DARE-TU Project
Co-creation of Affordable and Clean Pumped Irrigation for Smallholders

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Urban Rainwater Harvesting System: Possible Application for Car Washing

L. Andjelic*, N. Andjelic**, N. Jacimovic***, S. Petkovic*, M. Pavlovic*and D. Vlajic*

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INTRODUCTION

Rainwater harvesting (RWH) is the collection of rainwater runoff for use. Runoff can be collected from roofs and other impermeable areas, stored, treated (where required) and then used as a supply of water for domestic, commercial, industrial and/or institutional properties. The collected water can generally be used for a range of non-potable purposes, such as flushing toilets, washing machines (which may require adaptation) and for external uses such as car washing and irrigation (Woods Ballard et. al., 2015).

Rainwater harvesting (RWH) system

Rainwater Harvesting (RWH) is probably the most ancient practice in use in the world to cope with water supply needs. In recent decades, as a result of new technological possibilities, many countries are supporting updated implementation of such practice to address the increase in water demand pressures associated with climatic, environmental and societal changes (Amos et al., 2016).

In urban areas, RWH consists of the concentration, collection, storage and treatment of rainwater from rooftops, terraces, courtyards, and other impervious building surfaces for on-site use. Civil uses of collected rainwater are disparate, but all aim to reduce consumption of drinking water from centrally supplied sources (Campisano et al., 2017).

GhaffarianHoseini et al. (2016) suggest these uses can globally account for 80-90 % of overall household water consumption, and highlight the significant water conservation benefits associated with RWH implementation.

TESTING POSSIBLE APPLICATION OF RWH SYSTEM FOR CAR WASH

Input data

In this paper the application of RWH systems for car wash was examined for 3 different impermeable areas: rooftop of building with 20 apartments (cars), parking lot for 100 cars, and parking lot for 200 buses. Based on research and experience, the assumption is that the required amount of water for washing one car is 200 l (0.2 m^3), and for one bus is 1000 l (1.0 m^3). The examination was done for a period of five years, between 2013 – 2017, for “non-winter season” (March – November), with real recorded precipitation in the urban area of Belgrade, Serbia. In Figure 1 is shown the graphic view of precipitation in period March – November, 2013. For this work, different volume of water tank was tested, and in this paper is presented the results for the tank that will not be empty for more than 10 consecutive days, during the examination period, for the adopted conditions. Also, it is assumed that 10% of all users wash their car every “dry” day (day without precipitation).

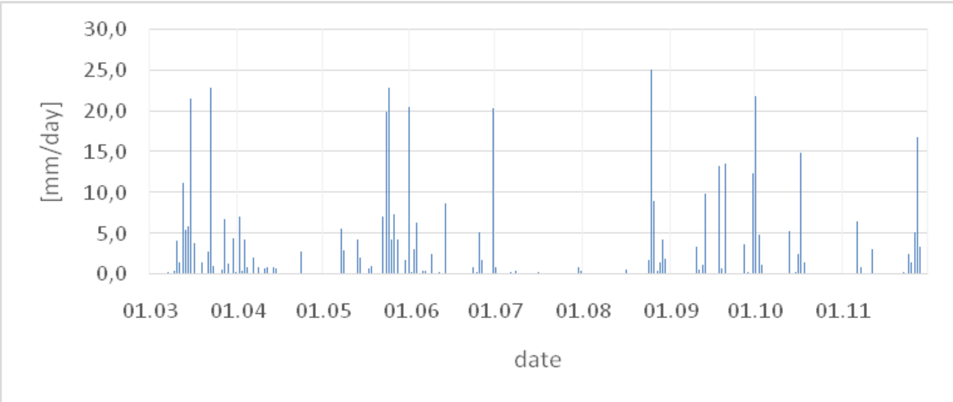

Figure 1. Daily recorded precipitation in the urban area of Belgrade, Serbia, for 2013 year

RESULTS

In this paper is shown that urban rainwater harvesting system can find good application for car washing. It is important to note, that in combination with other possibilities for using rainwater, the results could be much better, and the need for drinking water could be significantly reduced. As results, in this paper, is shown graphic view of water tank volume changing, for all three cases of impermeable areas, during all five years. According the results, in the paper is given the recommendation for tank size for all tree cases. Examples of results are shown in Figure 2.

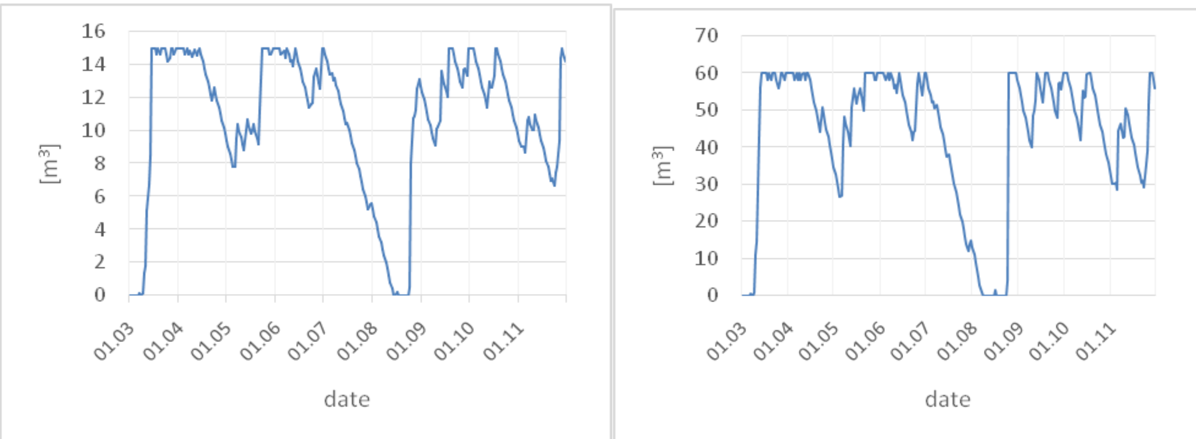

Figure 2.Water level in tank for 2013 year– volume 15m^3 for building rooftop area(left), and 60m^3 for parking lot for 100 cars (right)

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Application of SWMM Software Package for Management of Rainwater Drainage Systems of Urban Basins – Example of Drainage for Combined Cycle Power Plant

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INTRODUCTION

Nowadays, knowledge and using of software packages during the production and monitoring of condition of rainwater sewage at urban basins became very important and even necessary. EPA Storm Water Management Model (SWMM) is dynamic, physically based and conceptual model which serves for simulation of processes transformation of precipitation to flow, and which is based on the basic hydrodynamic laws. It can be used to simulate one happening or for continual simulation of flow quantity and quality, primary from urban basins. In this paper are shown possibility of application of this software package in domain of flow and rainwater sewage from urban basins with the example drainage at Combined Cycle Power Plant.

SWMM – introduction

The Storm Water Management Model (EPA SWMM) is a hydrologic and hydraulic model use to simulate flows in both storm water runoff and sanitary sewage (Martinez-Solano et al., 2016). It was developed by the United States Environmental Protection Agency, and it is a program that is able to solve the hydraulic equations of a network by using three different algorithms: steady flow, kinematic wave and dynamic wave (James et al., 2011).

SWMM is a conceptual model that is based on basic hydrodynamic laws (energy maintenance and mass maintenance laws). It can be used for for simulation of single event or long term (continuous) simulations. It is primarly used for runoff simulations from urban catchments.

Network design (Mays and Yen, 1975; Elimam et al., 1990), real time control (Van Nooijen and Kolechkina, 2013) are some examples of applications that require a hydraulic simulation of the sewerage network.

Within this simulation model, the flow calculation is done through the network of collectors, nodes and objects for flows distributions to nodes for outflow from system. In this case, further objects can be simulated: collectors, overflow, hole and outlflow objects.

When creating a model, the program requires defining the diameter, and the slope of the pipe. In addition to this information, each node introduces its inflow, which is calculated through the rational method. The surface runoff from the catchment areas, as well as the runoff from the roof surfaces of the facilities, was taken into account.

NUMERICAL CALCULATIONS

Storm waters from the new roadways, roofs and plateaus shall be collected by a special network of closed collectors installed beneath the road which gravitate towards the cadastral parcel boundary line, and then towards the recipient.

Calculation of discharge of the atmospheric water is done for rain return period 5 years, duration of 20 min, according to the data issued by the Republic Hydro-Meteorological Institute in Belgrade.

RESULTS

After a successful calculation, the result can be presented as a diagram or as a table. Depending on the interest, the need for further analysis and the transparency of the results, the following are presented:

- For collectors – flow, velocity, depth (filling), capacity, beveled volume,
- For nodes – volume, depth, lateral or total inflow,
- For catchments – precipitation, evaporation, infiltration, discharge or
- Longitudinal section with filling of the collector network in every time.

Figure 1 shows one of the longitudinal profiles of the atmospheric sewage network.

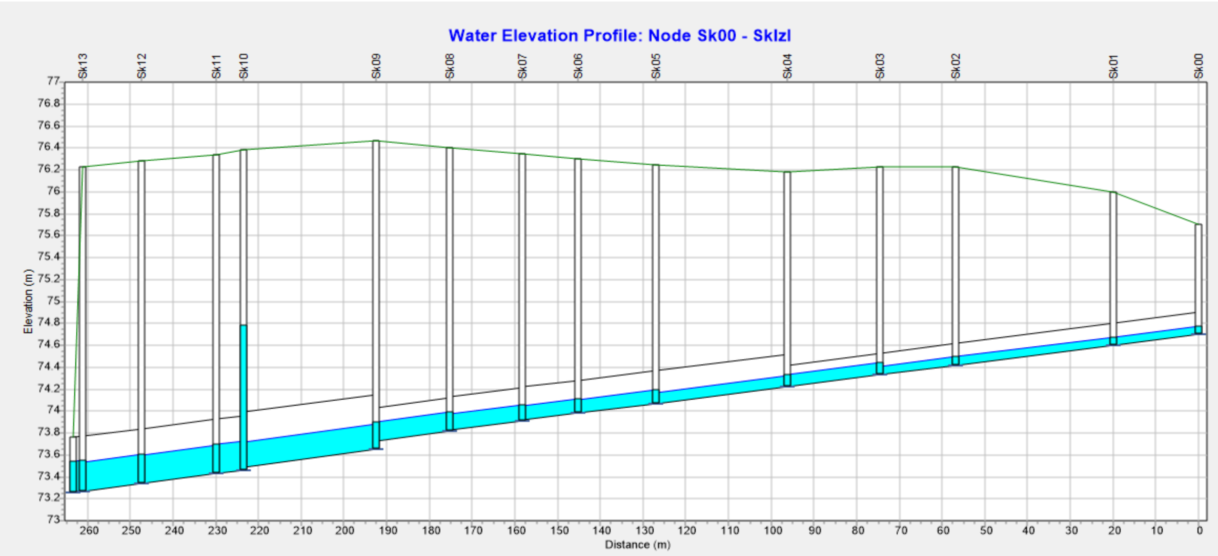

Figure 1. Longitudinal section from Sk00 to outfall SkOut

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The Rapid Biological Assessment of Ecological Status of Arpa River (Armenia)

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INTRODUCTION

Following the principles of EU Water Framework Directive (EU WFD 2000/60/EC), the decision 927-N of the Government of the Republic of Armenia (RA) has highlighted the necessity to ensure the ecologically balanced status, as well as the proper management and conservation of RA water resources. For that, 6 basin management areas (BMA) have been established in RA and baseline hydro-biological studies according to requirements of EU WFD have initiated since 2012.

Biological assessments of ecological status are mainly addressing the cumulative impacts of all stressors. The approach of assessing rivers' ecological state based on benthic macroinvertebrates is being testing in different river basins in Armenia (Fokkens et al., 2013), and Arpa River is one of the first studied by us areas. Thus, the aim of this study was the baseline assessment of the ecological status of Arpa River using RBA method/index established for the needs of Armenia and 5 other Eastern European countries (Cheshmedjiev, 2013).

Arpa River is the biggest surface water body in Ararat BMA and the main water vein of Vayots Dzor region. Being transboundary river between RA and Azerbaijan, it's intensively used for irrigation and production of electricity in the territory of RA. The baseline study is of high importance because since 2016 the works on exploitation of gold ore mining site Amulsar have begun in the upper course part of the river as well as because since the study ends up, 22 small hydropower plants (SHPP's) were established or planned to operate on the tributaries (National Statistical Service of Armenia, 2018). Thus, the manuscript could serve as a platform for assessments of changes in the structure of macrozoobenthos and ecological status of the river under the impact of SHPP operation.

MATERIAL AND METHODS

Studies were conducted during summer seasons in 2012 and 2013, which coincides with the minimum flow of the river. Sampling sites network includes all parts of Arpa River course and main tributaries. Sampling was carried out using Surber sampler with the frame of 0.09 m^2 and mesh size of 500 µm in accordance with the EU standards (EN ISO 10870:2012). Samples were fixed in 96 % solution of ethanol and transported to the laboratory for further processing and determination. Relative abundance and RBA were performed according to Cheshmedjiev (2013). Spatial interpolation of ecological status assessment by RBA method and mapping of the results was realized by ArcMap10.6 software.

In order to reveal quantitative changes in assemblage of benthic macro-invertebrates among different parts of the river, Sorensen-Dice index (Attwood et al., 2014) was used (1).

$$K = \frac{2J}{A+B} \tag{1}$$

where J is the number of species common for both sites, A and B are the total number of species at each site.

RESULTS AND DISCUSSION

The results of RBA have shown that, in general, water quality of river mouth parts of the left left-hand tributary Darb and the right-hand tributary Yeghegis as well as lower course part of Arpa River were not in compliance with the minimum requirements of EU WFD towards ecological status of surface water bodies. Spatial generalization of the results has shown, that the main course of Arpa River was mainly corresponded to "good" ecological status. Both the parameters of total number of taxa and RBA was corresponded to high ecological status only in the upper course parts of Darb and Yeghegis tributaries, which were initially chosen as reference areas for the basin. However, there was no part in the basin where the highest score of RBA was registered.

Although, the ecological status recorded at the lower course parts of Darb and Yeghegis tributaries was "moderate", but the negative effect of Darb on Arpa River is weaker because of differences in discharge of tributaries and stream gradient of Arpa River in parts of confluence. The main reason for worsening of ecological status of Darb tributary in the river mouth part could be the operation of SHPP as representatives of 3 "less sensitive" taxa were registered there, which prove the absence of strong pollution there. The situation with Yeghegis tributary is the most worrying now, as the density of population is the highest and many new SHPP's are being built there since the studies. The analysis of dominant groups of benthic macroinvertebrates at all stations showed that there were no A (sensitive) or B (less sensitive) group representatives in the studied parts. This means that pollution to some extent is present at all parts of the river.

Sorensen-Dice index calculation has shown that the composition of benthic macroinvertebrates has not been dramatically changed along the river course and even between the parts where water quality has worsened by two categories. However, the analysis of changes has revealed the main pattern of structural changes in the community of macrozoobenthos - sensitive and less sensitive taxa representatives have disappeared in lower course parts of both the river and its tributaries.

As the main direction of economic development were changed in the region and newly established industries was spatially allocated mainly close to the upper course parts of the river, it can be expected to have the changes in ecological status of hydroecosystem in a short time perspective.

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Fabrication and Characterization of Bipolar Membranes for Recovery Acid and Bases

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INTRODUCTION

The basic working principle of bipolar membrane is the separation of water molecules under electrical field (Shee et al., 2007). Separation of membrane water into hydrogen and hydroxyl ions by means of electrolyte solution due to electrical field effect (Amokrane et al., 1997). It is possible to produce acid and base salt from the salt without secondary salt pollution with bipolar membranes. It is therefore a technology that provides economic and environmental benefits. Due to its benefits, electrodialysis bipolar membrane systems (EDBM) are used in the chemical, food, biochemical and environmental protection sectors.

MATERIAL and METHODS

The polymers used in the study were polystyrene and polychloromethylstyrene for anion exchange layer and the polybutadiene-co-styrene for cation exchange layer. The functional group bound to the cation exchange polymer of bipolar was the sulfone, while the functional group bound to the anion exchange polymer was triethylene amin and diamine propane. H_2SO_4 was used as the sulfone source. And chloroform was used as the polymer solvent. While the bipolar membrane was formed, the cation exchange polymer layer was first cast and then the anion exchange polymer was poured onto it. It is then left in the oven at a certain temperature and left to the coagulation bath consisting of 0.1M NaCl solution. Each membrane has area of 10 cm^2.

RESULTS

In this study, characterizations of some bipolar membranes have been compared by considering different amine groups and membrane thickness. In total, 4 types of membranes produced which 1, 2, 3 and 4 bipolar membranes were shown in figure 1. Their electrical resistances were 6.45, 290, 8.7 and 25.65 ohm.cm^2 respectively. The initial water separation potentials of these membranes were 8.4, 31, 2.9 and 9.6V, respectively. Moreover, the thickness of these membranes was determined as 130, 290,120 and 220µm, respectively. In this study, four types of bipolar membranes were produced. The membrane cation side 1 was composed of a 20 % polybutadiene-co-styrene anion side of 17 % polystyrene and Polychloromethylstyrene mixture with NNNN diamine propane + trimethylamine. The difference of membrane 2 from membrane 1 was only thickness. The difference of membrane 3 from membrane 1 was the amine group, whereas the difference of membrane 4 from membrane 3 was only thickness. As the amine groups of membrane 1 and 2 were the same but the thicknesses were different, the electrical resistance of the membrane 1 was 6.45 ohm-cm^2 and the number 2 membrane was 290 ohm-cm^2. Although the thickness of the membranes 1 and 3 were close electrical resistance of the membrane 1 was lower than 3 because of different amine groups.

The result of the study was that the single kind of amine group was more effective on the electrical resistance on the membrane compared to the mixed amine groups. Another result was that membrane thickness was an important parameter in bipolar membranes.

Table 1. Characterization of bipolar membranes

Membran No	Anion groups	Thickness of membrane (mm)	Initial water separation potential (V)	Swelling (%)	Membran stress Mpa	Contact Angle
1	2ml NNNN diamin propan + 2ml trietilamin	0.13	8.4	18.4	786.52	68.93±0.29
2	2ml NNNN diamin propan + 2ml trietilamin	0.29	31	24.4	1271.34	64.69±0.93
3	4ml NNNN diamin propan	0.12	2.9	17.5	1076.46	67.61±0.23
4	4ml NNNN diamin propan	0.22	9.1	27	581.07	66.68±0.1

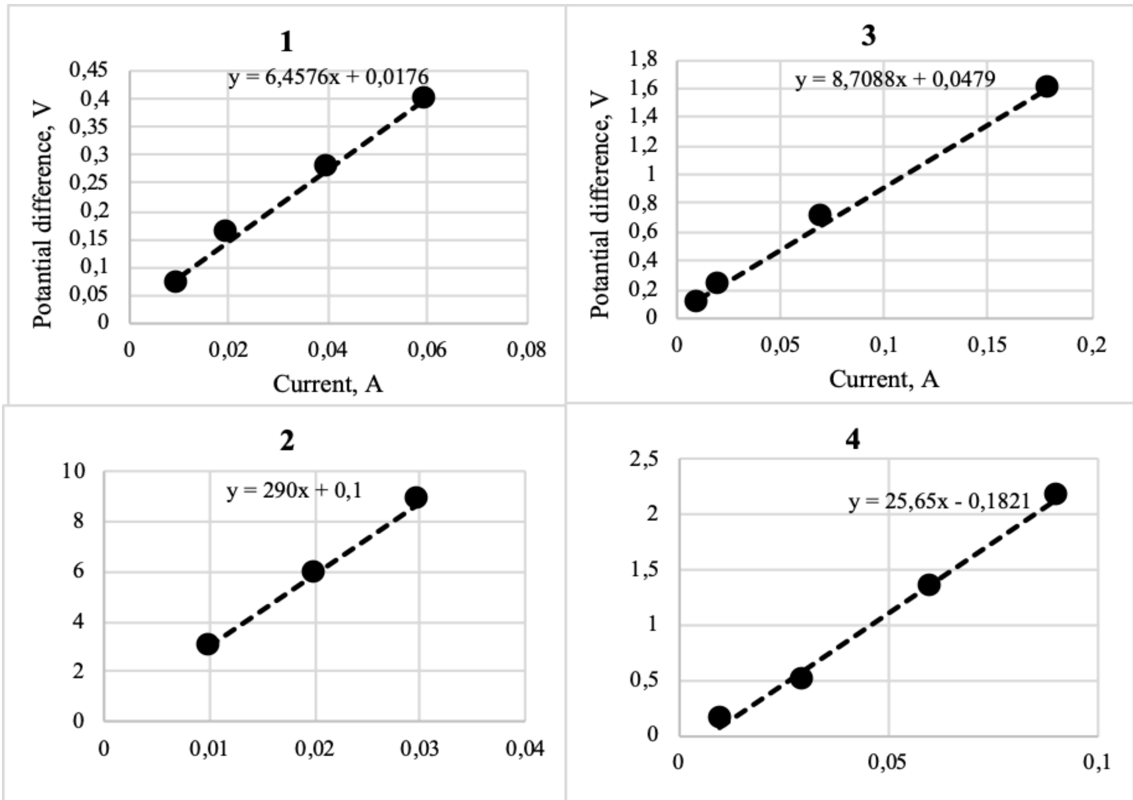

Figure 1. Electrical resistance of different bipolar membrane

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Evaluation of the Impact of Residential Urban Patterns on Water Ecosystem Services in Federal District, Brazil

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INTRODUCTION

The accelerated and large-scale urban growth leads to land use conversion and impacts on ecosystem services, which relationship between them depend on study area characteristics (Wang et al., 2019). Ecosystem services are the benefits obtained by people that are related to human well-being, whether directly or indirectly (MEA, 2005). By applying this concept to the urban sphere, this paper analyzes how the Water Ecosystem Services (WES) is affected by the urbanization in residential areas.

Landuse planning laws are applied to guide urban development and this demand detailed data about the built environment (Lam and Conway, 2018). Mapping using urban morphology examines the urban fabric details, observing the layout of buildings, infrastructure, and green spaces. Then, Urban Structure Types (UST) are defined as areas with homogenous characteristics, which are distinguished in the built environment by a specific form of buildings and open spaces (Wickop, 1998). The USTs also are characterized by urban density, buildings structure and constructive materials, amount of green areas, and surface imperviousness and it is a good classification to evaluate the ecosystem in an urban environment.

MATERIAL AND METHODS

The study area is the Riacho Fundo watershed, situated in Paranoá river's basin, in the Federal District, Brazil. Water resources availability is becoming critical, and thus preservation of water resources has extreme importance, therefore the evaluation of the impacts of urban morphology in ecosystem services such as groundwater recharge and infiltration is very relevant. The climate of the study area is tropical, with two very defined seasons: very dry from May to September with low precipitation rates and high evaporation rates, and a rainy season between October and April, with storms with and very high rainfall intensity. The average annual precipitation varies in the range of 1,200 to 1,700 mm in a territory of about 6,000 km², (Fonseca, 2001).

The Riacho Fundo watershed major type of soil is Latossol, very permeable, with low silt content and high clay percentage. Even though the high clay percentage, Latossol has a different hydraulic behavior, due to its structure, it can be classified as a soil of group A, in USGShidrological classification. (Reatto et al., 2004; Carvalho et al., 2012).

The purpose of this paper is to analyze the impact of urban residential patterns on water ecosystem services by using the Storm Water Management Model (SWMM) and the Urban Structures Types (UST) method, applied by GIS software. The rainfall return period of 10 years was adopted for runoff and infiltration analysis.

The residential structure types defined for this analysis and its characteristics are:

- RH1: high population density, units with residential parcels of less than 250m²;
- RH5: low/medium population density, units with residential parcels with area between 1000 and 2000 m².

Castro (2017) proposed a methodology to construct the Urban Water Ecosystem Services Provision Potential Index (UWESPI). The construction of this index is based on several water ecosystem services, such as groundwater recharge, erosion potential, overland flow, infiltration, flooding and green space area availability. Since there is no information available about the importance of different types of water ecosystem services, it is preferable to weigh them equally (Dobbs et al., 2014). Therefore, the results of runoff, infiltration, and land use were normalized between 0 and 1 to generate an index that indicates the degree of provision of urban water ecosystem services, varying between 0 (worst) and 1 (best).

RESULTS AND DISCUSSION

The results needed to build the UWESPI are presented below.

Table 1. Data used to build the UWESPI

	RH1	RH5
Max. potential infiltration (mm)	55.46	114.23
Water availability (%)	3.8	7.5
Groundwater recharge potential (%)	7.4	16.8
Runoff rate (cms)	1.1636	0.7218

After normalizing the results described in Table 1, the UWESPI obtained for RH1 and RH5 were, respectively, 0.038 and 0.083.

It was observed that the building density and allotment occupation affect directly in water ecosystem services, due to soil imperviousness, and green area available.

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Patterns of Changes in Soil Moisture Content Depending on Agrolandscapes Structure in Southern Ukraine

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INTRODUCTION

Anthropogenic changes within catchment areas performed without considering the structure of the landscapes being created have a negative impact on the restorative and self-regulating capacity of ecosystems, transformed agricultural and urban landscapes. Together with climate change, this causes a deterioration of the state of territories and increase aridization. Thus, there is an urgency to study the principles of how agrolandscapes should be spatially organized and how their components influence the formation and distribution of water resources. Such principles can be considered in regional scale planning of agrolandscapes development to minimize climatic and weather risks for local population and agricultural producers.

RESULTS AND DISCUSSION

For the arid conditions of the south of Ukraine, irrigation and shelterbelts should be emphasized as the most influential components of agrolandscapes. In this paper, within the above-mentioned broader context, we study the impact of these components on soil moisture availability.

Since the determination of statistical descriptions of such impact requires a large amount of ground measurements, the use of selectively verified remote sensing data is relevant. For this purpose we use the Vegetation Temperature Condition Index (VTCI) (Wang et al., 2001) which can be considered as a generalization of the Temperature Vegetation Dryness Index (TVDI) (Sandholt et al., 2002) and combines the assessments of surface temperature and biomass state. We calculate the values of VTCI index using the images acquired by the Landsat-8 satellite. Their resolution allows evaluating the moisture content within a separate field and, to some extent, tracing the impact of agrolandscape components on it.

To verify the reliability of VTCI usage for evaluating soil moisture content in the considered conditions, we obtained the correlations between its values and the average moisture content in the layer of soil with the depth up to 50 cm measured on August 10, 2018 by a portable moisture content sensor MG-44 on the experimental field of the State Enterprise Farm "Brilivske" located in the Kherson region of Ukraine. A linear correlation with R^2=0.48 was observed between the values of VTCI and NDVI indices. The similar correlation between VTCI and moisture content has R^2=0.65.

To study the changes in the correlations between biomass and moisture content for the different structures of agrolandscapes, on the studied territory we selected areas that have up to four shelterbelts around the fields. Then, for satellite images acquired on May 27, 2018, July 11, 2018, and August 10, 2018 the correlations between NDVI and VTCI indices were obtained.

For an image with low average biomass (NDVI <0.4) acquired in May, there were inverse linear correlations between NDVI and soil moisture content indirectly estimated using VTCI index. With an increase in the number of shelterbelts up to two, slope of the correlation increased. This fact can be explained by the extraction of soil moisture by shelterbelts and, thus, a decrease in moisture with an increase of biomass. In the case of three and four shelterbelts, the slope of the correlation decreased comparing with the case of two shelterbelts. This may be due to the reduction of evaporation from the fields surrounded by shelterbelts caused by the lowering of wind velocity and their other reclamation effects.

For the image taken in July, trends were similar to those observed in May. However, the inverse correlation here persists only when no shelterbelts are present. When irrigation was used and in the presence of shelterbelts, the greater biomass corresponded to higher moisture content. The distributions of NDVI and VTCI values for the image taken in August behave the same way. Moreover, primarily due to intensive irrigation, the correlations had a weak exponential form.

The distribution of index values in July and August can be divided into three groups in which the nature of the correlations between them varies. These groups include areas of weak or absent vegetation (NDVI<0.3), areas of rainfed crop cultivation (0.3<=NDVI<0.6) and irrigated areas (NDVI>=0.6). The linear correlations between VTCI and NDVI values for the three NDVI ranges computed based on the image acquired on August 10, 2018 are shown in Table 1. The correlations in the case of absent or weak vegetation are close. In the case of rainfed crop cultivation, the number of shelterbelts substantially affects the slope of correlation: it is negative when number of shelterbelts is less than two and positive when there is a complete or almost complete contour of shelterbelts. This can be explained by the retention of moisture by shelterbelts which leads to an increase of moisture content with the increase of biomass when two or more shelterbelts are present in the structure of the plot.

Table 1. VTCI=a+b*NDVI correlations for different number of shelterbelts and different NDVI ranges for the image acquired on August 10, 2018

	NDVI<0.3		0.3<=NDVI<0.6		NDVI>=0.6		
Number of shelterbelts	a	B	A	B	a	b	
	0	-0.23	1.59	0.91	-1.65	-1.54	2.67
	1	-0.09	1.12	2.73	-7.07	-0.62	1.35
	2	-0.12	1.22	-1.58	4.90	-0.32	0.96
	>=3	-0.22	1.53	-0.58	2.18	-0.74	1.47

The correlations for the irrigated fields are close in all cases of shelterbelts presence. The greater slope of the correlation between moisture content and biomass for the areas with no shelterbelts is due to the fact that these areas are small private fields where excessive watering is usually applied. As in the considered region irrigation is mostly performed by center pivot sprinkling machines, this behavior of the correlations shows that the impact of irrigation is a key factor for the development of biomass that levels other factors, particularly the influence of shelterbelts.

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Influence of the Internal Protective Coatings Surface Texture to the Transport Capacity of the Pipelines

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INTRODUCTION

The problem of sediment deposition in pipelines can lead to multiple problems; many being environmental. Formation of a dense layer of sediment in the tray part of the pipeline can lead to certain problems, besides the high increase in friction losses. One example would be the potential microbiological corrosion under the deposit layer, as well as needed of more frequent cleaning of the pipeline, which in turn increases the cost of sewage networks operation.

The main idea of design is to create a microturbulence effect in pipelines with low speed flows. This can be achieved by placing obstacles on the inner surface of the pipeline tray. This will create microturbulence in the flow, forcing suspension of sediment up into the flow instead of enabling deposition (Ebtehaj and Bonakdari, 2014; Grossmann and Lohse, 2017). Thus, experimental research of improving the transporting ability of non-pressure sewage pipelines at low water flow can be considered as an actual direction of scientific research and an extremely important aspect for development of pipelines reconstruction projects (Santiago and Durango, 2013).

MATERIALS AND METHODS

The research and its results were aimed to study the behavior of fluid flow around various artificially-created obstacles with the identifying of the optimal patterned structures as to ensure microturbulence due to the geometric shape and location of the obstacles and the increase of the flow transferring ability. In parallel, the aim was to investigate the influence of fine and coarse sediments (loose and cohesive sand) to the vortex formation in the transition from laminar to turbulent flow (Loisel et al., 2013; Kleinstreuer, 2017).

The experimental research of turbulence on corrugated surface has been studied on a purpose-designed and built, patented, testing bench. The experiments were carried out based on the light-shadow effect with relevant cameras. The corrugated surfaces in the tray sections of the pipeline were created by sets of different obstacles (wedges, corners, etc). Obstacles were located in the middle of the flow or with some relative displacement (small and large) from the tray axis. It was critical to detect the sizes (the nature, length, width of turbulence zone) of vortices (per object) and overpressure, in the form of ripples, in front of the obstacle.

RESULTS

Experiments were carried out to study the hydraulic parameters of single-phase and two-phase flows in the open trays without a textured surface and with different relief of their inner surface in a wide range of water level in the pipeline (0.05-0.6) and velocities (0.1-0.6 m/s) of fluid flow, as well as transportation of various sand fractions (0.1-3.0 mm).

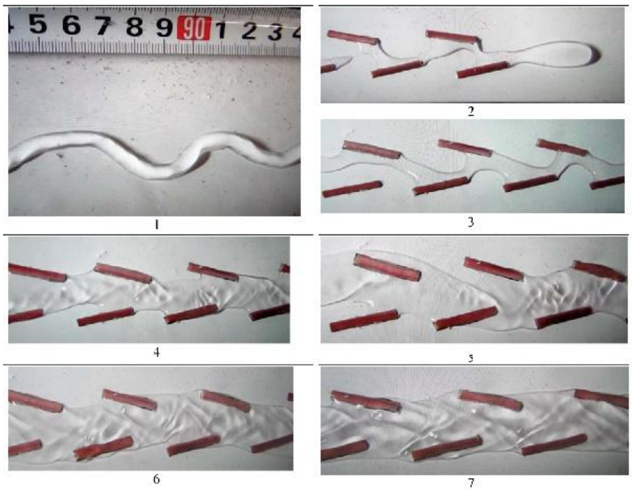

Figure 1. Dynamic of the flow pattern change on a hydrophobic surface with obstacles with a gradual increase of the flow speed from 0.08 to 0.35 m/s.Specific nature of the flow is observed on a hydrophobic surface with the group of obstacles

The results of experiments are described and interpreted in the form of the formation of vortices (coherent flow or vortex flow), considering the sizes of the vortices and geometric characteristics of the turbulence zones (both lengths and areas, before and after obstacles).

It has been established that the obstacles in form of the wedge or semicircular, located with a sharp end to the flow, are the most effective solutions for transportation of sand fractions along tray. Ranges of their transporting abilities are in the speed range (0.345-0.5 m/s) and water levels (0.377-0.446) for sand with a fraction size of 2.5-3 mm were their transporting abilities, respectively, per the dune areas 1.336-1.482 mg/s per cm^2 and per dune lengths 6.01-6.67 mg/s per cm.

It was found out that depends on the type and location of obstacles, the transporting ability of sand removal significantly differs for a fraction size of 0.1-0.3 mm and for a fraction size of 2.5-3.0 mm. The difference per unit area is about 53.1 %, and per unit length of the dune is 46.6 %. Thus, the smaller the size of the sand fraction is, the more efficient is the transporting.

CONCLUSIONS

The main conclusion is that the active turbulization of the flow can be observed at speeds of 0.4 m/s, i.e. below the self-cleaning speed, which was used for subsequent experiments. Based on the obtained results, it is shown that practically any obstacle can in some way influence the turbulence effect of the flow at less than its rate of self-cleaning.

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Toxicology Assessment of Emerging Contaminants Found in Secondary Effluent of Prague's WWTP on Aquatic Species with Ecological and Economical Relevance

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INTRODUCTION

The increase in the global population and the need to cover more food and services requirements, have redirected our attention to a new and growing environmental threat known as Emerging Contaminants (ECs). These new pollutants are not monitored nor regulated in a consistent matter, however they pose negative effects on human health and ecosystem balance (Geissen et al., 20015). The main concern is that their effects can start manifesting from concentrations as low as µg/L (Jurado et al., 2012). Common products, such as pharmaceuticals and personal care products are one of the main sources of these contaminants, and the current wastewater treatment plants (WWTPs) do not have the capacity to retain, treat or eliminate the great majority of them (Tong et al., 2011). *In vivo* studies are also needed to establish possible effects and the concentrations in which the repercussion are relevant in an ecological and economical level.

In a previous study, we analysed the secondary effluent of the WWTP of the City of Prague, and, to the best of our knowledge, among the ECs that did not have records of toxicity on *Artemia salina* were: furosemide, hydrochlorothiazide and tramadol; all of them are known and commonly used pharmaceuticals. *Artemia* was chosen as study model because of its great economic relevance in aquaculture and its important role in marine ecological balance. Therefore, this project aims to evaluate the effect of the three ECs above mentioned and characterize their toxicity.

MATERIALS AND METHODS

*Artemia Salina*cysts (Biogrow, Proaqua® - Mexico) were hatched in a glass container with marine water (Instant Ocean® 29.9mg/L distilled water) under constant aeration for 24 hours. Chemical contaminants were supplied by Sigma-Aldrich® (MO, USA). These were dissolved in milli-Q water (tramadol) or methanol (furosemide and hydrochlorothiazide). Marine water was used for dilutionsto maintain salinity. Toxicity testswere performed in *Artemia* nauplii at two temperatures: room temperature (ranging from 20.5 to 23.5 ^{o}C) and at 28 ^{o}C, and two exposure times: 24 and 48 hours. Experiments were performed in 96-microwell cell culture plates using 250 µl as working volume. Negative and positive controls containing marine water or potassium dichromate, respectively, were included in all the experiments. Each compound was evaluated bytriplicate for each condition and the survival was recorded. Lethal concentration for half the population (LC50) was determined by linear regression.

RESULTS AND DISCUSSION

The mean LC50 values obtained are showed in Table 1. Furosemide was the most toxic compound as the median lethal concentrations were the lowest of the three contaminants tested. This effectremained quite stable for all conditions tested, with concentrations ranging between 225 and 274 mg/L. Tramadol followed the expectation that LC50 would be lowerat 28 °C than at room temperature, as even the negative control tends to have lower survival at this temperature; however, furosemide and hydrochlorothiazide had an inverse behaviour. LC50 for these two compounds were always higher at 28 °C, although for hydrochlorothiazide at this temperature and 24 hours exposition was not possible to obtain this indicator in an accurate way as it exceeded 3000 mg/L, concentration, where the compound tended to precipitate in the dilution, interfering with the results analysis. Tramadol showed the least toxic effects in terms of killing half of the population, although the concentrations reached were very high. However, the effects of tramadol could be seen almost immediately as *Artemia salina* started swimming very slowly, almost like trembling. Survival for negative control was over 95 %, and the LC50 for the positive control $K_2Cr_2O_7$ranged 4.36 to 37.07 mg/L depending of temperature and time of exposition.

Table 1. LC50 mean values, at two different temperatures and at 24 and 48 hours exposition. The LC50 of potassium dichromate (positive control) is also shown along with the survival on the negative control (marine water)

Emerging Contaminant	**Temperature**	**LC50 (mg/L)**	**LC50 (mg/L)**	**LC50 $K_2Cr_2O_7$ (μg/L)**	**LC50 $K_2Cr_2O_7$ (μg/L)**	**Control Survival (%)**	**Control Survival (%)**
		24 h	**48 h**	**24 h**	**48 h**	**24 h**	**48 h**
FUROSEMIDE	28°C	273.95	242.27	22.73	5.92	98±4	96±7
	Room Temperature	256.63	225.01	37.07	8.62	96±5	90±8
HYDROCHLORO-THIAZIDE	28°C	>3000	957.99	22.49	5.40	97±7	96±6
	Room Temperature	1564.13	918.42	35.78	5.29	98±5	90±9
TRAMADOL	28°C	4419.41	838.46	26.73	4.36	99±3	97±6
	Room Temperature	>14000	1748.57	36.42	9.28	98±4	98±4

CONCLUSION

From these results, we conclude that the three pharmaceutical compounds tested, and included in the Emerging Contaminants classification, are indeed toxic for *Artemia Salina* in a higher or lower degree depending on the environmental conditions and the compound itself. The concentrations found for LC50 range from 225.01 mg/L for furosemide up to above 14.000 mg/L for tramadol; these concentrations are quite high compared to the ones found in the secondary effluent of the City of Prague in our previous study, which range from 810 to 2700 ng/L. However, it is important to emphasize that the three pharmaceutical compounds tested are very commonly used and have been found in water bodies around the world, therefore the accumulative effect of them must not be ignored, requiring further and intensive studies.

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Removal of Different Viruses in Water by Plasma

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INTRODUCTION

The increasing global population and food demand, together with higher standards of living and climate change are driving forces that lead to water scarcity (WWAP, 2018). Another very important factor is the emerging number of various non-biological and biological water pollutants. Of the former, viruses are particularly problematic as they are usually resistant to wastewater treatment processes and disinfection methods that have been developed to target mostly bacteria. Moreover, viruses can survive in water for long periods of time, can be infectious at low doses, and are the source of numerous human, animal and plant infections and epidemics (Id et al., 2019; Mehle and Ravnikar, 2012). Various methods are currently used for water decontamination, however, they all have some downsides. They can be expensive, time consuming, require large infrastructure, frequent maintenance, produce undesirable side components or need additional decontamination steps (Stewart-Wade, 2011). In today's polluted world, we need relatively cheap and efficient environmentally friendly method that does not produce waste. One such method is cold atmospheric plasma.

Plasma is the fourth and the most abundant state of matter in the visible universe. It is a complex mixture of charged particles (ions and free electrons), reactive species, UV photons and neutral particles (molecules or atoms in their excited or ground state). Cold atmospheric plasma (CAP) is generated under atmospheric pressure and has a temperature of less than 40 °C. That is why it can be used for treating biological samples. CAP has been used for decontamination in different fields like medicine, food processing or agriculture due to the antimicrobial properties resulting from the plasma mediated generation of reactive oxygen and nitrogen species, charged particles and UV radiation (Hoffmann et al., 2013)

METHODOLOGY

Viruses

In our experiments we used two different water-transmissible viruses: potato virus Y (PVY) and bacteriophage MS2. PVY is a filamentous, RNA virus that can infect different plants but is the most important potato virus pathogen and it can cause up to 80 % loss in potato production, which is a big problem since potato is one of the most important crops in the world (Kogovšek and Ravnikar, 2013). MS2 is an icosahedral, RNA virus used as a surrogate for enteric viruses transmitted by water. Enteric viruses infections are associated primarily with diarrhea and self-limiting gastroenteritis in humans, however they may also cause respiratory infections, conjunctivitis, hepatitis, and diseases that have high mortality rates in immunocompromised individuals (Fong and Lipp, 2005). Genome sizes of PVY and MS2 are ~10000 bp and ~3600 bp, respectively.

CAP

We added viruses in 10 ml of water and treated them with CAP for various amounts of time. We used CAP system in the single electrode configuration connected to a low-frequency generator (31 kHz) that operated at a peak-to-peak voltage of 6 kV, with total average output power of ~3 W.

Methods used to describe success of viral inactivation

We combined various methods to determine the success of viral inactivation with CAP. Reverse transcriptase droplet digital PCR (RT-ddPCR) was used to determine absolute viral concentrations. Infectivity test with tobacco plants coupled with RT real-time PCR (RT-qPCR) was used to test infectivity of PVY, while for the MS2, double layer plaque assay was used. RT-PCR of longer RNA fragments was used for all viruses to determine the integrity of nucleic acids after the treatments, while transmission electron microscopy was used to describe the integrity of viral particles.

RESULTS and DISCUSSION

Despite their structural differences, we were able to inactivate or sufficiently decrease the infectivity of treated viruses, even at high initial concentrations, after very short treatment times, depending on the treatment properties and virus type. We inactivated PVY after only 1 min plasma treatment, after which it was not able to infect tobacco plants. Based on the USA EPA regulative, which states that a proper water disinfection method should reduce the viral load in 4 logs, we were able to do so for MS2 after only 1 min. We confirmed that plasma treatment is able to degrade viral RNA, after only 1 and 5 min treatment times for MS2 and PVY, respectively.

CONCLUSIONS

CAP has a great potential as a decontamination tool of water sources. It could be used as an alternative, environmentally friendly method to remove viruses from water. Additional tests are needed to provide the evidence of the CAP effect on other water pollutants, however, based on the research done by many groups, CAP cold be a useful tool for water decontamination that could make water safer for everyday use.

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Evaluation on the Fate of Heavy Metals in Low Impact Strategies Treating Urban Stormwater Runoff

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INTRODUCTION

Multi-beneficial approach where several objectives drive the design and decision-making processes in management of urban drainage has been apparent in the recent years (Fletcher et al., 2015). Specifically, nature-based solutions such as low impact development (LID) technologies and green infrastructures (GI), which mimic natural processes for the improvement of urban stormwater runoff were utilized. Decentralized technologies such as LID and GI control stormwater from the source to mimic the pre-developed water cycle through mechanisms of microscale stormwater storage, increased infiltration and lengthening of flow path and runoff time (Damodaram et al., 2010). However, studies about the factors affecting the performance for heavy metal fate in these technologies were still lacking. Therefore, in this study, eight LID have been investigated considering the management and treatment of heavy metals in stormwater runoff.

MATERIALS AND METHODS

Eight different LID technologies were monitored from May 2009 to October 2016 with catchment, monitoring and design characteristics summarized in Table 1. These LID technologies were installed inside Kongju National University, Cheonan city, South Korea to catch urban stormwater runoff from 100 % impervious road, roof and parking lot areas. Hydrologic and hydraulic parameters were recorded during each storm event monitoring. Water samples collected were analyzed according to the standard method of the examination of water and wastewater (APHA, AWWA and WEF, 1992).

Table 1. Catchment, monitoring and design characteristics of LID technologies

Green Infrastructure	Parameters						
	Runoff source	Catchment area (m^2)	N storm events	Infiltration capability	Filter media	Facility aspect ratio (L:W:H)	SV/TV (%)
Infiltration Trench 1 (IT 1)	Road	371	24	Yes	Sand, woodchip and gravel	1:0.2:0.26	45.4
Infiltration Trench 2 (IT 2)	Parking lot	481	20	Yes	Sand, woodchip and gravel	5:1:1	26.7
Tree box filter (TBF)	Parking lot	379	26	Yes	Sand, woodchip and gravel	1:1:0.87	36.6
Rain Garden (RG)	Roof	161	29	No	Sand, soil, woodchip and gravel	2.47:1	38.3
Bioretention 1 (BR1)	Parking lot	139	16	Yes	Sand, soil, bottom ash and woodchip	2.5:1.08:1	48
Bioretention 2 (BR2)	Roof	81	12	Yes	Sand, soil and gravel	1.33:1	40
Hybrid constructed wetland 1 (HCW1)	Road and parking lot	323	21	No	Sand, woodchip and gravel	1:0.15:0.1	33.9
Hybrid constructed wetlands 2 (HCW2)	Road and parking lot	425	22	No	Sand, bioceramic and gravel	1:0.14:0.1	30.6

*ratio of facility storage volume to total volume

RESULTS AND DISCUSSION

Rainfall depth was found to be highly correlated to hydrologic and hydraulic parameters including rainfall duration, mean rainfall intensity, total runoff and discharged volume, mean inflow and outflow rates, peak inflow and outflow rates, discharged volume and hydraulic loading rate for all LID technologies. Antecedent dry days (ADD), on the other hand, is correlated with volume reduction of HCW2 (r: 0.6; $p<0.01$). In addition, ADD was found to be inversely related to average inflow rate, peak inflow rate and runoff coefficient (r: -0.80 to -0.99; $p< 0.01$) implying that longer ADD affects the hydrologic characteristics of runoff before entering TBF. Among these LID technologies, IT 2, BR 1 and RG significantly reduced runoff volume, mean inflow rate and peak inflow rates of storm events monitored ($p<0.01$). Figure 1 shows the relationship between volume reduction and heavy metal reduction of infiltration (IF) and non-infiltration (NF) technologies. For IF, 50 % volume reduction corresponded to 15 % to 60 % heavy metal removal while 50 % volume reduction corresponded to less than 5 % to 50 % heavy metal removal for NF. Among the heavy metals, IF significantly reduced Zn ($p<0.05$). It was found that IF heavy metal removal efficiency is greater than NF.

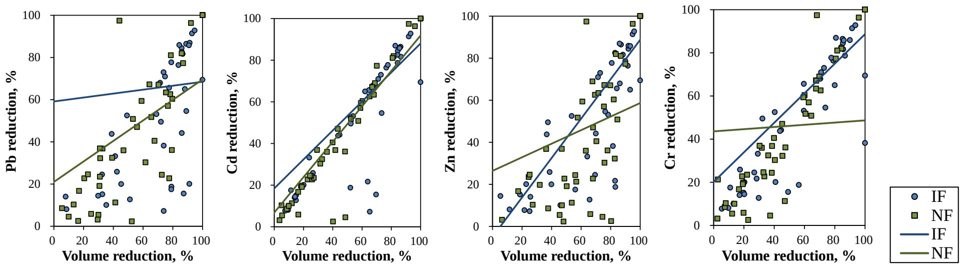

Figure 1. Relationship of volume reduction and heavy metal reduction by the filtration and non-filtration LID technologies

CONCLUSIONS

Eight LID technologies developed showed efficiency in achieving heavy metal reduction based on the monitoring conducted from 2009 to 2016. ADD was found to be one of the affecting factors for LID's performance where in intermittent wet and dry days increased volume reduction of the facility. The infiltration capabilities employed in several LID technologies resulted to greater heavy metal reduction compared to non-infiltration types. This research provided significant understanding of the factors affecting urban stormwater management using LID technologies that were useful for future application of similar technologies.

ACKNOWLEDGEMENT

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Simulation of Sensorless Flow Measurement System for Centrifugal Pump System

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INTRODUCTION

Centrifugal pumping equipment is widely applied in modern industrial activities, like water production and distribution, sewerage systems, oil industries, and many others. These centrifugal pumping plants are one of the major electrical power consumers nowadays. It is estimated that pumps consume from 10 % to 40 % of total produced electricity. The automation of the processes that take place in the centrifugal pumping plants will certainly help to improve their performance. It makes the centrifugal pump system a subject of intensive study for efficiency improvement. One of the most important parameters of the pumping systems is flowrate. It is necessary to find ways for affordable and at the same time effective flow estimation possibilities.

The main goal of this paper is to represent the model of the centrifugal pump system that is designed to calculate the flowrate of the pumping unit. The calculated data can be used later for the stabilization and maintenance of flow at a determined level or regulation in accordance to needs of specific industrial conditions. The main advantage of designed model is that it contains standard functional blocks and, therefore, is easy to readjust for various pumping systems with different parameters. The developed algorithm for a programmable logic controller allows implementing the real flow calculation based on the model parameters. Thus helping to tune real pumping control system respectively.

The structure of the paper is following. At the beginning, a functional circuit of developed Simulink model is described. Next, the developed method of sensorless flow calculation system is presented with the received simulation data. At the end, the experimental outcomes of developed model are discussed and the conclusions drawn.

MATERIALS AND METHOD

A conventional topology of centrifugal pumping system consists of several main components: the pipeline for fluid transportation, centrifugal pump, variable speed drive (VSD), feedback with pressure or flow sensor, regulation valve, fluid tank.

Every centrifugal pump can be described with the help of its main parameters, capacity Q (m^3/s), energy head H (m) and pressure p (bar) at a certain rotational speed n (rpm). Every manufacturer usually supplies pumps with manuals that include working characteristics. These characteristics consist of nonlinear dependence between Q and H, Q and P - power for the nominal rotational speed n_{nom}.

The dependence between energy head and capacity is given by equation:

$$H_{pump} = H_{static} + KQ^{m}, \tag{1}$$

where K is a pipeline resistance coefficient and m is 1 if the flow is laminar or 2 if the flow is turbulent.

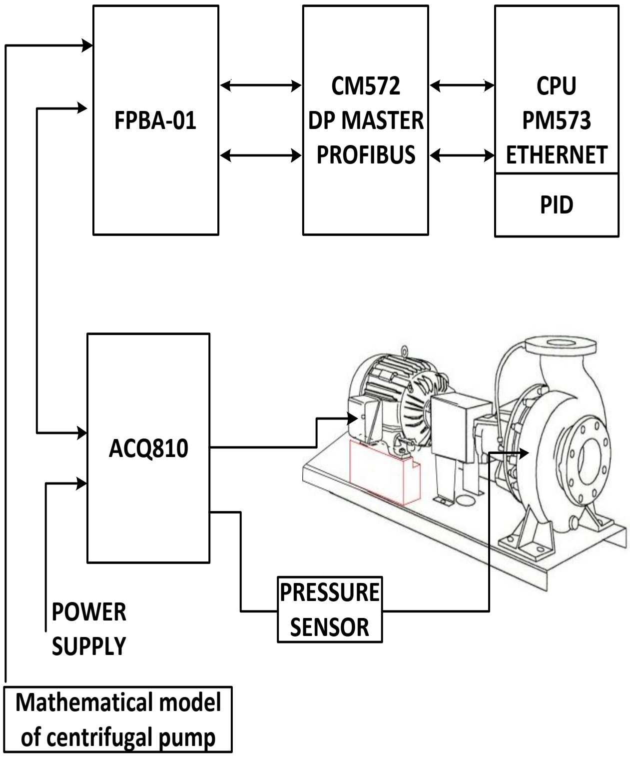

Figure 1. Structure of sensorless flowrate measurement system for centrifugal pump system

CONCLUSION

The developed model of centrifugal pump and related simulation approach are proposed in the paper. Simulations show that designed model is quite flexible and easy to tune. High accuracy of the model during dynamic and static modes, allows using this model for sensorless flow-measurement system for centrifugal pumps.

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Fostering Sustainable Development by Empowering Indigenous Abilities: the Border Zone Case of Rural South Lebanon

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INTRODUCTION

Humans have the capacity to formulate rules to guide cooperative behavior relating to each other and to their surrounding environment and that is why customs are not simply reflex responses to outside stimuli, but are developed intuitively by humans who seek to benefit by cooperation (Ørebech, et al., 2006). Lebanon has built its water sector on foundations laid down by the great fluvial civilizations of antiquity such as the Roman Empire and the Moslem world, that have contributed much to the art of water use and management in the region. Mesopotamian, Roman, Ottoman, and French water laws were superimposed on Muslim customs and practices and traditional Arab social water arrangements in Lebanon through a long history of conquests or mandates. In Lebanon annual precipitation is equivalent to three million Olympic pools, or eight billion cubic meters. However, only 17 % of the country's water resources are used, more than half of the rainwater is wasted to the sea and about 40 % is unaccounted for due to the lack of maintenance of the water supply networks (MEW, 2014). Experts agree that Lebanon will be the first country in the Middle East to be affected by climate change (MoE, 2016). Indeed, the distribution of the rains has changed, the density of snow is decreasing and the forest fires are multiplying leading to a decrease in infiltration and groundwater recharge. In rural South Lebanon, the development of agriculture required good practices for the conservation of water resources. Rural communities in the region have historically adapted to the characteristic water scarcity by harvesting and storing rainwater. How can we effectively prepare rural communities for the impacts of future water management problems, and what can be done to strengthen traditional social water arrangements?

MATERIALS AND METHODS

The focus of this study is on the role of indigenous water arrangements, customary law and inherited practices in developing the water sector in Lebanon. Indigenous water practices are the result of the complex interactions of changing practices imposed over time, combined with lessons learned regarding successful techniques, forming a palimpsest of legislative and administrative water competence that are potentially better able to address climate change because of their tested adaptive capacities. This work researches the influences and effects that strengthening customary, locally developed water arrangements could have on community resilience and adaptation to climate change. For this purpose, an appraisal of all ancestral social water arrangements that were developed in the region for the conservation of property and for the periodic distribution of water between interested parties was conducted through field visits to the rural areas of the countries and discussion with villagers and water users. Oral history was here the most important method of data collection as well as literature review of old books from Levantine poets or orientalist travellers. Then, a survey of all the ancestral *birket*-s of South Lebanon were identified using very old maps dating back to the year 1881, GIS maps, and land cover maps, and their status assessed using comparison with modern aerial images, and field verification.

RESULTS

During this research, we were able to identify several ancestral social water arrangements that were developed in the region for the conservation of property and for the periodic distribution of water between interested parties, which allowed for the mediation of disagreements between users and assured each of the equitable allocation of water to match needs. These include: *Urf:* Customs and Habits in the Islamic world // *Hima:* Ancestral Charter for the Protection of Nature // *Mushaa:* Communal land tenure // *Sabil:* water endowment for religious *waqf* // *Birket:* Ancestral communal rainwater harvesting // *Mastaba:* Indigenous water conservation and soil protection agricultural practices // *Aouna:* Rural mutual aid // *Sulha:* Traditional Arab tribal dispute resolution // *Murabaa:* share tenancy in farmlands // *Mugharasa:* landlord-farmer partnership for land vivification // *Chaoui:* informal water users' associations. Following the application of a series of criteria relevant to resilience and climate change adaptation (e.g.: democracy, equity, equality, fairness, spontaneity, transparency, participatory, replicability, adaptability, flexibility, efficiency, effectiveness) particular focus was made on communal pools (*Birket*). Moreover, ninety-nine *birket*-s were identified across eighty-five villages and cities in three administrative regions and nine sub-regions. Studies found that thirty-two of these pools are currently filled, fifteen have been transformed into buildings (mainly municipal buildings), six asphalted into parking, two transformed into sports facilities, and seven transformed into parks and gardens. The rest have either disappeared altogether or are empty. The case of the pool in the village of Marwaheen is of special interest: it was abandoned thirty years ago and transformed into a dump site, but was then restored by the municipality and currently functions as a communal water reservoir to which all farmers have access to irrigate their fields. This fact has contributed to a remarkable increase in vegetable farming which has risen from 12 to 25 ha in one year.

CONCLUSIONS

Rainwater harvesting and storing has long been a traditional approach to water management in South Lebanon. Here, precipitation occurs ordinarily only during winter (e.g. in Jebel Amel, Bilad Beshara, Northern Galilee), so it is important for the inhabitants to conserve this water into the dry season. This is done in cisterns beneath the surface of the ground and in reservoirs above ground. Open-air village reservoirs (Arabic, *birket*) collect rainwater for communal use in agriculture and for the use of herds and cattle. Moreover, location, form and capacity of traditional water reservoirs embody sophisticated and complex knowledge inherited over hundreds of years. They are located in the center of the villages and built on *mushaa* lands. Formerly, their usage included: drinking, irrigating, swimming, and washing (clothes, wool, grains, kitchenware, house ware, car….), whereas their modern usage is limited to irrigation, tourism (coffee shops, restaurants, promenade), water for construction, and for use by water tankers. They are usually located near a village in a depression where the water can readily be conducted into them. In light of the recent threats on water security in Lebanon and the Levant, understanding social water arrangements in rural areas of Lebanon, exploring their future potential in the management of water, and reclaiming local autonomy will definitely have a positive impact on community resilience and adaptation to climate change.

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Eutrophication of Bathing Waters in Prague: the Modeling of Causes and Proposals of Remedial Measures

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INTRODUCTION

The rapid rise of industry, household consumption and intensification of farming practices leads to significant increase of environmental pollution caused by nutrients, pharmaceuticals and heavy metals in the second half of the 20th century. In the Czech Republic, farming practices have improved, and different measures to decrease the content of polluting substances in surface water have been implemented since the 1990s. However, these measures seem to be not sufficient. Consequently, the trophic status of water bodies, which are burdened with increased nutrient intake, may change, e.g. from oligothropic to euthropic.

Phosphorus and its compounds are key factors of eutrophication. The increased intake of phosphorus can come from point and non-point pollution sources. The massive development of cyanobacteria and green algae is the most common accompanying phenomenon in water polluted with phosphorus. High concentrations of cyanobacteria and algae in the water cause problems mainly due to deterioration of the organoleptic properties of water. Another negative impact is the production of toxic substances that cause health issues.

Identification of pollution sources in given catchment is essential for consequent reduction of their intake into a water reservoir. The detailed survey of the catchment area is an important initial component of identification of different pollution sources. Then, the ratio between the point and non-point sources has to be determined in the overall pollution load. The motivation for recognition between the point and non-point sources is that even the complete elimination of point sources is not sufficient solution how to achieve the desired water quality in a reservoir (Gregar et al., 2019). Prevention is the most appropriate approach here, i.e. the limitation of nutrients intake.

The water quality parameters of bathing water have to be monitored during the season in the framework of Directive 2006/7/EC of the European Parliament and of the Council of 15 February 2006 concerning the management of bathing water quality and repealing Directive 76/160/EEC in order to determine the potential health risks.

CASE STUDY

The presented study focuses on the Hostivar Reservoir in Prague which is threatened by phosphorus pollution from various sources. The reservoir is situated on the watercourse Botic. The catchment area is 94.8 km^2. The catchment of the Hostivar Reservoir is located in the Prague agglomeration. Therefore, it is significantly built-up with a dense network of transport infrastructure. The remaining areas are intensively farmed. Only a very small part of the catchment area is forested. An extensive pond system is present in the catchment. Its impact on phosphorus load in the reservoir was also investigated. Moreover, these ponds are important inoculum of phytoplankton into the reservoir.

METHODS AND DATA

The Soil & Water Assessment Tool (SWAT) was used here. SWAT is focused on hydrological balance; it can be used also for modeling nutrient dynamics in a catchment. The model input data are land use, soil data, climatological parameters (air temperature, precipitation, humidity), information about farming practices on agriculture land and available data on point pollution sources (discharge of waste water from waste water treatment plants). The SWAT model of the catchment was optimized in order to achieve proper functionality.

RESULTS

The main focus of the study is to identify the pollution sources of reactive phosphorus and nitrogen forms in the sub-catchments, which is the fundamental prerequisite to being able to identify suitable remedial measures to achieve good ecological and chemical status of surface water in the catchment of the Hostivar Reservoir. Remedial measures have been proposed to decrease the intake of phosphorus into the reservoir.

The total permissible concentration was determined on the basis of a limnological assessment, namely to reduce nutrient intake 10 times: from current 0.1-0.2 mg/l to 0.02 mg/l. Therefore, the intake of phosphorus should decrease from 10 g/m^2/year to 1.5 g/m^2/year.

In addition to measures directly at waste water treatment plants (additional precipitation of phosphorus at the outlet), other potential measures are considered: e.g. the construction of biological ponds downstream from the plants. Biological ponds would provide post-treatment of the water from plants. Moreover, biological ponds are important revitalization measures.

Different scenarios were proposed to assess the potential of different measures to reduce the phosphorus intake into the reservoir. The considered measures are: reducing the use of agricultural fertilizers, eliminating diffusive sources, and improvement of the technology in waste water treatment plants.

CONCLUSION

Using the model, it was possible to verify individual scenarios and choose the most appropriate combination of measures that should reduce the input of phosphorus into the reservoir and thus prevent the increasing level of eutrophication in it. The same modelling approach is applicable in variable context, e.g. in the assessment of resources of potable water.

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Assessment of the Applicability of SWMM`s Water Quality Module for Green Roof

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INTRODUCTION

While green roof is known to be a good practice of runoff reduction for urban areas, it also is known to be the cause of water quality degradation as the effluent from it can have high nitrogen and phosphorous concentrations due to media type and age of green roof. In order to minimize this negative effects that green roof has on water quality, modelling of green roof water quality is necessary during the design phase. SWMM is one of the most popular stormwater models that is capable of modelling low impact development practices including green roof. Although assessment of SWMM model's applicability for runoff has been studied before, its predictability for water quality has not yet been studied. Therefore, this study aims to investigate the applicability of SWMM`s water quality module for green roof.

MATERIALS AND METHODS

In this study, the Portland Building Ecoroof, 488 m^2 in size, in Portland, Oregon, USA was selected as a study site where green roof characteristics and observation data for the green roof runoff and water quality were available. In order to conduct the study using SWMM, it is necessary to construct input data using the general characteristics of the green roof. This information was obtained from previous research on the study site and other relevant literature (Krebs et al., 2016). In addition, monitoring data for rainfall, total effluent volume and effluent concentrations were necessary for the calibration of the model, and they were provided by International Stormwater BMP Database and Oregon Water Science Centre.

Sensitivity analysis of the model parameters were performed for runoff volumes using the condition number. Sensitive parameters were then calibrated from using the harmony search algorithm, which is a popular metaheuristic optimization algorithm, for a range of recommended values. The objective function used was Nash–Sutcliffe model Efficiency coefficient (NSE). The closer the value of NSE is to 1, the more predictive the model is.

For the assessment of SWMM`s water quality module for total nitrogen (TN) and total phosphorous (TP), "rain concentration" was first used, which is the only water quality parameter available for green roof as the SWMM`s water quality module for green roof does not have any other mechanism to change constituent concentrations. For improvement, imaginary subcatchment of the same size as real one was installed to simulate pollutant buildup and washoff on the surface of green roof. This was made possible by using the buildup and washoff within Land Use Editor in addition to rain concentration. The flow and pollutant concentrations from the imaginary subcatchment were then fed into real subcatchment. The range of buildup and washoff and rain concentration parameter values were obtained from relevant literature.

RESULTS AND DISCUSSION

From the sensitivity analysis for runoff volume, porosity, conductivity slope, wilting point, conductivity and filed capacity were found to be sensitive (listed in the order of sensitivity). These parameters were then utilized for the calibration of SWMM LID Control for runoff volume. The applicability of the SWMM`s runoff module for green roof was found to be “very good” with an NSE value of 0.95. After the calibration for runoff volume, calibrated parameter values were used for the assessment of SWMM`s water quality module. First, assessment of SWMM`s water quality module was performed only using “rain concentration” as a calibration parameter. The applicability of the SWMM`s water quality module for green roof was found to be “not satisfactory”, with NSE value of 0.24 for TN and -1.45 for TP.

Another assessment of SWMM`s water quality module was performed using the Land Use Editor for imaginary subcatchment to simulate buildup and washoff from the surface of green roof. Exponential relationship was chosen for washoff equation in Land Use Editor, which is the only equation that is tied to buildup equation. Buildup in Land Use Editor includes three equations (Power, Exponential and Saturation). These three equations were utilized for simulation, respectively, to assess their relative performances. Table 1 shows NSE values using rain concentration and three different buildup and washoff combinations.

Table 1. Comparison of NSE values for TN and TP (with rain concentration and buildup and washoff)

	TN	TP
NSE[a]	0.36	0.64
NSE[b]	0.24	0.31
NSE[c]	0.29	0.37

[a] Power buildup equation, [b] Exponential buildup equation, [c] Saturation buildup equation

From the comparison of the three results, both TN and TP results were best with NSE values of 0.36 and 0.64 respectively when using power buildup equation. The reason for this is thought to be due to the ability of power buildup equation to cut off buildup growth when upper limit is reached, giving it the flexibility of choosing either a constant buildup or power growth depending on the events that need to be fitted. There was also a difference in the degree to which the applicability was improved for TN (“satisfactory”) and TP (“good”). This was seen to be due to the difference in the correlation between the observed values of the runoff volume and TN and TP. The simulated value of water quality load in the SWMM is, in general, proportional to the simulated value of runoff volume. In case of TP, the observed values of the runoff volume and water quality load were highly correlated with an R^2 value of 0.93, so the applicability of the SWMM`s water quality module can also be high. However, TN has little correlation with an R^2 value of 0.28, so the use of buildup and washoff in Land Use Editor did not seem to improve its applicability much.

Though improved, it was seen that buildup and washoff alone cannot properly help represent pollutant load characteristics from green roof. Further study should address this research gap by coming up with new kinetics formulations for internal processes of change in constituent concentrations.

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Long-term Monitoring of Rain Garden for Urban Parking Lot Runoff Treatment

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INTRODUCTION

Although rainfall runoff treatment and nonpoint pollution source management are carried out through LID facilities in urban areas, there is a possibility that the efficiency of facilities due to the accumulation of pollutants and sediments in the facilities may decrease over time. Therefore, the efficiency of the facility was analysed through long - term monitoring. As a result, the average d volume reduction was found to be 96 ± 3 % while the pollutant reduction efficiency of the facility were 85 ± 10 %, 91 ± 8 %, 74±16 and 85±13 for TSS, COD, TN and TP, respectively, for five years. The difference in heavy metal concentration in sediments collected from the inflow part and outflow parts were about 32 %, 39 % and 74 % for Cr, Cd, and Pb, respectively. It is analyzed that the efficiency is gradually lowered due to the limitation of the physical treatment mechanism brought about by pore clogging of the inflow portion and the upper filter material layer. The increase in impervious area due to urbanization causes water circulation distortion affecting the peak flow rate and the peak flow period occurrence during rainfall. In addition, changes in rainfall patterns due to climate change have been reported to affect the natural water cycle (Yoo, 2015). In order to solve the urban water environment problem, the Korean Ministry of Environment has applied the low impact development (LID) that can reduce the nonpoint source (NPS) pollution through infiltration, storage and utilization since 2004. In applying LID technologies, sedimentation basins, a pre-treatment technique, is included to remove particulate matters, reduce runoff, and increase hydraulic retention time. In addition, NPS pollutants are managed through Physico-chemical functions and ecological functions by treatment mechanisms including infiltration, filtration and storage through filter media and vegetation. However, over time, pollutants and sediments accumulate in the facility, resulting in problems such as filter pore clogging and decrease in permeability resulting to reduced efficiency of the facility. Therefore, this study evaluated the performance of rain garden through analysing the characteristics and behaviour of pollutants inside the facility.

MATERIALS AND METHODS

The rain garden technology was installed in Kongju National University, Cheonan campus to treat stormwater runoff from parking lot. The rain garden consists of sedimentation basin (pre-treatment technique), vegetation part and outflow part. Filter media including gravel and sand were used in the rain garden. Storm event monitoring was conducted including water quality and soil quality testing for a total of five years from 2014 to 2018. Water quality monitoring was performed by collecting water samples from inflow and outflow parts of the facility, and flow measurement was performed every five minutes after the runoff and discharge was observed in the rain garden. Water samples were collected at intervals of 0, 5, 10, 15, 30 and 60 minutes and every 60 minutes thereafter. Sediments were collected from sediments and analysed for soil.

RESULTS AND DISCUSSION

Figure 1 exhibited the annual pollutant removal efficiency of rain garden. Monitoring was carried out for rainfall depths ranging from 0.5 mm to 40.3 mm with mean antecedent dry days and average rainfall intensity of 5.46 ± 4.7 days, 5.33 ± 6.7 mm/hr, respectively. For pollutant removal, it was found that TSS, COD, BOD, TN and TP removal efficiencies gradually increased due to vegetation and plant stabilization after the first three years. However, it was also observed that the reduction efficiency for TSS, COD, TP and heavy metals through physical treatment mechanisms such as filtration, sedimentation and adsorption decreased by 10 to 60 % after operation of the facility for four years. Heavy metal concentrations in sediments were analysed to be 0.21 mg/kg, 0.21 mg/kg and 3.67 mg/kg, for Cr, Cd, and Pb, respectively which was about 14 to 74 % higher than the heavy metal concentrations at the outlet (Figure 2). It is considered that the sediments flowing along with the stormwater runoff during rainfall accumulate in the settling basin and the inflow part of the facility thereby affecting the physical treatment mechanism due to the pore clogging on the upper part of the facility and the filter material layer over time.

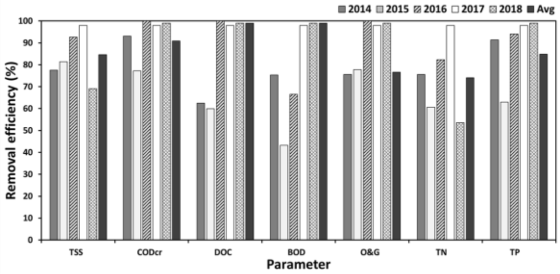

Figure 1. Annual pollutant removal efficiency of rain garden

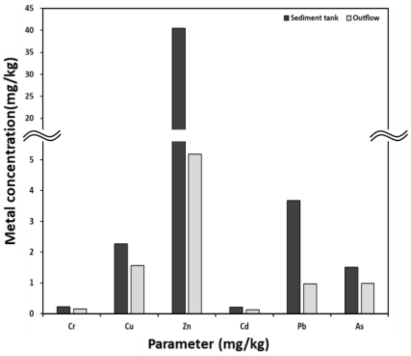

Figure 2. Heavy metal concentration in sediment

CONCLUSIONS

1) Based on the long-term monitoring of the rain garden, the following conclusions were derived: The rain garden exhibited relatively high average volume reduction amounting to 96 ± 3 %. This efficiency was observed to decrease after long facility operation without proper maintenance.

2) The difference in heavy metal concentration in sediments collected from the inflow part and outflow parts were about 32 %, 39 % and 74 % for Cr, Cd, and Pb, respectively. Due to the clogging of the filter media pores, physical treatment mechanisms decreased over time

ACKNOWLEDGEMENT

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Beach Wrack Management as Example of Circular Economy

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BEACH WRACK PROBLEM

Beach wrack is a natural occur phenomenon, which is observed on the beaches around the word. The sea throws out organic material by waves, tides and wind. These factors are also responsible for recycling it back to the sea (Macredie et al., 2017).

Impact of beach wrack on environmental and social

Beach wrack thrown out the shore is rich in nutrients, which released to the sea cause the eutrophication process. Organic material quick decompose on the shore, giving off unpleasant smell, which deter tourists (Szymelfenig et al., 2005). Beach wrack is not only environmental problem for eutrophicated water reservoir but also a specific social problem for local authorities. Gdańsk University of Technology (Poland) is involved in the project CONTRA- "Baltic Beach Wrack- Conversion of Nuisance to a Resource and Asset", which raise the problem of beach wrack, as part of the Interreg Baltic Sea Region program.

Occurrence and quantity of beach wrack

The lack of monitoring in the area of polish shore of the Baltic Sea as like seasonal changes in occurrence of beach wrack contribute on difficulties the accurately estimate of the quantity of it. According to Maritime Institute in Gdańsk , the amount of biomass of algae lying on the beach in Sopot (North Part of Poland, famous place for holidays) ranges from 160-800 tons dry weight per year (Schultz-Zehden Matczak 2013). According to MOSiR Sopot (Municipal Sports and Recreation Center) it is possible to collect from 180 to 796 tons of wet weight from beaches for the season. IO PAN (Institute of Oceanology, Polish Academy of Sciences) estimated this amount at 220 - 440 tons per season (Hansson et al., 2012).

BEACH WRACK AS COMPOST IN FERTILIZER PRODUCTION

One of the idea of beach wrack utilization is used a reed beds system to obtain final product- more likely as fertilizer or as a additions / enrichment to compost. The reed system is related on the simulation of processes occurring in natural wetlands ecosystem. To array of this method's advantages could be included: simple construction of reed system; low invest and exploitation costs (Kołecka and Rohde, 2018); natural look, which is enable easy fit in existing landscape (Sobczyk and Sypuła, 2011); lack necessity use of chemicals; low emission and energy consumption (Obarska-Pempkowiak et al., 2015).

Technological aspects

Planned pilot reed system will used cubes, situated on the wooden pallets. As a filing will be used some aggregate, gravel and sand. On the layer of sand will be situate reed. Each cube will be divided into four parts. From the bottom of each part of cube will be lead out drain pipe, which will drain away reject water and will introduce air to the reed system. In different parts of cube will be put different form of algae structure or mix algae with addition of compost in the different ratio.

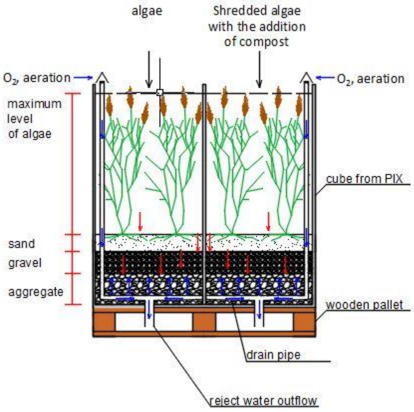

Figure 1. Scheme of pilot reed system based on cube's modules (own study)

Management aspects

Different amounts and seasonally occur of beach wrack are not problems for the reed system, because it works in an alternating cycle. Such a solution would cause the reuse of biogenic compounds, thus entering the circular economy. What's more, the reed system can be built close to the beach, which reduces the distance needed to transport the beach wrack. The system can be used to build and reconstruct the dunes. Reed system produced fertilize, which could be income and additional advantage for potential users. The reed system will be profitable, if it will be situated in neighborhood of place where beach wrack is collected. High water content makes transport for a long distance too expensive. For the reed system necessary is adequate surface. It could be a problem for potential interested invest. In addition different amendments like mature compost or biopreparates to enhance the decay are to be tested.

SUMMARY

Beach wrack is a specific problem. It is necessary to do research to management material from beaches located at highly eutrophicated water reservoirs such as the Baltic Sea. Collecting beach material and using it on a reed system, seems to be good idea.

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Performance Assessment of a Constructed Wetland Treating Agricultural Drainage Water after a Decade of Operation

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INTRODUCTION

Agricultural drainage water is one of the most important non-point sources of pollution, and, besides other problems, it can cause eutrophication of water ecosystems because of nutrients presence (Bruun et al., 2016). Therefore, it is important to treat agricultural drainage water before it reaches other ecosystems. Constructed wetlands (CWs) are man-made technologies that use processes occurring in natural wetlands in a controlled way in order to treat wastewater (Vymazal, 2005), and they can be of two basic types: free water surface CWs (SFCW) (water flows above the substrate and is in direct contact with the atmosphere) and subsurface flow CWs (water flows through the substrate, below the surface) (Kadlec and Wallace, 2009). Their advantages are that they can deal with varied and not constant flow, low cost operation and the fact that they do not require constant maintenance.

SFCWs are the type of CWs that are usually used to treat agricultural drainage water (Lavrnić et al., 2018). However, due to presence of sediments and plants development its efficiency can reduce over the years and therefore increase pollutant load to the nearby ecosystems. The goal of this study was to compare performance of a SFCW built in 2001 during two different rain events (in 2005 and 2018) in order to estimate if its ability to remove pollution loads decreased after 13 years of opeation.

MATERIALS AND METHODS

The system monitored is a SFCW located near the village of Budrio (Bologna, Italy). It was built in 2001 in order to treat drainage water coming from a 12.5 ha experimental farm operated by Land Reclamation Consortium Canale Emiliano Romagnolo. The whole farm area is drained into the central ditch from where water is pumped into the SFCW, that has a surface area of 0.4 ha and a maximum depth of 0.4 m.

The system is equipped with an automatic sampler, flow meters and probes that measure level of water inside the ditch and SFCW itself. In addition, atmospheric conditions (temperature and precipitation) were measured onsite, 500 m from the system. The collected inflow and outflow samples were tested for concentrations of total suspended solids (TSS), total nitrogen (TN) and total phosphorus (TP). Hydraulic retention time during the two events was established using the following equation:

$$HRT = \frac{V}{Q_{average}} . \quad (1)$$

RESULTS AND DISCUSSION

The two events occurred during the same period of year, with similar duration and atmospheric conditions (Table 1). However, water flows at inlet and outlet of the system were rather different and the second event had 4 times higher inflow comparing to the first one. In addition, water losses (e.g. infiltration and evapotranspiration) were higher in 2005 (40 %) than in 2018 (25 %). One of the explanations is that the infiltration reduced over the course of years due to sedimentation and pores occlusion.

Table 1. Summary of the two events analysed

	Event 1			Event 2		
Duration	24th February - 5th May 2005			3rd February - 25th April 2018		
Rain (mm)	173			266		
Temperature (°C)	10.3			8.5		
	Inflow	Outflow	Difference	Inflow	Outflow	Difference
Volume (m^3)	4.840	2.924	40%	16.463	12.285	25%
TSS (kg)	-	-	-	2030	927	54%
TN (kg)	67	51	24%	202	122	40%
TP (g)	916	1305	-42%	327	617	-89%

The removal efficiency of TN was higher during the second event, although it had a much lower HRT than the first event (8.4 d < 27.0 d). TP load, on the other hand, increased from inlet to outlet for both events, probably as a result of a sudden flush out of the soil particles containing this nutrient (Kynkaanniemi et al., 2018). As for TSS removal, it was rather high during the second event (54 %), but unfortunately its values for the first event were not measured and therefore it was not possible to make a comparison.

The results obtained suggest that the system did not lose its efficiency after 13 years of operation and that it can still be considered as a viable treatment option for the agricultural drainage water coming from the farm.

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Geo-statistics for Understanding Groundwater Conditions and Lateral Movement of Contaminants

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INTRODUCTION

Availability of safe drinking water has created a challenging situation around the world. Today preservation of natural resources has become a vital issue due to an exponential increase in their demand to support sustainable living scenario over earth (Caizhi et al., 2016). In addition to climate change, over exploitations of groundwater to meet need of increasing population, urban sprawl with increasing pervious surfaces and modern living standards are also casting bad impacts on this precious resource (Abbas et al., 2015). Therefore, conservation of groundwater resources has gained an inevitable attention of many policy makers and researchers regarding their monitoring and quality control. Rather than the fact of invisibility of groundwater, sampling of groundwater provides a deep insight in its quality assessment (Jang et al., 2017). Many studies have proposed that geostatistical spatial algorithms provide effective toolset to examine local ecological factors caused by any variable using their spatial distribution. Although interpretation of groundwater quality of a region is important but determination of potential regions of influencing events is equally significant (Mahmood et al., 2016). This work has been done to expand potential utilization of geo-statistical techniques to understand subsurface aquifers.

MATERIALS AND METHODS

Residential area of Lahore metropolitan, Pakistan has been chosen as the region for test case study of the proposed idea. Spatial statistics based hotspot analysis has been performed over evenly distributed point observations generated from existing randomly distributed drinking water supply units. Transformation of observations from random samples to uniform grid has been made using optimized spatial interpolation. For the purpose of regularizing hotspot input data all the available interpolators have been compared using least Root Mean Square Error (RMSE) and Mean Error (ME) and finally the best option has been used. The Gettis ord Gi* statistics (Ord and Gettis, 1995), used for hotspots identification is dependent on the distance of neighbourhood of each of the observation point in the grid.

RESULTS

The study is based on the hypothesis that optimization of this neighbourhood distance to achieve clarity in the hotspots can be a parameter to describe nature of the underlying aquifer and spread of a particular contaminant through it. For the purpose of this study Ca and Mg have been taken as the test water quality parameters. Results of spatial distribution of Gettis ord Gi* statistics at various test neighbourhood distances have been shown in Figure 1 and Figure 2. Clarity of spatial distribution and segregation of major water quality zones in the study area for both of the parameters have been obtained at 700 m as a radial distance of neighbourhood. This long distance dependency of values is showing that the aquifer is contiguous in its nature with no lithological barrier to prevent any horizontal movement and hence, mixing of water and these contaminants throughout the area.

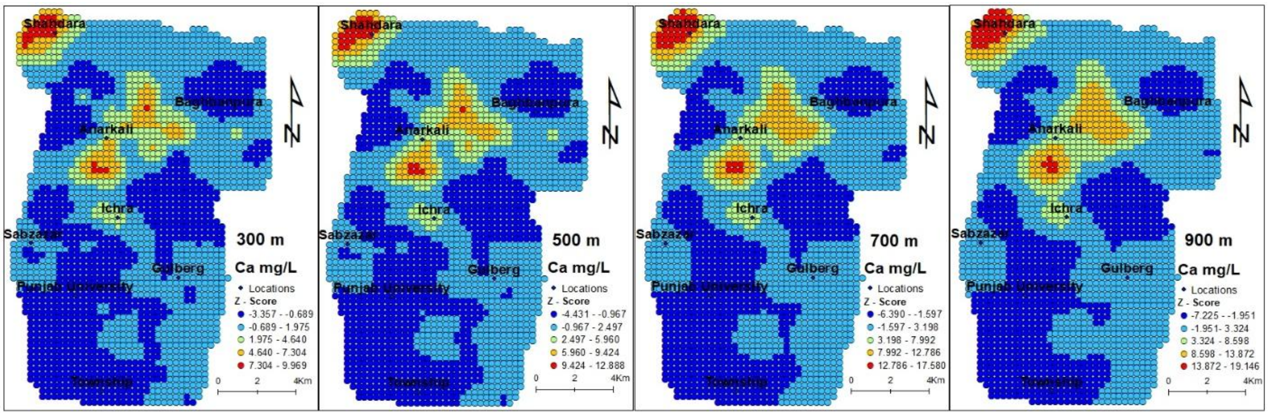

Figure 1. Comparison of different distance threshold values for Ca

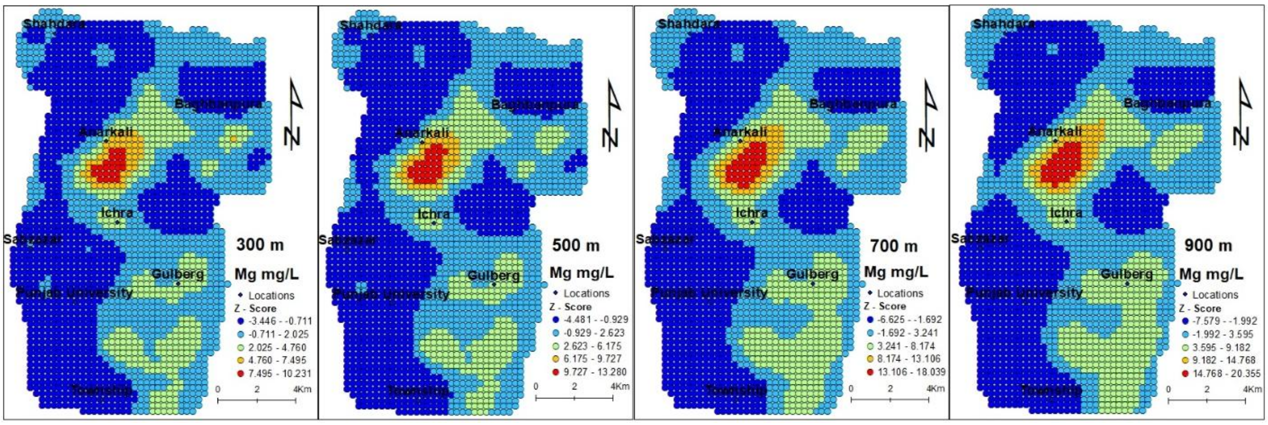

Figure 2. Comparison of different distance threshold values for Mg

CONCLUSIONS

On the basis of results proving study hypothesis, it is recommended that optimization of the neighbourhood radius in Gettis ord Gi* statistics can be an alternate method to understand type of groundwater aquifer and spread potential of a particular contaminant through it.

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Sensitivity Analysis and Vulnerability Assessment of Aquifer Using DRASTIC Model

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INTRODUTION

Groundwater is the most important source of several demands in most regions of Iran. Intensive agriculture activities caused water pollution on regional scale of the western Iran. DRASTIC is the most widely method used to evaluate potential contaminations of aquifers (Al-Abadi et al., 2017). The purpose of this research was to analysis a framework to use in groundwater protection and also to evaluate the vulnerability of these resources for contamination, using the DRASTIC index as well as the GIS capabilities. This study involves generation of an ArcGIS-based mapping system designed to allow evaluation of local contamination potential of groundwater, especially on the area such as Malayer plain of Iran.

MATERIALS AND METHODS

The Malayer plain aquifer is unconfined alluvial (519 km^2) situated over a schist bedrock. Its thickness varies from 8 to 66 m, with a water table depth of 3-10 meters. The transmissivity of the groundwater ranges between 261 and 1549 m^2/day. The main agricultural products in the region include wheat, barley, sugar beet and vegetables. Also, horticultural products include grape, almond, walnut, apricot and apple. The dataset included maps of soil texture, rainfall, lands using, water table level, soil permeability, digital elevation model, wells logging and nitrate rate of 32 monitoring wells. The water table dynamic was observed from 39 monitoring wells during 2017-2018. The nitrate concentration data were classified into low, moderate and high rate groups. A GIS-based DRASTIC model applied in order to evaluate vulnerability of the aquifer. The observed nitrate value was used for the model validation process (Akhavan et al., 2010). The DRASTIC local vulnerability classification consisted of the area with low, moderate and high rates of nitrate in the groundwater. The correlation coefficient (r) was calculated between the 3 groups nitrate data (as the independent variable) and the 3 groups of vulnerability potentials of the area resulted by DRASTIC model (as the dependent variable), in order to show the relationships ($p < 0.05$) between the 7 model parameters and water nitrate as an important contamination indicator. In order to identify the more vulnerable area of the plain, the sensitivity procedure of the model verified using two tests: i) the map removal sensitivity analysis and ii) the single-parameter sensitivity analysis. During this analysis, the effective weight (real) of each parameter and its theoretical (assigned) weight was compared.

RESULTS

The DRASTIC vulnerability index

The vulnerability map was obtained as a sum of the seven provided maps, after multiplying each map with its standard ratings and weights. The map multiplication and summation was conducted using the raster calculator of Spatial Analyst Tool in ArcGIS. As a result of potential of pollution (based on the DRASTIC index), 21.2, 77.4 and 1.4 % of the area were located in the low, moderate and high vulnerable zones with, respectively. This high vulnerable area was located in the southern part of the plain. This was due to the combination effect of gentle slope, high-porous vadose and aquifer milieu, as well as the other DRASTIC parameters that carried out a high potential of contamination. The r rate between the model parameters and the nitrate layer was about 0.67 (p <0.05) that mostly confirmed the accuracy of the results of DRASTIC model.

Map removal sensitivity analysis

Sensitivity of the model was analysis by the removing data procedure. The raster map of the area included a topography network constructed of 51889 cellules (100 m×100 m). The most sensitive parameters of groundwater contamination were net recharge, impact of vadose zone, soil media, water table depth, aquifer media and topography, respectively. The hydraulic conductivity illustrated the lowest sensitivity value. All of the parameters had a very similar effect but the higher rate of the vulnerability index performed from removal of the net recharge from the computation, while Mohammadi et al. (2009) found the topography as more important parameter in another study area. Also, the results of the sensitivity analysis in the studies of Rahman (2008) showed that the net recharge layer had the most important parameter in assessing the vulnerability of their study areas that was in agreement with the result of our research.

Single-parameter sensitivity analysis

The single-parameter sensitivity analysis was normally used to compare “theoretical” weights with “effective” weights. The effective weights of the DRASTIC parameter of this research showed some deviation from that of the theoretical weights (averagely about 4.52). Net recharge (24.09 %), aquifer media (14.42 %) and topography (8.79 %) were the most effective parameters in the vulnerability assessment, respectively, that were in agreement with the result of the map removal sensitivity analysis. The effective weights of this two parameters exceeds the theoretical weights assigned to it by DRASTIC model (17.39 %). All other layers showed lower effective weights when compared with their theoretical weights. The difference between these two weights was highly noticed in the water table depth that means the theoretical weight of this parameter should be revised for vulnerability index.

DISCUSSION

This paper has focused on the aquifer vulnerability of plains by employing the empirical index of DRASTIC model. Seven environmental parameters of the study area were used to represent the natural hydro-geological setting of the aquifer. The results revealed that a large part of the groundwater in Malayer plain was under moderate vulnerable zones. The sensitivity analysis showed that all the parameters had important role in vulnerability index and should be used for assessing of aquifer’s potential of contamination.

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The Mobility of Heavy Metals in the Water Column with Reference to Sediments Deposited in Short Urban Streams - Possibility of Water Re-contamination and Health Risk

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INTRODUCTION

One of the most persistent and toxic pollutants associated with cities development are heavy metals (HMs) (Alahabadi and Malvandi, 2018). Large uncontrolled metal inputs from industrial and urban sources have contributed to increased rivers and streams contamination. Throughout the hydrological cycle, 99 % of HMs are stored in sediments, that, therefore, are the major sinks and carriers for contaminants in aquatic environments (Bartoli et al., 2012). Far less than 1 % of contaminants remain dissolved in water. The water quality is, therefore, a temporary reflection of environmental pollution (Omwene et al., 2018). However, HMs may also directly pollute the raw water, resulting in sublethal effects or death in aquatic organisms and accumulate in crops through irrigation (Pekey, 2006). Little is known as regards the influence of possible health risk due to HMs sediments contamination. The chemical forms and metal speciation are important factors for the fate and transport of HMs in sediments. The association of HMs with various geochemical phases in sediments influence the overall behaviours of HMs in the aquatic environment (Islam et al., 2015). The field study attempts to give a partial posted answers: (1) how spatial distribution of HMS changes during the flow in urban streams, (2) with what phase are the HMs connected - is there any possibility of water re-contamination, (3) how high is the health risk for human, and (4) how nearby area affect the sediments contamination.

MATERIALS & METHODS

Two urban streams in Gdansk were selected to investigation. Several retention tanks (RTs) located on the streams were investigated. The core samples of sediments (including the depths of 0-2, 8-10, 16-18, and 24-26 cm) were collected at two sites (I- inflow and O- outflow) from six retention tanks. The sequential extraction was performed using the the 3-step BCR® method. ICP-MS were used to assess the HMs (Zn, Cu, Pb, Ni, Cr, and Cd) concentrations.

RESULTS & DISCUSSION

The highest concentrations of Pb in sediments from Ogrodowa and Srebrniki were found in the top layer of sediments (0-2 cm): 217 and 309 mg/kg d.w. for I and O at Ogrodowa and 25.1 and 33.1 at I and O in Srebrniki RT. The concentration of Pb decreases with depth to 24.5 and 21.4 in the deepest layer (24-26 cm) at I and O in Ogrodowa and to 8.70 and 9.80 at I and O respectively in Srebrniki RT. The percentage share of four fractions distinguished by BCR method is presented in Figure1. In both sites, the greater part of Pb is connected with the immobile fraction – F4, the rest of them with F3 (organic fraction). The analysis did not distinguish any part of the mobile fraction. Basing on this we can exclude the possibility of re-contamination of water.

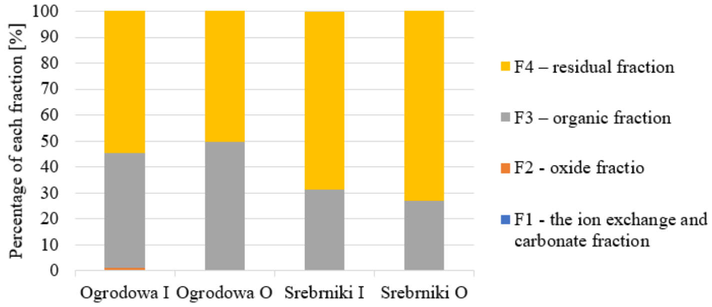

Figure 1. Sequential extraction results for Pb in top layer of core (0-2 cm) in Ogrodowa and Srebrniki RTs

Figure 2 shows the buffer zones which could be distinguished nearby each RT. For Ogrodowa RT the buffer zones 1 and 2 constitute only 6 % of the considered area, the remaining part is under urban pressures. However, in the case of Srebrniki RT both zones constitute about 60 % of the area. In accordance with Green Infrastructure aspects, the modern approach is to plan natural or semi-natural areas in the cities.

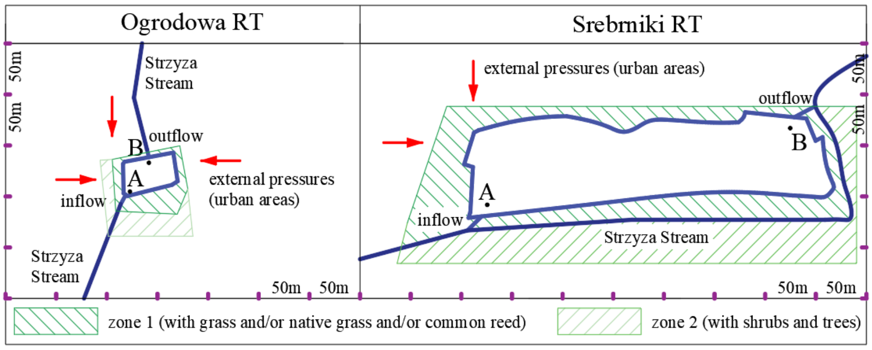

Figure 2. The location of I and O at Ogrodowa and Srebrniki RTs with establishing the buffer zones at nearby area of analyzed RTs

CONCLUSIONS

RTs retain the most of HMs transported with suspended solids along streams. The spatial distribution change in subsequent RTs, as well as the vertical distribution. Basing on Ogrodowa and Srebrniki RTs it can be conclude that Green Infrastructure fulfill environmental functions to protect the water and sediments contamination.

ACKNOWLEDGEMENTS

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Statistical Description of Time Series of Water Consumption in the Consumption Area

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INTRODUCTION

For the efficient operation and management of the drinking water distribution systems (DWDSs) it is necessary to have a detailed overview of the technical and hydraulic parameters of the network. One of the basic entry data is the water consumption in a consumption area. The analysis of water consumption determines the basic DWDS data, thanks to which we may consider other technical interventions (e.g. reduction or increase of pipeline capacity). Such data include determination of average and maximum consumption per day, maximum consumption per hour, minimum night flow, minimum water consumption per hour respectively. The determination of the minimum night flow, which is used to evaluate the water losses from the DWDSs, is essential. For DWDSs, the design or redesign is usually based on mathematical modelling and simulation methods (Kovar et al., 2014).

Reducing water losses has been one of the priorities of water utilities for a long time. With the reduction of water losses, the optimization of pressure conditions in the DWDS is very closely related (Tuhovcak et al., 2018). Water losses is unavoidable part of the MNF. The lowest technically achievable annual volume of Real Losses, at the current operating pressure, is the Unavoidable Annual Real Losses (Lambert and Fantozzi, 2005). In connection with the drought and the related decrease in the capacity of some water sources in the Czech Republic, the issue of reduction of water losses has become a populist slogan used for political purposes, which creates even greater pressure on water utilities.

Water losses in the Czech Republic

The level of water losses in the Czech Republic is generally very good even in comparison with economically more advanced countries. Water losses have been systematically reduced since 1994. One of the most used characteristic of water losses is % NRW (non-revenue water). The average value of % NFW was 16.4 % in the Czech Republic in 2017.

Water demand in the Czech Republic

Another characteristic of Czech water management is specific water demand (q_{spec}). Its level has been rapidly decreased during the past 30 years. In 1989, specific water demand of households was 171 litters per person per day, in 2017 it was only 88.7 litters per person per day. With actual level of q_{spec} per households, the Czech Republic is categorized to the group of countries with lower water demand. Water demand is influenced by several factors (Nguyen and Teller, 2018).

This article describes how to determine the basic characteristics of water consumption using statistical methods, thereby speeding up and simplifying the entire process of water consumption analysis.

METHODOLOGY

The statistical description of the time series of water consumption was performed using statistical functions of MS Office Excel software. Maximum water consumption per hour – Q_h and minimum night flow – MNF were described by quantiles (or percentiles) which are defined as statistical characteristics of the statistical file level indicating the magnitude of the phenomenon in a given set of data.

Verification of specified percentile levels

The water consumption values established as percentiles were compared with the MNF and Q_h determined by other methods to confirm the correctness of the selected percentiles. The following statistical methods and quantities were used:
Water consumption analysis and file cleaning under 3σ-rule. This methodology is based on the precondition that the relevant statistical set values are at a maximum distance of 3 times the standard deviation from the mean value.

Frequency analysis of MNF and Q_h values at a selected interval. The verification was based on the fact that the MNF occurs in the time interval 2.00–4.00 a.m. and the Q_h in 6.00–9.00 p.m.

Modus. The mode determination was only applicable to those input data files that were rounded by average hourly flow rates (to tenths, quarters, or half integers).

CASE STUDIES

The minimum and maximum consumptions per hour were determined on real DWDSs. The water consumption analysis of the above statistical methods was performed on a total of 9 district metered areas (DMAs). The rural character of the development is typical for all analysed DMAs.

CONCLUSION

The basic characteristics of water consumption can be determined in several ways. The advantage of the presented methodology based on the determination of the percentile is speed and simplicity. This methodology for the determination of MNF and Q_h does not need to sort the input data into 24-hour sub sets. At the same time, it is not necessary to create hourly averages if we have available flow rates in a shorter time step. The determined percentile values correspond to the MNF and maximum hourly consumption in selected consumption areas in the Czech Republic.

ACKNOWLEDGEMENT

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Sustainable Measures in Water Softening Technologies

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INTRODUCTION

Few countries have the natural and financial resources to continue increasing water supplies. The alternative is to make better use of available resources. The challenge is for developed nations to lower industrial water use and for developing countries to industrialize without substantially increasing water demand and water pollution (UN, 2018). This research is connected with finding ways for water softening technologies to become more sustainable. It touches mostly liming method combined with coagulation, which is usually held in clarifiers with suspended sediment and mechanical filters. Mentioned method requires heating of surface water to specific temperatures, technological scheme is bulky, uses additional pumping equipment, has big quantity of pipelines and valves, what are considerable disadvantages and cause significant costs for resources. Applying liming on expanded polystyrene filters with increasing layer of suspended sediment allows to make steps in to sustainability in water softening technologies.

MATERIALS AND METHODS

Experimental research of water softening consists in applying the ascending filtration type, what allows to accumulate sediment in the under filtering area (Orlov et al., 1999) with using lime solution, and expanded polystyrene granules. Water mixes with lime in the contact tube and then through a layer of suspended sediment which is performed gradually increasing, and after that passes through floating expanded polystyrene backfill (Orlov et al., 2013).

Experimental industrial plant, was installed and connected to the existing technological scheme of chemical water treatment department at chemical enterprise, represented on Fig. 1. We served river water and lime solution from lime preparation workshop with concentration of calcium hydrate 4 %.

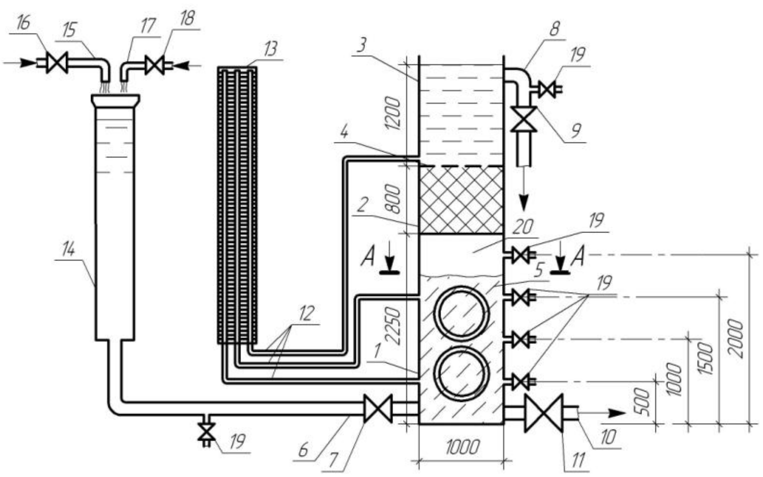

Figure 1. Experimental industrial plant for water softening: 1 – frame; 2 – expanded polystyrene filling; 3 – above filtering area; 4 – holding grate; 5 – suspended sediment layer; 6 – pipeline of river water mixed with lime solution;

7 – valve on pipeline of river water mixed with lime solution; 8 – softened filtered water offtake; 9 – valve on softened filtered water offtake; 10 – washing water offtake; 11 – valve on washing water offtake; 12 – piezometer; 13 – shield of piezometers; 14 – contact tube; 15 – river water supply pipeline; 16 – valve on river water supply pipeline; 17 – lime solution pipeline; 18 – valve on lime solution pipeline; 19 – samples valve; 20 – neutral area

RESULTS

In industrial conditions maximum achieved decrease effect on water quality characteristics was: for total hardness – 56 %, alkalinity – 84 %. Based on achieved experimental results the most optimal filtering rate was 3.5 m/h (Odud et al., 2017).

For calculation of the expected economic effect from the implementation of the developed method we use equation (1):

$$EE = E_{o.n.} + E_c + E_{e.c.} + E_e \text{, UAH/year} \quad (1)$$

where $E_{o.n.}$ – water expenses for own needs (washing, etc.), UAH/year;

E_c – expenses for coagulant(ferrum sulfate), UAH/year;

$E_{e.c.}$ – electricity expenses for coagulant (ferrum sulfate) dosing pumps, UAH/year;

E_e – electricity expenses for washing pumps, UAH/year.

Expected economic effect from the implementation of liming on expanded polystyrene filters with increasing layer of suspended sediment is 557010.7 UAH/year. Due to exchange rate for 24th December 2017 this amount wass 16861.5 EUR/year (Odud, 2017), for 1st May 2019 – 18806.59 EUR/year.

In quantity measures it was calculated that with applying proposed method we can reduce consumption of some resources:

- water expenses for own needs – 60 thsd. m^3/year;
- coagulant (ferrum sulfate) – 45 ton/year;
- electricity expenses for coagulant (ferrum sulfate) dosing pumps – 190080 kVt/year;
- electricity expenses for washing pumps – 38400 kVt/year.

CONCLUSIONS

The proposed method allows to keep water with required quality parameters for the exact needs at chemical enterprises and similar industries. Implementing of liming on expanded polystyrene filters with increasing layer of suspended sediment gives possibility to intensify, simplify and reduce resources and cost expenses of the existing technological scheme and shows measures that can be applied to achieve sustainability in water softening technologies.

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Fouling Index Change Characteristics during the Condensation Process of Algal Scum in the Sic Based Ceramic Membrane

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INTRODUCTION

Ceramic membranes have been used in water treatment plants and sewage treatment plants due to their small area requirement for installation and high solids separation efficiency. In addition, operational parameters such as critical flux and trans-membrane pressure changes have been widely studied in membrane filtration processes (Choi et al., 2005; Wu et al., 2018). In this study, we have investigated reversible and irreversible resistance for the various coagulant dosages and fouling capacity of the ceramic membrane in terms of Silt Density Index (SDI).

MATERIALS AND METHODS

Characteristics of the feed water. The feed water used in the experiment was at the bend of the lake located in the water source protection area, where algal bloom frequently occurs every year. Table 1 shows the characteristics of the feed water used in the experiment.

Table 1. Characteristics of the feed water

Item	Values	Unit
Total number of algal cells	262.434	cells/mL
Cyanobacteria	262.000	cells/mL
Chlorophyta	116	cells/mL
Diatom	318	cells/mL

Experimental Set-Up. The membrane used in the study was a submerged silicon carbide(SiC) flat MF (Microfiltration) membrane with an effective area of 0.0652 m^2 and a nominal pore size of 0.1 μm of which pure water permeability was 5,000 LMH/bar at 20°C.

The ceramic membrane was immersed in a 16.4L reactor filled with the feed water. The treated water was passed through a membrane module and discharged directly from the reactor using a peristatic pump (EMS-2000S, Korea). To monitor TMP changes over time, a pressure transducer (PTP708 Tuopo Electric, China) was installed. The membrane was operated to maintain a constant flux of 60 LMH at 20 °C.

PAC (Polyaluminum Chloride) was used as a coagulant and reversible and irreversible filtration resistance and fouling index were investigated while PAC dosage incrementally increased from 50 to 250 mg/L in increments of 50 mg/L.

RESULTS AND DISCUSSION

Figure 1 shows the change of filtration resistance when coagulant dosage varies. Both reversible and irreversible filtration resistance decreased rapidly when the coagulant dosage increased, and the degree of filtration resistance reduction was relatively small at the dosage of 150 mg/L or more.

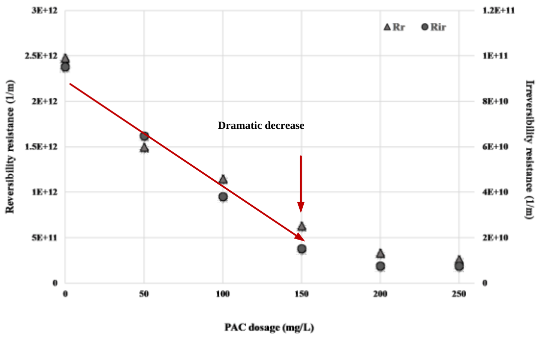

Figure 1. Filtration resistance with various coagulant dosages

Membrane contamination tendency can be easily evaluated using the following equation.

$$SDI = (1 - t_i/t_f) \times 100/t_T, \quad (1)$$

where T is total test in minutes, t_i is initial time (sec) to obtain sample and t_f is time (in sec) to obtain sample after 15 minutes.

As a result of this study using algal scum as feed water, it was found that the SDI decreased when the coagulant dosage increased (Figure 2).

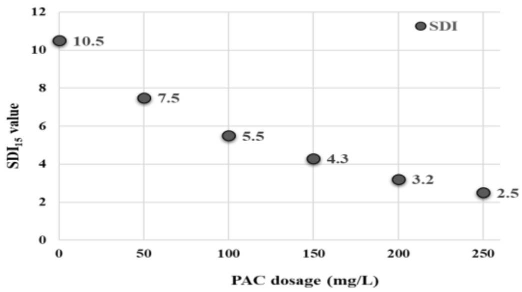

Figure 2. Comparison SDI15 values of SiC ceramic membrane permeate

CONCLUSIONS

This study investigated the fouling characteristics of algal scum using silicon carbide membrane. When the membrane flux was fixed at 60LMH, it was found that both reversible and irreversible resistance decreased rapidly as the amount of coagulant dosed increased until optimum coagulant injection (PAC 200mg/L) was reached, and membrane contamination tendency also decreased. In addition, as the amount of coagulant increased, the SDI(Silt density index) decreased.

ACKNOWLEDGEMENT

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The Use of a Check-List to Support Water Emission Limit Values in a Pulp and Paper Industry

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INTRODUCTION

On a climate change scenario the increase for water demand is showing that in a growing number of countries large quantities of high quality water may no longer be available at low cost. Therefore, some alternative water sources are being used with an increased attention to water recycling and reuse. This paper shows the results of a European project (Farabegoli et al., 2017) that aimed to deal with the water management and reuse inside Industrial Emissions Directive (IED) industries. One of the major outcomes of the project was that the water management inside industrial sectors should take into account that the water use efficiency must be seen from quantity perspective without jeopardizing the quality of wastewaters and water sources for direct use or reuse. The information collected on the project contributed for the development of a check-list to help permit writers, in particular, for wastewater discharges, that allows to verify the needs of going beyond Best Available Technologies (BAT) to not put at risk the receiving water bodies status. The aim of paper is to test the application of the developed check-list to a real case study, namely a pulp and paper industry, taking into account the complexity of balances needed in terms of quantity and quality of water in the industrial water cycle use.

CASE STUDY DESCRIPTION AND METHODOLOGY

The case study is an IED installation (pulp mill for the production of bleached craft) that discharges more than 95 % of the total organic load in the catchment area, where water body has a status less than good, due to problems linked with organic matter and nutrients (phosphorous). In 2017, a severe drought decreased significantly the water flow in the river and the treated wastewater (TWW) discharges from this installation negatively affected its quality, where, in a certain period, downstream (in a dam) near surface were observed levels of zero mg/l of dissolved oxygen.

The environmental permit had only included Emission Limit Values (ELV) supported exclusively on the BAT reference documents (BREF) that were being complied. However, to ensure that discharge of TWW complies with the Water Framework Directive (WFD) requirements, some aspects need to be checked to guarantee that the permitting process is both IED and WFD proof. Hence, to ensure the definition of ELV that avoids degradation of the water status a list of tasks, defined as check-list, was developed in the first phase of the mentioned European project, which links the water body characteristics, namely status and uses with the discharge, to access the need of different ELV from the ones defined on respective BREF documents. In this case study, the application of the check-list revealed the need of the definition of adjusted ELV based on a combined approach as established on the WFD, i.e., maximum discharge values that can be absorbed by the river without compromising the improvement of the water quality and the water body status. To ensure full protection, the discharge standards, besides the appropriate ELV also need to include specific compliance rules and an adjusted monitoring program for the water body, to access the real TWW discharge impacts. To ensure protection all over the year, due to the seasoning changes, three levels of ELV are also proposed: wet period, dry season and exceptional conditions.

The real impact of the TWW discharge was evaluated by the use of data from 2012 to 2017 from the installation self-monitoring program and from the water body monitoring program (downstream). A nonlinear regression model, expressed as exponential function, was applied for the parameters COD, BOD_5, Nt and Pt and a strong correlation (correlation coefficient, R, superior to 0.70) was found, when data from discharges and from the water body was ordered by its magnitude. For each of the periods mentioned above, three types of ELV with specific goals are also defined (punctual concentration, daily and yearly loads), with detailed compliance rules to guarantee the achievement of the goals i.e. protection of acute and chronic effects over the water body and the compliance of BAT-Associated Emission Level (BAT-AEL). Additionally to the ELV, a mixing zone is also provided to choose the location of the monitoring points in the water body and a complex monitoring program for it, upstream and downstream, is proposed to ensure that the discharge is not negatively affecting the surface water and at the same time rapidly detect any change on the pattern of the discharge. Another important aspect on this water management approach is that whenever is verified a decrease of the water quality downstream, the discharge conditions can be immediately turn into the more restrict ones. E.g., in wet season the water authority can indicate the need of the compliance of the dry season conditions or even the exceptional conditions.

CONCLUSIONS

From the application of the check-list it became clear that the use of the BAT-AEL would not allow the recovery of the water body, since the installation represents more than 95 % of the total discharged load in the catchment area. The use of a combined approach between the data from the receiving water body and self-monitoring data from the installation allowed the definition of new ELV that includes the real protection of the surface water, achieved by the management of several types of ELV and its variations according the seasons along the year, including severe climatic conditions. Another important aspect to consider is that the abstracted water needs to be balanced in situations where the river flow is very low. In this case, the discharge of TWW should be seen as a reuse to support the river and its ecosystems. However, this can only be achieved by an integrated water management inside installations to ensure the possible lowest abstraction and the highest discharge level quality to allow a lower consumption of water resources and a greater abatement of pollutants with a positive feedback on the quality of the water body.

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Constructed Wetlands as Nature-Based Solution for Stormwater and Agricultural Runoff Treatment

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INTRODUCTION

Agricultural systems are highly-dependent on artificial sources of nitrogen due to the absence of naturally-occurring nitrogen forms necessary for crop yield and production. Advancements in the field of environmental management, referred to as nature-based solutions (NBS), are new technologies devised to mitigate the negative impacts of anthropogenic activities in the ecosystem. Constructed wetlands (CW) are NBS for water used to treat agricultural runoff. CWs utilize physico-chemical and biological mechanisms to reduce the excessive nutrient concentration in water. This study evaluated the effectiveness of a CW treating runoff and discharge from an agricultural catchment area. The characteristics of accumulated sediments in the CW were also analyzed to determine the possibility of internal pollutant release within the system. Design considerations in developing agricultural CWs were also presented in this paper.

MATERIALS AND METHODS

The schematic diagram of the agricultural constructed wetland (ACW) located at Namsan-ri, Gongju City, South Korea was exhibited in Figure 1. The 3.282 m^2 CW treats agricultural and stormwater runoff from a 465 ha catchment area composed of 73 %, 25 % agricultural, and 2 % urban land use type. The CW has a total storage capacity of 2.957 m^3 and a hydraulic retention time (HRT) of 16.8 hours. A total of 28 events were monitored to assess the effectiveness of ACW in treating agricultural runoff and discharge. 17 events were monitored during dry days, whereas the remaining 11 events were observed on wet days. Water samples were collected on different treatment zones of the CW. Standard methods for the examination of water and wastewater were administered on the samples to determine the concentration of total nitrogen (TN) and total phosphorus (TP) in water. CW soils were also collected to determine the pollutant concentrations in the accumulated sediments.

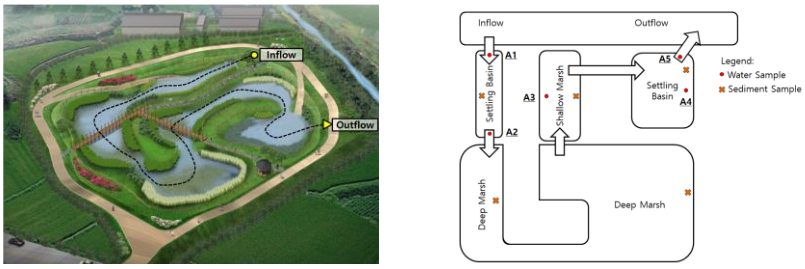

Figure 1. Schematic diagram of ACW

RESULTS AND DISCUSSION

For the monitored events, it was observed that the mean TN and TP influent concentrations were 17 % and 9 % higher, respectively on wet days as compared with dry days. Increased nitrogen (N) and phosphorus (P) concentrations can be attributed to the additional pollutant loading from the upstream catchment area. During storm events, runoff from agricultural areas may contain N- and P-enriched sediments that are directly deposited on natural streams resulting to elevated nutrient concentrations in water. As illustrated in Figure 2, the CW effectively reduced TN and TP concentrations in the influent. On dry days, the ACW was able to decrease mean influent TN and TP concentrations by 12 %, whereas an average of 21 % and 68 % reduction in TN and TP, respectively, were observed on wet days. Despite the higher pollutant concentrations on wet events, higher pollutant removal efficiencies were noted as a result of flow continuity and reduced HRT.

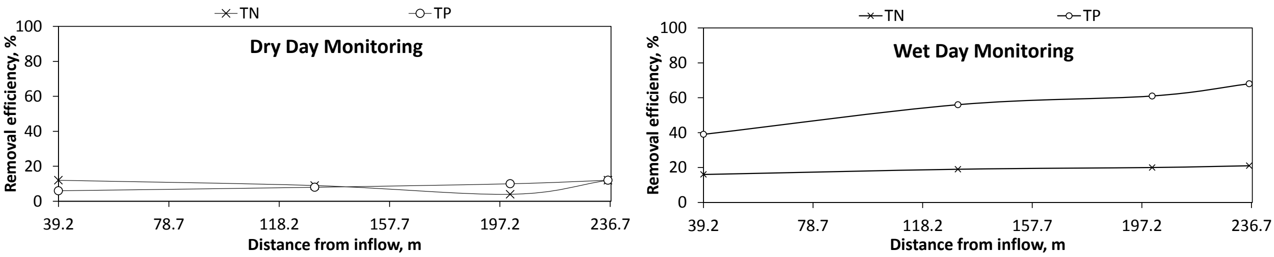

Figure 2. Average TN and TP removal efficiency for dry and wet day monitored events

Variations in sediment TN and TP concentrations were observed in each segment of the ACW. Mean TN concentration in the influent sedimentation zone (1542 mg/kg) was 238 % higher as compared to the mean sediment TN concentration in the effluent zone (457 mg/kg). On the other hand, mean sediment TP concentration in the effluent zone (1176 mg/kg) was 47 % greater in relation to the mean sediment TP concentration in the influent (797 mg/kg). Sediments tend to settle on the early stages of wetland treatment due to gravitational influence, thereby increasing the sediment nutrient concentration in the influent zone. Unlike some N forms (i.e. nitrate) that do not attach in soil particles and can move through the voids, P compounds are tightly-bound on sediments, resulting to accumulation in the effluent zone (Agriculture and Agri-Food Canada, 2016).

CONCLUSIONS

Untreated stormwater runoff and discharge from agricultural have adverse effects in aquatic ecosystems. For both storm and non-storm events, CWs were found to be effective means of reducing the excessive nutrient loads from agricultural activities. However, reduced N and P removal was observed on dry periods and low-flow events due to longer HRT. ACW functioned more efficiently with increased hydraulic loading due to the continuity of flow. Further analyses revealed that TN sediment concentration was reduced in the effluent zone due to leaching, whereas TP continuously accumulate throughout the treatment zones as a result of tight bond between sediments and P compounds. This study is beneficial in establishing the treatment mechanisms and design guidelines for CWs receiving surface runoff and discharge from agricultural areas.

ACKNOWLEDGEMENT

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Daily Rainfall-runoff Modelling by Support Vector Regression, Symbolic Regression and GR4J Models

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INTRODUCTION

Rainfall-runoff modelling is important for the improvement of water resources management and planning. In this study, performance of Support Vector Regression (SVR), Symbolic Regression based Genetic Programming (SR-GP) and Ge´nie Rural a` 4 parame`tres Journalier (GR4J) (Perrin et al., 2003) models were compared for daily rainfall-runoff modelling in two rivers, USA. As evaluation criteria, Nash Sutcliffe efficiency (NSE), root mean square error (RMSE) and Kling-Gupta efficiency (KGE) were used. Accordingly, it was obtained that GR4J lumped conceptual model yields better than SVR and SR-GP models in case of the utilization of same input variables. On the other hand, it was seen that selection of input variables affect the performance of SVR and SR-GP models, considerably.

DATA AND METHODOLOGY

To simulate runoff, daily precipitation (P), temperature (T) and streamflow (Q) data of Blanco River and Chunky River, which are located in USA, were used. Data cover the period of 01.01.1982-30.09.2002 for both rivers. 75 % of dataset was used for the training, whereas rest of dataset was used for testing. Statistical information about the precipitation, temperature and streamflow data was given in Table 1. Used data is part of the MOPEX dataset (URL 1, 2018). Evapotranspiration (E) was calculated by using the formula which was given by Oudin et al. (2005).

Table 1. Daily data statistics in used rivers

Rivers	Period	P		T		Q	
		Mean	Std.	Mean	Std.	Mean	Std.
		(mm)		(°C)		(mm/d)	
Blanco River	01.01.1982-30.09.2002	2.4	7.8	19	7.9	0.5	2
Chunky River	01.01.1982-30.09.2002	3.9	9.4	17.5	8	1.3	2.7

In order for rainfall-runoff modelling, SVR, SR-GP and GR4J daily lumped conceptual model were used. For SVR model, different kernel types such as linear and radial were chosen and cross-validation was performed to find the most convenient model. As for the SR-GP model, different parameter values of GP such as mutation and crossover probability were tried to obtain the most accurate prediction results. Finally, performance of GR4J model, which is lumped daily rainfall-runoff model, was investigated by using the airGR package (Coron et al., 2017; Coron et al., 2019) that is part of R software. To assess the performance of SVR, SR-GP and GR4J models, Nash Sutcliffe efficiency (NSE), root mean square error (RMSE) and Kling-Gupta efficiency (KGE) were used.

RESULTS

Forecasting results show that in case only P (t) and E (t) are used as input data, GR4J model performed better than SVR and SR-GP models. Daily rainfall-runoff modelling belongs to GR4J model for Blanco River was illustrated in Figure 1 as an example. However, it was also seen that choice of input variables has an important effect on the performance of SVR and SR-GP models.

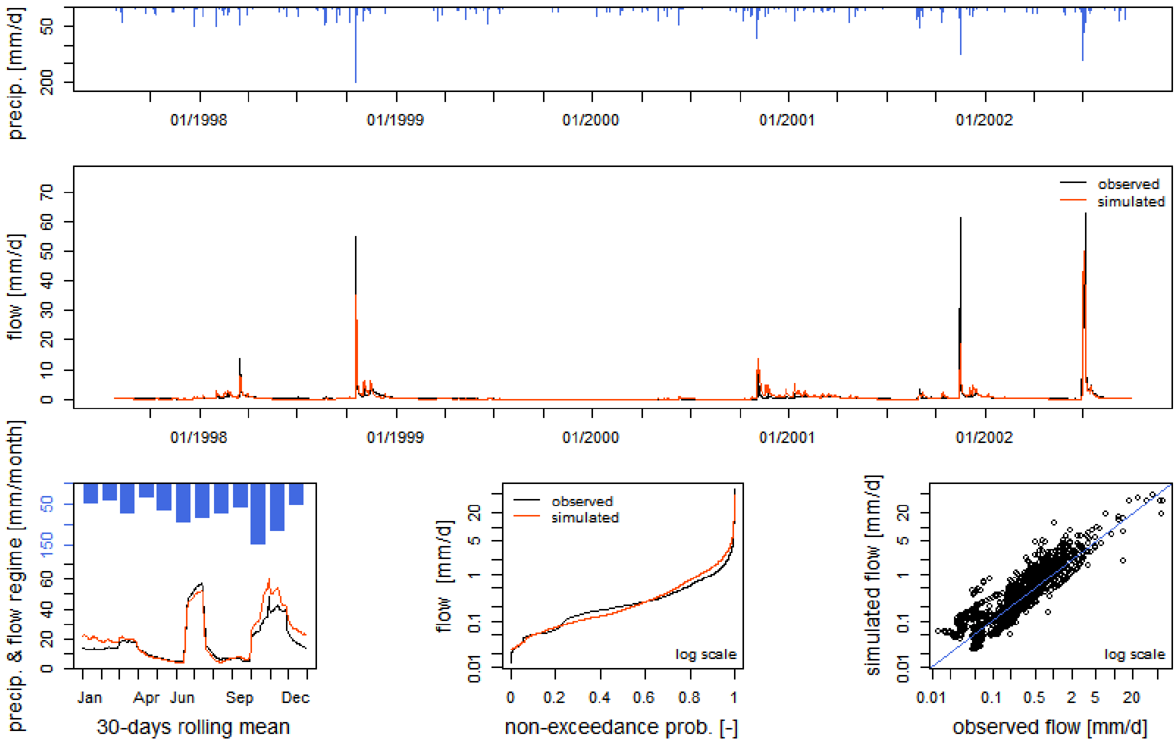

Figure 1. Simulation of rainfall-runoff modelling via GR4J model for test period in Blanco River

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Integrated Assessment of Technogenic Load on Water Ecosystems Based on Biodiversity and Hydrochemical Indexes

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INTRODUCTION

Existing methods for assessing the technogenic load do not allow an objective assessment of its level and the ecological state of water basins. The paper proposes an integrated approach to the integrated assessment of the ecological status of aquatic ecosystems. The data of seasonal long-term studies on indices and complex indicators for the northeastern part of the Gulf of Finland from 2015 to 2019 are summarized and analyzed.

METHODS AND MATERIALS

Assessment of technogenic load on aquatic ecosystems, due to the interaction of diverse factors, depends on a set of biotic and abiotic indicators and characteristics. This allows assessing the level of one or another technogenic impact, positive or negative, with specifying the list of impact indicators and methods for determining its absolute and relative values (Shishkin et al., 2018).

The methods of complex and integral assessments in the Russian and foreign practice are most widely disclosed by V. Shitikov with co-authors (Shitikov et al., 2003). The generalized assessment of the Shannon index and saprobity index by zooplankton, trophic state, and water pollution index (WPI) is given in Table 1.

Table 1. Generalized assessment of indices and water quality indicators (Stroganova, 2017)

Shannon Index	ITS	Environmental assessment of trophicity	Saprobity index	WPI	Pollution rate	Water quality class
>4.00	< 5.7 ±0.3	Ultraoligotrophic	≤0.50	<0.2	Very clean	I
2.51-4.00	6.3 ±0.3	Oligotrophic	0.51-1.50	0.2–1.0	Clean	II
2.01-2.5	7.0 ±0.3	Mesotrophic	1.51-2.50	1.0–2.0	Moderately polluted	III
1.01-2	7.7 ±0.3	Eutrophic	2.51-3.50	2.0–4.0	Polluted	IV
<1.00	> 8.3 ±0.3	Hyper-eutrophic	3.51-4.00	4.0–6.0	Dirty	V

The index of trophical state (ITS) is calculated on the basis of pH values and the level of water body saturation with dissolved oxygen. The Shannon index determines the species diversity of zooplankton and the trophic status of the water body.

The interrelation between WPI and the saprobity index is determined (Table 1.). The water pollution index is calculated using 6 hydrochemical indicators – ammonium, iron, phosphates, nitrites and limiting indicators - BOD_5 and dissolved oxygen:

$$\mathbf{WPI} = \frac{1}{n}\sum\nolimits_{n=i}^{n}\frac{c_i}{TLV_i}, \quad (1)$$

where C_i is concentration of the i^{th} component; n is the number of indicators used for calculating the index (n = 6); TLV_i is the established threshold limit value for the i^{th} component for the appropriate water body type (Shitikov et al., 2003).

RESULTS AND DISCUSSIONS

Based on theresearch results, the curves of seasonal changes in water quality indices of 20 water bodies of the Kurortny District of St. Petersburg and the Vyborgsky District of the Leningrad Region were plotted.

With the direct participation of the authors in conducting environmental monitoring of water bodies in the basin of the north-eastern part of the Gulf of Finland from 2015 to 2019, data were processed and the results obtained are presented in the diagram.

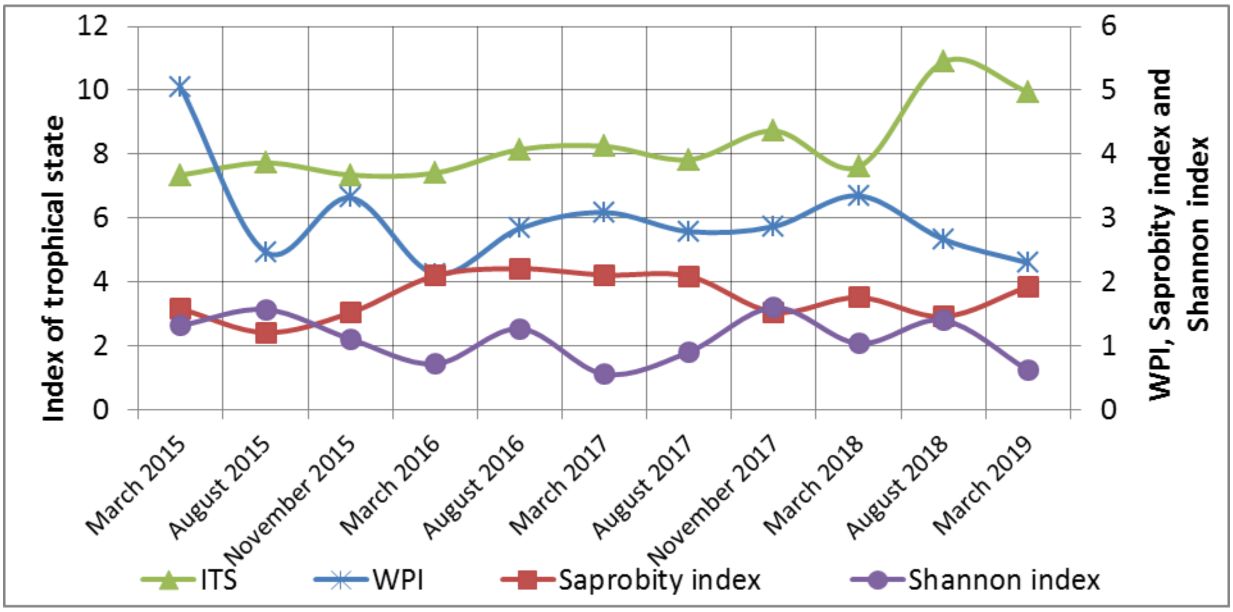

Figure 1. Seasonal changes in water quality indices of the studied aquatic ecosystems

The results of such studies are one of the basic information that predetermines the quantitative and qualitative assessment of the quality of water in water bodies and the visible anthropogenic load of the Kurortny District of St. Petersburg and the Vyborgsky District of the Leningrad Region. Seasonality was taken into account, on the basis of which it is possible to make a forecast of future values of pollutants in the water bodies. The combined use of hydrobiological and hydrochemical indicators allowed making the comprehensive assessment of water quality with its applying to regulation and load distribution among groups of water consumers.

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Synthesis and Performance Evaluation of Chitosan Membrane Filled with UiO-66 Nanoparticles for Dewatering of Biobutanol by Pervaporation

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INTRODUCTION

Butanol is mainly obtained from biomass by the fermentation technique. After the fermentation, the butanol is obtained as less than 3 % concentration. Therefore, the purification of butanol comprises of two stages: (i) the recovery of butanol from dilute aqueous solutions by distillation in order to obtain a high butanol-enriched mixture, and (ii) the dewatering of butanol in order to obtain a greater than 99.5 % concentration of butanol. In literature, enrichment of butanol had been studied greatly, but application of dewatering of butanol is limited. Dewatering of biobutanol has been carried out by using distillation, extraction, adsorption processes. These are very energy intensive and quite costly. In this study, pervaporation was used for dewatering of biobutanol in order to fill the knowledge gaps in literature. Pervaporation has recently gained great interest because of their unique properties such as low energy consumption, easy operation, low cost and high selectivity (Jie et al., 2018). In this study, mixed matrix membranes were prepared by using hydrophilic chitosan polymer and UiO-66 nanoparticlesfor the dewatering of butanol. UiO-66 loaded mixed matrix chitosan membrane showed a successful separation performance for the dewatering of butanol.

EXPERIMENTAL METHODS

UiO-66 Nanoparticle Synthesis

Zirconium (IV) chloride ($ZrCl_4$), terephthalic acid and acetic acid were mixed into dimethylformamide. The solution was stirred at 100 °C for 24 h. The UiO-66 nanoparticles were obtained by centrifugation and further purified by washing with fresh DMF (Naixin et al., 2017).

Membrane Preparation

1.1 wt.% of chitosan solution was prepared in aqueous acetic acid solution under stirring at 25 °C for 24 h. Chitosan membrane filled with UiO-66 nanoparticles were manufactured by certain amount UiO-66 addition. Firstly, UiO-66–water was mixed for 3 h. A little amount of chitosan membrane solution was added to the UiO-66 solution and UiO-66 particles were coated by the chitosan membrane solution. The mixed matrix membrane was poured on a clean plate and dried at room temperature. The obtained mixed matrix membrane was crosslinked with H_2SO_4 in 50% v/v aqueous acetone solutionfor 5 min.

Pervaporation Experiment

Pervaporation experiments were carried out in a laboratoryscale pervaporation system. It consisted of a membrane cell, agitator, thermocouple, Dewar flasks and a vacuum pump. Performance of pervaporation process was determined by calculation of flux and selectivity. The flux and selectivity values were determined as follows equations:

$$J = \frac{m}{A.t}, \tag{1}$$

$$\alpha = \frac{(y_a / y_b)_{permeate}}{(x_a / x_b)_{feed}}, \tag{2}$$

where J is theflux, m is the permeation mass, t is the time in Equation 1, y_a and x_a is the weight fraction of phenol in the permeate and feed streams, and y_b and x_b is the weight fraction of water in the permeate and feed streams in Equation 2.

RESULTS AND DISCUSSION

Pervaporation performance of UiO-66/Chitosan mixed matrix membranes for biobutanol dewatering

UiO-66 nanoparticle amount is an important factor for the separation performance of mixed matrix chitosan membranes. The separation performances of different UiO-66 nanoparticles loading membrane for butanol dewatering were investigated. As shown in Figure 1, with the loading of UiO-66 particles increased from 10 wt% to 30 wt%, the separation factor of the composite membrane increased while the permeate flux decreased. However, when the amount of UiO-66 particles further increased to 40 wt%, the separation factor of the mixed matrix chitosan membranes decreased while the permeate flux increased. This is probably due to the excessive amount leading to agglomeration of nanoparticles, they cannot be completely wrapped by chitosan. Therefore, the resulting defects will lead to the decrease of separation performance.

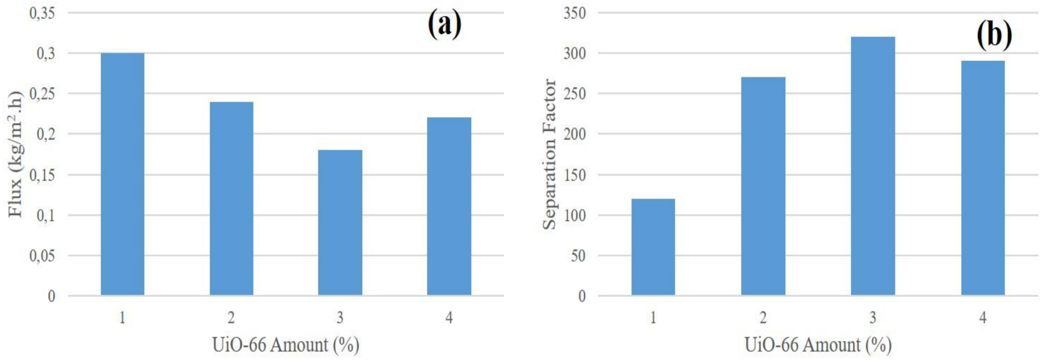

Figure 1. Effect of UiO-66 amount on flux and separation factor

CONCLUSIONS

In conclusion, UiO-66 nanoparticles were fabricated as porous fillers incorporated into chitosan because of their high thermal, water and acid stability. The mixed matrix membranes used for dewatering butanol/water mixtures. The obtained results showed comparable separation performance with the membranes reported in the reference. Therefore, these results indicated that UiO-66 nanoparticles can be used as a new membrane material for biobutanol dewatering.

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Agricultural Nutrient Inputs to the Bay of Puck from Small-size Watersheds in Relation to Agricultural Practices

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INTRODUCTION

Eutrophication continues to be one of the priority problems of many coastal marine waters and estuaries (Álvarez et al., 2017). Poland, as a large, densely populated state of the Baltic Region with dominating agricultural land use largely contributes to river-borne loads of N and P. While several studies concentrate on the catchments of major Polish rivers, the small catchments of Pomerania region are monitored extensively, even though some watercourses discharge to the areas of particular vulnerability, like the Bay of Puck. Herein, we examined the input of nutrients from three small first-order agricultural watersheds (Bladzikowski Stream, Gizdepka river and Mrzezino canal) in Pomerania region to the Bay of Puck in the view of the goals of the Baltic Sea Action Plan (BSAP) and Country Allocated Reduction Targets (CART).

MATERIALS & METHODS

Three watercourses in northern Poland located in Puck Municipality were analysed: Bladzikowski Stream (BS), Gizdepka river (G) and Mrzezino canal (M). All analysed watercourses outflow directly to the Bay of Puck and have artificially shaped and straightened river beds. Stream waters samples were collected between July 2017 and January 2019.

RESULTS & DISCUSSION

The structure of land use in the surveyed farms is diverse, clearly reflecting the differences between analysed watersheds. In all watersheds the arable farming constitute the majority of watershed (85 %, 70 %, and 49 % for BS, G, and M respectively). The rest part is covered by meadows (BS-9%, G-29%, M-49%), pasture (BS-4%, G-0%, M-3%), and remaining. The farm nutrient balance in the BS (Table 1) showed very broad range with max values for N – 172 kg/ha and for P – 24.9 kg/ha. In 3 of all 20 analysed farms consumption of N in mineral fertilizers exceeded 170 kg N/ha recommended in the ("Nitrates Directive," 1991). The average N and P surpluses for surveyed farms were equal to 96.4 kg/ha and 4.4 kg/ha, respectively, while the highest mean and median N surplus was found in Gizdepka river catchment.

In Figure 1 box-plot charts for nutrient concentrations: N_{tot} and P_{tot} in Bladzikowski Stream (BS), Gizdepka River (G) and Mrzezino (M) is presented.

Table 1. Characteristic values of farm nutrients balance and surplus of N and P in Bladzikowski Stream (BS) (Min - minimum value; Max - maximum value; SD – standard deviation)

Catchment	Mineral fertilization per unit of cultivated			Surplus			
	N, kg/ha	P, kg/ha	K, kg/ha	Surplus N	Surplus N kg	Surplus P	Surplus P kg
Min/ BS	16.3	1.3	4.2	5.8	323	-13.0	-732
Max/ BS	172	24.9	58.4	147	5283	21.6	505
Mean/ BS	111	12.5	29.9	89.5	2337	5.2	13.61
SD/ BS	45.1	6.6	15.9	41.9	1682	9.8	322

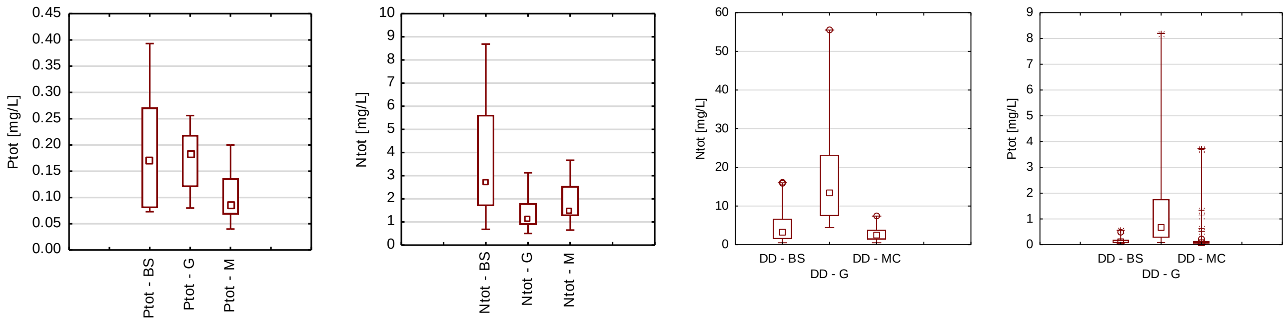

Figure 1. Box-plot charts presenting P_{tot} and N_{tot} concentrations in streams and drainage ditches located in Bladzikowski Stream (BS, DD-BS), Gizdepka river (G, DD-G) and Mrzezino canal (M, DD-M) watersheds

N and P surpluses in agricultural production were proved to be strongly related to emission of nutrients to rivers. In our study, we confirm such correlations in all analysed catchments. The surplus of nitrogen in EU countries shows decreasing trend, dropping by 18 % from an average 62.2. kg/ha in the period 2000-2003 to 51.1. kg/ha in the years 2012-2015 (European Environment Agency, 2018). In Poland the nutrient surpluses in the period 2008-2010 varied in the range 53.8 – 62.7 kg/ha for N and from 3.6 kg/ha to 7.2 kg/ha for P. According to prognosis performed by Pastuszak et al. (2014) they show a minor growing tendency and would reach 55.8 kg N/ha and 7.0 kg P/ha in 2020. In our study, the nutrient surpluses in the analysed farms were highly dispersed, however average and median values were higher than EU mean as well as those predicted by Pastuszak et al. (2014) in case of N and markedly lower in case of P.

CONCLUSIONS

Agricultural practices in analysed watersheds in northern Poland generally were in compliance with the requirements of the Nitrates Directive and recommendations set in the Codes of Good Agricultural Practices. The one major discrepancy regarded the uses of after-crops and winter crops, that was only reported by 19.4 % of surveyed farms. Consumption of fertilizers as well as nutrient surpluses were higher than average in Poland.

ACKNOWLEDGEMENTS

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A Hydrological Model for Ayamama Watershed in Istanbul, Turkey Using HEC-HMS

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INTRODUCTION

Floods are among the most common natural disasters which result in both big economic loss and human life. Especially, in urbanized regions with high population density, the effect of floods becomes more pronounced. One of the fatal events occurred in Ayamama River in Istanbul on September 9, 2009. In this study, a hydrological model for the Ayamama Watershed is generated by using Hydrologic Engineering Center Hydrologic Modeling System (HEC-HMS). The rainfall data measured during the said flood event is used in simulation and the results are evaluated in light of observations after the flood event.

Flood events have been more frequently observed as a result of climate change, global warming and urbanization. In order to investigate the physical mechanisms of floods and take precautions, flood simulations of the regions are necessary. Therefore, generation of hydrological models for different watersheds has gained importance. The flooding event occurred in Ayamama River in Istanbul was the result of successive and persistent storm with high intensity over a 3-day period which generated more than 250-mm rainfall over the region. The flood resulted in fatality of 32 people and caused extensive environmental and infrastructural damage in the region. The aim of this study is to generate a hydrological model for the Ayamama Watershed and investigate effects of urbanization on flood events in this region. HEC-HMS is employed for simulation of the flood event. Hydrographs for the subbasins, which are heavily affected by the flood event, are compared with the results of the hydrological model generated by WMS in a former study (Gülbaz et al., 2019) and with observations.

STUDY SITE

Ayamama watershed is located on the European Continental side of Istanbul in Turkey. The main stream length is 21 km with many tributaries feeding the river. The surface area of the watershed is 74 km^2. TEM highway, International Atatürk Airport and Ikitelli Organized Industrial Zone are located in this region and the basin is exposed to rapid urbanization.

HEC-HMS MODEL OF AYAMAMA WATERSHED

HEC-HMS models precipitation-runoff processes of dendritic watershed systems. It has the capability of simulating the floods and natural watershed runoff as well as meteorological phenomena such as evapotranspiration, snow melting and precipitation. The modelling results are employed in evaluating current water budget, and flow estimations (Scharffenberg, 2016).

For modelling of the Ayamama Watershed with HEC-HMS, a topographical map, cross-sectional area of the main river, soil properties of the study area and precipitation data for the flood event are used. The basin area is divided into the subbasins; the sections and specifications of the natural water channel are defined; infiltration is taken into account with Green-Ampt method and Clark Unit Hydrograph method is used for calculation of the hydrograph over the watershed.

RESULTS

The flood hydrograph is obtained at different locations along the Ayamama River for the flood event occurred on September 9, 2009. Atatürk, Evren, İnönü, and Çobançeşme districts are represented with 10C, 13C, 14C, and 15C, respectively which were heavily influenced by the flood. Flood peaks are obtained as 35.7 m^3/s, 73.4 m^3/s, 93.9 m^3/s and 98.9 m^3/s in these locations. HEC-HMS model of the watershed and rainfall intensity of the storm and flow rate at the outlet of the basin are shown in Figure1.

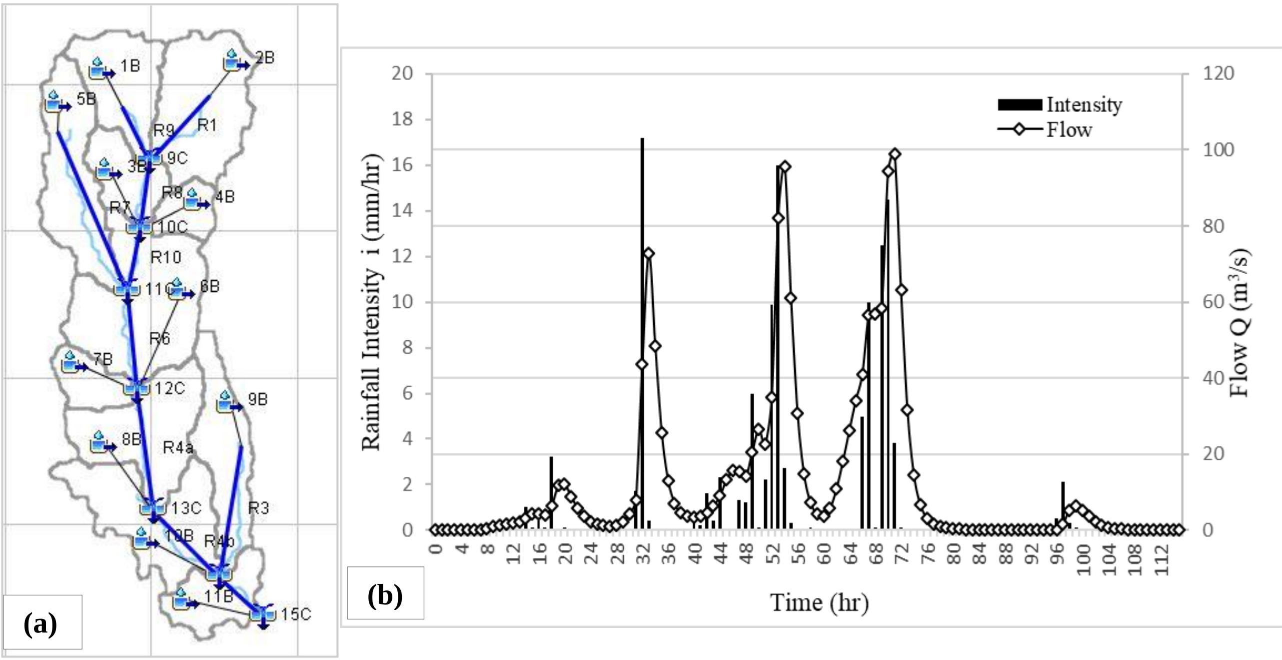

Figure 1. (a) Hydrological model of the Ayamama Watershed with HEC-HMS, and (b) hyetograph of storm event on September 7-11 2009, and hydrograph at the outlet (15C)

CONCLUSIONS

In this study, a hydrological model is generated for Ayamama River Watershed in Istanbul using HEC-HMS. Hydrographs for the subbasins are obtained and compared both with the results of the hydrological model generated by WMS in a former study (Gülbaz et al., 2019) and with observations. The results obtained by HEC-HMS model are in good agreement with the results obtained by WMS and with observations. Advantages and disadvantages of two models are presented. Moreover, the subbasins located downstream of the Ayamama River are determined as the most critical regions. The model produced in this study can be used to develop flood management studies for this region.

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Nutrient Assessment in Low Impact Development Technologies

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INTRODUCTION

Nutrients in urban stormwater runoff were assessed at a university in Cheonan City, South Korea. Infiltration trench and rain garden were evaluated to determine their effectiveness on nutrient removal. Both facilities have same structural main component except that rain garden have vegetation. The two low impact development technologies were monitored to collect stormwater sample. Water quality assessment showed that both facilities were effective in reducing the amount of nutrients. The study also cited that plants contributed in reducing the nutrients because the results showed that rain garden is more effective in nutrient removal than infiltration trench. In addition to that, higher CA/TV ratio of RG implied that smaller amount of rainfall entered the facility and 100 % volume reduction and pollutant reduction due to major of rainfall events did not produced outflow.

Low impact development (LID) has been introduced as one of the solutions on urban stormwater runoff problems. Problems in urban areas were addressed by LID technologies using natural hydrological functional site through increasing the infiltration ability of soil and evapotranspiration of plants. Various LID technologies such as infiltration trenches and rain gardens were applied to treat non-point source (NPS) pollutants in urban areas. Rain gardens (RG) and infiltration trenches (IT) provide pollutant reduction such as nutrients through media filters. Excessive amount of nutrients can cause unbalanced growth of plants and algae and leads to eutrophication (Bratieres et al., 2008). This research evaluated the effects of vegetated and non-vegetated LID technologies on nutrient removal on urban stormwater.

MATERIALS AND METHODS

Two LID technologies at Kongju National University were monitored to assess the nutrients present in a collected stormwater sample. IT captures stormwater runoff from adjacent road with a catchment area of 371 m^2 and has a CA/TV ratio of 47.5 %. While, RG captures stormwater runoff from parking lot with a catchment area of 481 m^2 and has CA/TV ratio of 55.6 %. IT and RG have an aspect ratio of 5:1:1.3 and 5:1:1 (L:W:H), respectively. The two LID technologies have similar main structural components: sedimentation zone, filtration zone and final effluent zone. Water quality parameter such as NO_2, NO_3, NH_4, total nitrogen (TN), PO_4-P and total Phosphorus (TP) were analysed based on Standard Methods for Examination of Water and Wastewater Treatment (American Public Health and Association et al., 1992).

RESULTS AND DISCUSSION

Figure 1 showed the event mean concentration of inflow and outflow for nitrogen (N) and phosphorus (P) on the monitored rainfall events. Among the nutrients, nitrite (NO_2) has the greatest percentage reduction on the removal of nutrients on both IT (60 %) and RG (73 %). PO_4-P has the least percentage reduction for IT (6.62 %) and RG (22 %). RG noticeably reduced the amount of nutrients present in the stormwater more than IT. Higher CA/TV ratio of RG indicated that smaller amount of stormwater entered the facility. Moreover, majority of the monitored events did not produced outflow, implying 100 % volume reduction and pollutant reduction. The vegetation of RG contributed to the nutrient removal when the rainfall event produced outflow. Plants improved the effectiveness of the pollutant removal on stormwater particularly nitrogen and phosphorus. Though there is a clear outcome that plants improved water quality effluent, there is no specification on what particular plant will be the most suitable for biofiltration system (Read et al., 2008).

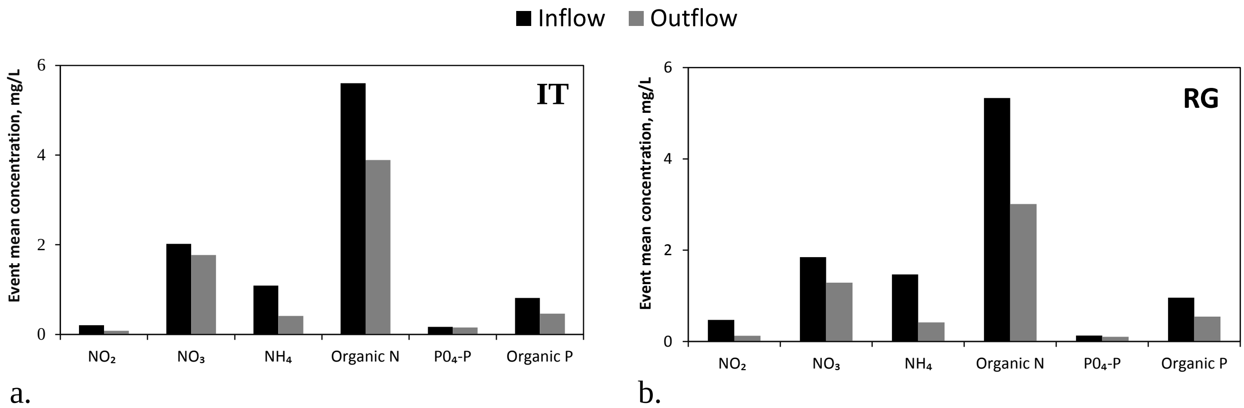

Figure 1. Characteristics of event mean concentration a) Infiltration trench b) Rain garden

CONCLUSIONS

N and P forms were generally lowered in both vegetated and non-vegetated LID technologies. Moreover, vegetated facility reduced more nutrients present in stormwater sample collected than non-vegetated facility. Analyses indicated that IT and RG were effective in nutrient removal especially on NO_2 and NH_4. In addition to the filter media layers, plants and CA/TV ratio contributed to the mitigation of pollutants in the stormwater for RG. Continuous monitoring will be conducted for rainfall events with higher rainfall depths.

ACKNOWLEDGEMENT

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Human Adenovirus as a Possible Indicator of Viral Contamination of Drinking Water

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INTRODUCTION

Microbiological water quality is usually assessed by determining the presence of bacterial indicators of fecal contamination such as *E.coli*. However, nowadays it is common knowledge that pathogenic intestinal human viruses can be detected in water with its normative quality according to bacteriological indicators, which often leads to waterborne outbreaks of various sizes (Bofill-Mas, 2013). The reason of viral occurrence is connected with their high resistance to disinfecting procedures, as well as their lower infectious dose compared to bacterial and protozoal pathogens. On this basis, there is flagrant necessity of using direct virological indicators in the study of water quality and the assessment of its epidemic safety.

Control of drinking water quality in respect to viral contamination remains an unsolved problem. According to the current Belarussian sanitary-hygienic standards, drinking water suppliers must conduct virological quality control for pollution by the following index pathogens: enterovirus (EV) and coliphages. Despite of the existing standard there is another one candidate for control viral contamination of both water sources and drinking water.

Human adenoviruses (HAdVs) are important pathogens that are responsible for wide range of waterborne diseases including enteric and respiratory infections. Illness tends to occur sporadically and without demonstrated seasonality (Mena and Gerba, 2009). Recently, these viruses have been found to be prevalent in rivers, coastal waters, swimming pool waters, and drinking water supplies worldwide. Some studies showed that their presence could be indicative of fecal pollution, according to relationships between fecal indicator organisms and adenovirus concentrations. Probably due to the double-strained DNA HAdVs show enhanced survivability under RNA-containing viruses included in the EPA's Drinking Water Contaminant Candidate List during UV water treatment (Jiang, 2006).

The aim of this study was to evaluate the qualitative and quantitative indicators of source and drinking water contamination of samples supplied by main Belarusian companies with EV and HAdV.

MATERIALS AND METHODS

Samples of underground and surface water sources, drinking water (bottled and tap), n=173 were collected during 2016-2019. The capture of viruses and their concentration were performed from 1000 liters of water using Kit for adsorption and concentration of viruses from drinking water using trap device (RRPCEM, Belarus) in accordance with the instructions for use. Viral nucleic acids extraction was carried out with RIBO-prep (AmpliSens, Russia).

Detection of EV's RNA was performed by using EV-PCR (RRPCEM, Belarus) with reverse transcription stage conducted with REVERT-L Kit (AmpliSense, Russia). Detection of HAdV's DNA and quantity estimate were performed by using quantitative real-time polymerase chain reaction (PCR) with designed and evaluated set of primer and probe sequences for a conserved region of the HAdV's hexon gene. The design of oligonucleotide primers and probes for identification HAdV's DNA in PCR-RT was carried out using the software Primer3 (v. 0. 4. 0) (Primer3, 2012), considering such parameters as degeneracy, Tm, GC%, ΔG, GC clamp, the formation of dimers and hairpins. Adjusted concentration dilutions of plasmid vector containing the target sequence for the primers were used as calibrators. Fluorescence levels were analyzed using the Rotor-Gene Q amplifier software (Qiagen, Germany).Identification of HAdV species F among the number of positive samples was realized with All screen-FRT (AmpliSens, Russia).

RESULTS

One hundred seventy-three samples of water were tested for the presence of EV and HAdV nucleic acids by real-time PCR protocols. Ten of them (5,78 %) were positive for HAdV and none for EV. Three of the 10 positive samples (30 %) were referred to HAdV species F. The analysis was done in duplicate in three independent assays accompanied by the presence of negative controls for confidence in the absence of false-positive results. The concentration of viruses was established using the developed calibrators in known concentrations. All positive for HAdV water samples were supplied by two organizations.

Table 1. Persistence of HAdV in source (n = 9) and drinking (n=1) water samples obtained from water organizations

	Water	Sampling date	Viral DNA concentrations (copies/ml)
HAdV in source water	Mineral underground	November 11, 2016	6 255
	Mineral underground	November 11, 2016	10 177
	Underground	November 11, 2016	1 659
	Underground	November 11, 2016	5 736
	Mineral underground	July 20, 2017	8 141
	Mineral underground	July 20, 2017	948
	Surface	October 25, 2017	1 163
	Surface	January 29, 2018	9 529
	Surface	April 15, 2019	2 462
HAdV in drinking water	Tap	April 19, 2017	1 567

CONCLUSIONS

Obtained data on the presence of adenoviruses in water samples in which enteroviruses were absent suggest a more appropriate use of HAdV as a relevant candidate indicator organism of drinking water contamination due to it enhanced survivability and lack of seasonality in its spread. In addition, viral load quantitative estimation may allow calculating the health risks associated with water use.

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Hydraulic Model Calibration and Performance Assessment of Pressure Managed Areas with Multiple Inlets

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INTRODUCTION

Pressure management is a widely adopted technique to decrease background leakage or to extend the lifespan of the pipe network (Knoblock et al., 2011). In some cases, it is inevitable to deploy multiple pressure reducing valves to supply a particular zone and keep the resilience of the network. In order to supply water to the customers with pressure close to the minimal service pressure, the precise setting of the parallel pressure reducing valves' (PRV) target pressure is required. Steady state hydraulic models like EPANET has the functionality to simulate pressure loss of a pressure-reducing valve (Rossmann, 2000). This can be simulated by adding minor-loss after the pipe, or by modifying the properties of the next link on the downstream side. Either way proper setting of the coefficients are essential to calibrate the hydraulic model. In this paper, two non-linear optimization methods were utilized to calibrate the hydraulic model with multiple input values (Bíbok and Fülöp, 2018).

MODEL SETUP

Instead of using minor loss coefficients, which show trade-off between discharge pressures, it is advised to use a combination of PRV (Pressure Reducing Valve)+GPV(General Purpose Valve) instead of a single PRV. The proposed model setup is not specific to a proprietary modeling software or framework. All the widespread commercial and open-source distribution network modeling tools are capable of implementing the proposed PRV scheme. The main reason behind it is the EPANET compatibility because most of the commercial software was forked from EPANET at some point. Figure 1 indicates the difference between the original modeling approach (above) and the proposed setup (below).

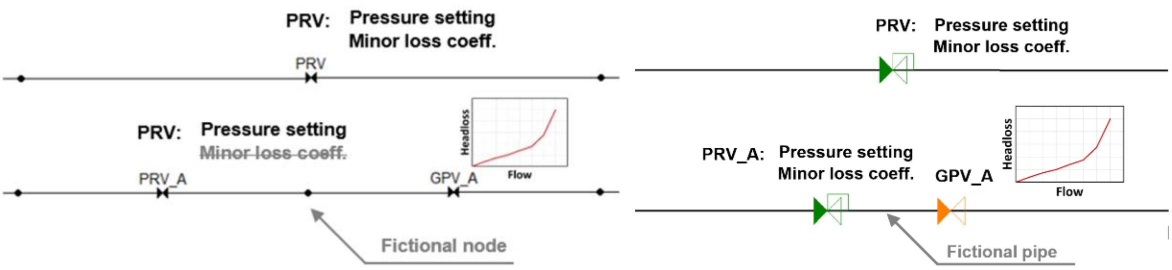

Figure 1. Implementation of PRV+GPV layout in EPANET (left) and WaterGEMS (right)

The calibration process includes iterating the following parameters to fit the pressure and flow-rate measurements: the discharge pressure setting which is required to open the valve for each valve, and the points of which the GPV flow-headloss curves consist. The number of parameters can be calculated by equation 1:

$$i = n + \sum_{j=0}^{n} S_j + 1, \tag{1}$$

where i is the number of free variables, n is the number of PRVs to calibrate and S_j is the jth segment of the valve headloss curve.

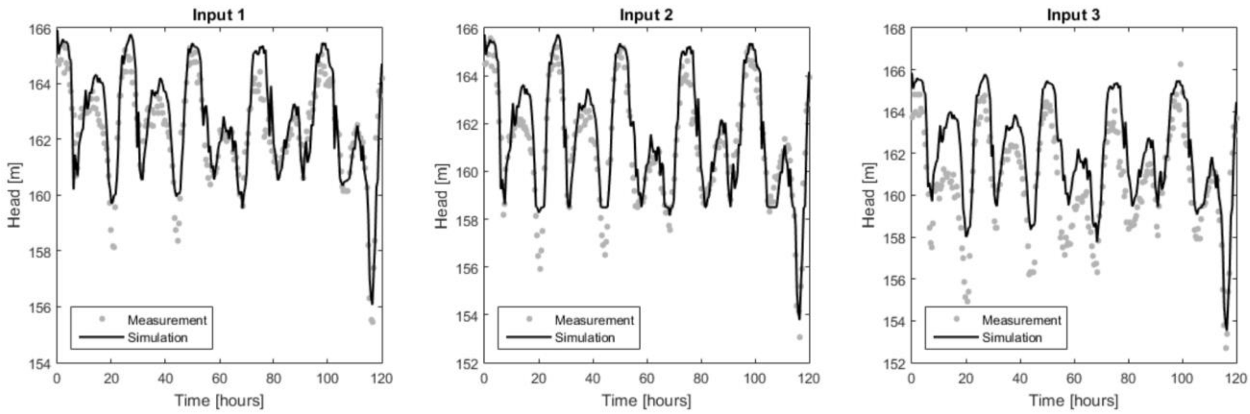

Figure 2. Calibration results of 5 days long simulation for discharge pressures

PERFORMANCE ASSESSMENT

The ratio of flow-rates and it's change by time is a good indicator of how stable the water supply is in the pressure managed zone. Flow-rate ratios in short (30min resolution) and medium (1day) length time-frames were analysed as performance indicators. If the theoretical flow coefficients (Kv) are known, it is possible to compare the operating point to the optimal valve using the relative valve closure curves. If the downstream pressure is biased before reaching the flow rate capacity for a given dP it means the valve is in sub-optimal operation

RESULTS & DISCUSSION

Both simulated annealing and the Nelder-Mead Simplex (Marios and Demetrios, 2010) method are capable of finding a near-optimal setting to fit the flow rates of PRVs to the measurement time series. Although direct validation of these solutions to the pressure measurement on the downstream side was less successful. The measured pressure losses compared to the valve setting were significantly higher than the simulated pressure losses. The investigation of the pressure loss and flow values showed that calibrating minor loss coefficients will not give a robust solution due to the different pressure loss characteristics of the valve. It is possible to overcome this issue, by applying rule based controls for parallel links downstream to the PRV, indirectly assigning different head loss coefficients to different domains of the flow range, though the resolution of this solution is limited by the number of parallel pipes downstream the PRV. Using the combination of a PRV and a GPV provides a robust solution for this complex problem. The valve's closing characteristics curve can be accurately calibrated based on the discharge pressure measurements.

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Automated Electrochemical Systems for Water Disinfection: A Review

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INTRODUCTION

In most developing countries and rural areas, water quality remains a serious problem due to potential pollution with a variety of microorganisms, including viruses, faecal coliforms, and protozoa; as well as due to lack in access to improved sanitation. As a result, about 500 000 people die of diarrhoea each year (WHO, 2018). The need for affordable and effective disinfection systems for the improvement of water quality in developing regions is still there.

Over the years, drinking water electrochemical disinfection has gained attention from the users and experts in water supply due to its high inactivation efficiency, environmental sustainability, and ability to generate free chlorine *in situ* (Martinez-Huitle and Brillas, 2008). The allow technology in its basic concept is suitable for disinfection purposes in point-of-use drinking water treatment, e.g., storage tanks or individual taps. Consistently, most of researches about electrochemical disinfection of water have been performed in batch mode (Ghasemian et al., 2017; Kourdali et al., 2018), which is often hard to control and scale-up in terms of reactive species generation and limitations which respect to productivity. Thus, the design of electrochemical systems that are able to operate at flow regime with no water recirculation and sufficient production of reactive species are essential.

The aim of the present review is to evaluate various commercially available and/or scientifically pointed automated electrochemical systems for water disinfection to establish the most sustainable operation/component setup. The effect of electrode material, electrolyte composition, current intensity, type of tested microorganisms, and bacterial inactivation efficiency have been taken into account in order to demonstrate the advantages and disadvantages of each system.

ELECTROCHEMICAL DISINFECTION SYSTEMS

Currently a wide range of different electrolytic systems have been developed and tested (Sarkka et al., 2015). However, there is no such system that simultaneously complies with high effectivity, rapid treatment (flow conditions), simplicity and economic sustainability. One of promising system is the EDI-001 system applicable for flow condition, operating at low current densities and using TiO_{2-x} electrodes (Denisova et al., 2017). Another alternatives are reactive electrochemical membrane (REM) system with Magnéli phase Ti_4O_7 ceramic membrane, operating in dead-end filtration mode (Liang, 2018); the CabECO® cell equipped with diamond electrodes (Isidro et al., 2018); and Ecodis® cell equipped with coated permanent titanium electrodes (Delaedt et al., 2008).

The comparison of different automated electrochemical systems for water disinfection is presented in Table 1.

The result showed that automated electrochemical disinfection systems have the potential to provide an environmentally responsible and effective method for water disinfection purposes. Moreover, most of the present studies have described bacterial inactivation in clean water and only some were performed using tap water or surface water. It is also important to develop new systems that will combine electrochemical disinfection with traditional water purification techniques to avoid the formation of by-products.

Table 1. The comparison of electrochemical systems for water disinfection

Electrochemical system	Electrode material	Experimental conditions	Microorganisms	Reference
Ecodis®	Titanium	0.5 – 0.75 A 0.3 – 0.5 A Flow rate – 20 l/h	*E. coli;* *L. pneumophila*	Delaedt, 2008
EDI-001	TiO_{2-x}	30.9 A/m^2, 25.1 V Flow rate – 30 l/h	*E. coli*	Denisova, 2017
REM	Magnéli phase Ti_4O_7	1 – 10 mA/cm^2 Flow rate – 0.3 l/h	*E. coli*	Liang, 2018
CabECO®	Diamond	0.83 – 833 A/m^2	Total coliforms; *P. aeruginosa*	Isidro, 2018

ACKNOWLEDGEMENTS

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Determination of Optimum Operational Conditions for the Removal of 2-MIB from Drinking Water by Peroxone Process: A Pilot Scale Study

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INTRODUCTION

Taste and odour in drinking water affect the perception of customers. Two of the most common taste and odour compounds, 2-methylisoborneol (2-MIB) and geosmin, are detectable even at concentrations below 10 ng/L (Srinivasan and Sorial, 2010). Previous studies have shown that conventional water treatment processes such as coagulation, flocculation, sedimentation and chlorination were ineffective, while powdered activated carbon, ozonation, and biofiltration have been found successful for the removal of these taste and odour compounds (Srinivasan and Sorial, 2010). Removal of the taste and odour compounds by peroxone process, that is a combination of ozone (O_3) and hydrogen peroxide (H_2O_2) was proven to be effective by several studies (Wang, 2014; WQTS, 2009). These studies have shown that removal of 2-MIB and geosmin compounds were quite higher with peroxone process in comparison to sole O_3 application at the same O_3 dosage.

In this study, optimum operational conditions such as peroxone ratio and contact time were determined for removal of 2-MIB at a pilot-scale peroxone system. Water samples used in all experiments were taken from the main drinking water source of a mega city. Other important parameters such as geosmin, total organic carbon and bromate were also determined along with the 2-MIB. During the experimental study, residual (dissolved) O_3 and residual H_2O_2 were monitored in order to investigate whether the applied chemical dosages were reasonable or not.

MATERIAL AND METHODS

Raw water that was obtained from the outlet of an aeration unit in a full-scale drinking water treatment plant was used in this study. 2-MIB and geosmin concentrations were lower than 10 ng/L during the sampling period, which is known as the limit concentrations to be perceived. Therefore, 2-MIB was spiked into the water samples to obtain a concentration of 90 ng/L. Chromatographic grade 2-MIB standard (Supelco, USA) (10 mg/ml) was used for maintaining the required concentration of 2-MIB in the water samples. Since 2-MIB is more difficult to be removed with O_3 in comparison to geosmin, operational conditions for 2-MIB removal were investigated to set the process design requirements.

Pilot system consisted of a raw water storage tank, reactor column (O_3 contact column with 2.4 m diameter and 5 m height), H_2O_2 dosing system and O_3 generator along with the required pipes and measuring equipments. The reactor contained an ultrasonic water level measuring sensor, gas phase O_3 measuring device, dissolved O_3 measuring device, thermometer and pH meter. O_3 was produced by the O_3 generator that was fed with the air. H_2O_2 solution was dosed by a solenoid dosage pump into a pipe. Gas phase O_3 was measured at the inlet and outlet of the reactor. Surplus (off-gas) O_3 was destructed by an O_3 destruction unit before reaching to the atmosphere.

Different H_2O_2:O_3 ratios (0, 0.1, 0.3 and 0.5) were tested in order to find the ideal ratio for the removal of 2-MIB. Inlet O_3 dose was set as 4 mg/L and the reactor was continuously fed with 2-MIB spiked water. Average water temperature in the pilot plant was recorded as around 16 °C. After the determination of the optimum H_2O_2:O_3 ratio, reactor was operated at different contact times including 5, 10 and 15 min. TOC and geosmin removal efficiencies were also determined throughout the experimental study. Additionally, variations in residual H_2O_2 concentration were measured during each experiment.

RESULTS AND CONCLUSIONS

Variations in dissolved O_3 and residual H_2O_2 concentrations

Dissolved and consumed O_3 concentrations were measured for each H_2O_2:O_3 ratio at a contact time of 10 minutes. It is essential that the residual O_3 concentration in the water leaving the reactor should not exceed 0.1 mg/L for safety reasons (WQTS, 2009). According to the results, dissolved (residual) O_3 concentration was around 0.05 mg/L, below the residual O_3 limit, for each H_2O_2:O_3 ratio, while consumed O_3 concentration was around 4 mg/L.

Residual H_2O_2 concentration in the peroxone process was recommended not to exceed 0.5 mg/L (Oturan and Aaron, 2014) since higher concentrations might cause operational problems such as residual chlorine consumption in the water treatment plants. The results showed that limit residual H_2O_2 was not exceeded during the experiments with a contact time of 10 min at H_2O_2:O_3 ratios of 0.1 and 0.3. However; concentrations over 0.5 mg/L residual H_2O_2 was observed even by the 4th min during the experiments with a H_2O_2:O_3 ratio of 0.5.

Impact of H_2O_2:O_3 ratio on treatment performance

Results obtained from 10 min experiments with each H_2O_2:O_3 ratio show that 2-MIB removal efficiency was found to be between 42.5-64.3 %. TOC removal efficiencies were below 10 % during the experiments with each peroxone ratio. Geosmin removal efficiencies could not be evaluated depending on the low initial geosmin concentrations close to detection limit. High residual H_2O_2 concentration was observed in the reactor effluent during the experiments with H_2O_2:O_3 ratio of 0.5. According to the results, ideal H_2O_2:O_3 ratio was determined as 0.3.

Impact of contact time on treatment performance

Optimum contact time for the ideal H_2O_2:O_3 ratio was determined regarding 2-MIB removal efficiency. Removal of TOC were below 9 % during the experiments conducted with each contact time. According to the results, 2-MIB removal efficiency had linear correlation with the contact time. Thus, contact time of 15 min resulted in the best removal efficiency (81 %) at an O_3 dosage of 4 mg/L. Overall results confirmed the significance of contact time on the removal of 2-MIB.

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A Pilot-Scale Experimental Study on the Adequacy of Filtration Mode of Operation and Filter Media in the Brasília Water Treatment Plant - Federal District - Brazil

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INTRODUCTION

High levels of turbidity may protect microorganisms from the effects of disinfection and it requires a multiple barriers system for ensuring safe drinking water (WHO, 2017). All too often, filtration is the last, and sometimes the only, physical particulate barrier for removal of turbidity (pathogens and impurities) not removed during the preceding water treatment processes. The Ordinance No. 5/2017 of the Brazilian Ministry of Health establishes that filtered water turbidity should be maintained below 0.5 NTU in at least 95 percent of samples (Brasil, 2017). However, keeping filtered water turbidity consistently below 0.5 NTU requires significant improvements in filtration performance. It is well known that the filtration rate, filter media characteristics and rate control play an important role in maintaining optimal filter performance. In the Brasília Water Treatment Plant (Brasília WTP), the constant-rate rapid downflow filtration system has been operated with negative pressures decreasing the filter run length and the effluent quality, and it is probably caused by problems related to the head available and rate control system. According to Cleasby (1990) gravity filters operated under variable declining-rate filtration (VDRF) mode demand less total head and have less tendency for terminal breakthrough than constant-rate filters. Therefore, using a pilot-scale filtration system, the aim of this study was to compare the performance of two different filter media, regarding turbidity removal and filter run length, operated under variable declining-rate filtration mode, in order to evaluate the feasibility of changing the rate control system at Brasilia WTP.

EXPERIMENTAL PROCEDURES

Teixeira (1991) proposed a method, in which it utilizes a mathematical model of variable declining-rate filtration developed by Di Bernardo (1993), for estimating the filter run length under VDRF mode, based on a single pilot filter operated under a constant-rate, variable head mode. The pilot filter should be operated at the maximum filtration rate and the filter run should be terminated when the maximum allowed head loss has been reached. Both maximum filtration rate and maximum allowed head loss are obtained by using Di Bernardo's model.

This work was carried out using two pilot filters (filter column of 200 mm ID and 3 m height) with different filter media. The first one was a sand filter media bed (80 cm depth, effective size of 1.25±0.05 mm and uniformity coefficient of 1.2). The second one was a dual-media filter bed, consisting of anthracite (50 cm depth, effective size of 1.00±0.05 mm and uniformity coefficient of 1.4) over sand (30 cm depth, effective size of 0.53±0.20 mm and uniformity coefficient of 1.5). The rapid gravity pilot filters were supplied with clarified water from Brasilia WTP (clarification by dissolved-air flotation). The pilot filters operated in parallel, at two filtration rates, 15 $m^3/m^2.h$ and 19 $m^3/m^2.h$. The filtration performance was evaluated at coagulation pH values in a range of 6.4 to

7.1 and coagulant dosages of polyaluminum chloride (PAC) in a range of 4.0 to 7.5 mg/L.

Piezometers for measuring head loss, sampling points and backwash accessories were properly installed. The influent and effluent turbidity and head loss were monitored every 15 minutes during the filter run in order to determine the treatment efficiency and the filter run length, respectively.

RESULTS AND MAJOR FINDINGS

The highest values of filtered water turbidity were observed during the ripening period and also when a filter has reached the end of its run. Averages of turbidity removal efficiencies at filtration rates of 15 $m^3/m^2.h$ and 19 $m^3/m^2.h$ were, respectively, 86 % and 80 % for the sand filter media and around 92 % for the dual-media filter, independently of the rate. For the dual-media filter, turbidity was removed to values below the Brazilian drinking water quality standard in all experiments.

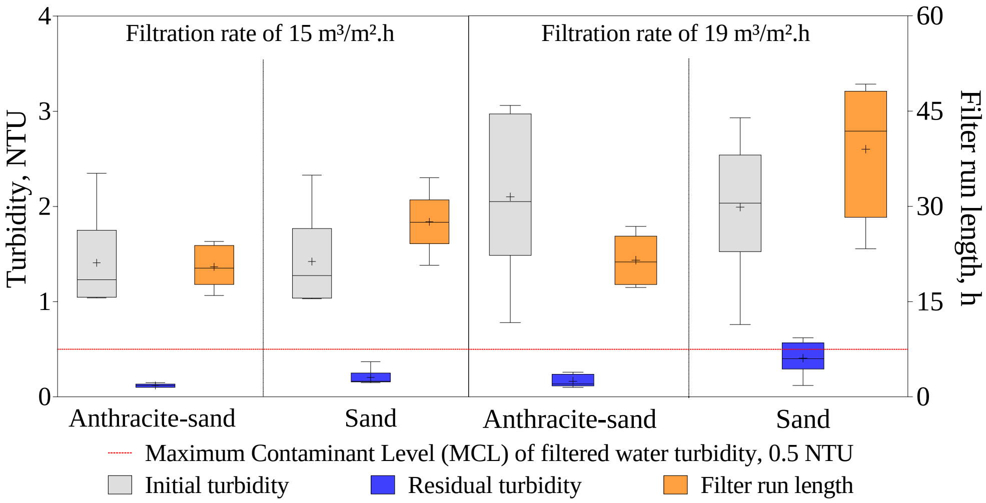

Figure 1. Descriptive statistics (box plot) of turbidity values and filter runs under VDRF mode

Filter run length was more affected by variation in coagulation pH and coagulant dosages than filtered water turbidity, indicating that the filters were able to produce stable effluent quality by dampening fluctuations in clarified water turbidity. The longest filter runs were obtained at higher filtration rate (19 $m^3/m^2.h$), by favouring depth filtration, despite an increase in the clarified water turbidity. Based on the comparison of the averages of filtration runs obtained by using the method proposed by Teixeira (1991), 27.6-39.0 h for the sand filter media and 20.5-21.5 h for the dual-media filter operating under variable declining-rate filtration mode, with the filtration runs observed in the actual filters at Brasilia WTP, 16.0-20.0 h operated under constant-rate filtration mode, it is suggested that filter media and rate control system of Brasilia WTP should be changed.

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Removal of Cylindrospermopsin by Adsorption onto Activated Carbon Synthesized from Coconut Shell

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INTRODUCTION

Cyanobacterial blooms producing toxins have been reported all over the world. Favourable geographic spreading of toxic blooms and adequate environmental conditions emphasizes the need for increasing monitoring of cyanotoxins in drinking supply reservoirs in Brazil (Bittencourt et al., 2014). As example of one of these toxins is cylindrospermopsin (CYN) which may cause diseases in humans related to liver disfunction. The removal of large concentrations of CYN by conventional treatments is hampered by its hydrophilic property, especially when its founded in extracellular form. Faced with the challenge of removing these toxins, there is a need for the use of advanced water treatment techniques. As a method of advanced water treatment, the use of activated carbon (AC) in pulverized and granular form stands out. These activated carbons can be synthesized starting from different raw materials, which will develop different physical and chemical characteristics in their structure. Studies must be developed to find which characteristics an activated carbon must have to ensure safety against CYN, leading to the aim of this study which is evaluate what synthesis conditions and carbon activated characteristics are more favourable to remove this cyanotoxin.

EXPERIMENT PROCEDURES

Carbon synthesis started using dried endocarp of coconut origin from Brazil as precursor, which particles were sieved in the range of 0.177 to 0.105 mm. Two sorts of carbon were produced following Prauchner and Rodríguez-Reinoso (2012) study. Both were activated by chemical activation using phosphoric acid, the difference consisted on acid ratio utilized where AC 1 used 0.54 g of precursor per gH_3PO_4 and AC 2 0.27 g/g. First the precursor was impregnated with the acid under the temperature of 85 ºC for 2 hours and then the temperature was increased to boiling point to force the incorporation of the acid. Second, the mixture was carbonized in a tubular horizontal furnace up to 450 ºC and stayed at this degree for 2 hours. After completing the synthesis, both carbons were submitted to characterization analysis, such as BET surface and adsorption-desorption isotherms of N_2 to evaluate superficial area and pores volume, respectively.

The second part of this study consists in analysing the adsorption capacity of both activated carbons, following the requirements of ASTM (2014). The experiments were conducted using two study waters: ultrapure water and Paranoá Lake water, both contaminated with an extract obtained from freeze dried cells of a strain CYN producer in order to reach an initial concentration of approximately 60 μg/L of CYN dissolved. To reach a better adsorption performance, experiments were done to set the contact time. After settled, adsorption experiments were done using AC doses of 0, 3, 6, 9 and 12 mg/L. All samples were analysed using ELISA method produced by Abraxis.

RESULTS AND DISCUSSION

The results showed that AC 1, which used a higher fraction of the phosphoric acid presented a lower BET surface area but the highest volume of mesopores in its structure, representing 35 % of total pores volume. Moreover, AC 2, which received a lower fraction of H_3PO_4, presented a greater BET surface area with a predominance of micropores in its structure, as shown in Figure 1.

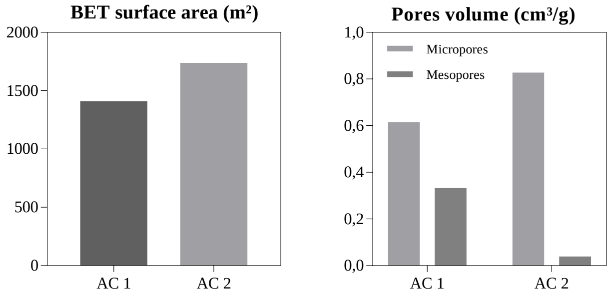

Figure 1. Physical characteristics of synthesized activated carbons

After experiments, 4 hours was used as contact time. Adsorption capacity results showed a similar removal of CYN for both carbons in ultrapure water (Figure 2). Although pores distribution was different, AC 1 and AC 2 remaining values for 12mg/L dose were alike, correspondingly to averages of 59,90 % and 53,53 % for ultrapure water. On Paranoa Lake experiment, the organic matter presented a high influence on adsorption capacity of CYN molecule.

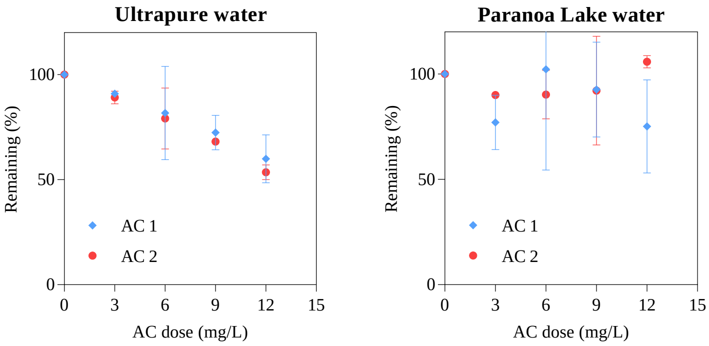

Figure 2. Remaining values of adsorption capacity for both waters. Initial CYN concentration in ultrapure water for AC 1 and AC 2 were 57,85±3,31 μg/L and 59,32±0,89 μg/L, respectively. For Paranoa Lake initial concentrations were 67,25±8,31 μg/L for AC 1 and 62,27±0,51 μg/L for AC 2.

In summary, synthesised carbons presented physics characteristics favourable to adsorption performance. Furthermore, the study leads to a necessity of producing others activated carbons under different conditions such as acid ratio or incorporation of functionals groups on carbon surface that could have more affinity with CYN molecules.

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Energy Consumption Reduction and Utilization of Renewable Energy in Pump Stations

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INTRODUCTION

One of the main focuses of water utility companies is the energy efficient supply of drinking water. Pump stations are key locations in energy efficiency. They have the highest velocity values of the water network system and the highest pressure loss values are also present here. Reduction of pressure loss at these facilities is the most feasible and most advantageous solution. Pump houses also provide an accessible location for the utilisation of the drinking water's excess heat capacity which can be used for the heating of the surrounding facilities.

ENERGY CONSUMPTION REDUCTION

A theoretical research was conducted from 2016 to 2018 which aimed to reduce the head loss of pipe networks in the pump stations. The results were promising and predicted an average of head loss reduction by 30 %. Afterwards physical experiments were carried out to test the effectiveness of the new pipe designs. Two new prototype pipe sections were installed into one of our pump stations, during a R&D project. The experiment was successful as two unique pipe section installed in the discharge section reduced the head loss of the pump station by 25-26 %.

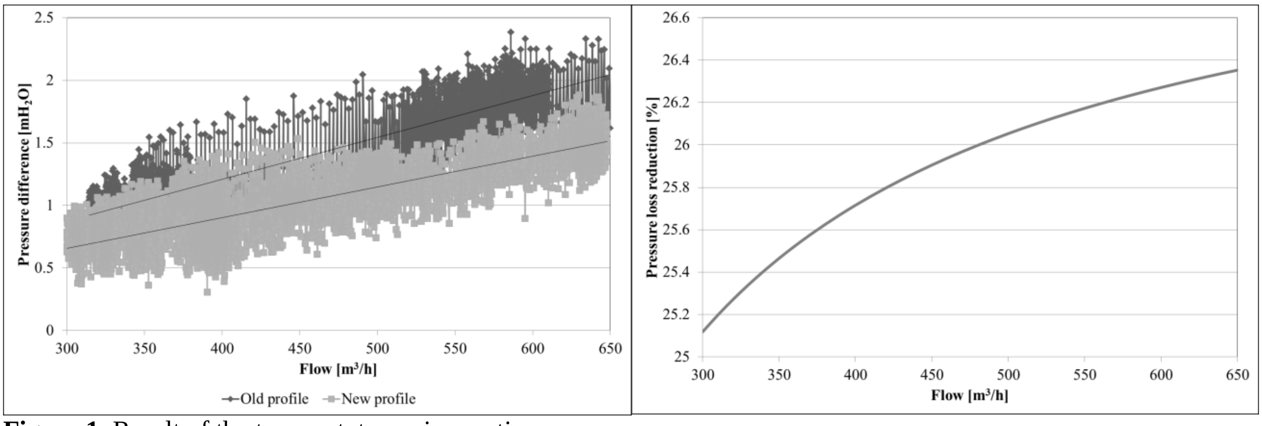

Figure 1. Result of the two prototype pipe sections

According to these results we can set a target value of 30 % head loss reduction at full pump station pipe reconstruction, this makes the technology financially recoverable. The electrical costs of the pump station operation can be reduced by 1 % (this means savings in the magnitude of multiple thousands Euros) with the reduction of pressure loss. Furthermore the new pipe elements reduce the chance of impeller damage caused by instable flow and it also reduces the damage caused by highly turbulent flow on valves and check valves.

UTILIZATION OF RENEWABLE ENERGY IN PUMP STATIONS

The utilisation of the excess heat capacity of drinking water in pump stations is not a new concept. Multiple studies were made in this topic. All of them highlighted the heat exchanger as the primary problem of the system. The role of the heat exchanger in the system is crucial as it “takes out” the excess heat capacity from the drinking water so it has to meet multiple strict operational and water-safety criteria which are the following:

- The material of the heat exchanger must be stainless steel.
- The device must withstand 150 % of the operational pressure. The pressure must be different in the primer and secondary circuit of the heat exchanger.
- The pressure of the secondary circuit pump cannot exceed the operational pressure of drinking water pipe system even at valve closing peak pressures.
- The operation of the circulatory pumps must be immediately stopped and the safety valves should be closed when pressure fluctuates over 0.5 [bar] from the pre-set values.

Currently there are no serial production heat exchangers on the market that meet all the criteria and can be installed in pump stations without any modification. Our newly developed heat exchanger for discharge pipe installation meets all the criteria and works without drinking water extraction, it can be attached to heat pump systems available on the market.

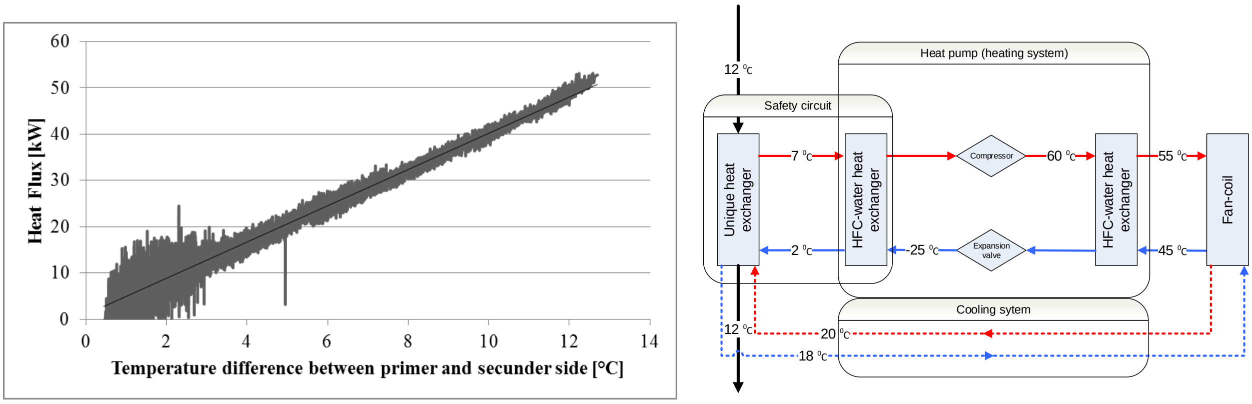

Figure 2. Left: performance of prototype heat exchanger; Right: schematics of the system

After the conception design a prototype heat exchanger were constructed and tested at one of our pump stations. The unique heat exchanger was connected to a heat pump system and provided heating for the pump station and the surrounding offices. The utilisation of the excess heat capacity of the drinking water was highly effective as the coefficient of performance (COP) value of the test system was 4.6, which is above the average COP value of the corresponding heat pump systems. With this technology the efficient heating of the pump houses and surrounding offices is achievable.

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Modelling Study of Arsenate Removal by Iron (Hydr)oxide Coated Pumice Stone

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INTRODUCTION

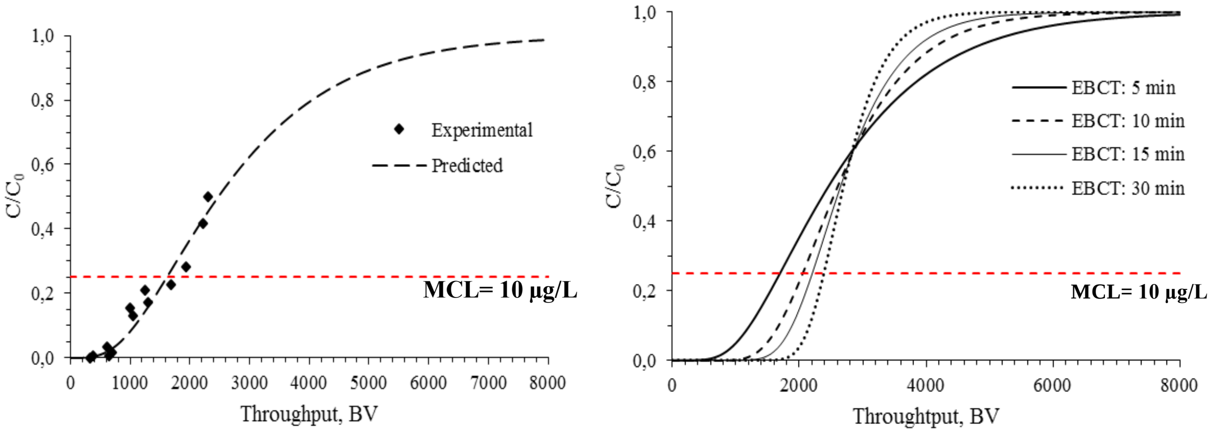
Iron (hydr)oxide coated pumice stone has been used for drinking water treatment to remove arsenate with promising results (Slokar and Petrusevski, 2016). However, there is no modeling studies of its behavior onto fixed bed adsorber. These can simplify the design of systems reducing the number of pilot scale tests. The Homogeneous Surface Diffusion Model (HSDM) and its modifications have been used widely to predict performance of adsorption systems (Summers et al., 2011). The aim of this research was to evaluate the feasibility of using the HSDM to predict the arsenate breakthrough of fixed-bed adsorber with Iron (hydr)oxide coated pumice and demonstrate its filter media potential at realistic inlet arsenic concentration.

MATERIAL AND METHODS

Natural pumice stone sieved to 0.85-1.18 mm was impregnated with iron (hydr)oxide following the procedure described by (Kumar et al., 2014) using ammonium hydroxide as precipitating agent. The resultant material was oven dried at 50 °C. The bottle-point method was conducted to obtain the Freundlich equilibrium parameters. Different doses of adsorbent ranging between 0.5 and 5 g L^{-1}, were placed in contact for 24 h with 0.2 L ultrapure water spiked with an arsenate concentration ~ 250 µg L^{-1}. The test was conducted in an orbital shaker at 100 rpm stirring rate, 25 °C and pH 6.5 ± 0.3. The film diffusion coefficient was estimated using the Williamson correlation (Crittenden et al., 1987). The determination of the surface diffusion coefficient was performed using a differential column bed reactor (DCBR), as indicated by (Badruzzaman et al., 2004). Fixed-bed adsorption experiments were conducted using a laboratory scale column (1.55 cm i.d., height 15 cm) at room temperature. Ultrapure water was spiked with an initial arsenate concentration of 40 µg L^{-1}. The solution was pumped at 1.5 m h^{-1} through the system according to an EBCT of 4.4 minutes. The software Fixed-Bed Adsorption Simulation Tool (FAST 2.1) was used to generate the theoretical HSDM predictions for the validation. The HSDM was used to simulate the performance of full-scale fixed bed adsorber at different EBCT. To achieve the desired EBCT only the loading rate was changed. The modeling was conducted with an initial concentration of 40 µg L^{-1}. The software FAST 2.1 was used to simulate the behavior.

RESULTS

The Figure 1(a) shows the experimental data of the breakthrough curve recorded up to 0.5 C/C_o and the HSDM predictions. The HSDM model yield a deviation of 15 % of the experimental data. The breakthrough point at maximum contaminant level (MCL) of 10 µg/L presented 10 % of deviation. Accordingly, the adsorption onto the pumice surface can be described by the assumptions of the HSDM described by (Worch, 2012).



a) **b)**

Figure 1. (a) Arsenate experimental data of the breakthrough curve test and its HSDM adjustment. (**b)** Arsenate breakthrough predictions at different EBCT

As can be seen in Figure 1(b), the higher EBCT, higher the quantity of BV produced at the MCL. However, the quantity of BV produced (1700 – 2400) is low compared with commercial adsorbents like titanium dioxide with around 42000 BV at 40 µg L^{-1} (Bang et al., 2005). The produced media could be implemented as a point of use filter for contaminated groundwater with realistic arsenic concentration. In order to use the material as a centralized system for small communities more studies are needed to improve the capacity of the coated pumice. However, the modeling approach shows a simple way to predict the breakthrough curve.

CONCLUSIONS

The adsorption onto the iron coated pumice surface can be described by the assumptions of the HSDM allowing to estimate the breakthrough curve. The produced media could be implemented as a point of use filter for contaminated groundwater with realistic arsenic concentration.

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Improving Quality of Drinking Water in the Water Treatment Plant by Decrease of Hardness with Respect to Sodium Concentration Control

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WARTER QUALITY IN EXISTING WATER TREATMENT PLANT: CURRENT STATUS

In this research the object of the analysis was water quality that is produces in the existing water treatment plant in Serbia, which at the present moment doesn't meet the standards for drinking water quality, according to the national regulation (National regulation on hygienic quality of drinking water, Official gazette of Republic of Serbia 42/98 and 44/99). The results of the analysis obtained for the water of interest, are presented in Table 1.

Table 1 Water quality analysis

Analysed parameters	Unit	Proscribed values	Inlet water	Outlet water
pH	-	6,8-8,5	7,25	7,66
Conductivity	µS/cm	<1000	**1297**	**1387**
UV	1/cm	/	0,048	0,062
p-alkalinity	mg $CaCO_3$/L	/	0	0
m- alkalinity	mg $CaCO_3$/L	/	555,5	580,0
HCO_3^-	mg/L	/	677,7	680,8
Total hardness	mg $CaCO_3$/L	/	524,5	542,5
TOC	mgC/L	/	2,82	3,22
Consumption of $KMnO_4$	mg/L	<8	3,77	1,26
Cl^-	mg/L	200,0	69,58	96,34
SO_4^{2-}	mg/L	250,0	53,54	65,54
Ca^{2+}	mg/L	200,0	131,14	133,15
Mg^{2+}	mg/L	50,0	47,85	**51,01**
Na^+	mg/L	150,0	/	111,0
K^+	mg/L	12,0	3,99	4,16
$Fe^{2,3+}$	mg/L	0,3	0,07	<0,005
$Mn^{2,4+}$	mg/L	0,05	**0,11**	**0,09**
Ba^{2+}	µg/L	700,0	256,9	256,9
Be^{2+}	µg/L	/	<5	<5
B^{3+}	µg/L	300,0	<20	<20
Cu^{2+}	µg/L	2000,0	<2	4,6
Zn^{2+}	µg/L	3000,0	11,6	19,6
Si^{4+}	µg/L	/	29,6	29,3
Se^{4+}	µg/L	10,0	<20	<20
Sr^{2+}	µg/L	/	690,1	720,1
Hg^{2+}	µg/L	1,0	<1	<1
$As^{3,5+}$	µg/L	10,0	<20	<20
Al^{3+}	µg/L	200,0	<40	<40

*values presented in red color and in bold format are above the regulation for drinking water

Within Table 1, list of analysed parameters is presented, as well as water quality before existing treatment, and after the treatment. Together with measured values, the values that are proscribed by the regulations are also presented.

As it can be noticed the parameters that are above the maximal proscribed values are: $Mn^{2,4+}$ content, Mg^{2+} content, conductivity, and even though water hardness is not limited it needs to be taken into account as it will affect the reliability of water supply network and cause precipitation of $CaCO_3$. Also, it can be noticed that Na^+ concentration is very high. It is obvious that water needs additional treatment in order to meet the drinking water quality standards.

TECHNOLOGIES FOR IMPROVAL OF WATER QUALITY: REMOVAL OF WATER HARDNESS AND SODIUM

For improval of existing water quality, or even more precisely, for meeting the standards for drinking water quality, and for reaching adequate water quality in distribution network and for drinking water supply several technologies have been considered.

Since manganese concentration, magnesium concentration and conductivity are above the maximum permissible value and sodium concentration and water hardness are very high (it gets higher than 500 mg $CaCO_3$/L), one of the options for improved water treatment is ion exchange technology. As mentioned before, water hardness is not a parameter that has defined maximum value, but what is important is that for high values of water hardness there are lots of negative effects. The most pronounced are negative effects on:

- the functionality of process equipment (it is rapidly destroyed),
- the distribution network that manifests through precipitation of carbonates on the surface of pipes, and
- the quality of drinking water, which can be observed by the complains of the consumers.

The ion-exchange processes are applied for removal of Ca^{2+} and Mg^{2+}-ions from water. In the ion-exchanger these ions are substituted by Na^+-ions. For this reason, the option of using ion-exchange technology for removal of water hardness is not the best option. In analysed water concentration of Na^+-ions is already relatively high. When additional Na^+-ions are released in water it is more than probable that the maximal concentration for Na+-ions in drinking water will be exceeded.

CONCLUDING REMARKS: RECOMMENDED TECHNOLOGY

For water with relatively high Na^+-ion concentration the best option of treatment are membrane separation technologies. In this case the recommended membrane technology is reverse osmosis (RO) (Magara et al., 2000). Possibly the quantity of water that needs to be treated by RO doesn't have to be the whole amount of drinking water, which will be subject of further analysis. Planned RO capacity is 15 L/s.

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Thermal Aging and its Impact on the Quality of Drinking Water

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INTRODUCTION

The objective of this research is to study the effect of thermal aging on the quality of bottled drinking water used in Tabuk region, KSA, and compared with Zamzam groundwater.

MATERIALS AND METHODS

Four recently-produced samples of drinking water were randomly selected from those available in the market. A fifth sample of Zamzam groundwater, KSA, was added. All samples were packed in transparent plastic bottles made from polyethylene terephthalate (PET). Selected physical, chemical and biological properties of these samples were measured before and after thermal aging up to 52°C, which is a summer temperature in several area in KSA, for time intervals (3, 5, and 11 days).

RESULTS AND DISCUSSION

With exception of heavy metals, the results revealed that the physical and chemical properties didn't exceed the values recommended by World Health Organization (WHO, 2006) or Saudi Arabian Standard Organization (SASO, 1984) for drinking water. No bacterial contamination was detected upon aging. The Inductive Detection of heavy metals by Couple Plasma- Mass Spectroscopy (ICP-MS) revealed an increase in the concentration of antimony and lead up to 0.020 and 0.011 mg/L, respectively, after 11 days at 52°C. The value of antimony exceeded the maximum values allowed by WHO and SASO (005.0 mg/L) while in the permissible value in case of lead, as shown in Table 1. These results were confirmed by the morphological changes on the surface of the plastic water bottles using scanning electron microscopy (SEM) (Azetsu-Scott, 2006). Thermal cracking of the packaging components and deposition of these elements, which are used as auxiliary agents during manufacture, may also lead to the possible deposition of carcinogenic substances such as dioxin and melamine used during the manufacturing stages of plastic bottles (Guart, 2011). In contrast, results showed that there was no trace of elemental antimony and lead in Zamzam water before and after exposure to the same conditions (Fig.1). This may be attributed to its high value of electrical conductivity.

CONCLUSION

PET plastic water bottle contains toxic heavy elements which could be passed on to drinking water with aging. Zamzam water didn't mix with the toxic elements in the plastic packaging. More laboratory studies should be conducted on Zamzam water to clarify its unique properties.

Table 1. Comparison between the concentrations of heavy metals in drinking and Zamzam groundwater after and before aging to 11 days at 52°C

Elements	WHO (2006)	SASO (1984)	Drinking water before aging	Drinking water after aging to 11 days at 52°C	Zamzam water before aging	Zamzam water after aging to 11 days at 52°C
Antimony (Sb) mg/L	0.005	0.005	0.012	0.020	0.000	0.000
Lead (Pb) mg/L	0.050	0.050	0.002	0.011	0.000	0.000

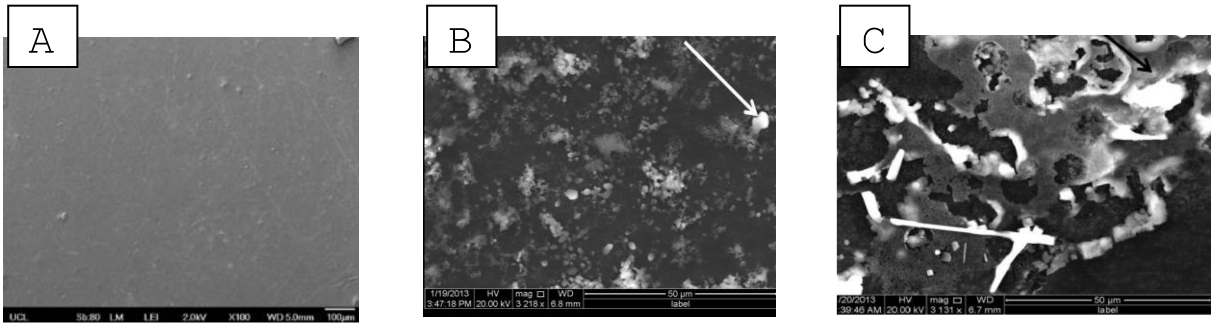

Figure 1. SEM of (A): untreated plastic PET; (B) Plastic PET bottle filled with water sample and aged to 11 days at 52 °C; Plastic PET bottle filled with Zamzam water to 11 days at 52 °C

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Fire and Drinking Water Capacity Enhancement in Water Distribution Networks

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INTRODUCTION

Water distribution systems are critically important elements of the infrastructure of every settlement (from small villages to large cities); therefore, pressure fluctuations originating from the consumption variation and uncertainties might result in significant discomfort to the customers and financial drawback for the providers. On the first hand, if the pressure of the water distribution system falls under a critical level (typically, 1.5 bar), the consumers experience insufficient flow capacity (that is, shortage of water). Due to this phenomenon, the providers of such areas experience a growth in the number of retail compliments and also a financial decrement because of the decrease of the consumed water. On the other hand, in low-pressure areas the utility company might have difficulties with fulfilling the prescribed fire hydrant regulations (e.g. NFPA 291-2019). This paper explores the minimal topological modification (that is, adding a single pipeline to the system) which leads to the most significant increase in the pressure robustness of the network. We demonstrate the proposed technique on real-life hydraulic networks.

APPROACH

To determine the location where the installation of a new pipeline eventuate the most significant pressure sensitivity decrement, and through that – as it later turned out – the largest capacity increase in the water distribution network, a new method is proposed. The implementation of this novel technique is built on the existing "Staci" one-dimensional hydraulic modelling software (www.staci-hds.com).

Objective measures of sensitivity

Finding an objective measure for the pressure sensitivity of a water distribution system is essential when analysing the network robustness. We have employed the sensitivity matrix, which includes the nodal pressures derivatives with respect to the demands. Based on the sensitivity matrix three new parameters – local, average and peak sensitivity – were developed. The local sensitivity characterises how much each nodal pressure changes if the demands are equally varied over the whole network. The peak sensitivity is the maximum local pressure sensitivity, while the average sensitivity describes the entire system through the average value of the local sensitivities. We found that these parameters exhibit a strong correlation with the topology and the robustness of the network.

Implementation of the method

Consider the problem of finding those two nodes in a water distribution system, which, if connected, results in the largest possible increase in the robustness. Direct enumeration (that is, evaluating all possible pairs) is impossible for large (real-life) networks due to the exponential increase in the computational time, hence, a faster technique is needed. The main novelty in our method is that we have found that the local pressure sensitivity difference between two nodes (in the original system, without a pipe connection between them) predicts the possible achievable average and peak robustness growth by the pipeline connection. With the help of this connection, the identification of the pipeline which maximises the pressure robustness of the system can be determined only with one hydraulic simulation. To achieve an economically optimal pipeline, not just the best, but the top ten solutions have been computed and compared, to reach an optimum between the investment cost and robustness growth.

RESULTS

The above method was tested on real-life water distribution networks, which were built using the utility company's GIS data. We found that our technique, even in the case of an extensive network (more than 6000 nodes), needs only a few seconds of runtime.

A network is presented in Figure 1 that is located in Western Hungary. The system provides water for 3500 people and has 2700 nodes. The figure below shows its pressure sensitivity map, on the left without, and on the right with the proposed new pipe connection. The allowed built-in pipe length was maximised in 120 m. As a result, the algorithm found a pipeline that resulted in 25 % decrease in average, and 28 % decrease in peak sensitivity. Moreover, the capacity tests with hydrant models showed more than 20 % average gain in the critically sensitive region.

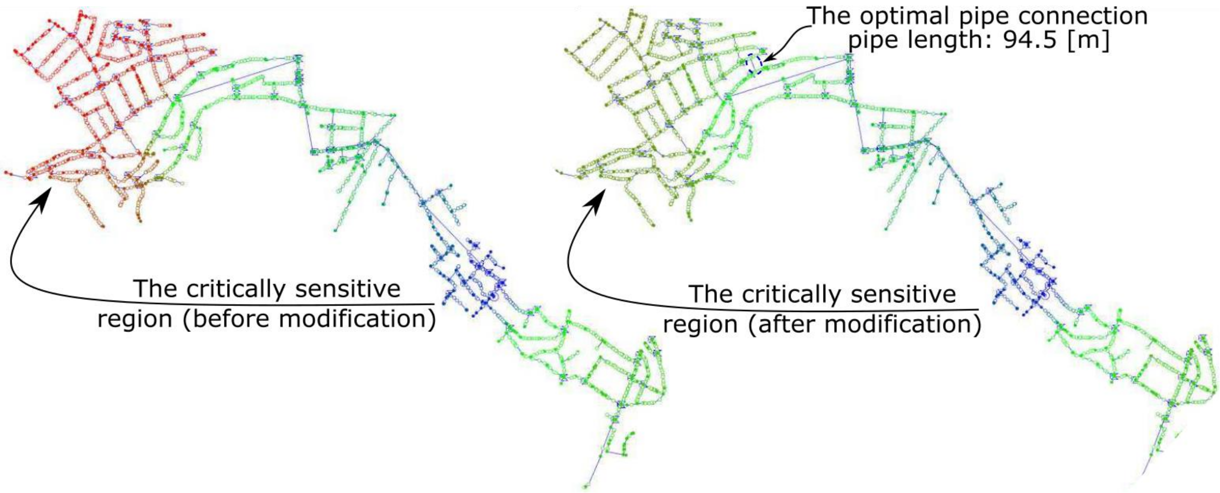

Figure 1. The effect of the determined pipe connection. The two sensitivity maps were created with the same colour scale

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Methodology for Drinking Water Protected Area Test Applied in Slovakia

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INTRODUCTION

Maintaining suitable water quality for human consumption (drinking water) is of great importance. In Slovakia, 84 % of drinking water is exploited from the groundwater sources (SHMI 2018). The abstracted amount of groundwater in 2017 was 10 600 $l.s^{-1}$ while the exploitable amount of groundwater was over the 76 500 $l.s^{-1}$ (SHMI 2018). Therefore it is crucial to defined and established drinking water protected areas (DWPA) and safeguard zones (SZ) of water sources to protect the water for human consumption. Legislatively 10 DWPA are set that is 14 % of the state area and 1734 of drinking water sources with 1269 SZ (zone I-III, in accordance with the decree no. 29/2005) that represents 7.6 % of the state area (RBMP 2015). According to Water Framework Directive (WFD, 2000/60/EC), the member states should ensure the protection of groundwater body (GWB) identified as DWPA in order to prevent the deterioration of water quality and to reduce the level of purification treatment in the production of drinking water. Therefore, the DWPA test was developed to assess whether the protection of DWPA/SZ is sufficient.

The DWPA test (also referred to as the test of water quality for human consumption) is one of the quality classification tests to assess whether the GWB is in good or poor status. This test was not performed in Slovakia so far. The proposed methodology includes the assessment of deterioration of untreated water quality at the abstraction point, that can be attributed to anthropogenic influences. The identification of significant change of untreated water is evaluated through trends considering the baseline levels and annual arithmetic mean values. Moreover, the impact of deterioration (increasing trend) on the level of treatment in water purification is assessed.

TEST METHODOLOGY

The DWPA test based on WFD requirements, guidance document no. 18 (CIS GD 18) and classification methodologies developed in the United Kingdom (UK TAG 2012) and Czech Republic (Hrabánková, 2014) was modified for the particular hydrogeological conditions in Slovakia. The aim of the test is to evaluate whether the protection of DWPA/SZ is sufficient, in order to avoid deterioration of groundwater quality and to decrease the necessity of water treatment.

The input data were obtained from monitoring managed by 14 water companies provided drinking water. The test was performed on all relevant chemical, microbiological and radiological parameters of untreated groundwater, measured at points of abstractions. In the initial screening, we directly identified parameters at good status, when their arithmetic mean of the last two years did not exceed 50 % of the threshold value (TV) (UKTAG 2012). The TV for inorganic ions/parameters were set as half of the sum of background value plus limit value (drinking water standard, DWD) for each particular GWB. The TV for other parameters were derived as 0.75 of DWD. The first step of the test procedure was to evaluate the existence of an increasing trend that could potentially lead to an increase in water purification treatment. The statistically significant trend was assessed by Mann-Kendall and regression analysis. If the increasing trend was present the second step assesses whether the arithmetic mean of the last two years or the predicted value to the year 2027 exceeds the TV. The classification of the particular parameter whether is in good or poor status also with the level of confidence is depicted in figure 1. The whole monitoring point was at poor status if only one relevant parameter was identified as poor. The classification at GWB level was done by considering the volume of abstracted untreated water (Hrabánková, 2014). The methodology was applied to 75 quarternary and pre-quarternary GWB of Slovakia. We will present the results from one representative GWB.

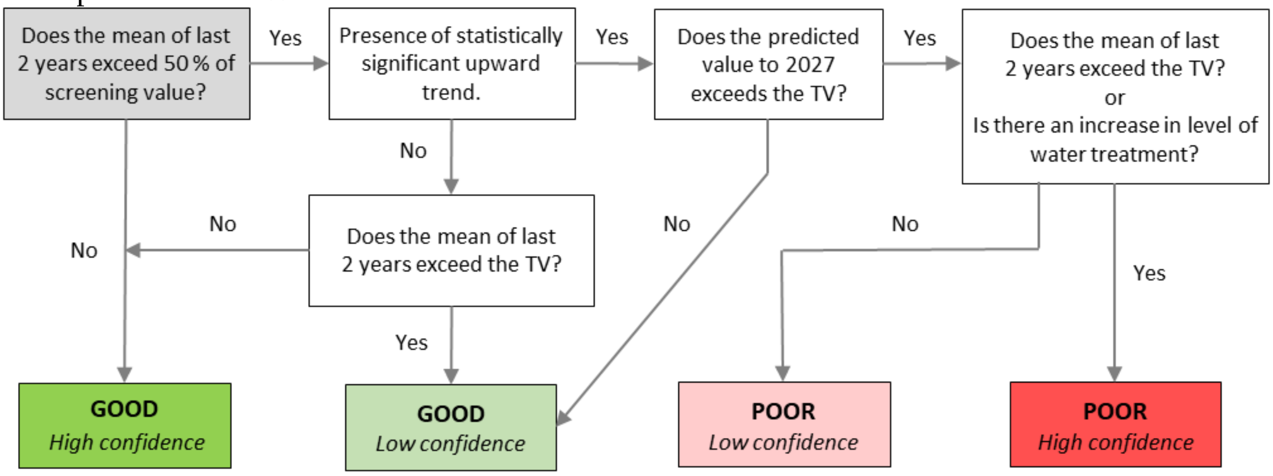

Figure 1. Schematic representation of the procedure for drinking water protected areas test

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Chlorine Presence Influence on Transformation of CECs During UV-based Processes

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INTRODUCTION

The chlorination process is still one of the most effective methods for water disinfection during the treatment of drinking water. The chlorination is performed using Cl_2, ClO_2 or NaOCl reagents. These agents not only lead to the removal or deactivation of pathogenic microorganisms but also react with compounds present in the disinfected water matrix. The most known chlorination by-products are trihalomethanes (THMs) and haloacetic acids (HAAs) (Legay et al., 2019; Villanueva et al., 2015). However these intermediates are not the only that are present in water after disinfection. Also chlorination by-products of several organic micropollutants, belonging to the group of contaminants of emerging concern (CECs), are identified in chlorinated water. The occurrence of these compounds especial in drinking water can have an harmful impact on human health. The paper presents the identification of decomposition by-products of selected CECs formed during UV-based oxidation processes preformed in the presence of chlorine.

EXPERIMENTAL

The research subject constituted CECs water solutions prepared on deionized water and surface water matrices. Solutions were spiked with 500 μg/L of benzocaine (BE), acridine (ACR) and 17beta-estradiol (E2) standards from Sigma-Aldrich (Poznań, Poland). pH of the tested matrices was adjusted to 7 using 0.1 mol/L NaOH. All water matrices were subjected to the chlorination process, which was carried out by the use of sodium hypochlorite (NaClO) with a nominal free chlorine content of 6 % (w/v). The chlorine dose used in the experiment was equal to 0.5, 1.0, 2.0 and 3.0 mg/L. The samples were subjected to single chlorination and UV irradiation supported by the presence of H_2O_2 and O_3. The H_2O_2 and O_3 dose was equal to 3 mg/L. The single chlorination process was carried out 10, 20 and 30 min and stopped by sodium thiosulphate ($Na_2S_2O_3$) at a dose of 100 mg/L, which act as an excess chlorine removing agent. $Na_2S_2O_3$ with a purity of 98.0 % was purchased from Merck KGaA (Darmstadt, Germany). Furthermore the UV irradiation was carried out by the use of a 150 Watt mercury lap by Heraeus (Hanau, Germany). The time of irradiation was set on 2, 5, 10, and 20 min. The analytical procedure of investigated compounds was performed according to guidelines presented in (Kudlek, 2018). Toxicological evaluation was carried out by the use of bioluminescent bacteria in the Microtox® test by Modern Water (Warsaw, Poland).

RESULTS AND DISCUSSION

The effectiveness of compounds decomposition occurring in both deionized and surface water solutions increases with the increase of the chlorine concentration (Fig. 1). The implementation of the $UV/Cl_2/H_2O_2$ and $UV/Cl_2/O_3$ allowed for a complete removal of E2 after 10 min of process duration (Fig. 1b). However several by-products formed during the reactions with the parent compounds and chlorine and/or reactive radicals were detected. The by-products were identified based on their mass spectra by the use of the NIST v17 data base (Table 1). The identified intermediates decompose more slowly than the parent micropollutants and were detected even after 20 of UV-based process implementation. The toxic nature of formed chlorination by-product was confirmed by the results obtained for the Microtox® test. The toxic effect decreased with the increase of the time of UV irradiation (data not presented).

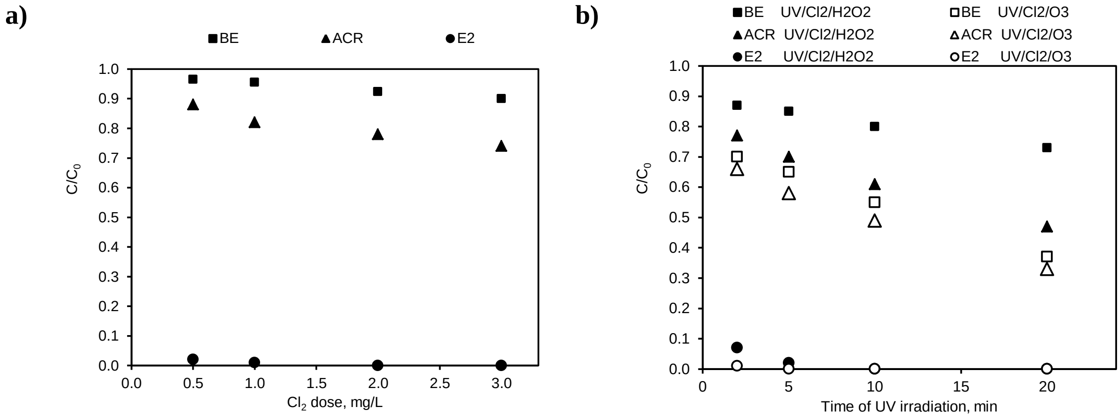

Figure 1. Change of compound concentration during a) chlorination and b) UV-based processes

Table 1. Identified CECs by-products during the performed experiments

Parent compound	Identified compound	Similarity,%	CAS-RN	Structural formula	Molecular weight
BE	ethyl 4-hydroxybenzoate	74	120-47-8	$C_9H_{10}O_3$	166.17
	ethyl 4-chlorobenzoate	84	7335-27-5	$C_9H_9ClO_2$	184.62
	4-chloroaniline	86	106-47-8	C_6H_6ClN	127.57
	4-chlorophenol	99	106-48-9	C_6H_5ClO	128.55
	3,4-dichlorophenol	98	95-77-2	$C_6H_4Cl_2O$	163.00
	chlorohydroquinone	75	615-67-8	$C_6H_5ClO_2$	144.55
	2,5-dichlorohydroquinone	80	824-69-1	$C_6H_4Cl_2O_2$	179.00
ACR	acridone	70	578-95-0	$C_{13}H_9NO$	195.22
	acridine-10-oxide	75	10399-73-2	$C_{13}H_9NO$	195.22
	2-hydroxyacridine	90	22817-17-0	$C_{13}H_9NO$	195.22
	9-chloroacridine	72	1207-69-8	$C_{13}H_8ClN$	213.66
	salicylic acid	80	69-72-7	$C_7H_6O_3$	138.12
E2	2-hydroxyestradiol	92	362-05-0	$C_{18}H_{24}O_3$	288.40
	estradiol-3,4-quinone	78	144082-88-2	$C_{18}H_{22}O_3$	286.40

CONCLUSIONS

The chlorination process of organic contaminants occurring in deionized and surface water lead to their decomposition and the formation of several intermediates. With the increase of the chlorine concentration a decrease of compound concentration and an increase of the forming by-products were observed. The implementation of the UV radiation in the presence of oxidants results in the decrease of the number and concertation of forming by-products. The UV-based processed had also a beneficial influence on the toxicity of the post-processed solutions.

ACKNOWLEDGMENT

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Bioremediation of Arsenic Contaminated Groundwater through Bioaccumulation of As(V)

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GROUNDWATER ARSENIC TREATMENT

Laboratory scale studies were carried out to study removal of Arsenic(V) using *Rhodococcus* bacteria procured for our work from Arsenic contaminated regions of West Bengal. Arsenite(As(III)) oxidation were carried out as a preliminary study in our earlier paper (Kumari et al., 2019). The process of biological arsenite oxidation leads to formation of arsenate(As(V)). Therefore a composite treatment by the same bacterial cells is done by studying their capacity to bioremediate As(V).The bioaccumulation of arsenic by the means of extracellular adsorption and intracellular accumulation of As(V) is studied. Response surface methodology using central composite design with the varying groundwater parameters were used to analyze the bioaccumulation capacity of *Rhodococcus* cells. Statistical analysis was carried out by applying the appropriate model and its validation was carried out. Contour plots was derived and the interaction effects of different groundwater parameters were studied.

BIOACCUMULATION

Accumulation of heavy metals by microbial cells involves physisorption at the cell surface which may be followed by metabolism dependent entry into bacterial cells. Aliquot 10 mL of pre grown bacterial cells is centrifuged and used as inoculum for synthetic groundwater as used in earlier study (Kumari et al., 2019). The bioaccumulation % of As(V) is evaluated by the following equation:

$$\text{Bioaccumulation\%} = \frac{C_i - C_f}{C_i} * 100, \tag{1}$$

where C_i, C_f are initial and final concentrations of As(V) in the groundwater solution. In this study maximum bioaccumulation capacity of 95.42 % was obtained at pH 7, Iron concentration 2.5 mg/L, Initial As(V) concentration, 0.65 mg/L and Humic acid concentration 5.5 mg/L.

CHARACTERIZATION

FE-SEM (Field Emission Scanning Electron Microscopy), AFM(Atomic Force Microscopy) and were used to differentiate between the untreated and treated samples to mark the physiological changes in bacterial cells after treatment process. FE-SEM shows marked morphological changes in bacterial cells after exposure to arsenic toxicity the treated cells are stunted and the outer surface appears smoothened. AFM images show the 3-D images of the cells and the cellular surface morphology change is clearly visible as the treated cells appear entirely smoothened.

BIOACCUMULATION IN REAL GROUNDWATER

The treatment method was also studied in groundwater to establish the feasibility of this composite treatment. The bacterial cells were also able to bioaccumulate As(V) proficiently, even in real groundwater, these cells remove 93.52 % of 0.5 mg/L As(V) in 12 h and 94.30 in 24 h.

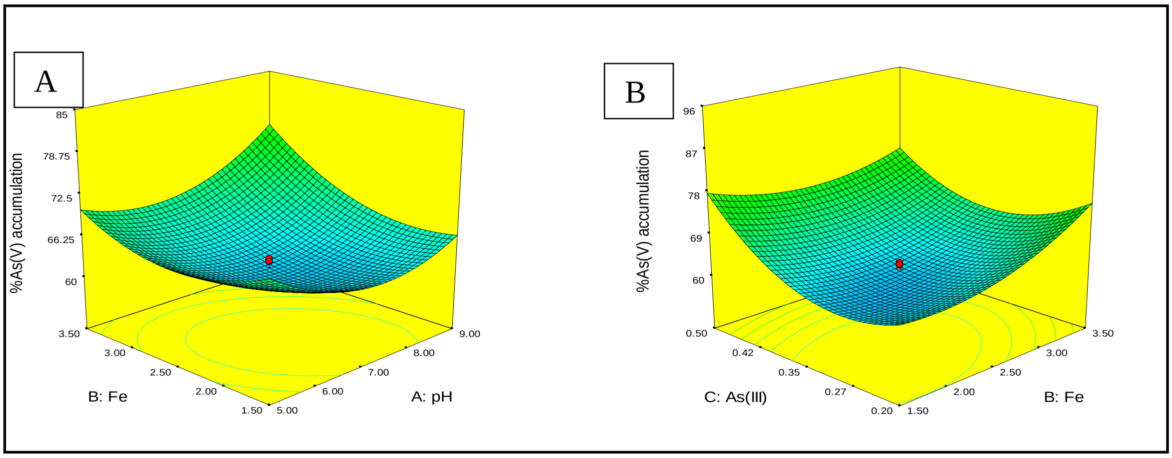

Figure1. Effect of (A) pH and Iron (B) As(III) and Ironon % As(V) accumulation

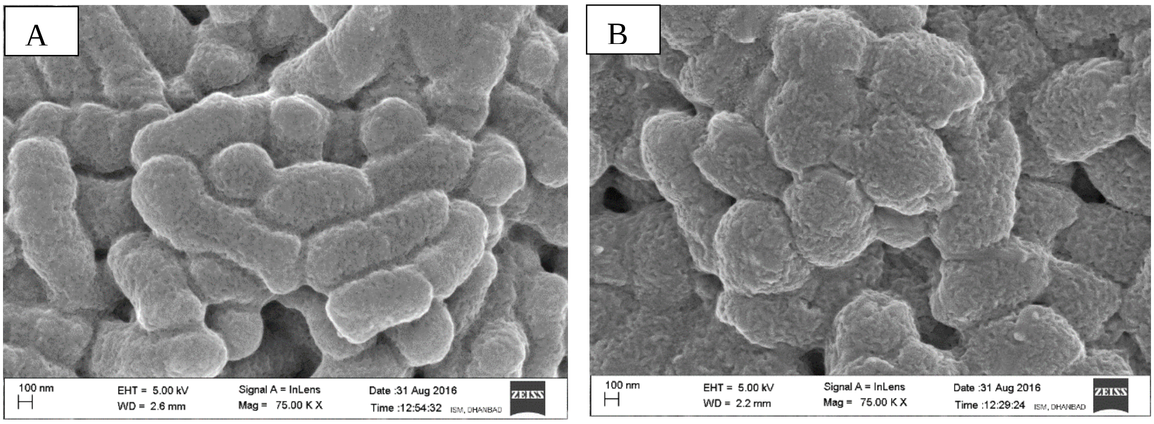

Figure 2. FE-SEM images of *Rhodococcus* cells (A) Untreated cells (B) As treated cells (Kumari et al., 2019)

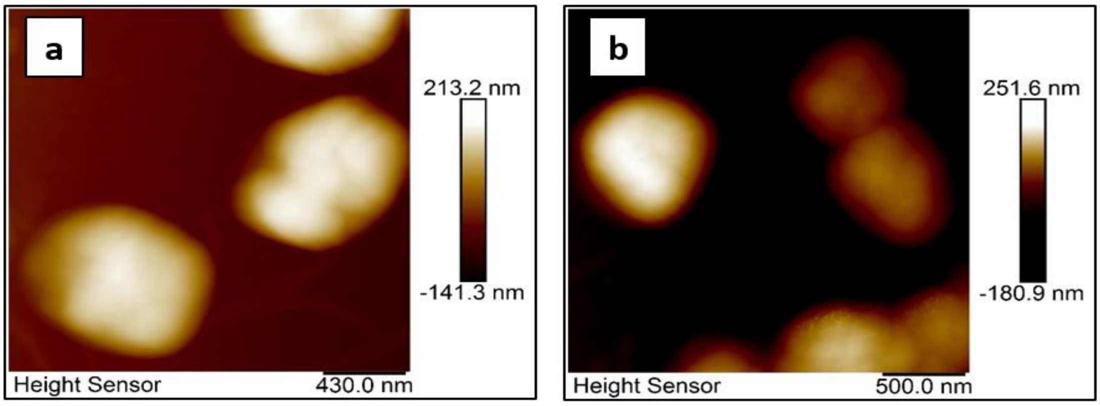

Figure 3. AFM images of *Rhodococcus* cells (A) Untreated cells (B) As treated cells (Kumari et al., 2019)

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Near Passive System for Generation of Water Condensate from Atmospheric Water

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INTRODUCTION

Atmospheric moisture is abundantly present in our ambient air and is emerging as an important source of potable water, especially in areas with little rain but relatively high humidity. (Lee et al., 2012). The *Near Passive System For Generation of Water Condensate from Atmospheric Water* is needed as a fresh water supply element in a closed loop process. A unit called *Water Flower* (Figure1) will come in use in water-scarce areas with arid climate conditions to capture water on its surface and storing it in a tank. The obtained water can be used for agricultural purposes, ecosystem services and potentially be remineralised to gain drinking water. In this paper, various materials and effects (like cooling) will be tested for their performance on water condensation. All of them will be shaped as a water flower taking advantage of passive radiation, cooling, wind braking and edge effect. The aim is to generate at least two liters of water per system per day (2 L/d) in water-scarce areas. The worlds ever-increasing need for fresh water has led to the use of non-conventional sources such as rain and fog water collection. Although rain water collection is relatively simple, the supply is often erratic. Dew occurrence, however, is far more widespread, can form in most climates and geographic settings, show high frequency and prevalence throughout the year. (Beysens, 2018).

Figure 1. Design of a Water Flower

MATERIAL INVESTIGAITON DESIGN AND CONSTRUCTION

A good understanding of water condensation, a phase change process in which water vapor is transformed to liquid water and which involves both heat and mass transfers, is a key to an effective atmospheric water harvesting. (Jin et al., 2018) This paper investigates dew formation by energy balances and material heat flux simulations in order to obtain major water output (Figure 2B).

In short terms, an easy way to increase condensation is to reach surface temperatures well below the dew point. This can happen by cooling using e.g. Peltier elements. The cooling effect is simulated with thermodynamic software and engineered for a good effect. The Water Flower will be powered by a homemade wind turbine and/or photovoltaic panels with intermediate power storage in small scale batteries. Thus, a nearly passive system. Without extra cooling, this system will operate entirely without any electric supply. Performances of 4 different settings will be tested and analyzed. Besides effectiveness, durability will be a criterion too due to environmental exposure as wind, solar rays and salinity on Greek Islands.

A) B)

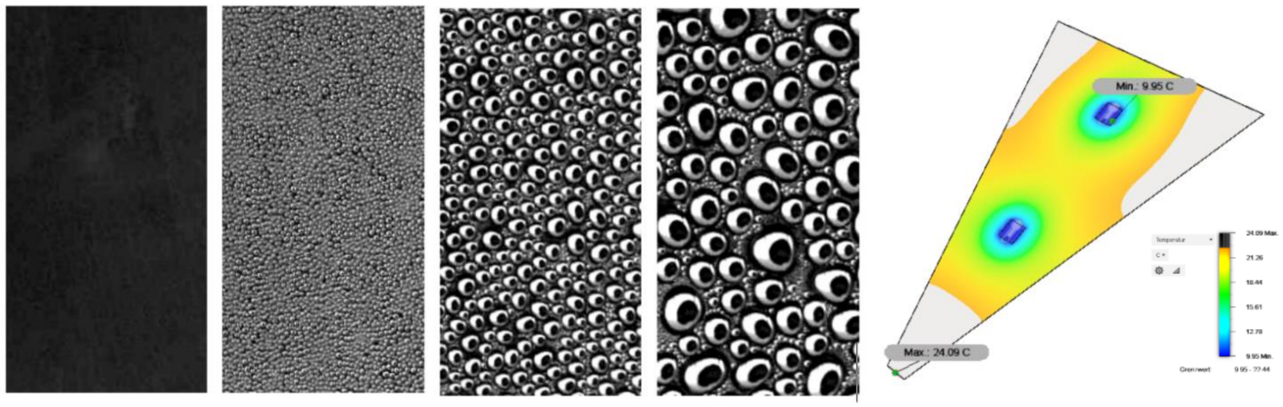

Figure 2. A) Dew formation on a smooth surface (Bintein et al., 2019); B) material simulation

Based on the tests a prototype will be built in a relevant scale for final troubleshooting. Hereby, the focus lies on low material and production costs. An easy to assemble system is important for flexible adjustment to different environmental conditions. Furthermore, the system shall operate in less favored regions where production technologies are limited. A simpler construction is also economically advantageous because it can also be installed by laymen. The use of cost-effective materials increases the opportunities of use across a wide range of users. By multiplying from one to several Water Flowers on location, a higher water turnover can be ensured.

The Water Flower is designed to adapt to local conditions, needs, and availability (climate, materials, building sites, foundation). The system can collect, harvest, and store water for humans, animals and/or plants. If necessary, the construction can be removed without residue and rebuilt at another location. The longevity aspect is also a decisive factor in the choice of materials.

SOCIAL ASPECTS

Like a tree, the Water Flower can provide shade for plants, animals and people and offer a place for gatherings of all kinds as the construction can serve as a flexible, adaptable open-air community centre.

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Comparative Analyzes of Hydro-chemical Properties of Bottled Waters in Serbia

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INTRODUCTION

A long time ago in amphorae - today in glass or plastic bottles - back then as a medicine, and today - for daily usage. Regardless of the age in history, commercially bottled groundwater always differed from the "plain" groundwater intended for public water supply. With the evolution of the market economy, changing and adapting to customer demand, the term "bottled water" changed as well. Today, consumers of bottled water expect as low mineralization as possible and consume this product daily. Bottled water often completely replaces the tap water even though it has a much higher price. The question is: how did we get here? Is it necessary and justified for the bottled water to replace entirely the public water supply? This paper examines bottled waters available in Serbia: their chemical characteristics, the effect they have on the consumer's health as well as the role of the advertisement on the consumer's choice.

METHODS

During the summer of 2018, 74 different bottled water samples were acquired, mostly from Belgrade's supermarkets. The analysis was done based on the data from the labels. Since all the info consumers get is the info provided on the product itself. Chemical properties of each sample were analyzed first, followed by the determination of the water type: concentrations in mg/l were converted to %eq and only ions with the content > 20%eq were considered. Data were plotted using AquaChem software (Schlumberger Water Services). Regarding medical information, the author has consulted a nutritionist from the Clinical Center of Serbia, Ljiljana Putniković. The aspects of bottled water advertising were analyzed using sent messages by different brands to their consumers, commercials and internet pages. Finally, a survey was taken to determine the choices people make regarding their preferred sources of drinking water.

RESULTS AND DISCUSSION

Out of 74 analyzed samples, 54 were *natural mineral waters*, 14 were *natural spring waters*, while the only *table water* found on the market was "Smart water". Among natural mineral waters, the majority (30) were carbonated. The comparative analysis of carbonated and non-carbonated natural mineral waters was conducted. The results were shown on the Piper diagram (Figure 1). In the diamond part of the diagram, the size of the circle was proportional to the mineralization of the sample. Verbal consultations were made with a nutritionist from Clinical center of Serbia, Ljiljana Putniković (9 August 2018), who stated that: *"…the mineral content of public water supply, if it fulfills all the established quality criteria, suits everyone. Moderation is one of the basic principles of a healthy diet, therefore bottled water should also be consumed in moderation."* The concept of "wellness" is one of the greatest trends in the 21st century. It has influenced all the aspects of modern ways of living. One of its aspects is the concept of "healthy diet", and together with it the idea of "healthy water" which is referring to pure, drinkable water with characteristics beneficial to human health. None of the brands has missed the opportunity to market their product in such a way. By becoming a part of the mentioned concept, bottled water brands have taken a prominent place in consumer consciousness (Mandić, 2018). A survey was taken in order to determine which water people in Serbia drink daily and why. There were 77 participants of whom 57.1 % stated that the public water system is their preferred source of drinking water.

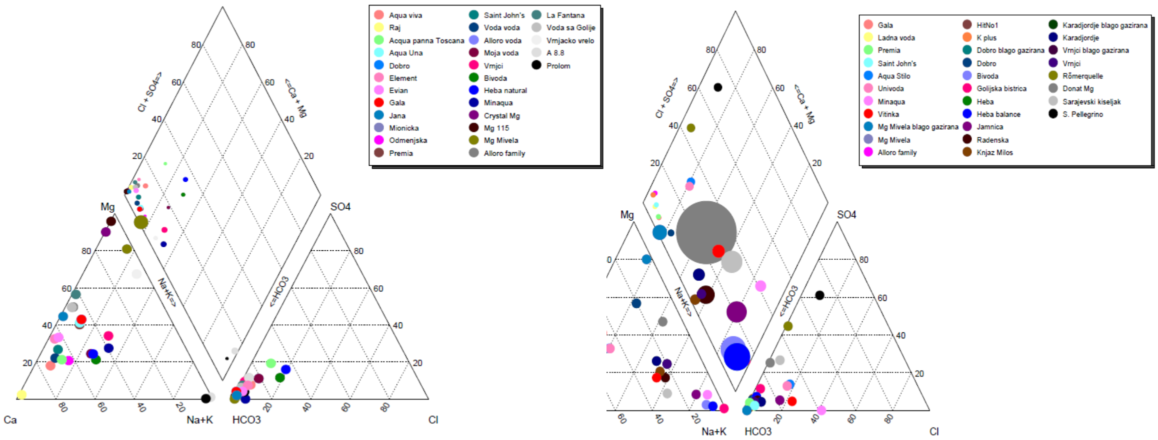

Figure 1. Piper diagrams for non-carbonated and carbonated natural mineral waters (Mandić, 2018)

CONCLUSION

Bottled waters available on the Serbian market are characterized by a diverse chemical composition, wide range of mineralization, as well as different dissolved gas contents. Regardless of their quality, availability and overall appeal, we should always keep in mind that bottled water is a commercial product whose primary purpose is to make profits. Public water systems, on the other hand, have a goal of providing drinking water for the population in whole. Therefore, it is unacceptable for bottled water to become the primary source of drinkable water. One of the most important issues every country should address is providing quality drinking water for its citizens. Hydrogeologists play an important and irreplaceable role in water supply projects.

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The Influence of Fine Sediments on the Quality of Drinking Water in the End Sections of the Water Supply Network

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INTRODUCTION

The paper deals with the assessment of the influence of fine sediments on the re-growth and occurrence of bacteria in drinking water, especially in the end sections of the water supply network. The sediment in the water supply network may come from a variety of sources. The fine material in the pipeline either occurs or comes from the outside. (Kooij, 2014) The presence of sediments in the water supply network is undesirable as it has a negative effect on both the quality of the water transported and may cause operational problems, particularly turbidity. For example, in 2014, 47,986 complaints were filed by customers of water supply companies supplying drinking water in England and Wales. These complaints concerned turbid water supplied to households and industry, with customers reporting turbidity as "dirty tap water" (DWI, 2015). Water supply networks have a certain self-cleaning ability, this self-cleaning ability is achieved by exceeding a certain threshold rate in the pipeline. At present, this threshold rate is considered to be 0.4 $m.s^{-1}$. (Husband et al., 2008). Sediments can serve as a source of nutrients for bacteria, can support bacterial re-growth (Kooij, 2014). Although the sediment is predominantly of inorganic origin, it may contain particles of organic origin, which can be strongly colonized by microorganisms and macroorganisms. The sediment also protects the microorganisms from the effect of the disinfectant and causes its higher consumption (Kooij. 2014). The composition of the sediments and their effect on bacterial re-growth and their diversity largely influences the pipe material. (Douterelo et al., 2014) Water supply network sediments can be removed to a certain extent by a controlled flushing of the pipeline. In order for the flush to be effective, the flush should respect the controlled flushing rules. (Rucka and Kovář, 2014).

CASE STUDY

The monitoring of selected end sections was carried out on the municipal water supply network in the Czech Republic. Within two months, samples were taken for the microbiological analysis. Thereafter, a controlled flushing of the entire water supply network was carried out. Sediments released by the controlled flushing were expressed by the turbidity value and microbiological indices. After the controlled flushing, the dependence of re-growth and bacterial occurrence on the achieved turbidity peak during the controlled flushing of the section was examined.

METHODOLOGY

The monitoring of water in the water supply network and sampling was carried out in a pre-determined procedure. Samples were taken from underground hydrants through a hydrant extension. Before the sampling, 30 litres of water were always drained so that the flow rate of water in the pipeline was not more than 0.02 $m.s^{-1}$. The controlled flushing was performed according to the methodology developed at the Faculty of Civil Engineering of Brno University of Technology within the project TA02020604. Subsequently, for each sampling site, the results were analysed as the number of non-compliant samples according to Czech Decree 252/2004 and the maximum detected turbidity peak when performing a controlled flushing of the entire network, respectively at the selected end sections.

RESULTS

As it can be seen from the following graph, there is a certain correlation in the occurrence of bacteria or the exceeding of their permitted amount according to the legislation currently in force and the detected maximum turbidity value during the controlled flushing. The size of this peak corresponds well with the total amount of sediment in each of the monitored sections. While this sediment, as mentioned above, plays a vital role in creating the conditions for the occurrence and growth of the monitored bacteria in drinking water.

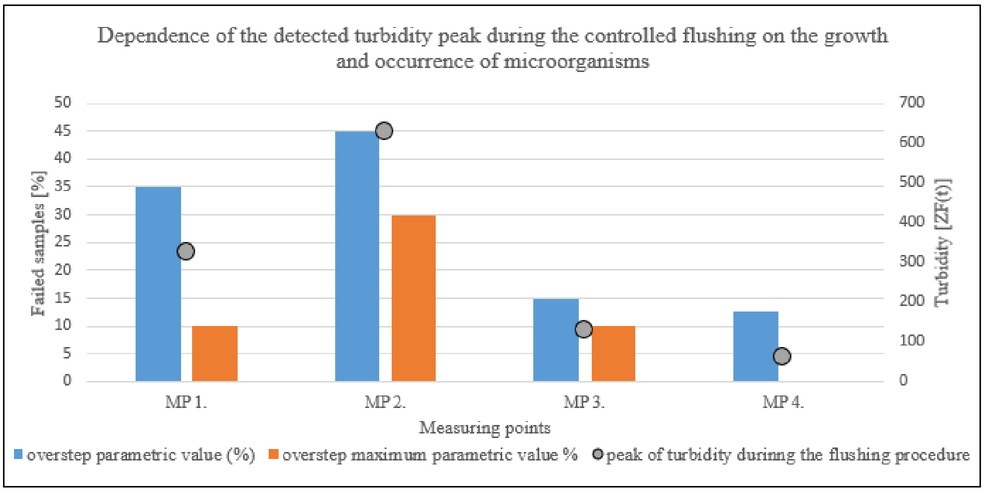

Figure 1. Dependence of the detected turbidity peak during the controlled flushing on the growth and occurrence of microorganisms

AKNOWLEDGMENTS

The work was funded from the budget of the BUT grant project "The influence time of the controlled water pipe flushing on the selected indicators of a drinking water quality", Registry No. FAST-J-19-6066, as well as with financial support of TAČR Zéta Project No. TJ01000296 "Drinking Water Quality Management in Water Supply Networks".

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Chemical and Green Zero Valent Iron Nanoparticles as Arsenic Remediating Agents: A Comparative Study

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GREEN ZERO VALENT IRON AS ECO-FRIENDLY ALTERNATIVE

Recent advancements in the field of nanotechnology has led to an increased application of nanoscale Zero Valent Iron (nZVI) in environmental remediation by virtue of its distinct physical and chemical properties. Choice of their synthesis technique plays a key role in determining the effectiveness and catalytic properties of nanoparticles. Due to the generation of toxic by-products associated with conventional chemical reduction methods, a green approach utilizing plant extracts has been employed for the synthesis of nanoparticles. These extracts contain phytochemicals such as polyphenols, flavonoids, tannins, proteins, vitamins reducing sugar, amino acids as reducing agent as they contain high antioxidant property.

Characterization of CS-nZVI and GL-nZVI

In this study, a comparison of characteristics of chemically synthesized (CS-nZVI) and guava leaf extract synthesized particle (GL-nZVI) and their Arsenic (As) remediation efficiency has been investigated. Particles were characterized on the basis of size distribution, UV-Vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM) and powdered XRD. Arsenic is a naturally occurring hazardous metalloid affecting millions of people around the world. Inorganic arsenite (As(III)) is usually present in reducing environments such as groundwater and has been found to be 60 times more toxic than the arsenate (As(V)) form. In developing countries such as India wherein groundwater contributes a major source of drinking water, sustainable As remediation techniques should be practiced.

As(III) remediation employing CS-nZVI and GL-nZVI

Effect of pH and kinetics of arsenic remediation are also studied and it was observed that green nanoparticles (GL-nZVI) are capable of oxidizing (>70 % within 10 min) the toxic and soluble form of arsenic (As(III)) into less toxic form of As (As(V)), which subsequently adsorbed onto in situ generated ZVI corroded products such as iron(hydr)oxides. Our earlier studies showed that As(III) oxidation kinetic model fitted well to a first order with K_{obs} values of 0.3444 s^{-1}, 0.0482 s^{-1} and 0.0155 s^{-1} at pH 3, 7 and 9 respectively (Rana et al., 2018). In contrast, for chemically synthesized nZVI, adsorption of As(III) was the main arsenic removal mechanism. The adsorption of As(III) onto ZVI could be described by a pseudo-second order kinetic model, indicating chemisorption. CS-nZVI was found to be a better adsorbent which adsorbs more than 50 % of As(III) within 30 min in comparison to about 20 % adsorption with GL-nZVI . However, use of green nanoparticles in environmental remediation should be encouraged as these nanoparticles considerably reduces environmental toxicity caused during CS-nZVI synthesis and application.

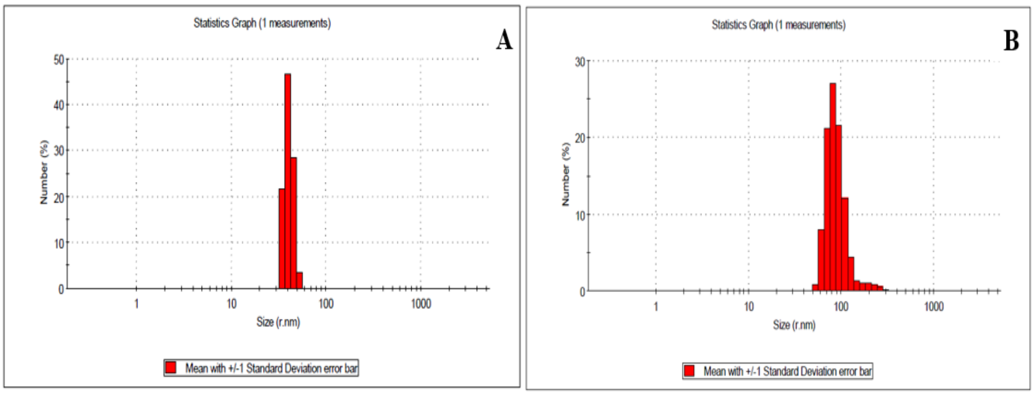

Figure 1. Histograms of nanoparticle size distribution by number of (A) GL-nZVI (Rana et al., 2018) (B) CS-nZVI

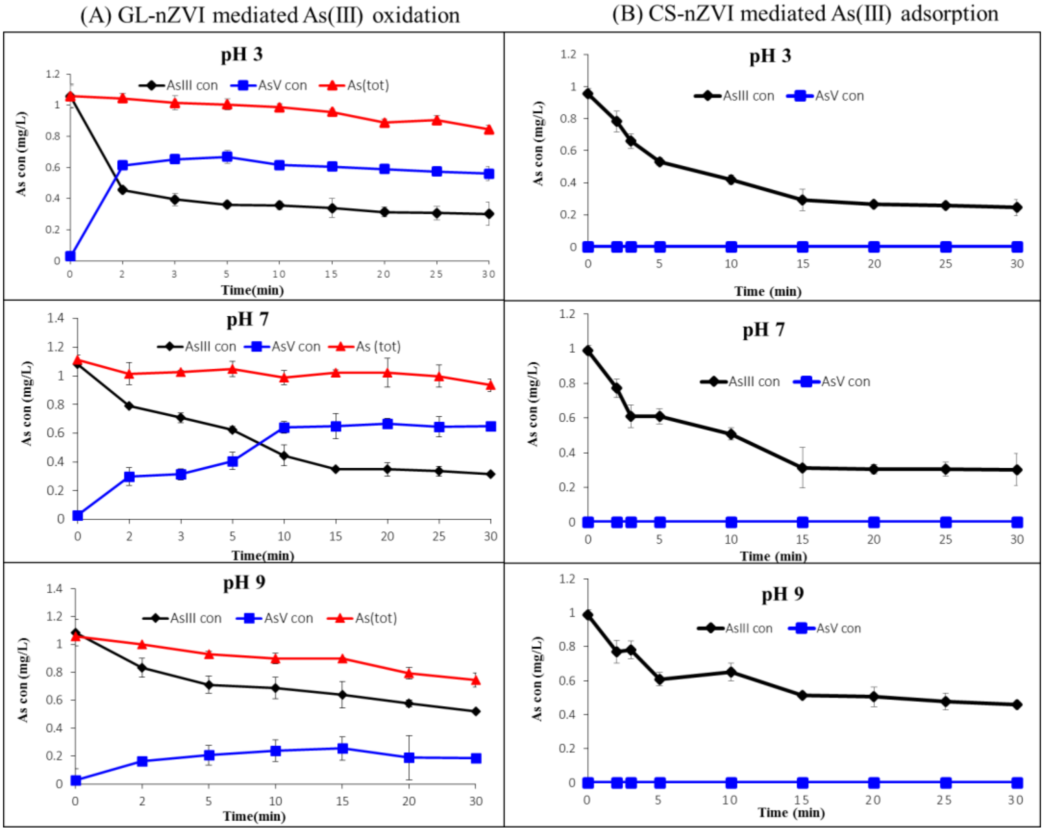

Figure 2. Arsenite oxidation and adsorption by GL-nZVI (Rana et al.,2018) and CS-nZVI at different pH values (3,7 and 9)

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Investigation of the Effect of Pre-ozonation on Organic Matter Removal via Flocculation

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INTRODUCTION

Ozonation of natural organic matter (NOM) yields major changes in its structure. There are many studies in literature reporting the effects of pre-ozonation on organic matter flocculation and removal, however many of them contradict one another. Some researchers indicated that pre-ozonation diminished the organic matter removal (Hailong et al., 2007; Bose and Reckhow, 2007), while others claimed the opposite (Pei et al., 2007; Jasim et al., 2008). And some informed that effect of ozonation depended on the concentration of organic matter (O'Melia et al., 1999) and ozone dose (Edwards et al., 1993). The studies revised were carried out with natural waters. However, the structure and characteristics of NOM may exhibit significant regional and seasonal variations. Hence, a study in which all conditions are controlled, as in this study, is essential to investigate the effect of ozonation on the removal of organic matter.

MATERIALS and METHODS

In this study, humic acid was chosen as the model NOM because humic acid part of NOM is more aromatic and has a larger molecular size, therefore it is hydrophobic, highly reactive and relatively easily removable by coagulation. Humic substances constitute the major part of NOM and are more determinative in NOM's behaviour.

Synthetic raw waters were prepared by adding designated amount of humic acid to deionised water. Before humic acid addition 0.1 M $CaCO_3$ and 0.1 M $NaHCO_3$ were added to deionised water to give hardness and alkalinity (both 100 mg/L as $CaCO_3$). Finally, necessary amount of H_2SO_4 was added to keep pH around 7.0 in order to modelise Istanbul tap water.

A series of O_3 doses (0, 2.5, 5 and 10 mg/L) were applied to synthetic raw waters containing different humic acid concentrations prior to flocculation. Aggregation process was monitored dynamically by using a Photometric Dispersion Analyser (PDA2000). Residual organic carbon measurements were done via a TOC analyser (Tekmar Dohrmann Apollo 9000).

RESULTS

A series of jar tests employing aluminium sulphate and polyaluminium chloride (PACl) were performed using synthetic raw waters with a range of humic acid concentration (5, 10 and 20 mg/L) pre-ozonated with different ozone doses (0, 2.5, 5 and 10 mg/L). Online monitoring of floc formation (Figure 1; floc formation at 10 mg/L humic acid concentration is presented only) showed that increasing pre-ozone dose led to gradual reduction in floc size. The onset of flocculation was delayed the time required to reach a steady-state fully grown floc size distribution was longer with increasing ozone dose. With PACl relatively larger flocs were formed. PACl also exhibited faster floc formation and earlier reach to steady-state fully grown floc size distribution, both make its performance superior to alum (Figure 2). Consistent with floc size data, lower residual TOC values were measured with PACl.

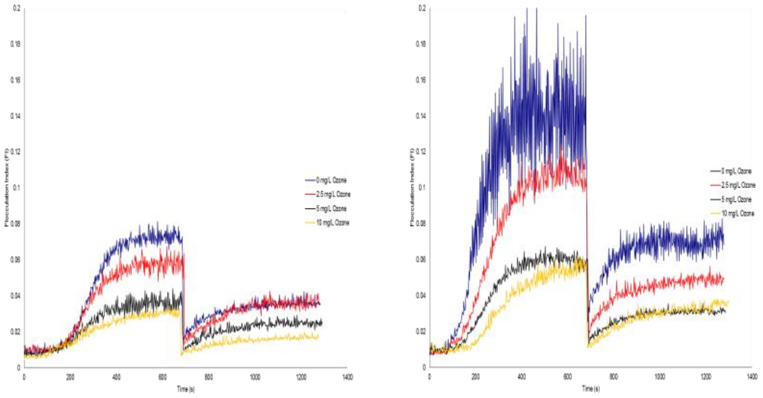

Figure 1. Floc growth and regrowth with alum (left) and PACl (right) in flocculation of pre-ozonated synthetic waters containing 10 mg/L humic acid

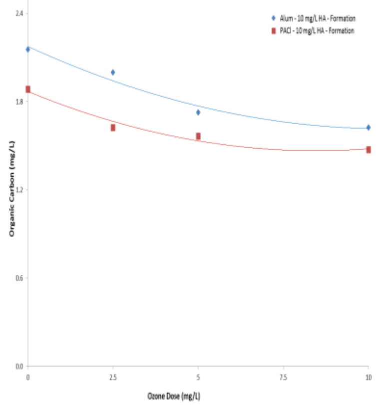

Figure 2.Residual total organic carbon change with ozone dose at 10 mg/L humic acid conc

On the other hand, TOC removal was found to be enhanced with increasing ozone dose. The results were quite similar to those in our previous publication (Sam et al., 2010), also to several others (Singer et al., 2003; Pei et al., 2007; Yan et al., 2007). Oxidation of humic acid by ozone brings out degraded organics, more oxidised organics (i.e more anionic charge) are introduced as the ozone dose is increased, which increase coagulant demand, and thus floc formation is hindered. Coagulant species are likely to first interact with those oxidised organics, neutralise their charge and form insoluble metal-organic complexes. This is thought to be the reason for the observed better TOC removal with increasing humic acid concentration even though smaller flocs were formed.

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Water Disinfection from Microorganisms Using Chitosan

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INTRODUCTION

The problem of clean water is closely related to the quality of water sources used in water treatment systems. The main source of centralized water supply is increasingly becoming artificial reservoirs and freshwater seas, which are formed owing to the riverbed blocking, flooding of large areas of land. As a result of human activity in the aquatic environment soil microscopic fungi, i.e., micromycetes, have appeared (Goncharuk et al., 2004). Micromycetes are widespread in the environment. They are an integral part of the human environment. Recently, however, micromycetes often become the cause of infectious and inflammatory diseases. Besides, it is known that micromycetes are capable of producing mycotoxins (Rudenko, 2015). When systematically injected into the human body, mycotoxins even in small doses are capable of provoking oncological diseases. They also have neuro-, nephro- and hepatotoxicity, show mutagenic activity, and have an immunosuppressive effect (Naresh and Olsen, 2004).

Taking into account the spread of micromycetes in the environment and their danger to human health, the aim of the work was to study the disinfecting effect of high molecular weight chitosan CTN_1 and low molecular weight CTN_2 with different degrees of deacetylation on *E.coli* and *C.albicans* microorganisms depending on the physicochemical parameters of the medium.

EXPERIMENTAL TECHNIQUE

Studying the disinfecting effect of CTN cups of 100 cm^3 capacity were filled with water contaminated with microorganisms, the necessary amount of CTN was added so that it concentration constituted 0.1, 0.5, 1.0, 5.0 or 8.0 mg/dm^3. At certain time intervals, an aliquot of the treated water was taken and sown on a nutrient medium with further counting of the colonies. Studying the joint bactericidal and flocculating effect of CTN on the process of water disinfection cups of 100 cm^3 capacity were filled with water contaminated with microorganisms, the required amount of CTN was added so that it concentration constituted 0.1, 0.5, 1.0, 5.0 or 8.0 mg/dm^3. At certain intervals, the treated water was passed through paper filters (i.e., a white tape – Whatman Grade 40 filter paper 8 μm, which simulates filtration through a sand filter), an aliquot of the filtrate was collected and sown on a nutrient medium with further colony counting. The survival of microorganisms of *Candida albicans* was determined by the presence of CFU during the process of sowing water samples in question on the Saburo agar medium, while for the determination of the survival of microorganisms of *Escherichia coli* the Endo agar medium was used. Microorganisms were cultured for 14-18 hours at 37 °C. The result was presented as the logarithm of the ratio of the test microorganism concentration in the solution after CTN treatment (Nt) to the microorganism concentration in the initial solution (N_0).

RESULTS AND DISCUSSION

It is found that the degree of inactivation of the culture of *E.coli* does not depend on the types of chitosan studied in the work (i.e., CTN_1 (its molecular weight (Mw) constitutes 100–300 kDa) and

CTN_2 (Mw constitutes 50-60 kDa) with the degree of deacetylation reaching 95 and 75-85 % respectively) whereas in the case of *C.albicans* culture a high molecular weight CTN with a deacetylation degree of 95 % is a more effective disinfecting agent. This confirms our conclusion made in previous studies on *C.albicans being* a more suitable test object of disinfection processes compared to *E.coli*.

It was shown that the highest degree of inactivation of the culture of *C.albicans* with CTN_1 is achieved in a weakly acidic medium (pH 5.0), whereas at pH 8.5 the disinfecting effect is insignificant. For the first time, the significant contribution of the flocculation of microorganisms with chitosan to the total effect of water disinfection is shown, which is especially noticeable at relatively short periods (< 1 hour) of culture contact with chitosan (Figure 1). This factor is essential when choosing a rational scheme of water disinfection with chitosan, because it indicates the possibility of reducing the dose of chitosan required for disinfection in the case of applying the water filtration after treatment with chitosan.

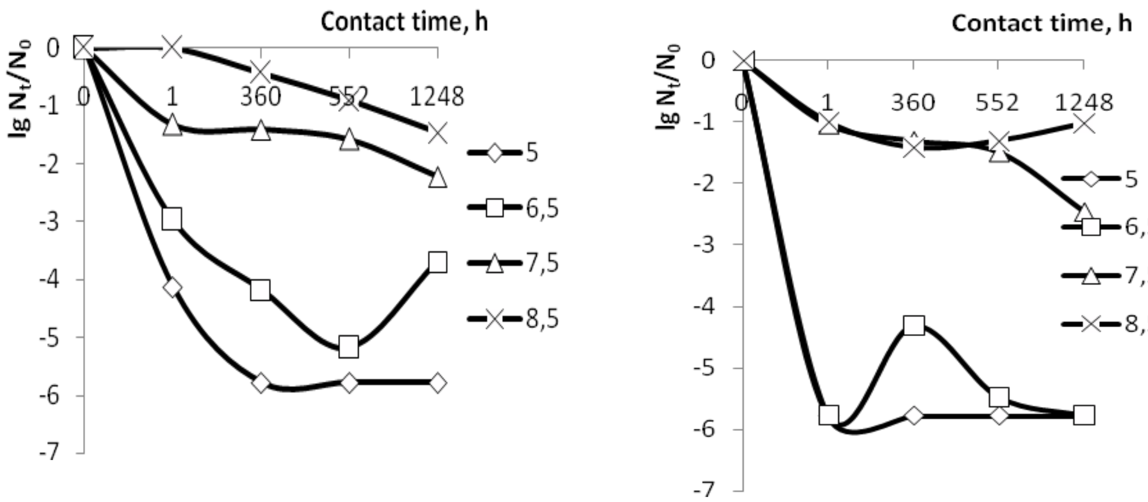

Figure 1. The kinetics of disinfection of distilled water with CTN_1 (0.1mg/dm^3) from C.albicans at different pH values: a) the bactericidal effect of CTN_1; b) joint bactericidal and flocculating effect of CTN_1

It is found that the presence of organic and inorganic impurities in water reduces both the disinfecting and flocculating effect of the polysaccharide on the microbiological object, which is obviously due to the competing influence of these impurities on the interaction of CTN molecules with microorganisms. It is shown that the antimicrobial effect of chitosan increases along with the increase of temperature from 7 °C to 42 °C. Achieving a high degree of water disinfection at low temperatures requires to increase the dose of chitosan. Thus, the results obtained convincingly indicate that chitosan can be used to effectively purify water from a number of microorganisms. The use of investigated dependencies will improve the quality of water purification.

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Effect of Agitation Strength and Time on Non-Aqueous Solvent Desaliation

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INTRODUCTION

Worldwide, water supply is not adequate to meet demand. Based on the current consumption rate, it will reach 90 % of fresh water withdrawals by 2025 in water stressed areas. The development of seawater desalination technology is considered to be essential to prevent regional and international conflict due to water shortage. The desalination process is widely used for removing salt ions present in seawater and industrial wastewater. Typical methods include the evaporation using heat and the process using membrane. However, the evaporation method requires a high heat energy to evaporate, and the separation membrane process also consumes enormous electrical energy for high pressure. Accordingly, various technologies are being developed to reduce energy consumption of desalination process. Recently, Bajpayee et al. (2011) has reported the possibility of removing the salt ion present in the water through the solvent extraction of pure water from the seawater. The solvent extraction desalination process is a technique using the difference in solubility between water and solvent according to the temperature change. However, main factors affecting this desalination process has not been studied much. In this study, the effects of the agitation strength and time on the water recovery and salt removal by the secondary amine (non-aqueous solvent) were investigated.

MATERIALS AND METHODS

We selected 0.5 M NaCl as brine and Dipropylamine [$C_6H_{15}N$, >99 %, Tokyo Chemical Industry, Tokyo] as non-aqueous solvent, which was considered promising for solvent desalination. First, we mixed 20 mL of brine and non-aqueous solvent in a beaker at 300-700 rpms for 5-30 minutes using a magnetic stirrer. After completion of the mixing, the mixture of the solvent and the brine is rapidly separated into two layers. The upper solvent layer which partially absorbed water was then removed from the beaker by pipet. The removed solvent mixture was heated at 80 ℃ for 30 minutes to separate the water again from the solvent. The separated water was finally evaluated for the water recovery and the salt removal rates. The water recovery and the salt removal rates were calculated according to the Equations 1 and 2.

$$water\ recovery\ rate\ (\%) = \frac{V_2}{V_1} \times 100, \tag{1}$$

$$salt\ removal\ rate\ (\%) = \left(1 - \frac{c_2}{c_1}\right) \times 100, \tag{2}$$

where V_1 is a volume of brine, V_2 is the volume of recovered water and c_1 is a concentration of Cl^- in brine, c_2 is the concentration of Cl^- in recovered water. The concentrations of Cl^- ion in brine and recovered water were analyzed by Ion Chromatography (ICS900, Dionex). The water content in supernatant solvent was analyzed by Karl Fischer Titration (KF890, Metrohm).

RESULTS AND DISCUSSION

The objective of this experiment is to figure out the effect of agitation strength and time on the water recovery and salt removal rates. Figure 1 shows that water recovery tended to increase mostly with the agitation time until around 10 minutes. After 10 minutes of agitation, agitation time did not have much effect on water recovery rate but its strength became more important for the increase in water recovery rate. Figure 2 shows that the rate of salt removal was decreased with increasing agitation strength and time.

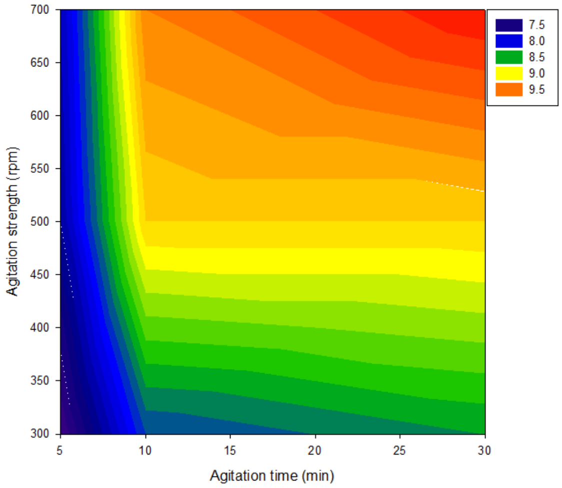

Figure 1. Water recovery rate (%) according to agitation strength and time

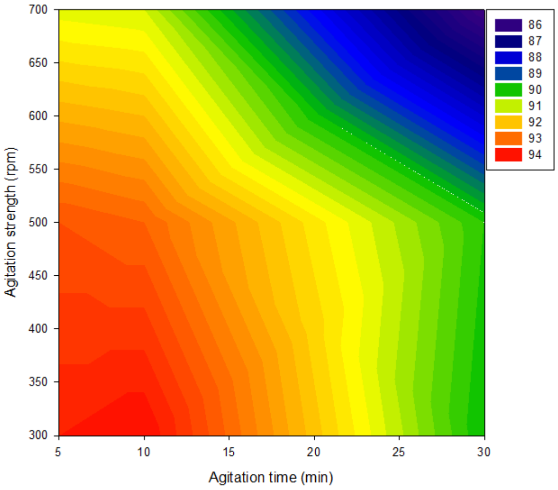

Figure 2. Salt removal rate (%) according to agitation strength and time

It is thought that the intimacy of contact and interfacial area between brine and solvent increase as the agitation strength and time become stronger and longer. This phenomenon suggests that the migration of both water molecules and salt ions to the solvent is increased so that the water recovery rate and the salt removal rate according to agitation strength and time show opposite trend.

The results in a chart form found in this study seem to be useful in determining the right operating conditions of solvent desalination for the water recovery and salt removal rates desired.

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Experimental Determination of Efficiency Adsorbent Bayoxide E33 of Removal Micropollutants from Water

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INTRODUCTION

Micropollutants are current topic in the water management field. In the world new technologies are tested to elimination micropollutants from water, because they are harmful not only for the environment, but also for people. Standard water treatment processes for removing micropollutants from water are: adsorption, advanced oxidation process and membrane process. For experimental determination of efficiency adsorbent Bayoxide E33 selected adsorbents were removed using adsorption. The efficiency of removing microfouling was determined comparised by removing three micropollutants namely removing a metal, a pharmaceutical and a pesticide. Bayoxide E33 removed metal successfully, but pharmaceutical and pesticide was not removed, because desorption occurred during removal.

MATERIALS AND METHODS

Sorption material

Bayoxide E33 is a dry crystalline medium developed by Severn Trent and designed for removal of arsenic, antimony and other metals, such as iron and manganese from water. The advantages of the material are long life continuous water treatment, low investment costs and long life dry medium (Ilavský and Barloková, 2008).

Selected micropollutants

Arsen was selected as a metal; which sometimes occurs in groundwater and can also be toxic for people in higher concentrations. Metal enrichment of water occurs by contact of water with rocks and soil. The anthropogenic source of metals in water can be wastewater from the mining and processing of ores, from metallurgy, rolling mills, from surface treatment of metals, the textile and leather industries (Pitter, 2015). Salicylic acid was selected as a pharmaceutical; which we classify to its anti-inflammatory effects in the group of non-steroidal anti-inflammatory drugs. Salicilyc acid is used as an ingredient for pharmaceuticals use for dermatological problems. Other groups of pharmaceuticals found in water include contraceptives, food supplements and personal care products. Pesticides can be introduced into drinking water sources primarily through agricultural activities. They can be found water in dissolved and undissolved form (Šíblová, 2017). Metazachlor ESA was selected as a pesticide to be removed; which is metabolite pesticide Metazachlor, belongs to classified a herbicides. This pesticide is used for agricultural activities for protection of plants. It is toxic for water organisms and may cause long-term adverse effects in water management (CHMI, 2019).

Process removing

In order to remove micropollutants from water glass column was used with above mentioned sorption materials. The height of sorbent was based as recommended by the producer of sorption material. Samples of filtered water were taken at different time intervals.

Determination of efficiency removing

Efficiency of removing micropollutants from water was determined by formula (Biela and Šopíková, 2017):

$$\eta = \frac{C_{RW} - C_F}{C_{RW}}, \tag{1}$$

where η is efficiency of removing, C_{RW} concentration of micropollutants in raw water and C_F is concentration of micropollutants after adsorption.

Figure 1. Sorption material Bayoxide E33, samples of filtered

RESULTS AND DISCUSSION

Efficiency of sorption material Bayoxide E33 in removing arsen from water was high, because the concentration of metal in water was reduced below the assay limit adsorption. The concentration of Metazachlor ESA was reduced after 30 seconds of removing, but afterwards the concentration was gradually approaching the initial value. Removed of salicylic acid had almost the same course as removed of pesticide. After 30 seconds, the sorption material was oversaturated and therefore gradually ceased to remove the acid. During removal, pharmaceutical and pesticide desorption occurred. This experiment showed that Bayoxide E33 is a very effective sorbent for metal elimination from water, but for removal pharmaceutical and pesticide, it was almost ineffective.

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Clean Karst Water Supply under a Big City: the Molnár János Cave

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INTRODUCTION

The Molnár János cave is a hypogenic cave situated under a densely populated area of Budapest, the capital of Hungary. The cave is the youngest member of the Buda Thermal Karst System. It's passages, extending several kilometers under the Rose Hill are almost completely submerged. Mixing corrosion is still active in the passages that are filled with waters originating partly from regional, partly from local/intermediate flow systems (Erőss 2010; Suranyi et al. 2010). The cave passages - evolved along tectonic fractures - form a multi-level maze, the cross section of the passages range from near impassable restrictions to tunnels large enough to pass for subway lines.

Figure 1. Scuba diver in Molnár János cave

The submerged part of the cave contains a huge amount of clean water - a potential water source for the city in case of emergency. Although the stream water filling the passages is probably originated far from the city, anthropogenic pollution can reach the cave via fissures in the host rock reaching from the surface to the ceiling of the passages, forming dripping sites. Drip waters are easily distinguishable from the stream waters based on their chemistry.

This research is focused on the characterization and monitoring of drip waters in order to determine their origin and to assess the severity of the pollution carried into the cave. For this purpose five ions were selected: chloride, calcium, magnesium, sulphate and nitrate. These ions may derive from the sewage system (NO_3^-), or from the chemicals used for de-icing the roads (Ca^{2+}, Mg^{2+}, Cl^-). With the exception of the nitrate ions natural sources can also contribute to these concentrations, for example by the degradation and dissolving of evaporite rocks (e.g. halite).

RESULTS

As seen on (Figure 2) the drip waters have significantly higher concentrations of all investigated ions than stream waters. The difference in nitrate concentration is remarkable, indicating that drip waters carry pollutants from the sewage system to the cave stream waters, especially close to the exit of the cave (1. sampling point) where the rock cover is thinner over the caves route.

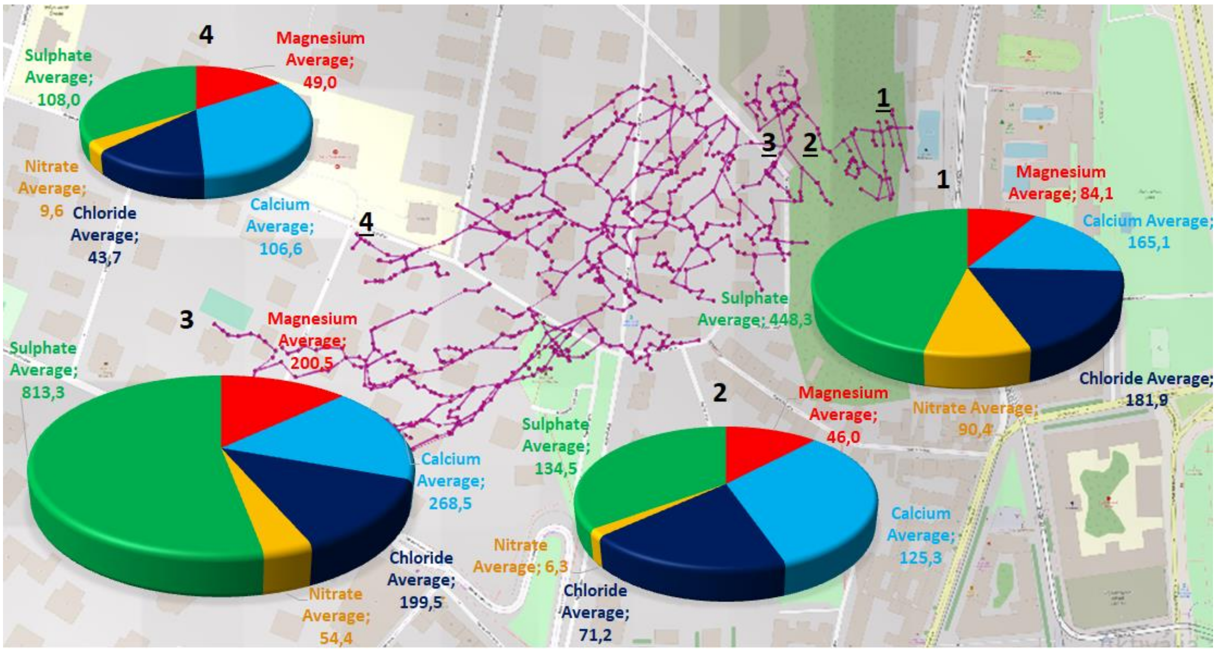

Figure 2. Map of Molnár János cave projected over the city map of Budapest, with the average ion concentrations [mg/l] at the most important sampling points (1-4). 1. and 3. are dripping waters, 2. and 4. are stream waters

The cave has colder (4.) and warmer (2.) inflows. Magnesium and nitrate ions are characteristics of the colder waters. According to our research the magnesium has a natural source, related to the contact time of the water with dolomite rocks. The nitrate ion is undoubtedly an anthropogenic pollutant, it is suitable for long term water quality monitoring. The presence of the chloride ion in high concentration in the warm waters shows that it derives also from the deeper flow paths, not only from surface pollution (e.g. de-icing agents).

The known amount of renewable water source of the cave system is at about 5000 m^3/d. This could be a possible drinking water source in the city close to the water consumers. The water quality fulfills the requirements of drinking water or even bottled mineral water.

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Investigation of Chlorine Wall Decay in Decommissioned Metallic Pipe Using Pipe Section Reactor

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INTRODUCTION

Free available chlorine decay in water supply networks has been associated with the occurrence of different chemical reactions. The mathematical model proposed by Rossman et al., 1994 is the most commonly used so far for description of this complex phenomenon. It assume, is that chlorine decay occurs in two places: in the bulk flow and on the contact surface (or very close to it) between the water and the inner wall of the pipes. Two parameters needs to be established in order to predict chlorine concentration over time: bulk (k_b) and wall (k_w) reaction coefficients. Hydraulic and physical conditions are also important, because they influence the transport of the substance from the bulk flow to the inner wall of the pipe. This process is described with the implementation of the mass transfer coefficient (k_f). For determining the values of the coefficients, different approaches and mathematical models were developed (Clark et al., 2010).

MATERIALS AND METHODS

Pipe section reactor

A laboratory pipe section reactor (PSR) was built, in accordance with the design of Digiano and Zhang, 2005. An old iron made pipe (internal diameter 150 mm, L = 300 mm), decommissioned from the water distribution network of Sofia city was used for the experiments. The sealing plates and the inner cylinder (diameter 120 mm) are made of acrylic. Eight rectangular shaped stainless steel baffles, BxL = 20x125 mm, are attached to minimize the vortex in the annular space between the cylinder and test pipe. A propeller of diameter 100 mm and variable speed (up to 600 r.min^{-1}) creates a circulating flow through the annular space. To prevent random errors due to the occasional introduction of air into the PSR during manual sampling (Hua at al., 2017), the system is equipped with a top-up reservoir.

Tests and measurement procedures

Water velocity. The flow velocity in the PSR was measured by detecting the flow travel for a certain time. For the purpose, a small piece of material with density, close to water is placed in the PSR and the time for 10 full circuits was measured.

Chlorine decay. A series of experiments was made using tap water from the distribution system of Sofia city. Each series included two parallel tests:

- Test 1: PSR test to determine the overall rection coefficient (K);
- Test 2: Bottle test for evaluation of the bulk reaction coefficient (k_b).

The model water solution was prepared with tap water and sodium hypochlorite, mixed in a 10 l bottle. The temperature of the solution and the initial chlorine concentration were measured before each set of experiments. The PSR was filled in with model water and a sample is taken from the system to define starting condition. Then the propeller is started, which time is considered to be the beginning of the overall chlorine decay test. Samples were taken from the PSR at random time intervals. The experiment ends when the chlorine concentration in the PSR drops below 0.05 mg/l. In parallel to the PSR tests bottle tests were also executed, as samples were taken from the rest of the model solution simultaneously with the samples from the PSR. Additional bottle tests were also performed to investigate the bulk reactions in greater detail.

Water quality. For chlorine concentration, a standard DPD colorimetric method is used with sensitivity of ± 0.02 mg/l (HACH, 2009). A thermometer with 0.1^{o}C reading intervals was used for temperature measurement. For other water parameters of concern (e.g. Iron, Manganese, Nitrites, Ammonia and TOC) standard laboratory methods (HACH, 2007) were used.

RESULTS AND DISCUTION

In the range 200 - 400 revolutions per minute of the motor, a linear dependence between the propeller rotation and the average velocity of the water in the PSR was observed. General first order models (first order bulk reaction and first order wall reaction) can predict precisely enough the chlorine decay only in case of low initial chlorine concentration, below 0.85 mg/l. However, new model is proposed, based on assumption of zero order bulk reaction and first order wall reaction. It provides best prediction of chlorine decay over time in the PSR for all 23 series of tests with initial chlorine concentration, ranging from 0.3 to 1.8 mg/l and annular space velocities of 0.27 m/s 0.39 m/s, 0.50 m/s and 0.62 m/s. Additional 24 hours bottle tests show, that parallel first order bulk reaction model describes much better the observed results, rather than simple first order. New parallel zero order bulk reactions model was carried out. It describes the laboratory results having Nash-Sutcliffe efficiency coefficients over 0.992, which confirms the assumption, for zero order bulk reactions. It was found out, that in the constructed PSR, mass transfer does not influence the chlorine decay at annular space velocity over 0.39 m/s. At 0.27 m/s there is a clear tendency for lower values of overall wall reaction rate compared to other results. This might be the consequence of a lower shear stress at the water-pipe contact surface. The values of wall reaction coefficient for all 23 series vary in the range of 0.008 ÷ 0.030 m/h. Exponential tendency for of decreasing of k_w with the increase of initial chlorine concentration was observed.

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Search for Materials Used for Tap Water Transmission Reducing the Capacity for Development of Biofilm – Preliminary Research

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INTRODUCTION

Biofilm developing on the internal surfaces of materials applied in the construction of the water supply system can be the cause of many serious problems, including technical and economic ones (Wolf et al., 2018). It contributes to a decrease in the sanitary quality of water, and as a reservoir of pathogenic microorganisms and viruses it can be a serious threat to the health and even life of consumers. The development of biofilm is possible on any material, but the type of material can determine among others its rate of development or structure. Synthetic materials proposed on the market are also subject to the phenomenon of microbiological corrosion. Both during production and particularly after their exploitation, as weakly biodegradable materials, they can pose a serious ecological threat to the environment.

The materials proposed in the study were produced at the Department of Sanitary Biology and Ecotechnics with the application of secondary raw materials. They are 3 materials based on polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC). The research on the materials was conducted in two aspects. The surface was analysed in terms of development of biofilm and its effect on the occupied surface. Potential toxicity of the new materials was also determined. The paper presents only results of selected analyses in the scope of the research.

MATERIALS AND METHODS

Multi-species biofilm culture – based on microorganisms from the water supply network. 100 μl of inoculum was introduced to flasks with liquid substrate R2A enriched with sodium citrate (own modification). Five developed materials from each type were separately introduced, namely PE, PP, PVC (with a surface area of 1cm^2 each). The culture was left for 30 days on a laboratory shaker at room temperature (22 °C). The inoculum was suspension of microorganisms isolated from tap water from Wroclaw. For this purpose, 3 litres of cold water were filtered through a Whatman filter with pore diameter of 0.2 μm. The filter was then transferred to 25 ml of sterile physiological solution (0.85 % NaCl) and shaken (160 rpm, Nocturne,) for 2 h. It was subject to the effect of ultrasounds for 30 seconds (35 kHz) for the purpose of detaching microorganisms from the filter cake.

A method of assessment of the metabolic activity and viability of cells subject to adhesion to the surface is adenosine triphosphate (ATP) determination (El-Chakhtoura et al., 2015). The analyses were conducted with the application of device luminometer EnSure, and the results were provided in Relative Light Units (RLU). The value of the units is directly proportionate to the content of ATP in a sample.

Pathogen adhesion to the surface of the materials was also analysed in *the multi-species culture with an addition of* 100 µl of pure strain of *Escherichia coli* (NCTC 12241 / ATCC® 2592 - BioMaxima). After 30 days, the materials were rinsed from excess agar with sterile distilled water (2 cm^3), placed in sterile test tubes with Tris buffer, and subject to the effect of ultrasounds for the purpose of isolation of genetic material of bacteria. DNA extraction from the biomass of microorganisms present on the surface was performed by means of an Isolate II Genomic Kit (Bioline). Measurement of the concentration and purity of genetic material was performed by means of a nano spectrophotometer (NanoPhotometer N60 Implen).

Detection of bacteria *E.coli* was performed with the application of the qPCR reaction (Mic, Bio Molecular Systems). For this purpose, an AmpliTest kit was used (Amplicon). It included reaction starters, specific TaqMan probe, and internal reaction control. The conditions of the reaction were in accordance with the producer guidelines.

RESULTS I CONCLUSIONS

Table 1. Measurement of the metabolic activity in the solution and on the surface of materials

	ATP, RLU		
	SURFACE OF THE MATERIAL		
Material	SUSPENSION (MICROORGANISMS DEVELOPING BIOFILM)	WITH BIOFILM	AFTER REMOVAL OF BIOFILM
PE	74	1117	22
PP	342	2260	165
PVC	37	356	50

The analysis of ATP content shows that the highest abundance of living microorganisms developed biofilm on the surface of Polypropylene (2260 RLU surface of material with biofilm, 342 RLU suspension). Their highest amount was also left after removal of biofilm by means of ultrasounds (165 RLU). Material the least prone to the development of biofilm proved to be polyvinyl chloride (37 RLU in suspension, 356 RLU in direct analysis of the surface with biofilm and 50 after removal of biofilm). The amount of isolated DNA, indirectly pointing to the degree of adhesion, was different for each material. For PE, the value was 10.08 ng/µl, PP – 10.85 ng/µl, and for PVC – 64.71 ng/µl. The conducted qPCR reaction showed presence of bacteria *E.coli* on PE and PP. No presence of the pathogen was detected on material made of PVC.

The preliminary analysis of results shows that PVC is a material least prone to the development of biofilm.

ACKNOWLEDGEMENT

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Reaction Mechanism for High Capacity Redox-Active Adsorbents for Selective Removal of Trace Hexavalent Chromium from Contaminated Drinking Water

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INTRODUCTION

Cr(VI), being a carcinogen, is regulated at concentrations greater than 50 μg/L in drinking water. With the possibility of USEPA changing the MCL to 10 μg/L, drinking water at many places shall be out of compliance. Although there exists various options for Cr(VI) removal from industrial wastewater, fewer options are available for contaminated drinking water since Cr(VI) is present at trace concentrations in comparison to other competing ions and secondly due to non-specificity of the adsorbent towards target ion. As a result, the treatment process becomes expensive due to the need for frequent replacement of exhausted adsorbent or regeneration. Thus, a material is required which would show high selectivity and removal capacity for such trace concentration of Cr(VI) from contaminated drinking water.

In one recent research project report to California Department of Public Health, it was observed that two weak base anion exchange (WBA) resins, i.e., Duolite A7 and SIR-700 have shown at least an order of magnitude higher capacity than other resins for trace Cr(VI) removal from contaminated groundwater (McGuire et al., 2006). The field results suggested presence of one or more mechanisms along with ion exchange. It is therefore intriguing to find out the mechanism behind such exceptionally high Cr(VI) removal capacity shown by these WBA resins. Motivated by all this, Cr(VI) removal by Duolite A7 was further investigated in the laboratory under different operating conditions and a novel mechanism has been reported for highly efficient chromium removal involving a combination of two mechanisms, ion exchange followed by redox reaction.

MATERIALS AND METHODS

Five synthetic anion exchange resins (INDION 810, INDION 820, INDION 860, Amberlite IRA 67 and Duolite A7) with different combinations of matrix and functional group were selected for this study. Fixed bed column runs were carried out using epoxy coated glass columns of 11 mm diameter and flow rate was maintained using peristaltic pumps. An initial Cr(VI) concentration of 200 μg/L and a background concentration of 100 mg/L of commonly occurring anions like chloride, bicarbonate and sulphate was kept in the influent. Cr(VI) in the effluent was measured by 1,5-Diphenylcarbazide method (APHA, 2012) and total chromium was measured using ICP-OES instrument. Surface morphology and elemental composition were studied using FE-SEM and EDAX. ATR-FTIR spectroscopy was used to study the changes in the molecular structure of the samples before and after Cr(VI) removal. XPS was also carried out to study the oxidation state of chromium present in the exhausted samples.

RESULTS AND DISCUSSION

The breakthrough curves obtained from fixed bed column study showed that strong base anion exchange resins performed better than weak base anion exchange resins at neutral pH, whereas at slightly acidic pH (pH = 5.0), Duolite A7 outperformed all the resins. For Duoilte A7 resin, breakthrough of 50μg/L (MCL for Cr(VI) in India) was observed around 35,000 BV(Bed Volume), whereas for all other resins, chromium broke through almost instantaneously at less than 1000 BV. Also, the performance of Duolite A7 resin improved with decrease in influent pH. The pH profile of Duolite A7 resin showed that from the beginning of column run, effluent pH was higher than influent pH indicating consumption of H^+ ions during the removal process, with continuous drop in the pH as the column run progressed. Perusals of literature has reported reduction of Cr(VI) to Cr(III) at acidic pH along with consumption of protons. Another breakthrough profile of Duolite A7 was plotted for column running at influent pH 7.0. Once the column was exhausted, it was left undisturbed and restarted after few days. It was observed that upon each restart of the column, there was a significant drop in effluent concentration and breakthrough curve instead of being steeper, became gentler long after restart.

From SEM image, it was observed that virgin Duolite A7 resin is highly porous and has a rough surface morphology, whereas after chromium adsorption, the surface has become very smooth and the visible pores have been filled up. New chromium peaks were observed in the EDAX spectra of exhausted Duolite A7 resin. The XPS spectrum of Cr 2p splits into Cr $2p_{1/2}$ and Cr $2p_{3/2}$ components attributed to spin-orbital coupling. Further, the Cr 2p bands were resolved into five Gaussian peaks, located at binding energy values of 575.46 eV, 576.78 eV, 579.83 eV, 584.47 eV and 586.48 eV which can be attributed to CrN, Cr_2O_3, Cr(VI), metallic Cr and $Cr(OH)_3$, respectively. Thus, XPS result suggested reduction of Cr(VI) to Cr(III) and simultaneous precipitation of Cr(III) into $Cr(OH)_3$. FTIR spectra showed evolution of C=O group in the exhausted samples. This observation leads to a conclusion that there has been oxidation inside the resin.

In the light of the above results, we propose a new reactive ion exchange mechanism taking place for the removal of Cr(VI) by Duolite A7 resin. When passed through a WBA column, chromate ions in the solution selectively bind to positively charged functional groups like secondary amine (-NH_2^+). The bound Cr(VI) anions thus approach closer to the polymeric matrix and being a strong oxidizing agent, it oxidizes the matrix of the resin. As a result, Cr(VI) anions got reduced to Cr(III) species, vacated the occupied sites and ultimately got precipitated as $Cr(OH)_3$. The vacated functional groups took up further Cr(VI) anions. Thus, the anion exchange sites got automatically regenerated, resulting in a huge capacity for Cr(VI) removal. On the other hand, strong base anion exchange (SBA) resins have quaternary amine functionality and thus the steric hindrance caused by bigger size functional groups did not allow chromate ions to approach closer to the matrix. As a result, Cr(VI) could not oxidize the polymeric matrix.

Although, the treated water needs to be characterized with respect to the byproducts of the redox reaction between Cr(VI) and the polymeric matrix, but this process opens the door for the design of new class of redox active agents for trace removal of Cr(VI).

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Effect of Conventional Pre-treatments on Natural Organic Matter Characteristics and Biodegradability in High DOC Waters

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INTRODUCTION

Many potable water sources in Canada have an exceptionally poor quality such as high concentrations of dissolved organic carbon (DOC) up to 25 mg/L and hardness often in excess of 400 mg $CaCO_3$/L (Goss et al., 2017). These waters are challenging to treat; especially the removal of DOC from the water requires excessive amounts of chemicals. High DOC in treated can have an adverse impact on drinking water treatment including the formation of potentially carcinogenic disinfection by-products (DBP) such as Trihalomethanes (THMs), and membrane fouling (Matilainen et al., 2010). Pre-treatments such as coagulation and oxidation can be used to reduce DOC and its biodegradable fraction (BDOC) prior to the membrane to alleviate fouling and reduce the concentration of THMs precursor (Volk and Lechevallier, 2002).

The purpose of this study was to assess changes in biodegradability of DOC, THMs formation potential (THMFP) or a real raw water source with an average DOC concentration of 18.3 mg/L during coagulation. A better understanding of the effect of chemicals and processes on DOC characteristics can help adapt water treatment techniques to improve drinking water quality specific for each different water source.

MATERIALS AND METHODS

The coagulants used include aluminum sulfate (Alum), polyaluminium chloride (PACl), aluminum chlorohydrate (ACH) and ferric chloride. The coagulation experiments were carried out at room temperature using a conventional method in six paddle standard jar testers. The BDOC test was performed according to a batch procedure developed by E. Khan (Khan, 1999); 230-mL water samples were filtered through 0.7 mm filters, inoculated with biologically active BOD seeds, and incubated at 20 °C for 28 days. The BDOC concentration was based on the difference in DOC reduction in the sample and the blank after the incubation period.

RESULTS AND DISCUSSION

According to Figure 1, a significant portion of DOC and BDOC, up to 70 % and 34 %, respectively, were removed after coagulation by 100 mg/L PACl. However, PACl had the lowest THMFP reduction from 810 µg/L to 364 µg/L, while alum had the highest reduction, reducing THMFP to 183 µg/L. (THMFP data are not shown here due to the space limitations of the abstract).

The results in Figure 1 also indicate that high removals of DOC do not necessarily correlate with high BDOC removal or low THMs formation. In fact, water samples with high BDOC concentration have formed less THMs. Therefore, it can be said that the formation of THMs can be controlled by changing water DOC characteristics that is a cost-effective alternative to removal of DOC with membrane filtration.

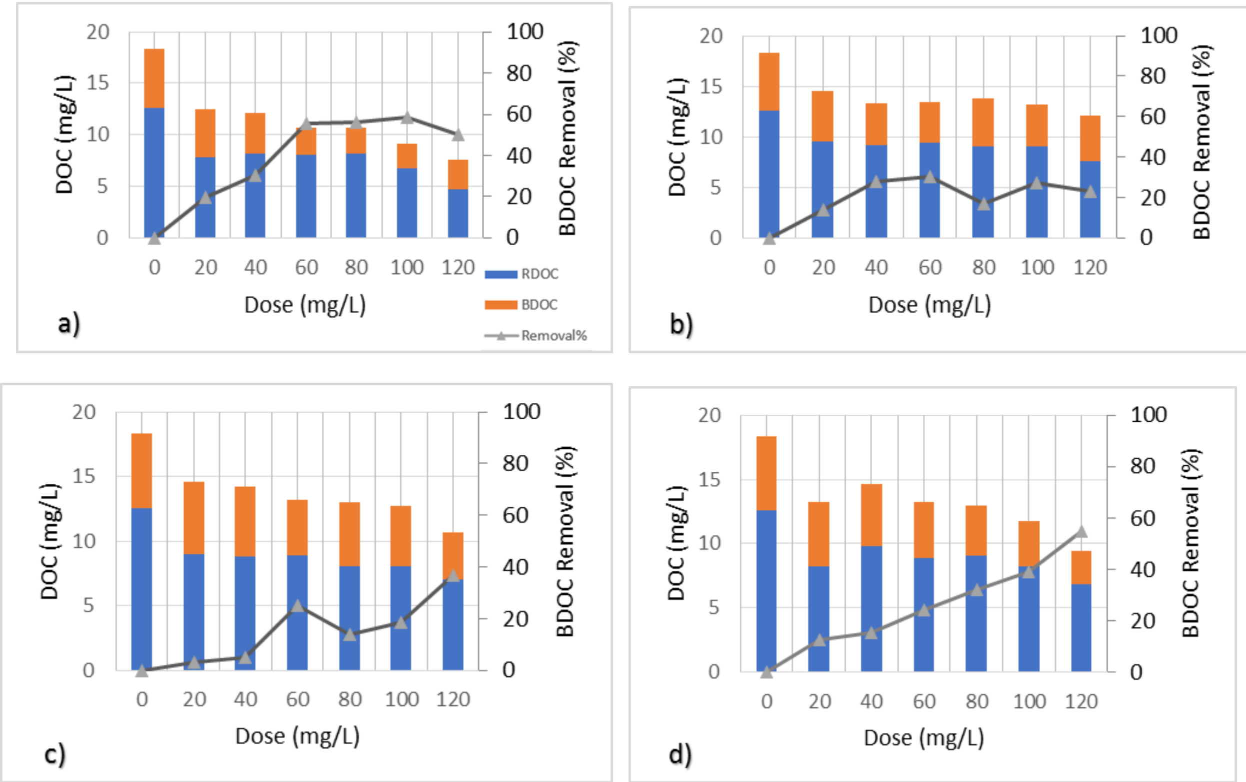

Figure 1. Removal of BDOC for a): Alum, b): $FeCl_3$, c): PACl and d): ACH at varying coagulant dose. The bottom and top bars are presenting BDOC and Refractory DOC, respectively. The line is showing the percentage of removal

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Comparison of Sensor Placement Strategies on Water Distribution Systems in the Aspect of Roughness Calibration

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INTRODUCTION

Water distribution systems (WDS) are typically ensuring clean drinking water for the industry, agriculture and population of cities in a wide range from a couple of hundreds to millions. For supervision purposes a hydraulic model is required that is capable of determining the pressure distribution across the system. The underlying mathematical model is a set of linear and nonlinear algebraic equations whose number nowadays can exceed even ten thousand. Before using such a model, calibration is necessary to reach the desired accuracy. In this study, we focus on calibrating the pipe roughness values, but it shall be stressed that the proposed framework is also suitable for calibrating other parameters e.g. nodal demands.

Even though there are several different sensor placement strategies presented in the literature, e.g. (de Schaetzen, 2000) or (Kapelan et al., 2003), an objective comparison between these is yet not available. Therefore, the main aim of our work is to fill this gap. Six different measurement layout techniques will be compared, including a novel one (HDS), on the widely known Anytown hypothetical test network.

CALIBRATION TECHNIQUE

Considering a real hydraulic network, the number of unknown pipeline roughness values are significantly larger than the available linearly independent measurements. A typical idea to overcome this issue is to create several groups and assign the same value for those pipes. However, our method takes every pipe friction value individually. In the first step an initial estimated parameter is needed for each unknown, that can be based on the material or diameter of the pipelines. Starting from this, we use the sensitivity matrix (Klapcsik, 2018) to build up a two-step iteration that can find those parameters which are the closest to the estimated ones and for which the computed pressure distribution matches with the measured pressure values. The proposed method is iterative, thus it is free from heuristic optimization strategies. This results in an advantageous computational time a dn is suitable for large, real-life networks containing more than ten thousand of pipelines.

SENSOR PLACEMENT METHOD

Intuitively, a "good" measurement layout fulfils two important requirements. On one hand, sensitive nodes are used for sampling where the “sensitive node” means that even small changes in roughness coefficients throughout the network will cause significant pressure changes at that node. On the other hand, it is inefficient to deploy pressure loggers close to water tanks, where the pressure is prescribed by the water level of the tank. Also, sensitive nodes tend to accumulate at certain locations within a WDS, thus simply choosing the most sensitive nodes often results in the accumulation of sampling points close to each other (Klapcsik, 2018). Thus, the installed pressure loggers should “far” from each other as well as from primarily defined pressure points.

For the first aspect, one sensitivity analysis is performed to determine the nodal sensitivity (Klapcsik, 2018). While for the latter issue a new approach has been defined, called *hydraulic distance*. This originates from graph theory, where the distance between two nodes is the number of edges along the shortest path between them. This quantity can be extended straightforwardly for weighted graphs: the distance stands for the sum of the weights along the shortest path. In case of WDS, the weight is the frictional pressure drop. In overall, we defined two variables for each node, one indicates how sensitive the node is, while the other shows how far it is from other nodes. Therefore, we will refer to this method as Hydraulic Distance with Sensitivity (HDS).

The method consists of the following steps. First, we perform a single hydraulic simulation with sensitivity analysis using nominal demands and estimated roughness values. Secondly, we calculate the hydraulic distance for each node and multiply it with the nodal sensitivity and choose the maximum value amongst them, then recalculate the hydraulic distances only. This method ensures that a) sensitive nodes are sampled, b) pressure loggers are “far” from each other and prescribed pressure points. Since only one hydraulic calculation is necessary, the technique can be applied on huge networks efficiently, e.g. cities with population over millions.

COMPARISON

Our novel sensor placement technique was compared to five different methods from literature using the presented calibration technique on Anytown network, see Fig. 1 left side. The steps of the comparison analysis are the following. First, we perform a hydraulic simulation with nominal roughness values and save all nodal pressure data. Then, we choose the number of sensors and designate a layout using one of the methods and perturb every roughness coefficients, then calibrate using only the “measured” pressure data. Finally, we evaluate the difference between the nominal pressure and the ones after calibration. As the right side of Fig. 1 shows, the *HDS* technique is amongst the best one with *Smax* (Klapcsik, 2018) method.

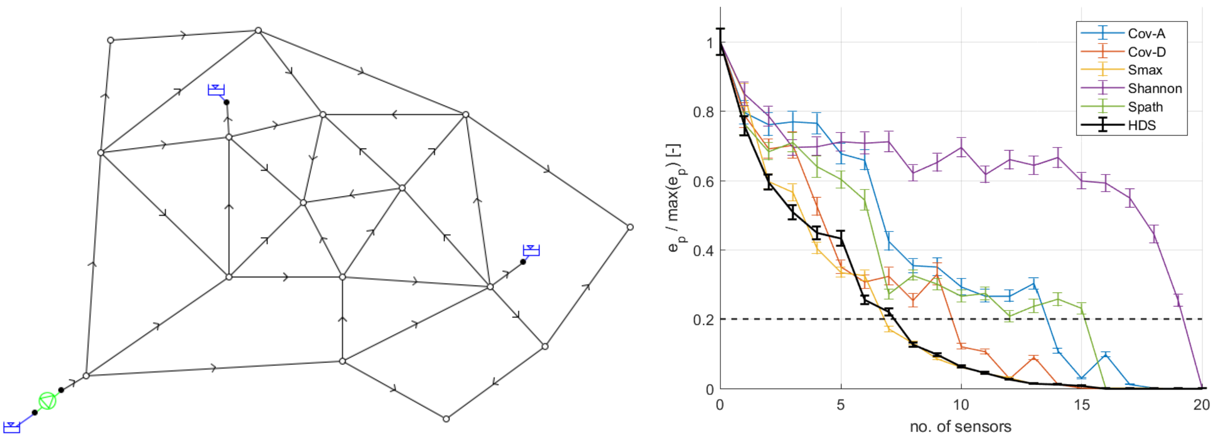

Figure 1. The layout of Anytown network on the left side and the results of the comparison on the right side

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Detection of *Legionella spp*. and *E. coli* Pathogens in the Water Supply System in Wroclaw

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INTRODUCTION

To date, the human health risk assessment of tap water is performed mainly by culture-dependent methods, what may lead to under-estimation of the issue. However, the potential solution of this problem may be the implementation of molecular biology techniques, such as next generation sequencing and quantitative PCR (qPCR) (Ashbolt, 2015). It is known, that trace amounts of pathogenic bacteria are present in natural water reservoirs such as lakes and rivers (WHO, 2017) and may enter water supply systems as a result of imperfection of water purification. Two examples of the most important species causing the waterborne diseases are *Legionella pneumophila* and *Escherichia coli* (WHO, 2017).

Some waterborne pathogens are resistant to disinfectant, able to grow on low organic concentrations and low oxygen levels and may adhere the pipeline surface, forming biofilms (Falkingham et al., 2015). Therefore, water supply systems provide optimal conditions for such bacteria. The presence of nutrients in sediments or biofilms, stable temperature, as well as insufficient amounts of chlorine remaining in a network may contribute to the multiplication of these pathogens. Another factor promoting the proliferation of bacteria, mainly within the biofilms, is water stagnation (Ashbolt, 2015; September et al., 2007). Therefore, the proper design, operating and maintenance of water installations, providing even minimal, but permanent water flows, is strongly recommended.

The aim of the article was the detection and quantification of the most important waterborne pathogens, i.e. *Legionella* and *Escherichia coli*, in the tap water samples collected from the water distribution system in Wroclaw by the qPCR approach.

MATERIALS AND METHODS

Tap water samples were collected from 15 different points of the water supply system in Wroclaw (Figure 1). 3 litres of each sample were filtrated on Whatman filters (mixed-cellulose esters, diameter 0.2 µm). Before the sampling, taps were disinfected by 96 % of ethanol (Sigma) and the water was flushed for 5 minutes.

Genomic DNA was isolated using the Isolate II Genomic Kit (BIOLINE) with small modifications. The amount of DNA was measured on NanoPhotometer N60 (Implen).

The real-time PCR (MIC, Bio Molecular Systems) was carried out using AmpliTest (Amplicon) with specific TaqMan probes dedicated for each type of the bacteria (*Legionella spp*., *L. pneumophila* and *E. coli*). All parameters for the qPCR run were retained as suggested by the manufacturer (initial denaturation 95 °C / 5 min; 45 cycles of: denaturation 95 °C / 30 sec, annealing 58 °C / 25 sec; cooling at 40 °C / 30 sec). In each sample the internal control was included. All reactions were conducted in triplicate.

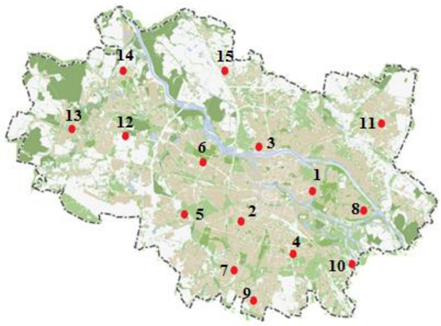

Figure 1. Map of Wroclaw with the location of collection points

RESULTS

In the performed reactions, *Legionella spp*. were detected and quantified (based on the standard curve) in samples collected from sampling points: 1, 2, 3, 4, 5, 7, 8, 9, 12, 14, 15. At no point the presence of *L. pneumophila* was detected. The *E. coli* was quantified only at one point (number 13). The results indicate the high occurrence *Legionella spp.* in tested tap water samples. Nevertheless, the presence of the most important human pathogens, i.e. *L. pneumophila* and *E. coli*, seems to be irrelevant. As the applied qPCR method do not differentiate between live and dead bacteria, the obtained results do not evidence directly any human health threat associated with tap water consumption. However, the results obtained by Bonetta et al. suggest that only minimal fraction of total *Legionella* bacteria detected by qPCR method were non-viable (Bonetta et al., 2018). In any sample, no inhibition of reaction was found, what confirms the reliability of the obtained results.

CONCLUSIONS

Tap water samples revealed to contain some species of bacteria of *Legionella* genus, but no *L. pneumophila*, which is the most known legionellosis causing factor. Moreover, *E. coli*, commonly recognized indicator of faecal contamination, was quantified only in one sample (with no evidence of viability of the bacteria), suggesting the overall good quality of tap water from the water supply system in Wroclaw.

ACKNOWLEDGEMENT

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Pollution of Urban Groundwater by Emerging Contaminants

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INTRODUCTION

Groundwater is an important source of drinking water worldwide and its role is growing due to the deterioration of surface water quality and quantity under the impact of climate variability, contamination, and reallocation of surface run-off (WWAP, 2015). There is a high concern regarding the low quality and quantity of available groundwater resources due to ongoing and increasing contaminations in Ukraine (Yakovlev et. al., 2015), and a lack of appropriate regulations (Vystavna et al., 2018a). Organic compounds, particularly pharmaceuticals, have been used to determine the sewage contribution in groundwater (Schaider et al., 2016). The research area is the densely populated Kharkiv city (1.4 M inhabitants), East Ukraine, where locals use groundwater as an alternative to tap water. The study area has limited local runoff and is located in zone under risk of military actions. Therefore, groundwater is considered as an important strategic drinking water source that can potentially replace the tap water in an emergency. We selected five urban (T1, S2, N3, Y4 and P5) and one peri-urban forested (O6) groundwater sites.

METHODS

Groundwater samples (1L amber glass bottles) for analysis of emerging compounds were collected in September 2017. The screening of chemicals was based on an exact mass in an open access library (over 2,000 compounds) by Liquid Chromatography Quadrupole Time-of-Flight Mass Spectrometry coupled to an Accela 1250 LC pump (Thermo Fisher Scientific®) and an HTS XT-CTC autosampler (CTC Analytics AG®, Switzerland), operated using Xcalibur software (Thermo Fisher Scientific®). Because of the nature of the screening analysis, exact concentrations could not be determined.

RESULTS

The identified chemicals were divided into three groups: drugs (caffeine, nikethamide, riluzole, phenazone, pilocarpine, pergolide, ajmaline, carbamazepine, moxonidine, dihydrocodeine, sulfathiazole, papaverine, and aripriprazole), pesticides (DEET (pentedrone), dodine, chlordimeform, atrazine, simazine and butraline) and food compounds (alternariol as a mycotoxin, chanoclavine and kojic acid as additives). All of the studied drugs can be abused and some are illicit drugs. The most frequently detected drug (in 5 out of 6 springs) was the alkaloid pilocarpine which was found even in the forest spring. The chanoclavine and chlordimeform were detected in 4 out of 6 studied springs. Caffeine, phenazone and alternariol were found in 3 out of 6 studied springs. Other compounds were found in 1 or 2 sites. However, each spring was characterized by a distinct group of detected compounds according to the principal component analysis (PCA) ordination (Figure 1) (Vystavna et al., 2019).

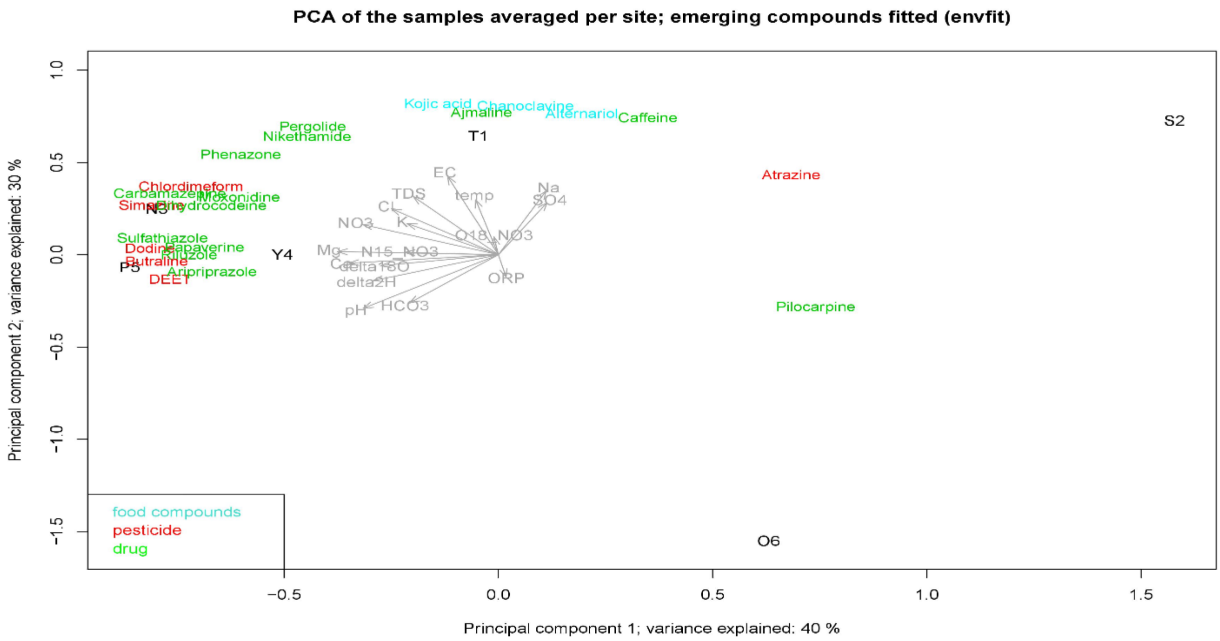

Figure 1. PCA of the samples of emerging compounds averaged per site (Vystavna et al., 2019)

DISCUSSIONS

The impact of anthropogenic land use was reflected also by the presence of drugs and food compounds in urban springs (Figure 1). The highest diversity of drugs and food compounds was found in springs with the high sewage contribution (T1, N3, Y4 and P5). The relation between the non-persistent chemicals caffeine, food compounds and some ions (SO_4^{2-} and Na^+) indicates that these emerging compounds continuously enter T1 with raw sewage likely from mains. However, the positive relation between persistent drugs and pesticides with NO_3^- at N3, Y4 and P5 may point to sewage leakages from pit latrines. Some persistent pesticides and food compounds were detected at sites with negligible sewage contribution (urban S2 and forest O6).

CONCLUSIONS

The chemical (major emerging compounds) analyses was useful to determine and partly quantify hydro chemical processes in the urban subsurface. Our findings clearly indicate strong contamination under the urban impact. High nitrate contamination of urban springs and the presence of potentially toxic emerging compounds indicate the health risk associated with the use of urban springs as drinking water sources.

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Comparison of Different Adsorption Materials for Pentavalent Arsenic Removal from Drinking Water

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INTRODUCTION

Arsenic (As) is toxic and carcinogenic and nowadays the arsenic occurrence is responsible for many diseases, where it occurs in drinking water. Its exposure to low or high concentrations can be fatal to human health (van Halem et al., 2009). Arsenic occurs naturally in water usually in the forms of the soluble arsenic species As(III) (arsenite) and As(V) (arsenate). Adsorption has been universally accepted as one of the most effective arsenic removal process (Zhu et al., 2013). In the present study, the possibility of using six granular commercial adsorbents (activated carbon-GAC, zeolite-ZEO, iron coated zeolite-ICZEO, ferric oxide-FeO, ferric hydroxide-FeOH and ferric oxide-hydroxide-FEOOH) and two non-commercial granular adsorbents (iron-impregnated activated carbon-IPGAC and iron-impregnated zeolite-IPZEO) for pentavalent arsenic removal from drinking water was investigated by batch adsorption studies. For each adsorbent the adsorption capacity was determined and mutually compared. In addition, for non-commercial iron-impregnated adsorbents the total iron content and stability were evaluated.

MATERIALS AND METHODS

Reagents

As(V) stock solution was prepared by dissolving an accurately weighed amount of sodium arsenate hydrate ($Na_2HAsO_4.7H_2O$) in distilled water to achieve a concentration of 1 g/L. The iron stock solution (0.5 M) for the iron impregnation was prepared by diluting of iron sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) in distilled water.

Analytical determination

Determination of As(V) was done by flow-through chronopotentiometry with using triple-electrode flow-through measuring cell (type 353c) with work electrode (type E-T/Au), platinum auxiliary electrode and argentochloride reference electrode.

Adsorbent preparation

The six commercial adsorbents was used without further purification. Their were just rinsed with distilled water to remove dirties and then oven-dried at 105 °C for 24 h. The two non-commercial materials reacted at room temperature with iron stock solution for 24 h in the orbital shaker. After 24 h, the materials were separated from the solution by gravity filtration and oven-dried, so the ferrous was oxidised to ferric getting a less soluble iron form. To reach high amount of iron in the material the impregnation procedure was carried out until the iron content from one impregnation to the other was kept constant.

Adsorbtion studies

Adsorption experiments were carried out by batch method at room temperature (20±2 °C). The time dependent behavior of arsenic adsorption was studied by varying the contact time between the adsorbate and adsorbent in the range 0 – 180 min. The 0.1 L solution of As(V) was taken in each Erlenmeyer flask of volume 0.20 L separately. The initial concentration of arsenic was kept at 1000 µg/L, while the dose of each adsorbent was 0,2 g. The adsorption capacity (q_t) of As(V) on adsorbent (µg/g) was calculated using the following equation:

$$q_t = \frac{c_i - c_t}{M} V, \qquad (1)$$

where c_i and c_t are the initial and final As(V) concentration in the solution, V is the volume of solution (L) and M is the mass of the adsorbent (g) used.

RESULTS

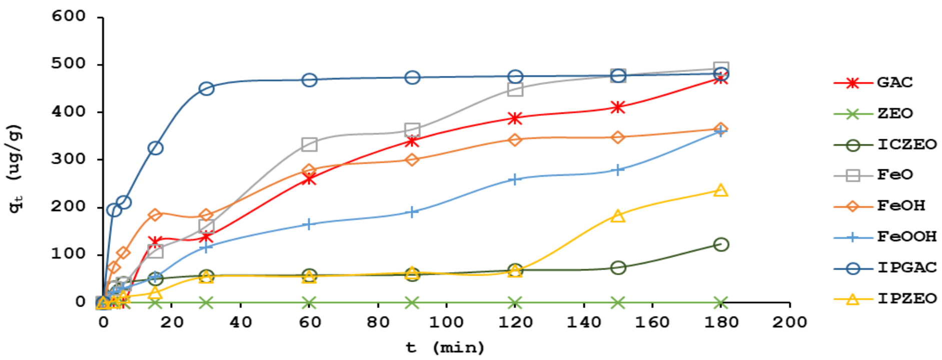

Figure 1. Effect of contact time on the adsorption capacity of different adsorption materials

CONCLUSION

The present study shows that the FeO, FeOH and FeOOH were successfully used as as an adsorbent for the quantitative removal of As(V) from the beginning of experiment. The GAC started remove As(V) after 15 minutes contact time, but the iron-impregnation improved its adsorption capacity. After impregnation, the IPGAC was the most effective material for As(V) removal. The iron-impregnation of ZEO also improved its adsorption capacity, but the achieved results compared with other materials were not so satisfactory. On the other side, the IPZEO removed after 120 minutes contact time more As(V) than the commercial ICZEO.

ACKNOWLEDGMENTS

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Study on PES Ultrafiltration Membrane Fouling Characteristics during Filtration of HA Solution under High Back Pressure

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SUMMARY OF KEY FINDINGS

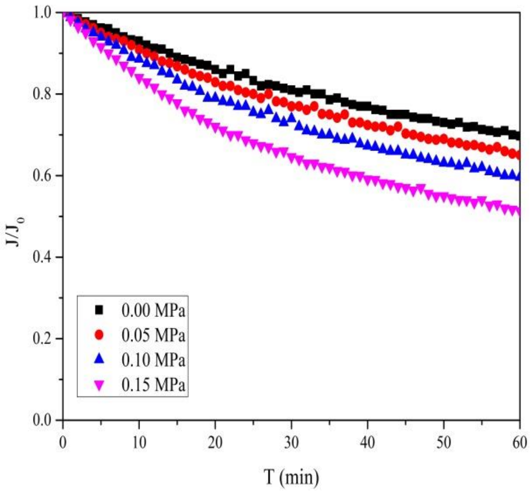
The results showed that the application of back pressure (pressure at the outlet) accelerates membrane fouling, gradually transforming the filtration mechanism from pore narrowing and pore blocking to cake filtration. And the back pressure application has an improving effect on rejection to humic acid (HA). When back pressure increased from 0 to 0.15 MPa and trans-membrane pressure remained constant at 0.069 MPa, the concentration polarization resistance, reversible fouling resistance and irreversible fouling resistance of the 30 kDa polyethersulfone ultrafiltration membrane increased 3.20 %, 4.14 % and 11.01 %, respectively. Scanning electron microscopy and atomic force microscopy indicated that HA particles deformed under high back pressure, changing from their original three-dimensional particulate state to a flattened sheet, which adhered to the inside of the membrane pore and were difficult to remove.

BACKGROUND AND RELEVANCE

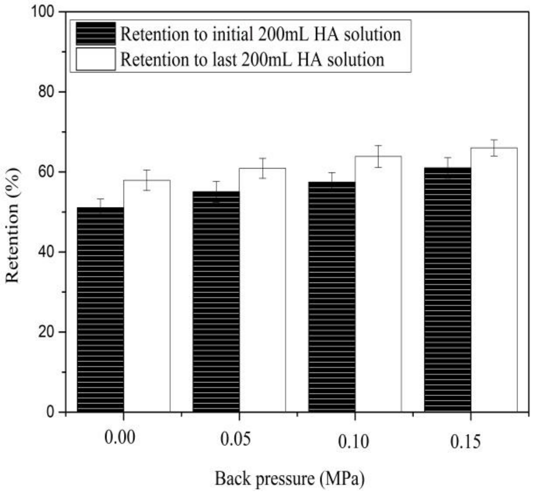
In recent years, ultrafiltration (UF) technology has become one of the most topical technologies in in guaranteeing drinking water quality during the treatment process. In addition, whether the pressure type or immersion type, UF technologies currently used operate without a pressure at the outlet (back pressure) of the membrane. Several limitations are encountered in absence of back pressure. First, UF effluent needs to be lifted (pumped) twice before it can enter the pipe network. Second, washer pumps need to be set up separately. Third, clean water tanks are needed for use with the pumps, all of which makes the system complex, costly, and inconvenient to operate and manage, especially in rural areas. However, if UF membranes can be operated under high back pressure, the above limitations would be solved. Therefore, in this research, the operating characteristics of the polyethersulfone (PES) membrane during filtration of humic acid (HA) solution at high back pressure were first studied (Zhu et al., 2018). The major objectives of the study were as follows: (i) to investigate the influence of back pressure on the UF membrane fouling characteristics. (ii) to evaluate HA fouling mechanism at high back pressure using filtration models (Zhang and Ding, 2015). (iii) to serve as a reference for the application of UF membranes at high back pressure for drinking water treatment.

RESULTS AND DISCUSSION

During the HA solution filtration of 60 min, the normalized flux of the 30 kDa PES membrane declined 30.28 %, 34.95 %, 40.36 % and 48.63 %, respectively (Figure 1a). The results indicated that the normalized flux declined as the back pressure and filtration time increased, which is because the back pressure application accelerates the fouling process. In addition, the retentions by the 30 kDa PES UF membrane to the initial 200 mL HA solution (5 mg/L) at back pressures of 0.00 MPa, 0.05 MPa, 0.10 MPa and 0.15 MPa were 51.06 %, 55.03 %, 57.42 % and 61 %, respectively, and comparable retentions to the last 200 mL were 57.94 %, 60.89 %, 63.87 % and 66 % (Figure 1b). The retention to the last 200 mL HA solution by the PES membranes was larger than that to the initial 200 mL because the membrane pores were gradually blocked during the UF process. And as back pressure increased, the retention to HA solution by the 30 kDa PES membrane increased. This result occurred mainly because that the back pressure application can narrow the membrane pores and aggravate blockage. Furthermore, the respective linear correlation coefficients (R^2) of pore narrowing and pore blocking regressions decreased gradually, while the R^2 of the cake filtration regression increased gradually (Table 1). These changes indicated that the application of back pressure promotes the filtration mechanism gradually transforming from pore narrowing and pore blocking to cake filtration.



a)



b)

Figure. 1. a) normalized permeate flux of humic acid solution as a function of time for various back pressures (trans-membrane pressure, 0.069 MPa; temperature, 25 °C); b) retention as a proportion of 400 mL HA solution under different back pressures (trans-membrane pressure, 0.069 MPa; temperature, 25 °C)

Table 1. Summary of coefficients and R^2 for different models

30 kDa PES membrane	Pore narrowing coefficient (K_n*E-4)	Pore blocking coefficient (K_b)	Cake filtration coefficient (K_c*E-4)
0.00 MPa	2.5104 (R^2=0.9934)	0.00595 (R^2=0.9897)	2.6018 (R^2=0.8000)
0.05 MPa	3.0173 (R^2=0.9910)	0.00701 (R^2=0.9856)	3.0588 (R^2=0.8635)
0.10 MPa	3.7251 (R^2=0.9889)	0.00843 (R^2=0.9812)	3.7314 (R^2=0.8760)
0.15 MPa	4.9509 (R^2=0.9811)	0.01071 (R^2=0.9679)	5.1944 (R^2=0.9239)

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The Effect of Irrigation Using Secondary and Advanced Treated Wastewaters on Soil Properties under Kikuyu Grass Production

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INTRODUCTION

Treated wastewater is a reliable water source for reuse in various areas to confront the water shortages (Pedrero et al., 2010). The objective of current study was to determine the effect of irrigation using different types of treated wastewaters on soli chemical properties. Membrane bioreactor treatment system is a secondary treatment of wastewater (STW) process (Judd, 2010) while intermittently decanted aerated lagoon provides an advanced treatment of wastewater (ATW) for removing nutrients, particularly nitrogen (Ngo et al., 2007). In the present study, kikuyu which is a very common and popular grass for urban areas and sports fields in Australia was irrigated with mentioned treated wastewaters and tap water for a period of 16 months (March 2016 - June 2017) in the absence of any sort of fertiliser. The source of TW was drinking water supplied to the Sydney Metropolitan area by the Sydney Water Corporation.

MATERIALS AND METHODS

The schematic set-up of the study is shown in Figure 1. The soil column tests were carried out at the Werrington Campus of Western Sydney University using three identical stainless steel columns filled uniformly with the soil with Loamy Sand texture.

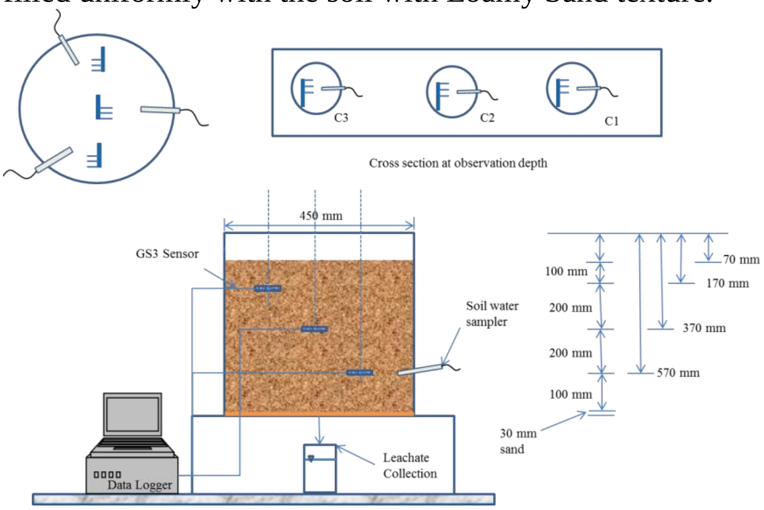


Figure 1. Schematic set-up of the columns

Table 1 lists selected parameters of the soil.

Table 1. Selected parameters of the soil

Soil properties	Value
pH_{SE} (saturated extract)	5.9
EC_{SE} (saturated extract), (ds/m)	0.38
Exchangeable Ca ($cmol_C$/kg air dry soil)	1.38
Exchangeable K ($cmol_C$/kg air dry soil)	0.08
Exchangeable Mg ($cmol_C$/kg air dry soil)	0.48
Exchangeable Na ($cmol_C$/kg air dry soil)	0.13

RESULTS AND DISCUSSIONS

Characteristics of irrigation waters

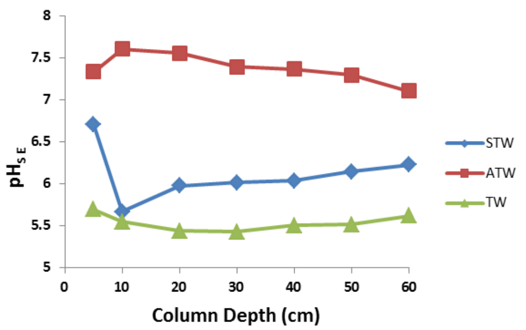
Mean values of selected parameters for irrigation waters are listed in Table 2.

Table 2. Mean values of selected parameters of irrigation waters

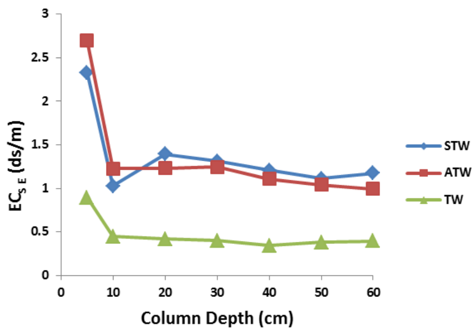
Parameters	STW	ATW	TW
pH	7.25 ± 0.41	7.52 ± 0.35	7.25 ± 0.46
$EC_{25°C}$ (dS/m)	0.99 ± 0.18	0.93 ± 0.073	0.26 ± 0.026
Ca^{2+} (mg/L)	29.59 ± 5.51	16.10 ± 1.70	20.33 ± 4.61
K^{+} (mg/L)	25.69 ± 7.28	28.58 ± 8.14	7.74 ± 5.42
Mg^{2+} (mg/L)	11.57 ± 3.39	26.04 ± 4.62	7.30 ± 2.57
Na^{+} (mg/L)	143.37 ± 31.23	113.68 ± 25.57	18.87 ± 5.51

Soil pH and EC

Over the period of study, soil saturated extract pH (pH_{SE}) and EC (EC_{SE}) changed in different depths of the soil varying from column to column (Figure 2).



(a)



(b)

Figure 2. Variation in oil saturated extract pH (a) and EC (b) in different depths of the columns

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Effect of C/N Ratio on N_2O Production in the Deammonification Process

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BACKGROUND AND RELEVANCE

The process of partial nitrification / anammox (PN / A) is a promising alternative to conventional nitrification and denitrification under mainstream conditions. However, it should be remembered that the N_2O evolved in this process is a harmful greenhouse gas. Wastewater treatment based mainly on biological processes generates huge amounts of N_2O and has been recognized as one of the most important sources of greenhouse gas emissions (Liu et al., 2014). Therefore, it is necessary to examine factors that can reduce N2O emissions in the PN / A process. A number of studies have been carried out which have determined the effect of dissolved oxygen (DO), C / N ratio, pH on nitrification and denitrification processes (Zhao et al., 2009; Hu et al., 2013; Merlin Christy et al., 2014). Hu et al. (2013) showed that with the increase in C / N from 7.5 to 14.5, N_2O production decreased from 6 % to 1.3 % in the anoxic–oxic biological nitrogen removal process. In turn, during partial denitrification (PD)-anammox process it was indicated that the ammonia was directly oxidized by nitrite to N_2 without producing N_2O (Cao S. et al., 2019). In the same study, high N_2O was observed at a low C / N ratio in PD. However, the PN / A process in terms of the impact of the C / N ratio on N_2O production has not been widely studied. The aim of this study was to investigate the effect of different C / N ratios on the production of N_2O in the PN / A process.

MATERIALS AND METHODS

The PN / A process was carried out in a sequencing batch reactor (SBR) with a working volume of 10 dm^3. Biomass was taken from long-term experiments on PN / A on sidestream reject water. The study lasted 90 days. The temperature was maintained at 20 ± 1 °C, DO at 0.7 (± 0.1) g O_2 / m^3, pH between 7.5 - 7.9 by 1.0 M NaOH additive. The reactor was fed with synthetic sewage as indicated by Dapena-Mora et al. (2004). The measurement of N_2O production was controlled continuously using a probe adapted for this purpose. The course of the long-term process was divided into 5 phases, during which the C / N ratios in the range of 1 to 3 were changed.

RESULTS

The gradual increase in the incoming C / N ratio resulted in a reduction of N_2O emissions. The comparison of emissions at a C / N ratio of 1: 1 and 3: 1 is shown in Figure 1. For the first two hours of the beginning of each cycle at each C / N ratio, the production of N_2O was insignificant. Then during the next 2-3 h it increased and at the end of the cycle it returned to the value close to 0. There is a huge difference in the production of N_2O at a C / N ratio of 1: 1 and 3: 1. The highest recorded N_2O production value for a C / N ratio of 1 was about 0.24 mg N_2O-N / L after 3h of the cycle. However, the highest value for the C / N ratio of 3 was about 0.07 mg N_2O-N / L. The total production of N_2O throughout the entire cycle is also significantly higher in phase with a C / N ratio of 1. However, during the process, also TN removal efficiency and AUR were tested for each C / N ratio and the process turned out to be broken at a C ratio / N equal to 3.

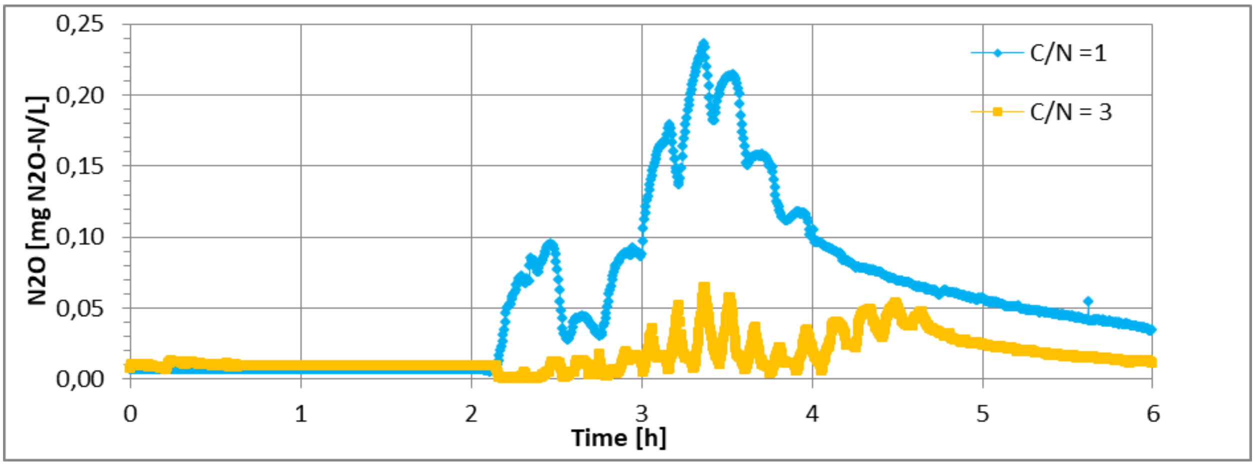

Figure 1. N_2O production at a C / N ratio of 1: 1 and 3: 1

DISCUSSION

The initial phase of each cycle of the PN / A process, which does not show a large N_2O production, may indicate the use of COD by heterotrophic bacteria. The use of elevated COD concentrations may prove to be an effective method of N_2O emission reduction. However, it should be remembered to correlate this method with the efficiency of the PN / A process, which also increases with the increase in the C / N ratio, but at some point it breaks down. In this study, the critical value was the C / N ratio of 3. It would be best to optimize the N_2O and production and TN removal efficiency in PN/A.

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Characterization of Leachate from Non-sanitary Municipal Solid Waste Landfill in Novi Sad

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INTRODUCTION

Complex chemical reactions, the infiltration of atmospheric water into the body of landfill, water contained in the waste, as well as the dissolution of pollutants from waste generate the landfill leachate which contaminate soil and groundwater (Pogo et al., 2016). The real composition of the landfill leachate is very difficult to predict due to the complex dynamics processes in the landfill body and the influence of a large number ofvariables. The qualitative composition of leachates is characterized by pollutants that can be divided into four groups: soluble organic compounds (volatile fatty acids, humic and fluvic acids), inorganic macrocomponents (ions of calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), ammonium ion (NH^{4+}), iron (Fe^{2+}), manganese (Mn^{2+}), chloride (Cl^-), sulfate (SO_4^{2-}), hydrocarbon (HCO_3^-), heavy metals (ions of cadmium (Cd^{2+}), chromium (Cr^{3+}), copper (Cu^{2+}), lead (Pb^{2+}), nickel (Ni^{2+}) and zinc (Zn^{2+})), organic compounds (hydrocarbons, phenols, chlorinated aliphatic compounds, pesticides, dioctyl phthalates) (Christensen et al, 1998; Kjeldsen et al., 2002). The main objective of the paper was to characterize the leachatefrom non-sanitary municipal solid waste landfill in Novi Sad in order to identify the groups of organic compounds contained in it.

MATERIALS AND METHODS

Campaigns of sampling leachate carried out in winter and spring periods in 2019 in cycles of 2 hours at the landfill in Novi Sad (Figure 1). For the needs of the realization of screening analysis of organic pollutants, 2 litres of leachate were collected. The samples were transported and stored at a temperature of 4 ^oC until the moment of preparing the sample for analysis. For screening analysis, the samples were prepared using liquid-liquid extraction and paired in Kuderna-Danish apparatus. QP2010-Ultra GC-MS, Shimadzu was used for the analysis. The screening analysis was carried out in an accredited Laboratory for monitoring landfills, wastewater and air of the Department of Environmental Engineering of the Faculty of Technical Sciences in Novi Sad.

Figure 1. Collecting of leachate at a non-sanitary municipal solid waste landfill in Novi Sad in winter (left) and spring (right) period of 2019

RESULTS AND DISCUSSION

Content of organic matter in leachate is directly conditioned by morphological composition of the deposited waste and its seasonal variations. Organic profile of leachate from the non-sanitary municipal solid waste landfill in Novi Sad, in winter and spring period of 2019 is shown in Table1.

Table 1. Organic profile of leachate from the non-sanitary municipal solid waste landfill in Novi Sad

Group of compounds	Winter period	Spring period
Hydrocarbons	5	6
Organic acids, esters and salts of organic acids	13	17
Phthalates	/	/
Alcohols, ketones and aldehydes	8	10
Phenols	2	1
Heterocyclic compounds	5	2
Organonitrogen compounds	5	5
Total detected	38	41

The obtained results indicate the dominant presence of two groups of organic compounds: organic acids, esters and salts of organic acids and alcohols, ketones and aldehydes. The stated groups of organic compounds are represented in the organic fraction of waste and products of degradation (fruit, animal waste, food products) and in industrial waste as well (pharmaceuticals, synthetic polymers, industrial solvents, essential oils).

CONCLUSION

Identification of specific polluting substances in untreated leachate of the landfill in Novi Sad is of great importance due to its negative impact on all environmental mediums, primarily on ground and surface water flows, as well as potential negative impact to people’s health. It is also necessary to know the composition of organic matter when planning and designing their treatment.

ACKNOWLEDGMENTS

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Optimizing Continuous Photo-Fenton Process for Removal Color and Organic Compounds From Textile Wastewater

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INTRODUCTION

Water pollution due to several industrial discharge is a global environmental problem. As the result of the rapid industrialization, the consumption of coloring chemicals also increases day by day. Therefore there is an increasing worldwide interest in developing of alternative water reuse technologies on textile industry. Currently, chemical method, such as Advanced Oxidation Process (AOP's). AOP's generally involve production of very powerful and non-selective oxidizing species, the hydroxyl radicals ($^{*}OH$) for the destruction of refractory and hazardous pollutants observed in wastewater. Especially after biological treatment, different AOP's were used to treat the real textile dyeing wastewater as a final step to remove color, COD and other refractory organic compounds, which were partially removed using a biological process. Among the AOP's, two of the most important processes to generate hydroxyl radicals are using Fenton and photo-Fenton (Fe^{+2}/ H_2O_2 and Fe^{+2}/ H_2O_2/UV) systems. In this reactions, H_2O_2 is added as the direct source of $HO^{\cdot}$. Fenton reagent leads to the formation of hydroxyl radicals using the reaction of hydrogen peroxide decomposition catalyzed by ferrous ions Fe^{+2}.

In this study, experiments were performed on biologically treated effluent obtained from a textile industry located in Tekirdağ-Turkey.

METHODS

The biologically treated effluent taken to the laboratory, filtered from sand and stored at 4 ºC. The characteristic of the wastewater is given in Table 1.

Table 1. The typical composition of raw wastewater

pH	**Color** (pt-Co)	**EC** (µs/cm)	**TOC** (ppmC)	**COD** (mg/L)
7.8 – 8.2	120 -250	1602 – 1720	30 – 45	90 – 110.5

For the photo-Fenton experiments optimal values of reagents such as concentration of Fe^{+2}, H_2O_2 and pH were investigated to increase the removal of COD, TOC and color of raw wastewater. All experiments for the photo-Fenton system was carried out in a lab scale reactor with continuous mode operations. Initial pH of the wastewater was adjusted to the optimal level pH 3 by using 6 N H_2SO_4 solution, added determined quantity of Fe^{+2} reagent and the sample was stirred continuously. The photo-Fenton reaction was started by adding an exact amount of H_2O_2 oxidant and the UV light was switched on immediately. After the reaction finished identified time, pH of the solution was measured and in order to stopped Fenton reactions by increasing the pH 9-10 level added $CaCO_3$. All the samples centrifuged 1000 rpm, 15 minutes, filtered with glass fiber filter and analyzed after filtering from 0.45 mm syringe filter. With the different dose of Fenton reagents, optimum conditions were decided to be doses of 10 mM H_2O_2 and 2 mM for Fe^{+2} in 40 minutes. For determining the optimal reaction time, photo-Fenton oxidation repeated at optimal doses of 10 mM H_2O_2 and 2 mM for Fe^{+2} to 280 minutes. Samples were taken from reactor in 5 to 280 minutes as given in Table 2.

Chemical oxygen demand (COD) determination was measured using Standard Method 5520 D closed reflux colorimetric method with the Hach Lange DR-6000 UV-vis spectrophotometer. The total organic carbon (TOC) content in samples was determined using a Teldyne Tekmar Lotix TOC analyzer. The pH measurements were carried out with Thermo-Scientific device. For the color determination samples were analyzed using UV-vis spectrophotometer, Hach Lange DR-6000.

RESULTS

Table 2. 10 mM H_2O_2, 2 mM Fe^{2+} Photo Fenton removal efficiency %

Time (min.)	Color (pt-Co)	EC (µs/cm)	TOC (ppmC)	COD (mg/L)	COD (%)	Color (%)	TOC (%)
0	215	1701	44.9	91.5	0.0	0.0	0.0
5	3	3008	19.2	61.3	33.0	98.6	57.3
10	0	2962	17.3	39.3	57.0	100.0	61.5
20	0	3040	16.2	48.3	47.3	100.0	63.9
30	1	3029	15.7	42.2	53.9	99.5	65.0
40	1	3002	16.1	42.2	53.9	99.5	64.2
60	0	3018	14.6	32.4	64.6	100.0	67.6
80	0	2968	13.5	30.4	66.7	100.0	69.9
100	0	2996	13.9	32.2	64.8	100.0	69.1
120	0	3055	14.1	36.7	59.9	100.0	68.7
160	0	3020	12.7	26.7	70.8	100.0	71.8
200	0	3058	11.8	28.5	68.9	100.0	73.8
240	0	3034	11.6	20.2	77.9	100.0	74.2
280	0	3064	10.6	20.0	78.1	100.0	76.4

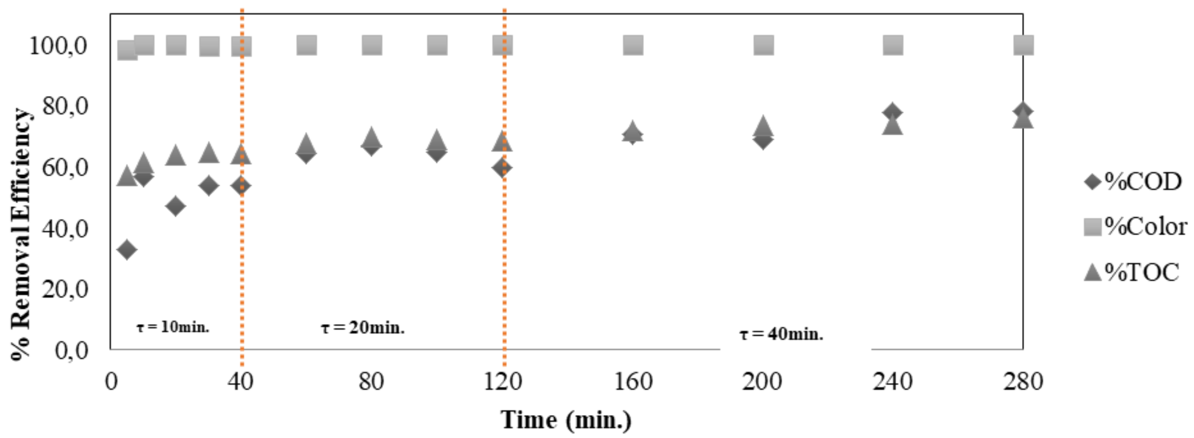

Figure 1. Removal efficiency of COD, Color and TOC according to time

Maximum color, COD and TOC removal efficiencies were obtained as 100 %, 78.1 % and 76.4 % respectively. But after 20 minutes removal efficiencies were increasing at a low rate.

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The Impact of Combined Sewer Overflows Activity on the Quality of Bottom Sediments of the River Jasień

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INTRODUCTION

The activity of combined sewer overflows has a negative impact on the condition of surface water being a receiver of the combined sewer. Pollutant load directed into surface water and change of hydrological conditions (hydraulic stress) pose a significant threat to the receiver's water quality and ecological balance of water ecosystems (Brzezińska et al., 2016). Pollutants directed via combined sewer overflows to the receiver can also affect the quality of sediments in rivers (Telse et al., 2013). The accumulation of contamination in sediments may cause secondary pollution of the receiver during the disturbance of the sediments structure at increased flow. The aim of the study was to analyse the variability of sediment quality from the River Jasień at different distances from the emitter.

METHODOLOGY

The paper presents the findings of the research of the bottom sediments quality from the River Jasień. The river, whose length is 12.6 km flows through the urbanized area within the administrative borders of Łódź city (central Poland). The River Jasień is the right tributary of the River Ner, and the area of its catchment equals 79,5 km^2. In the river catchment there are seven combined sewer overflows, which during intense or prolonged rainfall introduce excess of sewage directly into the environment. The River Jasień has the character of a canalized urban river, its bed has been regulated, deepened and strengthened. The function of the river was limited to the fast discharge of rainwater and combined sewer (coming from combined sewer overflows) from the city area. At present the river does not function as watercourse at all. There were selected five sampling sites of the bottom sediment on the uncovered section of the River Jasień, which is marked on figure below.

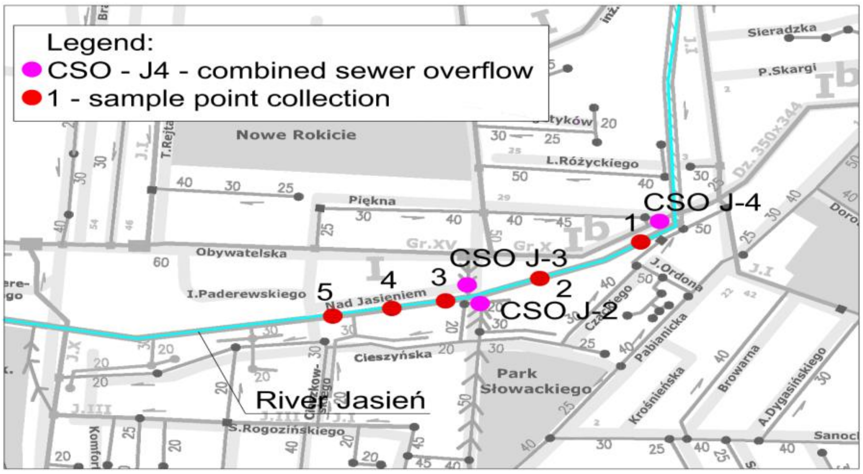

Figure 1. Location of bottom sediment sampling points from the River Jasień

The locations of the sampling sites were chosen due to the largest accumulation of sediment on a selected section of the river. There are three combined sewer overflows (J-2, J-3 and J-4) on the analysed section of the Jasień River that discharge sewage from catchments of various sizes. The assessment of pollutants amount in bottom sediments was made on the basis of selected parameters: pH, dry matter content (DM) [g·kg^{-1}], mineral (MM) and organic matter content (OM) [% DM], content of ammonium nitrogen (N_{NH4}) and total Kjeldahl nitrogen (N_K) [mg·kg^{-1}], content of total phosphorus (P) [mg·kg^{-1}]. The research was carried out in five series.

RESULTS

The quality of bottom sediments from the analysed section of the River Jasień varied depending on the sampling site. Table 1 presents the example values of the determined quality parameters of bottom sediments from the first series of measurements.

Table 1. Results of chemical analysis of the bottom sediments from the River Jasień (series No.1)

Sampling site	P (mg·kg^{-1})	N_K (mg·kg^{-1})	N_{NH4} (mg·kg^{-1})	DM (g·kg^{-1})	OM (% DM)	MM (% DM)	pH
1	2554.08	419.91	4.95	654.10	11.12	88.88	7.40
2	84.09	269.47	0.63	751.92	2.29	97.71	7.45
3	48.02	362.11	1.39	720.10	1.79	98.21	7.49
4	64.09	186.45	0.77	782.34	1.61	98.39	7.54
5	61.74	227.91	0.93	773.09	3.04	96.96	7.63

The determined results indicate the greatest accumulation of pollutants at the measurement point No. 1, which was located in the distance of 10 m from the combined sewer overflow J-4. The combined sewer overflow J-4 (with a 4.0 x 2.4 m cross section), discharging sewage from urban catchment of an area which equals 889.79 ha, is the largest in the analysed section of the River Jasień.

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Immobilization of Anammox Biomass in Sodium Alginate-polyvinyl Alcohol Carriers

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INTRODUCTION

Biological anaerobic ammonium oxidation (anammox) is a promising and cost – effective process for nitrogen removal from wastewater. Process consumes less oxygen with no need of external organic carbon source in comparison to traditional denitrification – nitrification processes. However, despite obvious advantages, application of the anammox technology is not without difficulties, as anammox bacteria are characterized by slow growth rate. Moreover, the optimal temperature for anammox bacteria in technological systems (30-35 ^oC) is higher than average temperature of wastewater (10-15 ^oC) (Ma et al., 2016). One of the ways to cultivate slow-growing bacteria and develop a stable and high rate nitrogen removing anammox system is to immobilize biomass in a reactor. Under unfavourable conditions in operating system, anammox biomass growth is often inhibited, wherein fast-growing heterotrophs start to dominate. Immobilization of anammox cells may lead to higher anammox biomass retention and will give possibility for anammox bacteria to growth inside the carrier. Selection of the best carrier for immobilization is crucial for each process efficiency. In case of presented study, we decided to use combination of sodium alginate (SA) and polyvinyl alcohol (PVA) to strengthen the effect of crosslinking, and thus enhance mechanical and chemical properties of the prepared carriers.

MATERIALS AND METHODS

Carriers characterization

Different combination of SA and PVA concentrations in the carriers were tested in terms of chemical stability, mechanical strength and water related properties (swelling ratio, water holding capacity and shrinking factor). Then, to anammox bacteria immobilization, SA (2 %) - PVA (7 %) solution was added to the concentrated anammox biomass in the ratio of 2:1 (v/v). The mixture was added by dropping through peristaltic pump to the calcium chloride solution (4 %). Bacteria were immobilized for 0.5 h. Subsequently, obtained pellets were washed in deionized water.

The morphology and structure of the immobilized samples were characterized via a scanning electron microscope (SEM, QUANTA FEG 250, Thermo Fisher). The samples were washed with the phosphate buffer solution and were completely dried at room temperature in a silica gel dryer. After that, the samples were treated with spray gold and were covered using a vacuum cover system for the evaporation of metals.

Short term anammox process performance

To evaluate specific anammox activity (SAA) and reveal short-term nitrogen removal, immobilized and non-immobilized biomass (control) were investigated in series of batch tests. Batch experiment was performed in triplicate. Tests were conducted for 6 h in 15 °C and 30° C with a pH value of 7.5. During the tests, samples were taken every 0.5 h and were prepared for nitrogen concentration measurements. The specific anammox activity (SAA) was measured by calculating the linear descending slopes of N-NH_4 and N-NO_2 concentration. To calculate the SAA, the removal rates for N-NH_4 and N-NO_2 were normalized by volatile suspended solids (Banach et al., 2018).

RESULTS

Anammox biomass was successfully immobilized in SA-PVA (Figure 1A), analysis occurred on SEM allow to observe the surface of the obtained carriers (Figure 1B). The specific anammox activity in the case of immobilized biomass was calculated at the level of 0.175 $gN \cdot gVSS^{-1} \cdot d^{-1}$ for the batch tests conducted in 30 °C and 0.138 $gN \cdot gVSS^{-1} \cdot d^{-1}$ for the batch test conducted in 15 °C. While, for the control was equal 0.206 $gN \cdot gVSS^{-1} \cdot d^{-1}$ in 30 °C and 0.12 $gN \cdot gVSS^{-1} \cdot d^{-1}$ in 15 °C.

A) 

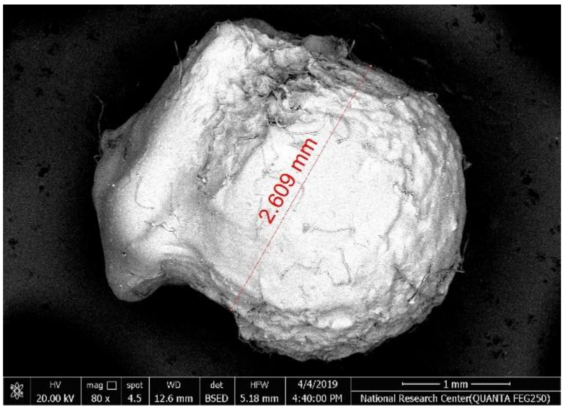
B) 

Figure 2. SA-PVA carriers; A – with immobilized anammox biomass after immobilization; B- under Scanning Electron Microscope

CONCLUSIONS

The pellets show similarly acceptable spherical shapes while the surface of SA-PVA showed some buckling, and some agglomeration can be faintly seen. This suggested that a good compatibility between SA-PVA and anammox biomass which resulted in uniformly distribution in the SA-PVE matrix. Both for anammox biomass entrapped in the SA-PVA carriers and for suspended anammox biomass, decrease of SAA in 15 °C was noticed. However, slighter difference between SAA calculated in 30 °C and 15 °C was observed in the case of biomass immobilized in SA-PVA carriers in comparison to the suspended biomass. Obtained results may indicate that immobilization in investigated carriers may have protective properties for anammox bacteria conducting anammox process at low temperatures.

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Understanding the Synthetic Leachate Fungal Degradation in Log-term Continuous Tests through Modelling

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INTRODUCTION

Nowadays, the achievement of sustainable technology for landfill leachate treatment is still a challenge due to its high concentration in recalcitrant molecules (Tigini and Varese, 2018). Among the innovative approaches for recalcitrant compounds removal, the use of fungi has gained considerable research interest (Spennati et al., 2018). However, long-term fungal applications are still poorly investigated (Spennati et al., 2019).

A reactor was operated under not-sterile conditions for the treatment of a synthetic leachate, prepared with tannic acid, being active for approximately 200 days, with promising performance in terms of soluble Chemical Oxygen Demand (sCOD) and toxicity removal (Bardi et al., 2019). The experiments were conducted using a selected fungal strain, *Bjerkandera adusta* MUT 2295, which was previously employed in other bioremediation studies, being effective on several difficult wastewaters, including leachate, tannery and pharmaceutical effluents (Bardi et al., 2017, Anastasi et al., 2010). *B. adusta* was inoculated in attached form onto PolyUrethane Foam cubes (PUFs).

Considering the poor knowledge regarding the kinetics of fungal-based systems for recalcitrant compounds removal, in this study, mathematical modelling was employed to analyse the reactor efficiency. In particular, the primary goal of the investigation was to understand and describe the behaviour of *B. adusta* attached biomass during a long-term process for recalcitrant compounds degradation.

MATERIALS AND METHODS

Experiments for synthetic leachate treatment have been performed using a packed-bed bench-scale reactor. The volume of the reactor was 5 L, with a working volume of 4.5 L. The reactor was equipped with a polyethylene cage in which 60 cubes, inoculated with *B. adusta* in attached form onto PUFs, were added. The pH was monitored using a pH controller and set-up at 6. The adjustments were performed with sulphuric acid (10 %). Air was provided continuously using a air diffuser with a flow of 2.0 L/min. The reactor was operated with a Hydraulic Retention Time (HRT) of 72 hours. Inlet an outlet were pumped in and discharged using a peristaltic pump (ISMATEC Reglo ICC, Digital Peristaltic Pump), with a pump cycle of 6 hours. The design of the reactor is shown in Figure 1.

Biomass growth, substrate inhibition, the decay and other kinetics parameters were estimated the software AQUASIM.

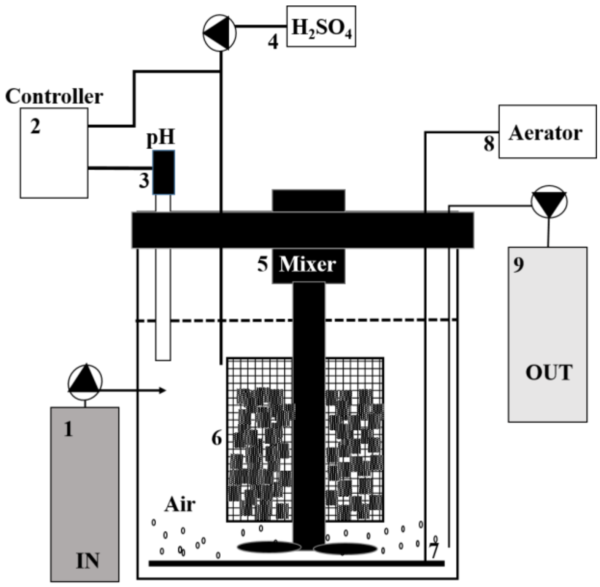

Figure 1. Schematic representation of the reactor from which the model was designed. 1: Inlet tank. 2: pH controller. 3: pH probe. 4: Acid solution for pH adjustment. 5: Mixing engine,6: polyethylene cage with PUFs,7: air diffuser, 8: aerator, 9: outlet tank

RESULTS AND DISCUSSION

The experiments on bench-scale proved the feasibility of fungal-based system for synthetic leachate treatment under not-sterile conditions (Bardi et al., 2019).

The fungal growth was described with a Monod kinetic and the reactor was described in the model as a modification of MBBR. The modelling results obtained represent the first step for ongoing designing of an up-scale application, suggesting the possible use of fungal-based process as pre-treatment for leachate, to mitigate the concentration and effects of its recalcitrant fraction.

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High Strength Slaughterhouse Wastewater Treatment by Sequential Anaerobic and Aerobic Batch Reactors (ASBR-SBR)

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INTRODUCTION

Effluent coming from slaughterhouse, food processing, dairy, brewery, tannery, and pharmaceutical industries are rich in impurities, and can cause detrimental effects on both human beings and aquatic flora and fauna. Particularly the slaughterhouse industry has elevated amount of organic matter, suspended solids, oil and grease (O&G), and nutrients (Bustillo-Lecompte and Mehrvar, 2015; Mittal, 2006). Biological treatment (anaerobic and aerobic) provides substantial amount of advantages over other treatment systems (discharge in sewers, land application, electrocoagulation, membrane separation, advanced oxidation, and physico-chemical processes). Hence, the objective of this study was to treat slaughterhouse effluent by installing two sequencing batch reactors (anaerobic and aerobic). Moreover, quantification of biogas and methane at steady state conditions were also the principal objectives.

MATERIALS AND METHODS

Anaerobic and aerobic sequencing batch reactors (ASBR-SBR) were employed for treating slaughterhouse waste. Figure 1 shows the actual and schematic reactor configuration.

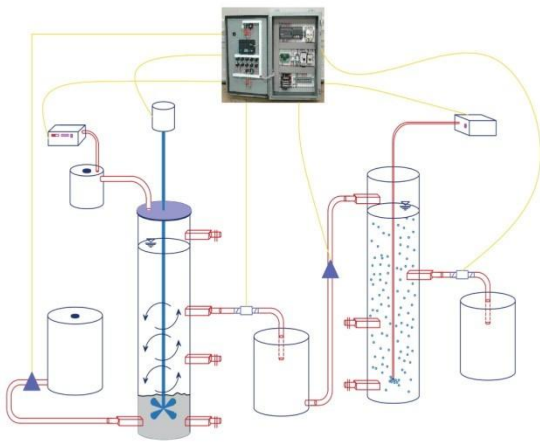

Figure 1. Actual and schematic diagram of entire reactor configuration

Around 40 % anaerobic sludge (UASB) and 30 % aerobic sludge (aeration tank) was used for feeding along with slaughterhouse wastewater in anaerobic and aerobic SBR respectively. The wastewater characteristics obtained during the course of study were pH = 7.2-8.4, alkalinity = 1950-3150 mg/l, COD = 3800-4700 mg/l, BOD_5 = 2300-3100 mg/l, TSS = 794-1116 mg/l, TN = 210-274 mg/l, NH_3 = 28-41 mg/l, NO_3^- = 9-20 mg/l, NO_2^- = 5-15 mg/l, SO4-2 = 92-148 mg/l, PO_4^{-3} = 140-229 mg/l, and O&G = 426-521 mg/l. Analysis of alkalinity, TSS, O&G, BOD, COD were done as per standard methods (APHA 2005). DR 5000 (HACH, USA) UV/V spectrophotometer was used for analysing sulphate, phosphate, total nitrogen, nitrite and nitrate. Biogas was analysed using low volume gas flow meter, while methane was examined with the help of methane analyser. The entire study was divided into four main phases. Out of total phases three were associated with acclimatization period. The HRT was maintained at 24 hr, while the loading rates were increased gradually in each phase by decreasing the dilution factor. The maximum OLR applied after steady state condition (4th phase) was 2.04 kg COD/m^3-d and 1.12 kg COD/m^3-d for ASBR and SBR respectively. The results obtained were significant, and the combined assembly removed considerable amount of organic content. Biogas was produced with an average methane content of 64 %. Apart from that formation of granules was also observed at the end of the research period (Fig. 2) they are able to remove nutrients due to their internal core structure.

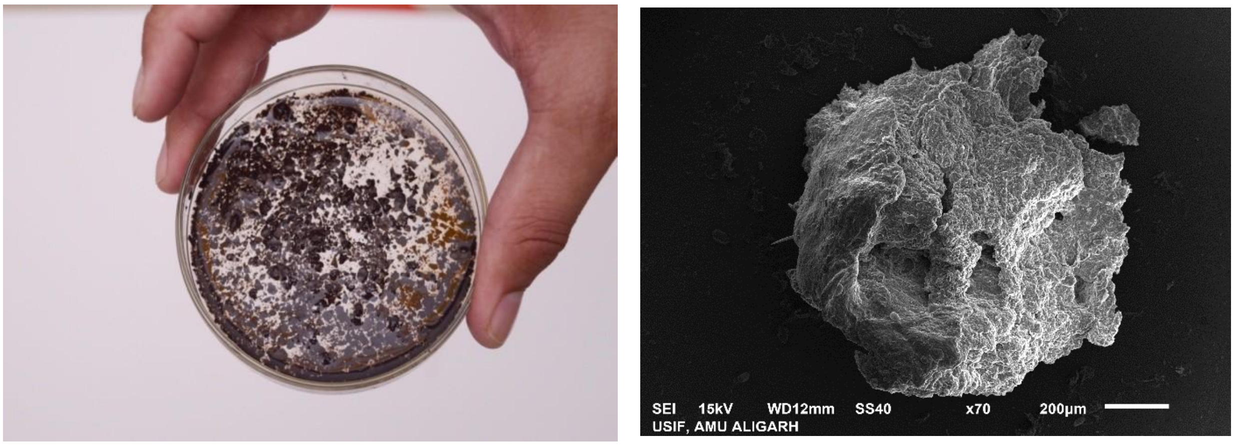

Figure 2. Granules formation along with SEM image on day 216

CONCLUSION

The ASBR-SBR system was exceptional in treating slaughterhouse wastewater effluent, and the removal efficiencies obtained from sequential treatment (ASBR+SBR) at steady state conditions were 92 %, 97 %, 90 %, 74 %, and 90 % for TCOD, BOD, TSS, PO_4^{-3}, and O&G respectively. Moreover, production of biogas rich in methane was also observed, and the average biogas and methane production at steady state from anaerobic SBR was 4-5 L/day and 70 % respectively. The post aerobic SBR on the other hand further enhanced the removal efficiency by eliminating the unsafe pollutants and colour. The results obtained were significant, and the combined assembly removed considerable amount of organic content. Future scope is that we can reduce the HRT of the sequential system and can go for higher organic loading rate and adopt different cycle conditions for better nutrient removal.

ACKNOWLEDGEMENT

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Changes of the Granulometric Composition of Particles in Wastewater Flowing through the Hydroponic Lagoon in III° Wastewater Treatment Plant

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INTRODUCTION

Total suspended solids are one of the most problematic pollutants that have to be sufficiently removed before discharging wastewater into the receiving water bodies (Remo et al., 2016). Using the three stage wastewater treatment with the use of hydroponic lagoon as an additional system for biogenic compounds removal may cause operational problems connected with the excessive TSS concentrations as a result of algae growth in the system. Monitoring of the changes of particles size and properties during the flow through the hydroponic ditch can be the basis of developing more effective methods of TSS removal from the sewage (Bawiec et al., 2017).

AIM OF RESEARCH

The aim of the paper was to analyse changes in the granulometric composition of particles in the hydroponic lagoon working as a third stage of wastewater purification in the Municipal Wastewater Treatment Plant (WWTP) in Poland. Measurement of the particle size was made with the use of laser diffraction method. The measurements include particle size distribution and calculations of mean diameters D(3.2) and D(4.3) as well as fractal dimensions of the particles.

MATERIALS AND METHODS

The samples of sewage were taken from the WWTP equipped with the III° of treatment – hydroponic lagoon, created as an artificial river to maintain the water self-purification processes. Samples were taken from the inlet (P1), middle flow (P3,P4) and the outlet (P6) from the hydroponic ditch. Granulometric composition of the wastewater was measured with the use of laser granulometer Mastersizer 2000. On the basis of measurements, particle size distribution, fractal dimensions and mean D(3.2) and D(4.3) diameters were calculated.

RESULTS

The changes in particles size distribution described by the changes in the % share of volume of suspended solids fraction with characterized *di* diameters in the total volume of polydisperse suspension shows variations within different wastewater samples. However, identified variations have no significant impact on the mean values of particles diameters (Figure 1). Identified mean diameters D(3.2) deciding of the absorption capacity of the particles and mean diameters D(4.3) conditioning the sedimentation capacity of particles are presented in Figure 2 and 3. Identified fractal dimensions (Df) of the particles shows that during the research period the lowest value of Df=1.483 occurred at the outflow of the hydroponic lagoon while the highest one – Df=2.857 was calculated from the sample from the middle point of the ditch.

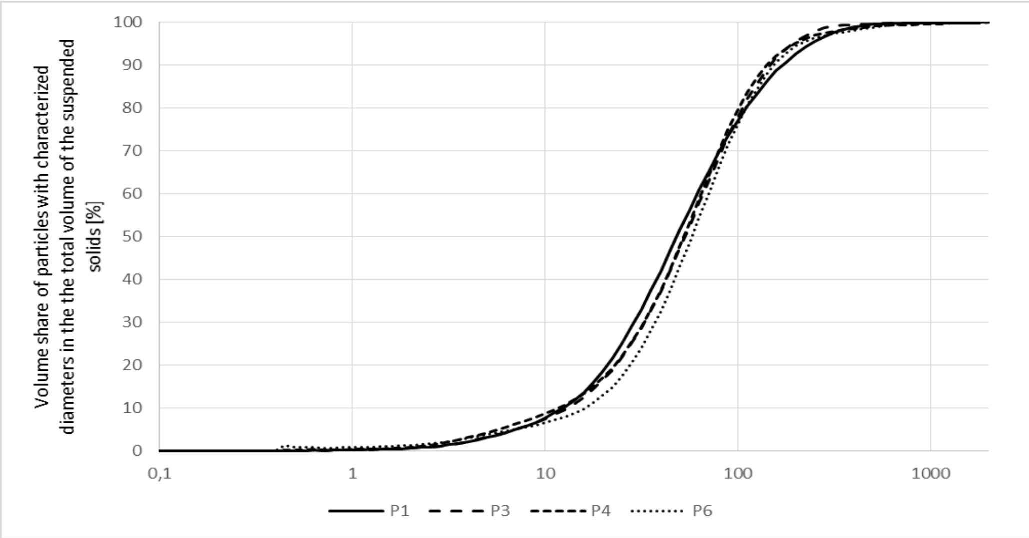

Figure 1. Cumulative volume frequency of particles diameter in wastewater taken from 4 sampling points

The mean values of Df in all sampling points varied from 2.112 to 2.173, and no significant changes of fractal dimensions during the flow through the lagoon was observed.

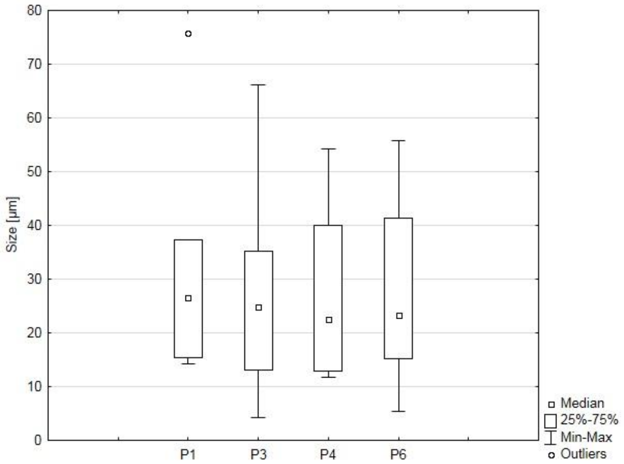

Figure 2 Sizes of mean equivalent diameters D(3.2) in wastewater taken from 4 sampling points (P1,P3,P4,P6)

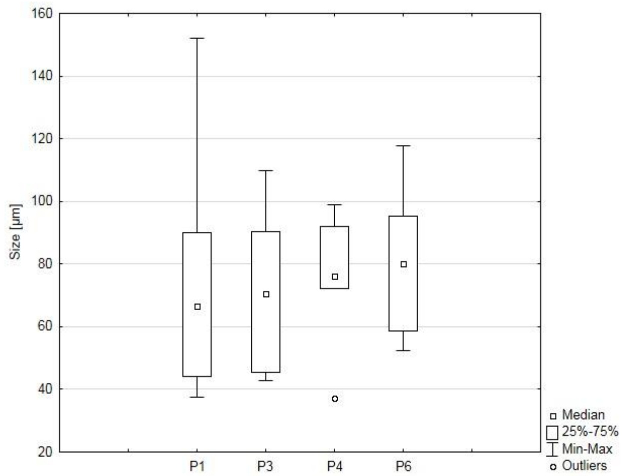

Figure 3 Sizes of mean equivalent diameters D(4.3) in wastewater taken from 4 sampling points (P1,P3,P4,P6)

CONCLUSIONS

The environment of hydroponic lagoon (present of plants, algae, invertebrates, protozoa) as well as physical conditions (intensive aeration) have huge impact on the size and properties of particles. On the basis on conducted calculations it can be concluded that identified particles have small reactivity (D(3.2) > 10µm) but good sedimentation capacity (D(4,3)>50µm) what can be the basis of development of new suspended solids removal system.

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Evaluation of Sentry Sensor for Real-time Biochemical Oxygen Demand Measurement Capabilities

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ABOUT THE SENSOR

The Sentry bio-electrode sensor by Island Water Technologies is mainly used in anaerobic digestor systems to prevent the effects of toxic shock, system imbalance and poor performance and result in better yield for biogas production. The sensor utilizes the metabolic pathways of microbes of the Proteobacteria genus commonly found in nature (Loveley et al., 2011) which can use metal surfaces as electron acceptor thus generating an electrical signal which can be measured.

The importance of BOD

A novel approach in the application of the sensor is in aerated wastewater treatment systems, especially to measure Biological Oxygen Demand (BOD) based on true microbial activity. Although BOD_5 is still the basis of designs and effluent limits in the wastewater industry, the standard manometric lab measurement for this biological parameter carries more error then a standardized measurement of a chemical parameter, e.g. Chemical Oxygen Demand (COD) and takes 5 days to complete (APHA, 2012). Our aim was to correlate the measured signal from the Sentry sensor (Microbial Electron Transfer - MET) to laboratory Total BOD_5 measurements and test if it's possible to get real time values correlated to the concentration of biodegradable material.

Toxicity monitoring

Another promising application is early warning for toxic materials. As opposed to usual COD-based online measurement methods (sensors and analyzers) which cannot indicate degradability or toxicity of the incoming material, changes in biodegradability can be reliably detected by the Sentry bio-electrode sensor. This means that wastewater treatment plant operators can see the changes of the influent in real-time and they are able to prepare their plant for the negative effects.

MEASUREMENT RESULTS

Correlation to standard laboratory measurements

The sensor was tested in an Organica Water facility in different locations along the treatment process: in the primary clarifier (influent), after the secondary clarifier (effluent) and in the beginning and end of the biological reactors. The measured value (MET) was correlated to standard laboratory parameters, such as Total BOD_5, Total COD and filtered COD.

The results for the influent showed an excellent correlation to $TBOD_5$ (R^2=80 %, MRE=7 %); the correlation was also good when all the obtained influent and effluent datapoints were plotted on the same graph. (R^2=98 %, MRE=13 %, Figure 1). In the aerated reactors the correlation was less ideal but the daily fluctuations were clearly detectable from the changes in MET.

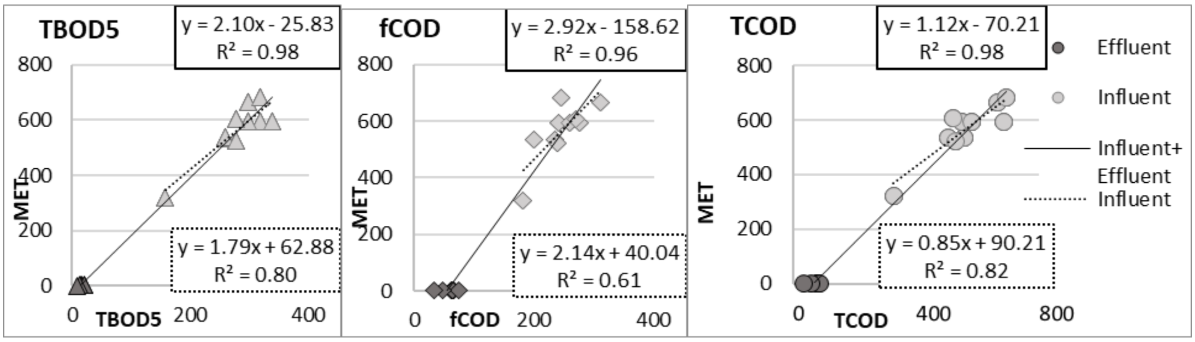

Figure 1. Linear regression for influent and combined influent and effluent TBOD5, fCOD, TCOD

Toxicity tests

The toxic effects of hypochlorite, hydrogen chloride, sodium hydroxide and saturated salt solution were examined. Apart from the first one, the addition of the chemicals caused distinct changes in the signal: after the addition of the acid and the base, the signal increased in a clearly distinguishable way from the baseline. When placed back to wastewater, the signal returned to the baseline. The addition of salt caused a gradual decrease in the signal from which the sensor recovered much slower after placed back to wastewater (Figure 2).

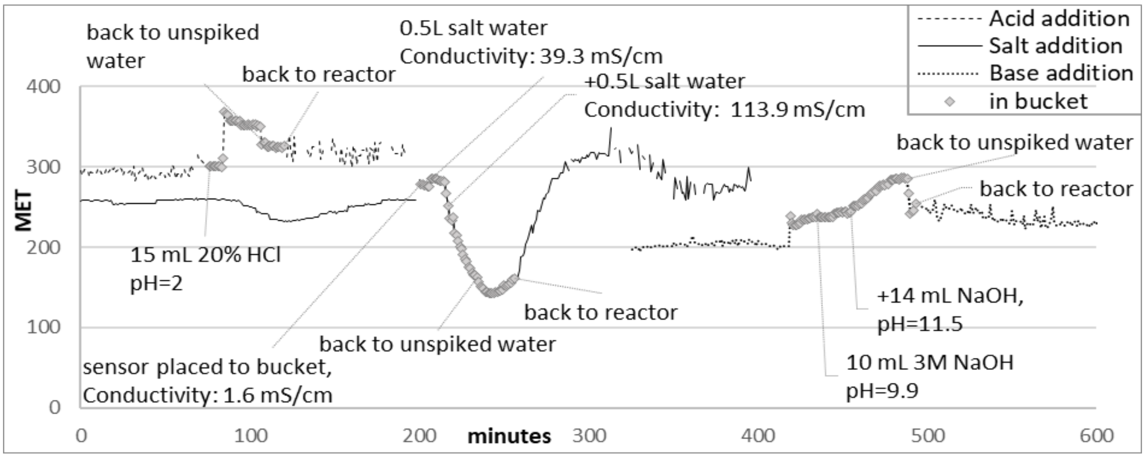

Figure 2. Responses in MET signal for different toxic events

POSSIBLE APPLICATIONS

As a conclusion, the Sentry bio-electrode sensor is suitable to measure TBOD5 concentrations in the influent and effluent of a municipal wastewater treatment plant, given that the proper measurement for correlating the MET and TBOD5 values are done. Even without correlation to TBOD5 or other parameters, the MET value can be used to indicate the concentration changes of biologically degradable materials in the water.

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Micropollutants Removal in Submerged Membrane Bioreactors at Different SRT Values: Variations of Extracellular Polymeric Substances

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INTRODUCTION

Endocrine disrupting compounds (EDCs) are becoming of primary concern, given their increased use and, in turn, their increased presence in our aquatic environment (Palacios-Rosas and Castro-Pastrana, 2017). These human-made micropollutants such as pharmaceuticals, hormones, phenolic compounds, phthalates and pesticides can be found in aquatic environment, and consequently were found in the effluent of conventional activated sludge processes at various concentrations from few nanograms per liter (ng/L) up to several micrograms per liter (μg/L) due to their limited capability to remove these contaminants (Nguyen et al., 2013). The biodegradation of micropollutants is influenced by SRT, which is considered as the most significant parameter for pharmaceuticals (Nasirabadi et al., 2016). This paper presents possible treatment of some micropollutants by submerged membrane bioreactor (sMBR) at 15 days and 90 days of SRT. The study also focuses on the production of EPS and SMP in MBRs.

MATERIALS AND METHODS

Two lab scale submerged MBRs made of plexi-glass were used in the study, having 5 L effective volume (R1: test MBR (micropollutants added), R2: control MBR). The MBRs were operated at a constant permeate flux (7.3 L/m^{2}xh) under the same hydraulic retention time (HRT) of 12 h. The reactors were fed with synthetic municipal wastewater. Ceramic membrane modules (pore size 0.1 μm; filtration area of 0.057 m^2) were used in the R1 and R2 MBRs. 4-tert-octylphenol (endocrine disruptor), fluoxetine (pharmaceutical), estrone (hormone), and atrazine, penconazole, chlorpyrifos ethyl, malathion, cypermethrin (pesticides) were selected as an organic micropollutants and mixture of these micropollutants were added to the synthetic wastewater in the R1 MBR after reached the steady-state condition. The R1 and R2 MBRs were operated between 0-50 days and 51-193 days at 15 and 90 days of SRT, respectively. The concentrations of each analyte in the synthetic wastewater were determined according to the detection limits in the GC/MS protocol (Caglak et al., 2019). EPS and SMP were conducted according to Tinggang et al. (2008).

RESULTS AND DISCUSSION

The MLSS concentrations of R1 and R2 MBR were about 3345 mg/L and 3215mg/L at 15 days, 13655 mg/L and 11380 mg/L at 90 days SRT. The COD, NH_4^+-N and PO_4^{3+}-P removal efficiencies were found to be over 96.7, 86.1 and 56.1 %, respectively. The micropollutants removal efficiencies were found between 82.6 % to 91.7 % except atrazine and penconazole at 15 days SRT. The atrazine and penconazole removal efficiencies were found to be 14.9 % and 57.0 % due to their lower biodegradability. On the other hand, removal efficiencies of micropollutants were found above 97.5 % except atrazine (17.5 %) and penconazole (45.0 %) at 90 days SRT. The EPS concentrations were presented in Figure 1. The protein fraction of EPS (EPSp) were found between 39.2 to 65.4 mg/g MLSS and 34.6 to 73.6 mg/g MLSS for R1 and R2 MBRs and it can be said that the EPSp of R1 were found lower from R2 MBR. Similar trends of EPSp were found at 90 days of SRT (Figure 1-b). When compared to obtained results of SRT 15 and 90 days, EPS concentration decreased with an increase of SRT from 15 days to 90 days. It be also said that the EPSp concentrations were found approximately 3 times higher from the EPSc concentrations at both SRT values.

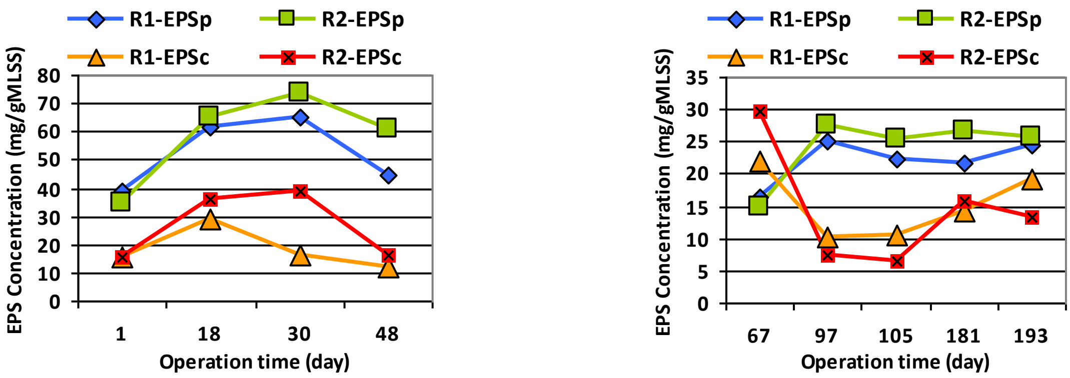

Figure 1. EPSp and EPSc concentration of activated sludge at different SRT values: (a) 15 days SRT, (b) 90 days SRT

The total SMP concentrations in the supernatant of 15 days SRT averaged around 16 and 17.1 mg/L for R1 and R2 MBR. The average SMP concentrations in permeates were found to be 3.6 and 4.1 mg/L for R1 and R2 MBRs. The SMP rejections of R1 and R2 MBR were around 77.5 % and 76 %. On the other hand, the average SMP concentrations of R1 and R2 supernatants at 90 days SRT were determined 9.6 and 8.4 mg/L. Total SMP of R1 and R2 permeates were found to be 3.1 and 4.0 mg/L with the rejection rates of 67.5 % and 52.1 %, respectively.

CONCLUSION

In this study, adding micropollutants in feed wastewater results in slight increase of EPS and SMP secreting by activated sludge in MBR. An increase in SRT also resulted in a significant decrease in EPS and SMP production. According to the SMP results in supernatant and permeate, it was understood that proteins and carbohydrate accumulated in the sMBRs.

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Accelerating Biofilm Formation in a Single Stage Mainstream Deammonification Moving Bed Biofilm Reactor (MBBR): The Use of nZVI and Polymers

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BACKGROUND

Biofilm reactors have gained more attention recently for deammonification systems which include partial nitritation and Anammox process. MBBRs developed in 1990s (Ødegaard, 2006) have distinct advantages over other technologies (e.g., high volumetric capacity, effective use of volume, stable operation, no short-circuting, no clogging). More importantly, they allow to formation of distinct oxic, anoxic and anaerobic layers on carrier, which allows allocation of different species. In MBBR systems, different microbial species are spatially distributed on plastic carriers that move in water with air supply and/or mixers. The main limiting step of MBBR applications is the initial biofilm formation. The usual trend for the start-up is to bioaugment reactors with seed carriers. However, deammonification seed carriers are usually not available locally in countries. Hence, the research activities should focus on the methods that may accelerate biofilm attachment on virgin carriers. This study aims to evaluate the effect of regular addition of cationic and anionic polymers and nano scale zero valent iron (nZVI) on initial biofilm formation stage MBBR systems. The effect of additives were evaluated both attachment and process efficiency wise.

METHODOLOGY

The experimental set-up contains 4 reactors operated under room temperature (20-23 ºC) as follows: 1st reactor: Blank (MB), 2nd Reactor (M1)- 5000 ppb nZVI dosing, 3rd Reactor (M2)- 1 mg/l anionic polymer dosing, 4th Reactor (M3)- 1 mg/l cationic polymer (Figure 1). The reactors were initially seeded with mixed activated sludge of Istanbul STP. They were initially filled with HDPE carriers with protected area of 550 m^2/m^3. All reactors were operated as SBR and fed with aerated grit chamber effluent of Istanbul STP. The additives were regularly added twice in a week. The oxic and anoxic periods were adjusted with intermittent aeration sheme. Daily influent and effluent samples were analysed regularly for COD, NH_4^+-N, NO_2^--N, NO_3^--N and PO_4^--P.

RESULTS AND DISCUSSION

Through 112 days operational period, the biofilm formation on carriers was monitored with naked eye (Figure 2). In all reactors, no biofilm formation was apparent in the first month. Afterthat, biofilm slightly observed on carriers. At the end of 112 days operation period, the most intense biofilm was seen in the reactors dosed with anionic polymer (M2) and nZVI (M1). The cariers in both anionic and cationic polymer dosed reactors (M2 and M3) demonstrated a homogeneous distribution of film on carriers. In all reactors, ammonia removal was observed in the sort of M2 (anionic poly)> M1 (nZVI)> M3 (cationic poly)> MB. The highest ammonium removal efficiency was observed as 77 % in the anionic polymer dosed reactor (M2). Based on removed ammonium, nitrate production efficiencies in the reactors was observed as M2≈ blank (MB)> nZVI (M1)> cationic poly (M3). In all reactors, nitrate removal was also observed. The highest removal efficiency (58 %) was seen in nZVI dosed reactor (M1). However, nitrate removal was more frequently observed in the MB (blank). COD removal was ranged between 43-53 % in all reactors. Phosphorus release and uptake patterns were different in all reactors. The highest phosphorus release was in blank MB (91 %) while the lowest phosphorus release in nZVI reactor M1 (27 %).

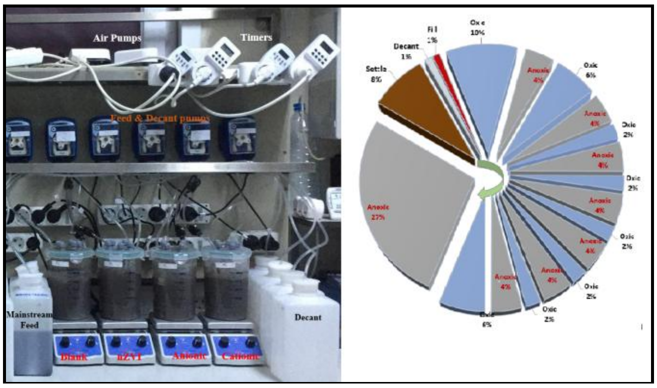

Figure 1. Experimental set-up (a) reactors (b) SBR cycle describing intermittent aeration

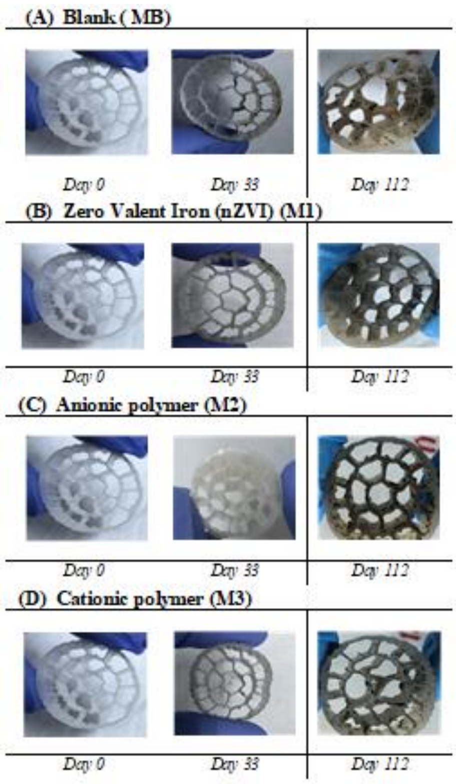

Figure 2. Biofilm formation on plastic carriers

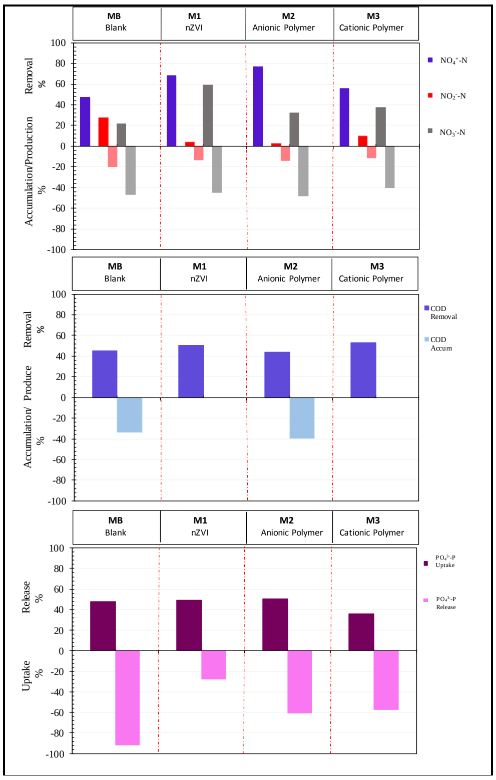

Figure 3. The effects of additives on process efficiency; nitrogen removal, organic carbon removal, phosphorus removal

ACKNOWLEDGEMENT

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Advanced Nitrogen Removal for Domestic Wastewater Treatment via Anammox Pathway in a Combied Biofilm Process

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BACKGROUND

High energy consumption is a pronounced challenge for the treatment of low COD/N domestic wastewater with conventional nitrification and denitrification processes. Anammox technology is regarded as the most potential process to make wastewater treatment energy-neutral or energy-positive. However, some problems need resolve for its application, including nitrite source, competition with AnAOB and denitrifiers, and the effective retention of AnAOB (Chen et al., 2018). Biofilter combines both physical filtration and biological treatment by biofilm attaching on the surface of filter media, and microorganisms can be retained in reactor effectively (Liu et al., 2017). In this study, a combined biofilm process was built up to treat domestic wastewater. Heterotrophic and autotrophic biofilm were enriched separately, 88 % nitrogen was removed via anammox and denitrification pathway, and effluent nitrogen was less than 10 mg/L.

MATERIALS AND METHODS

Reactors setup and operation

This combined biofilm process was consisted of four biofilters, the first biological aeration filter (BAF1) was used for COD removal, the second biological aeration filter (BAF2) was used for autotrophic nitrogen removal via anammox pathway, the third partial denitrification biofilter (PDN) was used for nitrite accumulation, and the last one was anammox filter (AXF) for advanced nitrogen removal via anammox pathway. This process was operated at 25~19 ℃. The gas and water ratio of BAF1 and BAF2 was controlled at 8:1 and 3:1, respectively. The effluent of BAF1 and BAF2 was mixed with the volume ratio was 1:3.25, and then it was pumped to PDN. Sodium acetate was also added to PDN as carbon source, and the COD/NO_3^--N was controlled at 3.

Analysis methods

The microbial community composition was analyzed by high-throughput sequencing based on 16s rRNA genes. N_2O was measured by gas chromatography with electron capture detector (Agilent 7890, U.S.).

RESULTS AND DISCUSSIONS

More than 80 % nitrogen could be removed from this combined biofilm process for domestic wastewater treatment. Effluent nitrogen was less than 10 mg/L, and COD was less than 50 mg/L. In BAF1, 17.8 mg/L nitrogen was removed via denitrification pathway. Autotrophic biofilm was enriched in BAF2, and 21 mg/L nitrogen was removed via anammox pathway, based on the interactions of AOB and AnAOB (Lawson et al., 2017). NO_2^--N was accumulated in PDN, and finally advanced nitrogen removal was achieved via anammox pathway in AXF. According to the calculation of nitrogen balance, 0.22 % of the influent nitrogen was released via N_2O, and 64 % nitrogen was removed via anammox pathway. In BAF2, *Candidatus Brocadia*, *Nitrospira* and *Nitromonas* were the dominant bacteria at genus level. In AXF, 25.4% *Candidatus Brocadia* and 6.6 % *Candidatus Kuenenia* were enriched. It was vital to enrich autotrophic and heterotrophic biofilm in separate reactors to avoid the inhibition of other bacteria to AnAOB.

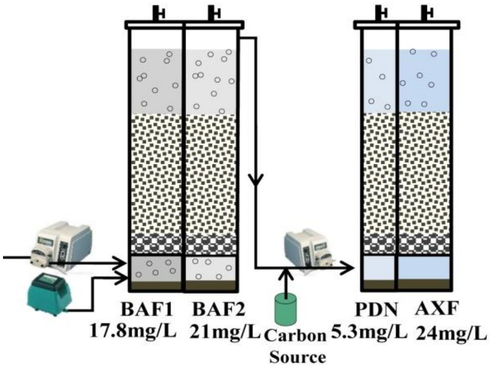

Figure 1. Schematic diagram of the combined biofilm process and nitrogen removal concentration in each biofilm reactor

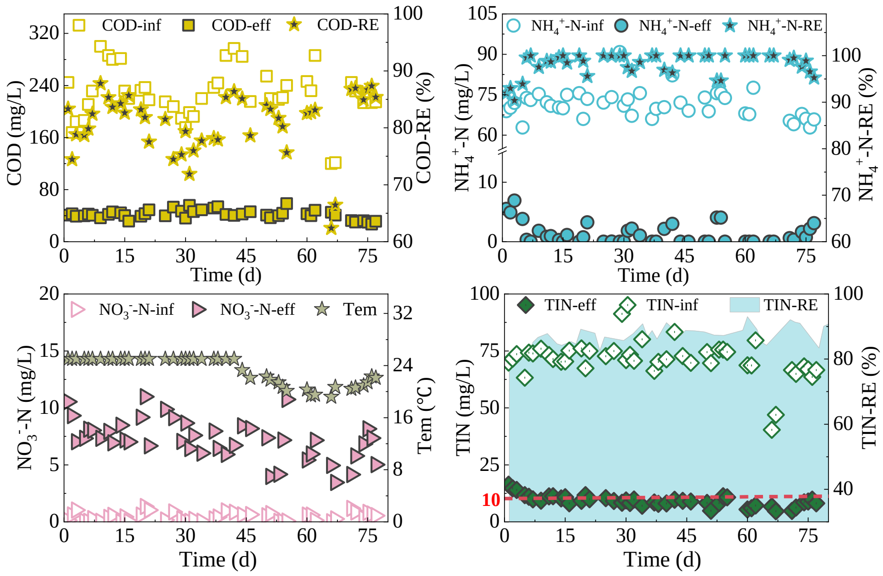

Figure 2 Variations of influent and effluent wastewater quality of the combined biofilm process

CONCLUSIONS

64 % of the influent nitrogen was removed via anammox pathway for domestic wastewater treatment in the combined biofilm process, and effluent nitrogen was less than 10 mg/L. Excellent interception of AnAOB, and separate enrichment of heterotrophic and autotrophic bacteria were vital to achieve nitrogen removal via anammox pathway. The combined biofilm process has great potential with saving 30 % aeration and 60 % carbon source addition, reducing 54 % excess sludge production and 43 % CO_2 emission.

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Potential Use of Filamentous Fungi for Diclofenac Removal from Municipal Wastewater

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INTRODUCTION

The conventional wastewater treatment plants not always can effectively remove the pharmaceutical substances such as diclofenac. Therefore, the search for new methods of removing pharmaceutical substances from wastewater needs to be carried out. In the last decade, the fungal treatment of wastewater has been shown as a promising approach. Thus, it is necessary to investigate and find the most appropriate fungal strains for pharmaceutical substance removal from wastewater. The aim of this study was to examine the potential of three selected fungal strains to remove pharmaceutical substances from municipal wastewater. Furthermore, during this study, the batch scale experiment was conducted under non-sterile conditions to increase more realistic action for further practical application. The results of the diclofenac removal, enzyme activity of laccase and pH changes during incubation time of 72 h were compared between the fungal strains and inlet wastewater as a negative control.

MATERIALS AND METHODS

Wastewater and fungal strains

The inlet wastewater (Inlet WW) was provided by Hammarby Sjöstadsverk wastewater treatment plant (Stockholm, Sweden) with the following composition: COD – 500-700 mg l^{-1} , N_{tot} – 40-50 mg l^{-1}, P_{tot} – 4,0-5,0 mg l^{-1}. The white-rot fungi of *Lentinus tigrinus* DSM 1016, *Phanerochaete chrysosporium* DSM 1556, and *Pycnoporus ciunabarinus* DSM 1184 were purchased from DSMZ Culture Collection (Leibniz Institute DSMZ-German Collection of Microorganisms and Cell cultures, Germany).

Removal of diclofenac in municipal wastewater

Removal of diclofenac in non-sterile municipal wastewater was run using K1 carrier units to achieve a higher initial concentration of biomass from selected fungal strains. Firstly, the fungal biomass was grown on carriers with potato dextrose broth media (Oxoid, United Kingdom) for 5 days. Subsequently, the fungal biomass was separated and added to non-sterile municipal wastewater (25 ml; pH 5,5). Finally, the diclofenac (Sigma-Aldrich, Gemany) was added to a final concentration of 2,5 mg l^{-1}. All flasks were incubated in a shaking incubator (50 rpm) at 25 °C for 72 h and samples were taken at 0 up to 72 h. Further, the concentration of diclofenac was measured by HPLC system of Alliance 2695 Separation Module (Water, USA) using Nova-Pak C_{18} column (4μm, 3,9 x 300; Waters, USA). All results were analysed using Empower 3 Chromatography Data Software (Waters, USA). The laccase activity was measured spectrophotometrically using a standardized procedure of the enzymatic assay for laccase by Sigma-Aldrich (Germany).

RESULTS

The results of *P. ciunabarinus* demonstrated complete (>99,9 %) removal of diclofenac after 6 h of incubation while *L. tingurinus* and *P. chrysosporium* were able to remove diclofenac completely after 12 h of incubation. Additionally, the inlet wastewater without fungal strains was also able to remove diclofenac after 48 h of incubation (Fig. 1A).

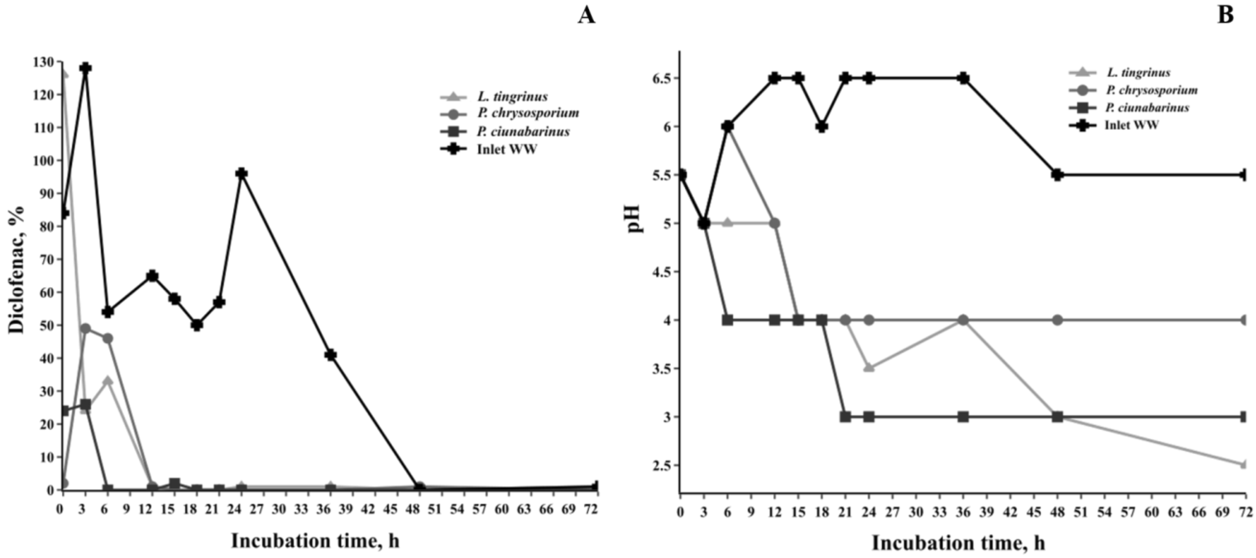

Figure 1. **A** Removal efficiency (%) of diclofenac in 72 h from non-sterile municipal wastewater with selected fungal strains; **B** pH changes during incubation time of 72 h for selected strains

During this study, the pH and enzyme activity of laccase was monitored to better understand the removal mechanisms of diclofenac. The results shown a pH decreasing of wastewater in the presence of fungal cultures, for instance, the pH of *P. ciunabarinus* decreased from 5,5 to 4 after 6 h of incubation when the complete removal of diclofenac was reached (Fig. 1 B). The same tendency was observed for the inlet wastewater without selected fungal strains, i.e., after 48 h of incubation, the diclofenac was complete removed (>99,9 %) when the lowest pH of 5,5 was reached (Fig. 1 A and B). However, none of the fungal strains shown laccase enzyme activity up to 72 h of incubation. Hence, it is speculated that tested fungal strains might use biosorption as a mechanism for removing diclofenac from non-sterile municipal wastewater. Further study in progress to analyse the extracellular production of enzymes like peroxidases to under the mechanism of diclofenac removal by fungal strains. Overall, the results from this study shown the ability of all selected fungal strains to effectively remove diclofenac from non-sterile municipal wastewater. Therefore, the use of these strains might be a promising approach for the development of advanced wastewater treatment technology.

ACKNOWLEDGMENT

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Enhancing the Accuracy and Precision in Quantifying the Pesticides Present in Complex Environmental and Food Samples by GC-MS Using Matrix Matching Calibration and Isotopically Labelled Internal Standard

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INTRODUCTION

The onslaught of pesticide usage has significantly increased the yield and quality of agricultural products, and helped to curb diseases that are transmitted by disease bearing pests. Different chemical classes of pesticides are synthesized to target specific organisms with different modes of action to weaken or kill pests (Chormey et al., 2017). Since pesticides are used all around the world and in large quantities, a high risk has been associated with non-target organisms getting exposed. Just as pesticides are capable of causing harm to pests, non-target organisms including humans when exposed to pesticides through inhalation, dermal contact or ingestion could manifest various health disorders. Both approved and banned pesticides need to be monitored in food and environmental samples to affirm that humans and the environment are protected from their detrimental effects. Gas chromatography mass spectrometry (GC-MS) offers high sensitivity and specificity for the monitoring of one compound in the selected ion monitoring (SIM) mode, or selectivity for different compounds at the same time in the scan mode (Kyle, 2017). Due to the complicated nature of environmental and food samples, false negative and false positive results could be reported for analytes that are suppressed or boosted by components of the sample matrix (Panuwet et al., 2016). Instrumental fluctuations and other systematic errors could affect measurement results and increase uncertainties (Alnouti et al., 2006). The aim of this study was to use matrix matching calibration method to enhance the accuracy of quantifying the selected pesticides in complex environmental samples, and to use a deuterated internal standard to increase measurement repeatability by offsetting systematic errors.

MATERIALS AND METHODS

The pesticides and internal standard used in this study (dioxacarb, flumetralin, tefluthrin, trifluralin, and deuterated bisphenol A) were purchased from Dr. Ehrenstorfer (Augsberg, Germany) and they were all of high purity (>98 %).The following temperature program was used for elution and complete separation of analytes within 7.0 min: 40 °C/min ramp from an initial temperature of 70 °C to 160 °C, then a final 50 °C/min ramp to 280 °C and held for 3.0 min. The capillary column (HP-5MS) used for separation of analytes was 30 m in length, 0.32 internal diameter and 0.25 µm film size. The column was fixed in the oven compartment of a 6890 model Agilent gas chromatograph coupled to a mass spectrometry detector (Agilent 5973) for analyte detection. The fragmentation ions (*m/z*) 224/223, 306/264, 177/197, 143/145 and 121/166 were respectively used to quantify/qualify BPA-D16, trifluralin, tefluthrin, flumetralin and dioxacarb. All aqueous samples were directly spiked with intermediate standards with concentrations 100 times higher than the intended spike concentration. The kiwi sample was homogenized and extracted by the QuEChERS method and the solid samples were extracted with acetonitrile by mechanical shaking for 2.0 min.

RESULTS AND DISCUSSIONS

BPA-D16 was added to all samples and calibration standards, and the ratio of sample/standard peak area to internal standard peak area was used in developing calibration plots and calculating percent recovery. The samples were spiked at different concentrations and three replicates were performed for each spike level to determine precision. The GC-MS method was validated for the analytes based on limit of detection (LOD), limit of quantification (LOQ), coefficient of determination (R^2), percent relative standard deviation (%RSD) and linear working range (LWR). Since the standard solutions used to validate the method were prepared in acetonitrile, the recovery results of all spiked samples were calculated with respect to calibration plots developed with acetonitrile based standard solutions. The recovery results of all aqueous spiked samples fell below 50 % against the standard solutions and matrix matching was therefore used to enhance the accuracy of quantification. The recovery results calculated for irrigation canal water, well water and wastewater at four different spike concentrations ranged between 94 and 107 %. The soil and sludge spiked samples recorded more satisfactory recovery results to the aqueous samples but the sludge sample was in turn relatively lower than the soil sample. The recovery results obtained by matrix matching for both solid samples ranged between 95 and 103 %. Kiwi extract obtained by the QuEChERS method produced recovery results between 102 and 124 %. Matrix matching was used to improve the results as shown in Table 1.

Table 1. Percent recovery results calculated for kiwi samples by matrix matching method

Analyte	**Kiwi samples (%)**			
	1.0 ng/mL	**2.5 ng/mL**	**5.0 ng/mL**	**10 ng/mL**
Dioxacarb	96.4 ± 5.5	102.2 ± 6.4	99.6 ± 4.6	100.0 ± 3.5
Trifluralin	96.8 ±2.9	100.0 ± 2.0	101.2 ± 4.9	99.7 ± 2.1
Tefluthrin	98.1 ± 3.9	97.6 ± 0.7	102.5 ± 5.3	99.5 ± 6.1
Flumetralin	103.2 ± 2.2	96.7 ± 0.1	99.6 ± 3.4	100.2 ± 0.9

CONCLUSIONS

The complexity of environmental and food samples requires accurate and precise analytical techniques for the determination of contaminants. To mitigate matrix interference and improve the accuracy of quantification, matrix matching calibration method was used for selected aqueous and solid samples and this produced satisfactory results for all analytes. The use of an internal standard augmented accuracy by given more precise results for replicate measurements.

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The Distribution of Bacterial Communities in Partial Nitritation Fixed Bed Reactor

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INTRODUCTION

The anammox process is widely accepted as a promising process for nitrogen removal from wastewater. The anammox process is more cost effective than the conventional nitrification–denitrification system due to the lower sludge production and low requirement for aeration.

During this process anammox bacteria combines ammonium and nitrite to produce nitrogen gas under the anoxic condition (Pathak et al., 2007).In wastewater treatment anammox needs to be combined with a precedent partial nitritation stage by ammonia oxidizing bacteria (AOB), namely the oxidation of NH_4^+ to NO_2^-(around one-half of NH_4^+ is oxidized to $NO_2^-$the other half is not).

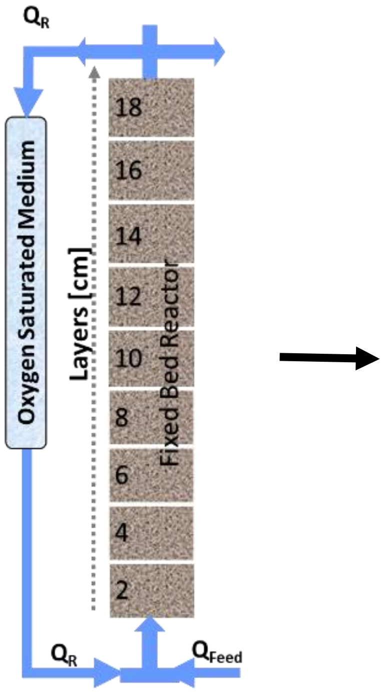
Anammox process was implemented at several wastewater plants mainly for reject water at different configurations: MBBR, DEMON and SBR (Lackner et al., 2014)a few reports deal with fixed bed reactors. In the last years the researches focused in the implementation of the anammox process in mainstream.

In order to achieve stable anammox process an efficient controlled nitritation is needed. There are several strategies to enable the occurrence of the first step of the aerobic nitrification, while inhibiting (minimizing) the activity of the nitrite oxidizing bacteria (NOB), such as temperature control, pH control and oxygen concentration. Achieve partial nitritation relies also on the knowledge of the abundance of (Ammonia oxidizers) AO over NOB and how they respond to different operational conditions. The abundance of the N-transformation bacteria is influenced by the different the environmental conditions.

MATHERIALS AND METHODS

In this study we developed reliable and efficient strategy to control nitritation in a continuous fixed bed up-flow biofilm reactor with recirculation and external aeration at main stream conditions. In aim to understand the effect of the limited nitritation on the bacteria communities, a shotgun metagenome sequencing was performed for the extracted DNA from the biofilm in the reactor at the different layers after 300 days of operation and from the source sludge of the reactor. Taxonomic profiling at phylum through species levels for the Prokaryotes was performed. The controlling strategy was efficient, the reactor conditions were suitable for anammox growth the dominant specie of N-transformation bacteria was Nitrospira defluvii, the dominant AOspecie was Nitrosomonas europaea. Despite the high abundance of Nitrospira defluvii,a stable performanceof the reactor was shown, this mostly related to their low activity. DO concentration had noticeable effect on the bacterial communities composition.

MATHERIALS AND METHODS



Shotgun metagenome sequencing was performed for the extracted DNA from the biofilm in the different layers, by NextSeq500 instrument of Illumina.

Figure 1. Schematic flow diagram of the partial nitritation split aeration/feed upflow-fixed bed reactor for limited nitrification, the reactor was operated for 300 days

Table 1. The abundance of the dominant N-transformation species (99 % of the communities) at the different layers and the source sample

Specie	PNR [%]	Source [%]
Nitrospira defluvii	46-80	60
CandidatusNitrososphaeraevergladensis	2.5-24	1
Planctomycete KSU-1	2.29-21.4	0.56
Nitrosomonas europaea	7-17	6
CandidatusBrocadiasinica	1-10.2	0.1
Nitrosomonas sp.AL212	1.4-3.3	0.24
Scalinduabrodae species	0.87-1.85	0.43
Nitrosomonas eutropha	*0.6-1.3*	*0.8*
Nitrosomonas multiformis	<0.1	14

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Industrial Wastewater Discharge to Municipal Sewer System in Countries of Baltic Sea Region

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INTRODUCTION

In terms of various industrial activities, the industrial wastewater is produced as a residue of produced or processed unit, in numerous cases it is more polluted than typical municipal wastewater. Due to the urbanization, industrial organizations tend to have the facilities in urban areas that lead to industrial wastewater discharges to public sewer systems, municipal wastewater treatment plants (MWWTP) / indirect wastewater discharges (Ntuli, 2012). In most of the cases, MWWTP are not designed to treat high polluted industrial wastewater. Thus the residuals might leak to receiving surface water bodies. In spite of legislation applied in European Union regards industrial wastewater discharges to MWWTP that clearly defines that "Industrial waste water entering collecting systems and urban waste water treatment plants shall be subject to pre-treatment" (European Commission, 1991) there is a lack of information on the total amount of discharges and impact on MWWTP. Therefore this research is done to estimate the potential number of indirect industrial wastewater discharges in the Baltic Sea Region (BSR).

MATERIALS AND METHODS

To evaluate the approximate amount of industrial wastewater discharges to public sewer systems and subsequently to MWWTP, a questionnaire have been developed and distributed in Estonia, Finland, Latvia, Lithuania, Poland and Kaliningrad region (Russia). The questionnaire is aimed to collect the data on industrial organizations by the implementation of a Statistical classification of economic activities in European Community NACE Rev.2.0 (Eurostat European Commision, 2008) for division and arrangement of industrial sectors (number, scale). An expert panel which consisted of scientists, engineers, consultants, and lawmakers was formed to distinguish the industrial categories that might be a source on industrial wastewaters. In total 21 categories and 9 subcategories in food production categories were selected as a source of industrial wastewaters and included in questionnaire. The experts in each country selected the "key industries" that have the major impacts on operating efficiency of MWWTP. The number of industrial organizations in each of the 30 categories was collected from the local bureau of statistics. Based on the data collected with questionnaire the most urgent "key industries" in BSR were selected and the number of potential industrial wastewater discharges to municipal wastewater systems established.

RESULTS

The results from the questionnaire showed that every of 9 subcategories from food production sector (C.10) was selected in at least 1 country (Figure 1.A) as a potential source of indirect industrial wastewater discharge (IIWD) in BSR. Consequently, it was concluded that the C.10 subsector in all of its scope is an essential source of industrial wastewaters in municipal wastewater systems. From the other 21 sectors, 16 (Figure 1.B) was selected in at least 1 country meaning that 5 of previously selected sectors are not relevant sources of IIWD in BSR.

Within the food production categories in BSR the meat production and dairy products manufacturing organizations were identified as the “key industries” since those were mentioned accordingly in 6 and 5 countries. From other industrial categories the beverage production, chemicals, and chemical products production and waste collection, treatment, and disposal activity categories were identified as the “key industries”.

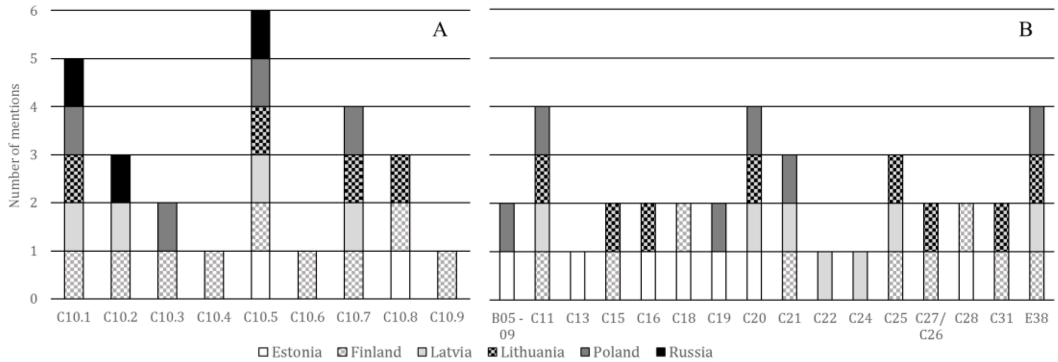

Figure 1. Industrial sectors and subsectors as a potential source of industrial wastewater in BSR
C10.1 - meat products, C10.2 - fish products, C10.3 - fruits and vegetables, C10.4 - vegetable and animal oils and fats, C10.5 - dairy products, C10.6 - grain mill products, C10.7 - bakery and farinaceous products, C10.8 - Other food products, C10.9 - Prepared animal feeds, B05-09 - mining and quarrying, C11 – beverages, C13 textiles and wearing apparel, C15 - leather and related products, C16 - wood and of products of wood, C18 - printing of recorded media, C19 - coke and refined petroleum, C20 - chemicals and chemical products, C21 - pharmaceutical products, C22- rubber and plastics products, C24 - basic metals, C25 - fabricated metal products, C27/C26 - electrical equipment, C28 - machinery and equipment, C31 – furniture, E38 - waste collection, treatment and disposal activities, materials recovery

According to the statistical information collected by questionnaire in 5 “key industries” sectors, there are 3 281 (excluding Kaliningrad due to availability of statistical data) industrial organizations that might be a potential source of industrial wastewater discharge to the public sewer systems. Likewise, if all industrial sectors that are mentioned in figure 1 are assumed as a potential source, the number rises to 25 986 industrial organizations in 5 BSR countries.

CONCLUSIONS

There are 3 281 industrial organizations in 5 “key industries” sectors of BSR and 25 986 in total. Therefore there is a high risk for potential contamination of MWWTP and subsequently Baltic Sea. The estimated number is just indicative since it is based on statistical and economic data. There is a lack of the data basis on industrial wastewater discharges in BSR that might lead to a more precise estimation of industrial wastewater sources and potential impact on MWWTP.

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Coupling Enzyme Technology to Improved Wastewater Treatment Processes

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INTRODUCTION

The water is a crucial resource for humanity, ecosystems and climate. Nevertheless, the water is limited, as in quantitative terms as qualitative, where climate change aggravate the situation. The Water Framework Directive (Directive 2000/60/CE) had been a radical change in the focus of management of water resources, changing utilitarian view to protective view of resource. Within main pressures which effect superficial water and subterranean water in the UE, founding waste from urban and industrial wastewater. The control of waste and the protection of recipient mass of water was regulated with the directive 91/271/CEE, today in force, which bind an adequate treatment of all wastes generate by urban congestion regardless size.

Wastewater treatment (WWTP) is commonly based on biological processes where determinate microorganisms digest organic or inorganic material from urban wastewater, which uses for their metabolism. Degradation of organic contaminants by microorganisms requires the pass across cellular membrane of these substances, where only monomeric and oligomeric substances (Lighter weight 1000 Da) are capable to cross by active transport. (Cadoret et al., 2002). For that reason polymeric substances must be degraded previously by the actuation of hydrolytic extracellular enzymes (Nybroe et al., 1992). The hydrolysis of high molecular weight substances will be limited step in the biological process of wastewater treatment.

The addition of hydrolytic enzymes in WWTP could stimulate the organic material assimilation. The improvement is expected like in conventional system (activated sludge) as natural or extensive systems (constructed wetlands). Enzyme’s hydrolysis has been applied in industrial effluents with high levels of fat and oils, with low level of biodegradability like alternative for conventional systems (Becker et al., 1999) and for sludge digestion (Aragón et al, 2009) to solubilize organic material reducing sludge production until 30% in pilot scale (Bermúdez et al., 2013). Nevertheless, enzyme catalysis in WWTP is limited by high cost of commercial enzymes. In this sense, previous works have allowed the production of enzymes from organic by-products’ fermentation, like sludge from sewage treatment (Rodríguez-Morgado et al., 2015). The addition of these enzymes could improve the process, obtaining water with better quality, in less time and with a low price.

This study aims at (a) the determination of the optimum conditions for the application of enzymes in the wastewater treatment and (b) the assessment of the effects on both intensive (activated sludge) and extensive treatment systems (constructed wetlands).

METHODS

In this study, lab scale pilot plants are employed for the assessment of the application enzymes to biological reactors. One pilot plant works as an activated sludge system (intensive tech.) and the other will simulate a constructed wetland (extensive tech.). Both pilot plants are fed with real wastewater. Commercial enzymes are tested initially, and later, with the by-product obtained in the fermentation of sewage sludge. Physicochemical and microbiological parameters are monitored in both systems to assess the effect of enzyme's addition on both systems.

RESULTS

Initial results show a slight increase in the treatment efficiency in both systems (larger organic matter removal) after the enzyme dosage. Besides, a reduction in sewage sludge production is observed in the SBR unit. Finally, it is observed a delay in the appearance of the clogging phenomenon in the horizontal flow constructed wetlands. Both effects are directly related to the solubisation of the organic matter.

ACKNOWLEDGEMENTS

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Application of Core-shell Bimagnetic Nanoparticles for Removal of Phosphorus from Aqueous Solution

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INTRODUCTION

An adequate concentration of phosphorus (P) in water bodies is key to maintain life in these environments. However, high concentrations of this nutrient may cause eutrophication of the receiving waters. A significant amount of P can be found in wastewaters (Verstraete et al., 2009). Thus, in order to avoid a possible uncontrolled increase of P in water bodies, this element must be removed from wastewaters before discharge. Among the P removal technologies, adsorption has been increasingly gaining attention from the scientific field due to its good performance at low concentrations, greater selectivity and simple operation (Yang et al., 2014). This work aims to investigate the adsorption capacity of core-shell bimagnetic nanoparticles ($CoFe_2O_4@\gamma\text{-}Fe_2O_3$) to adsorb P from aqueous solution in order to obtain a preliminary response regarding its use as a technology for wastewater treatment. It is important to highlight that the nanomaterial has magnetic properties, which enables an easy separation of the adsorbed nanoparticles from the medium through the appliance of a magnetic field.

METHODOLOGY

The first part of the synthesis of the nanoadsorbent corresponds to the production of ferrite cobalt nanoparticles ($CoFe_2O_4$) through a hydrothermal coprecipitation. In this step, in order to obtain samples of two different mean sizes, sodium hydroxide (NaOH) was used to synthesize the larger mean size nanoparticles (PaCoL) while methylamine (CH_3NH_2) was used in the synthesis of the smaller mean size nanoparticles (PaCoS). The second step of the synthesis is a surface treatment, in which a thin layer of maghemite ($\gamma\text{-}Fe_2O_3$) is formed around the ferrite cobalt nanoparticles. The shell of maghemite protects the nanoparticles from acid dissolution. X-rays diffraction measurements (XRD) were performed to provide information regarding the crystalline structure and the mean size of the nanoadsorbent.

Batch adsorption tests were performed to evaluate the influence of the solution pH, the contact time and the initial P concentration for both mean sizes of nanoparticles. A dosage of 10 mg of nanoparticles was added to 15 ml of an aqueous solution of phosphate under previously determined conditions. The tests were carried out on an orbital shaker. After the contact time, the nanoparticles were separated from the solution through the application of a magnetic field to the system for 15 minutes, using a permanent magnet (Nd-Fe-B). The concentration of phosphate in the supernatant was determined spectrophotometrically.

RESULTS AND DISCUSSION

The X-ray diffractogram pattern confirmed the spinel ferrites structure in according to the International Centre for Diffraction Data (ICCD) for both mean sizes of nanoparticles. The values of the average lattice parameter (0.835 nm for PaCoS and 0.837 nm for PaCoK) are in good agreement with the ICDD patterns. The mean diameter of the nanoparticle (dXRD) was calculated by applying the Scherrer's formula (Hammond, 1997) to the most intense line of the diffractogram (311). The dXRD obtained was 7.8 nm for PaCoS and 13.5 nm for PaCoL.

The influence of the pH on the adsorption demonstrated that, within the studied range, the lower the pH is the greater is the removal of P for both samples. This result was expected since the electrostatic interactions between the adsorbate and the adsorbent are favored in acidic medium (Campos et al., 2013).

The kinetics data were adjusted to the pseudo-first order, pseudo-second order and Elovich models. The Elovich model best fits the kinetics data for both samples. Figure 1 shows the kinetics of P adsorption, where t (min) is the contact time and q_t (mg/g) is the amount of P adsorbed at any time t. The equilibrium was achieved in a period of approximately three hours for the two samples with a removal of P pf 94% for PaCoS and 80 % for PaCoL.

In Figure 2, the equilibrium data is presented, where C_{eq} (mg/l) is the equilibrium P concentration and q_{eq} (mg/g) is the amount of P adsorbed at equilibrium. The equilibrium data were adjusted to the Langmuir and Freundlich model. The Freundlich model best fits the equilibrium data for both samples, suggesting that multilayers are formed in the adsorption process and that the adsorbent surface is heterogeneous.

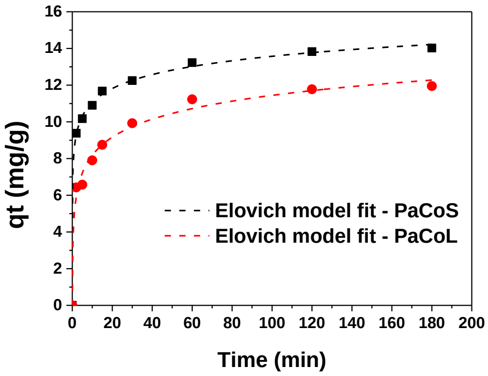

Figure 1. Kinetics adsorption data

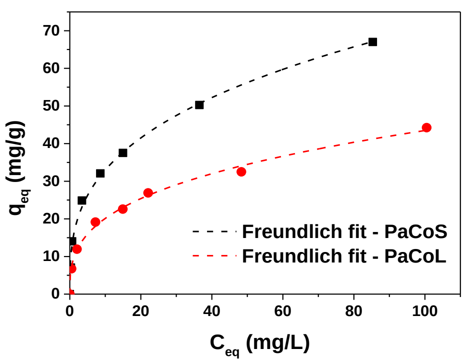

Figure 2. Equilibrium adsorption data

The nanoadsorbent mean size affects significantly the adsorption process. In all tests, the PaCoS sample adsorbed more P than the PaCoL sample under the same conditions. These results were expected since the smaller the mean diameter is the greater the available adsorption surface area per mass is.

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Limits of Increased Simultaneous Phosphorus Precipitation in WWTP Bílina

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INTRODUCTION

Increasing requirements on improvement of surface water quality press on the increase quality of wastewater treatment plants discharges. Limits of pollution at the outlet from WWTP are given by the Government Decree No. 401/2015 Coll., which has been widely discussed in recent years. The aim of this paper is not to evaluate whether and how stricter discharge concentration limits would affect surface water quality. The paper describes preparation of the operating company for possible change in legislation which will cause considerable costs – both investment and operational – to both operators and owners of water infrastructure. A WWTP belonging to the size category where the technological method of achieving possible stricter limits in the P_{tot} parameter is not clear was chosen for monitoring.

The paper is about pilot project which deals with the limits of simultaneous phosphorus precipitation in WWTP Bílina. After the new Government Regulation comes into force, the required concentration limits on the outflow of WWTP will be lower. The lower limit of P_{tot} concentration will be the major challenge of new legislation. WWTP in Czech Republic are divided into five categories depending on their projected capacity. Limits on the outflow of WWTPs are different for each category. The technical solution of phosphorus removal depends on the WWTP category. For the highest category (>100 000 PE) only tertiary treatment is possible. For the category 10 000 – 100 000 PE, which also includes WWTP Bílina, it is not clear. Pilot project lasted from January 2019 to May 2019 and outcome of the pilot project should be to verify the possibility of meeting the limit of P_{tot} without changing the current technology of WWTP – with simultaneous precipitation. The evaluation will also include an assessment what effect increased coagulant doses have on the WWTP operation and its economy.

WWTP CATEGORIES AND LIMITS ON THE OUTFLOW

How is written above, WWTP in Czech Republic are divided into five categories depending on their projected capacity. Each category has its emission standards for WWTP outflow quality. WWTPs categories and their outflow quality limits are in the Table 1.

Table 1. Categories of WWTP and their emission standard – concentration limit of P_{tot} on the outflow – current legislation (NV 401/2015 Sb.)

WWTP category (PE)	<500		500 – 2 000		2 000 – 10 000		10 000 – 100 000		>100 000	
P_{tot} (mg/l)	-	-	-	-	3[1]	8[2]	2[1]	6[2]	1[1]	3[2]

[1] means annual average concentration which cannot be exceeded
[2] means concentration which cannot be exceeded in any sample

Table 2. Categories of WWTP and their emission standard – concentration limit of P_{tot} on the outflow – upcoming legislation

WWTP category (PE)	50 – 500	500 – 2 000	2 000 – 10 000	10 000 – 100 000	>100 000
P_{tot} (mg/l)	1–3[1] ?[2]	1–2[1] ?[2]	1–1,5[1] ?[2]	0,2–0,8[1] ?[2]	0,15–0,5[1] ?[2]

[1] means annual average concentration which cannot be exceeded
[2] means concentration which cannot be exceeded in any sample

From the comparison of the Table 1. and Table 2. is clear that there is significant tightening of P_{tot} limits on the outflow of WWTPs. WWTP Bílina is in the category 10 000 – 100 000 PE and because of the water quality in the recipient the limit should be 0,8 mg/l P_{tot}. The main question for the owner and operator of the WWTP is: will WWTP be able to meet the limits with current technology (simultaneous precipitation) or will it be necessary to invest in a tertiary treatment?

MATERIALS AND METHODS

WWTP Bílina is mechanical-biological WWTP with two biological lines. Each line has regeneration, denitrification and nitrification tank and for each biological line there is two rectangular secondary settling tanks. Elimination of phosphorus is by simultaneous precipitation. Dosing point of coagulant is to the drain channel from nitrification tank. Dosage calculation is based on the online measurement of $P\text{-}PO_4$ and wanted outflow concentration. During the pilot project was one biological line reference – operated as usual – automatic dosing according to the online measurement. In the second, coagulation dose was set manually and was increased each 2 weeks.

During the pilot project the outflow from both pairs of secondary settling tanks was sampled. Parameters COD, BOD, SS, $N\text{-}NH_4$, $N\text{-}NO_2$, $N\text{-}NO_3$, N_{tot}, P_{tot} and Fe were monitored in the taken samples. Activated, returned and excessed sludge was sampled as well. In the activated sludge SS, Fe and P_{tot} were monitored, in the returned and excessed sludge only SS. Also activity and quality of the activated sludge was examined by kinetics and respirometric test and also by microscopis analysis.

CONCLUSIONS

Presumption is verification of the possibility to meet „new” limits of P_{tot} by current simultaneous precipitation, only with increased coagulant dosing. Project did not focus only on verifying this possibility but also on assessing the impact of increased coagulant dosing to the operation of WWTP, quality of outflow in other parameters than just P_{tot} and also sludge production as well as the impact of the operating costs.

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Modified Nanofibrous Carriers for Specific Growth of Bacteria and Modern Methods of Biofilm Evaluation

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MODIFIED NANOFIBROUS MATERIALS AS BIOMASS CARRIERS

Nanomaterials can be employed for immobilization of microorganisms (biofilm formation) utilizing their specific surface. With varying material compositions, preparations and modifications, the microorganisms (MO) can behave differently. For instance, MO metabolic processes can be promoted or suppressed. The properties of the nanofibrous biomass support (surface structure, wettability, charge and others) have a significant impact on the rate of microbial colonization and biofilm functionality (Liu, 2017). Bacterial strains can adapt to varying conditions according to their metabolism (nutrition). A suitably prepared and modified (physically, chemically, additively) nanomaterial can support the growth and reproduction of bacteria (even bacteria used in wastewater treatment). There is, however, lack of studies on application of nanofibers and their modifications for preferential growth of bacteria.

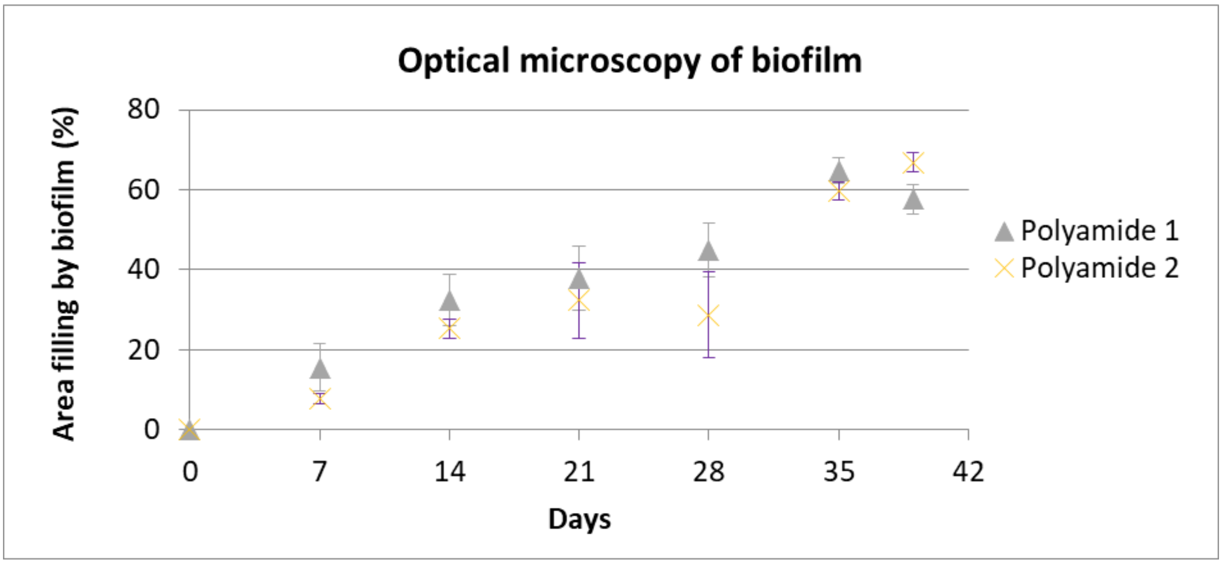
MATERIALS PREPARATION

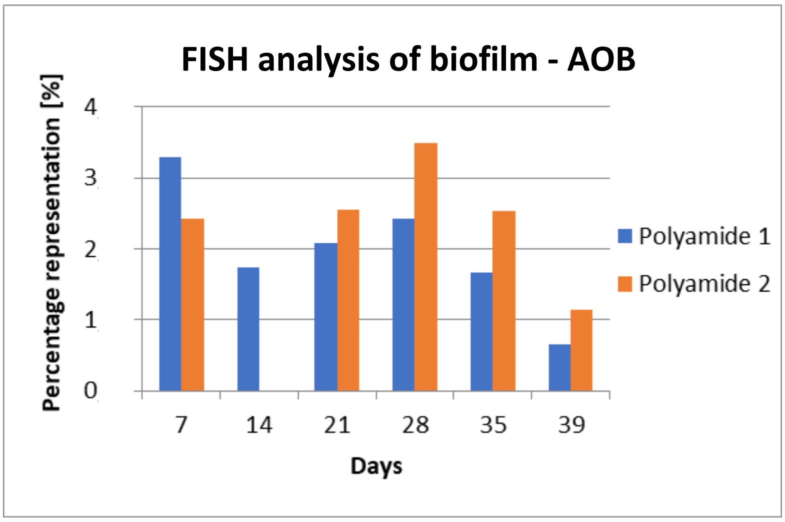
In this study, nanofiber carriers were prepared by direct (DC) and alternating (AC) electrospinning, using several polymers as polyvinyl butyral, polyurethane, and polyamide. The results showed large differences in fiber morphology, surface roughness, pore size, layer homogeneity, strength, size and fiber arrangement, depending on the spinning method and polymer used. The most suitable method for preparing nanofibers with required properties was Nanospider^{TM}, i.e. DC electrospinning. Moreover, modification of PVB nanofibers through addition of Fe_3O_4 nanoparticles showed as a very promising option for biotechnological applications, particularly for the growth of specific bacteria (for example for nitrifying and denitrifying bacteria). The PVB nanofibers doped by Fe_3O_4 nanoparticles were tested in a lab-scale bioreactor, and the results were unexpected. Respirometric tests showed approximately 2 times higher bacterial activity during the ammonia nitrogen removal when using composite carriers compared to activated sludge. In addition, a large number of nitrifying bacteria was detected on these carriers by FISH analysis. Nanoparticles Fe_3O_4 inside PVB polymer allow efficient binding of ammonia nitrogen to the carrier (biofilm) (Zhang, 2018), thereby accelerating its removal.

COMPARISON OF BIOFILM ANALYSIS METHODS

For biofilm evaluation, we use the FISH method, optical microscopy, molecular genetic method and respirometry. By comparing the results of individual methods, we can verify the correctness of the results, and we can modify the determination procedures for specific experiments.

It has been shown, that individual methods, although completely different from the nature of the assay, do not provide a fundamental difference in results and that, based on some modification of the evaluation, the methods can be used for mutual verification. During evaluating and comparing methods, it is important to take into account the nature of the determination, principle of evaluation, sensitivity of the methods and influence of the environment on the parameters monitored. Methods of analysis were compared in the experiment where the increase of biomass on fibers in the laboratory model of the biological reactor was studied.





qPCR heatmap - Polyamide	Total bacterial biomass	AOB
Day	U16SRT	amoA
7.	+++	+++
14.	++	+++
21.	++	+++
28.	+++	++
35.	++	+
39.	+++	++

Figure 1. Example of biofilm analysis (optical microscopy, FISH, molecular genetics) for one of the samples (polyamide fiber) from the experiment

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Efficient Aeration for Biological Wastewater Treatment

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MOTIVATION

In developed countries wastewater treatment is responsible for about 1 % of the total electric energy consumption, where deep tank aeration in the activated sludge process uses up to 80 % of the total energy budget. However, mass transfer and mixing are still the limiting factors for the energy efficiency of biological wastewater treatment (Wang et al., 2010). The bubble size is of great importance for mass transfer efficiency. It determines the surface area to volume ratio, which affects the volumetric oxygen transfer coefficient k_La and the oxygen absorption. The optimum diameter of bubbles in the typical aeration tanks is known to be between 0.75 and 1 mm to achieve 95% oxygen absorption from the bubbles (Motarjemi and Jameson, 1978). However, the bubble size of conventional fine-bubble aeration systems is between 2 and 5 mm (Hendricks, 2016) which results in a limitation of the oxygen absorption from the injected air bubbles below 50 % (Mohseni et al., 2019).

OPTIMAL BUBBLE SIZE

Towards increasing the efficiency of the aeration process, we propose two approaches. First, we suggest optimum diffuser concepts following the goal of bubble generation in the optimal range. Therefore, we studied the initial gas dispersion performance of diffuser concepts based on micro-orifices and needles with very fine orifice diameters in the range from 37 µm to 225 µm (Mohseni et al., 2019). Our study revealed that micro-orifices generate significantly smaller bubbles (Figure 1a), and thus an up to 22 % higher oxygen absorption at up to 51 % less power demand (Figure 1b). However, it was observed that small initial bubbles with diameters below 1 mm coalesce to bigger bubbles right above the orifice. A controlled bubble formation shows further potential to prevent the bubble coalescence and achieve optimum bubbles.

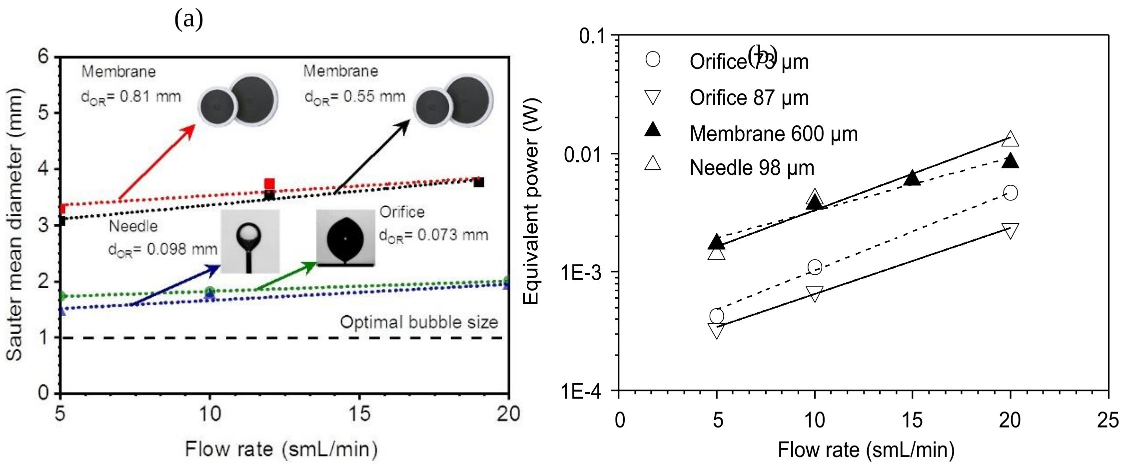

Figure 1. Performance of micro-orifices, needles and industrial rubber membrane diffusers (Mohseni, et al. 2019): (a) bubble Sauter mean diameter and (b) equivalent power demand to compress the air per orifice

IMPROVED GAS DISPERSION

Ideal dispersion of the generated bubble swarms in the bulk liquid by dynamic aeration is part of the second approach to further improve the mass transfer efficiency. We investigated the mass transfer of pulsed aeration modes in comparison to constant flow aeration in a test geometry in a numerical study (Herrmann-Heber et al., 2018). An increase of oxygen mass transfer rate by up to 24% is determined in comparison to continuous aeration (Figure 2). Further investigations show a potential reduction of the gas flow rate in pulsed aeration by 16 % while maintaining the mass transfer rate. Thus, air demand in compression and energy consumption can be reduced when dynamic aeration is applied. The intended combination of both approaches will be evaluated in further experimental investigations.

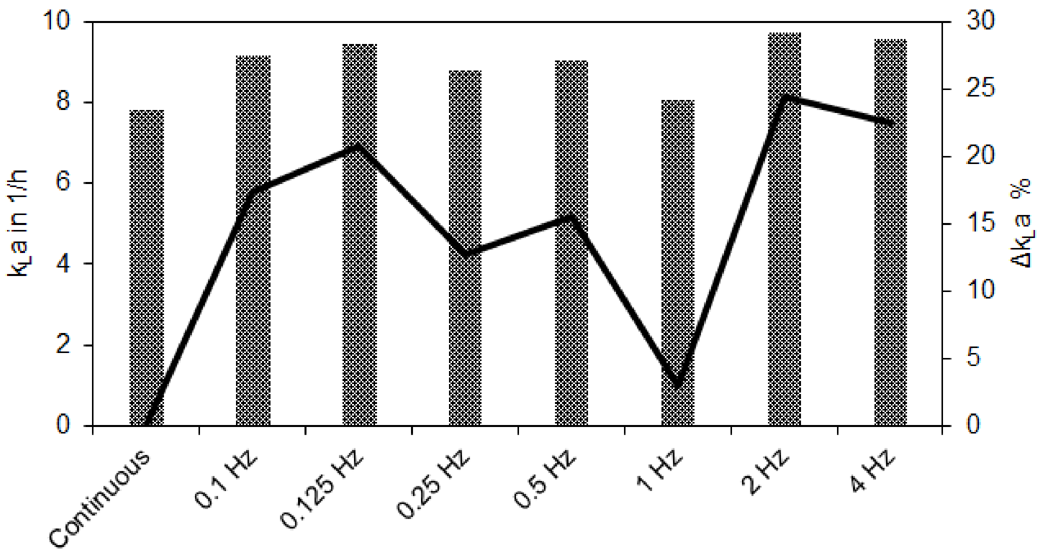

Figure 2. Comparison of volumetric mass transfer coefficients (bar chart) and its relative changes (line plot) for continuous aeration and dynamic aeration (Herrmann-Heber et al., 2018)

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Developments of Strategic Polymer / Ceramic Composites and Nanocomposites for Waste Water Remediation and Sustainable Utilization

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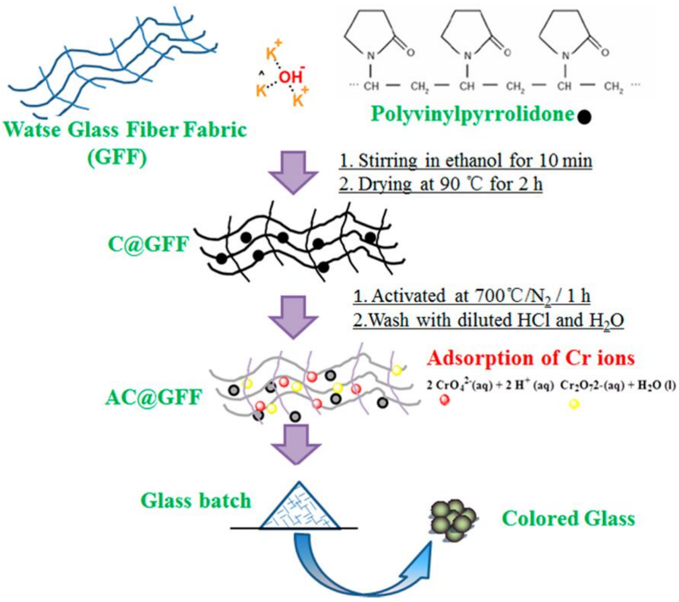
INTRODUCTION

The synthesis of activated carbon coated glass fiber fabric (AC@GFF) was carried out by the carbonization of polyvinylpyrrolidone with the assistance of KOH onto waste glass fiber fabric (GFF). The samples were analysed using XRD, SEM, N2-sorption, FTIR, XPS, TG, and DSC measurements. It is shown that KOH not only acted as an activator during the carbonization process but also facilitated the adherence of PVP onto the surface of the glass fibers by increasing the viscosity of the PVP precursor solutions. The prepared AC@GFF was applied to uptake Cr(VI) from synthetic wastewater, and the factors such as the pH, initial concentration of adsorbate, contact time, and adsorption temperature influencing the adsorption of the Cr(VI) were investigated. The adsorption data were fitted with the isotherm and kinetic models. The adsorption of metal ions by the AC@GFF from a real metal passivation wastewater proved that the synthesized adsorbent was highly selective to Cr(VI) against its inferring Zn(II). The spent adsorbent together with the adsorbed Cr ions was used as an effective glass colorant. The method provided a sustainable entrapment of toxic chromium ions in a glass matrix to produce a color glass, eliminating pollutions from the Cr(VI), waste GFF, and spent adsorbent.

EXPERIMENTAL DESIGN

Given below is the scheme (Scheme 1) showing the experimental design.



Scheme 1. Experimental design

RESULTS AND DISCUSSION

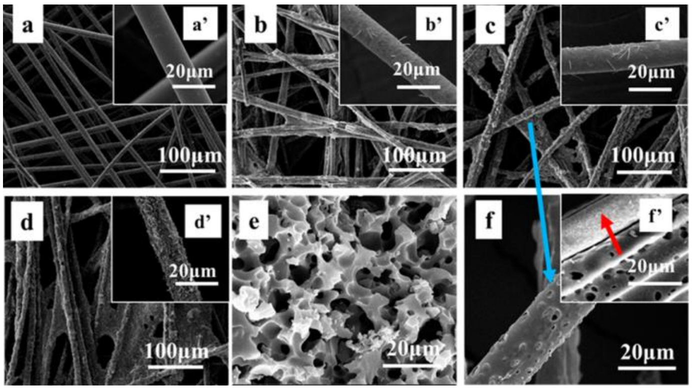


Figure 1. The SEM images

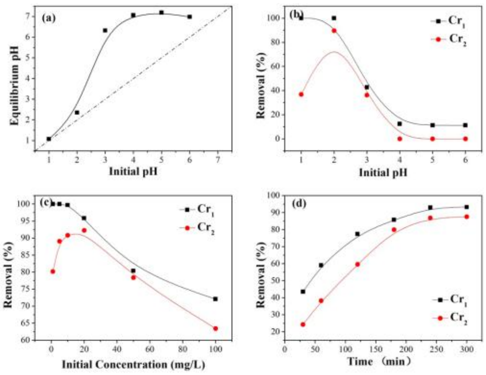


Figure 2. The adsorption tests

The SEM images Figure 1a show the diameter of the GFF is about 10−20 μm. After the formation of AC@GFF (Figure 1b−d), the fibers were rougher and the diameters were larger with the increase of KOH. Besides, there was some carbon material existing between the glass fibers in 1c-d. The amplified SEM image (Figure 1f) show broken holes on the surface of the AC@GFF sample, implying the emission of gas from the coated layer on the glass fiber. The adsorption tests were higher than the initial pH levels Figure 2a, indicating that the removal of Cr(VI) was accompanied by the consumption of H+ ions. Figure 2b shows that the removal of Cr1 by the AC@GFF decreases with increasing pH. The protonation of the surface of the carbon layer decreased with increasing the solution pH, and vice versa. Figure 2c shows that the removal efficiency of the Cr1 decreases with increasing the initial concentration and Figure 2d. It can be seen that the adsorption of Cr(VI) approaches equilibrium at about 4 h.

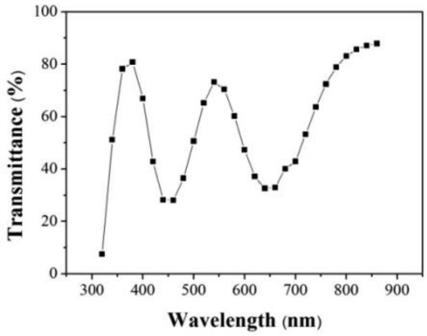


Figure 3. The transmission spectrum of the prepared glass

The transmission spectrum in Figure 3 of the prepared glass with the addition of spent AC@GFF adsorbent (3 wt %) show that there are two selective absorption bands at the wavelengths of 440 and 660 nm, respectively. Since the absorbance at 440 nm gives transparent glass a yellow colour, the one at 660 nm gives a green colour.

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Effect of Trace Metal Addition on Methane Production and Relation of this Effect to Diffusive Gradients in Thin Films (DGT) Metal Accumulation

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INTRODUCTION

Utilization of methane as a renewable energy source, through anaerobic digestion of organic matter is a well-established process in wastewater treatment. When wastewater and waste sludge are treated anaerobically, it is of great importance to maximize methane production by optimizing the activity of microorganism. The activity of the microorganisms can be hindered if trace metals, needed for enzymatic reactions, are not present in the bioavailable form in the reactor (Zandvoort et al. 2006). In order to optimize metal supplementation, the crucial step is to quantify the fraction of trace metals which is bioavailable to the microbial community. Our study focused on understanding the link between activity of the methanogens upon addition of different concentrations of Co, Ni and Fe and measured metal fraction by the diffusive gradients in thin films (DGT). The accumulated metals in the DGT devices represent labile metals, which we consider to be bioavailable for the anaerobic microorganisms.

MATERIALS AND METHODS

Activity of the methanogens was determined by biochemical methane potential test (BMP). The batch tests were performed in 600ml bottles with acetate as a substrate and anaerobic sludge (fed on cellulose) as the inoculum, with the initial organic loading of 1.2. In all the bottles, $NaHCO_3$ was added having concentration of 2.52 g/L and the pH was set up to 7.2. The control set had no metals added, where in the other bottles Co, Ni and Fe were added with the following concentrations: Co: 25, 50 and 100 µM, Ni: 100, 350 and 500 µM and Fe: 200, 500 and 1000 µM. Over time, we measured biogas production in the bottles and its composition. For the labile metal determination, DGT cells for metals in soil were used (for the characteristics of used DGTs, look at www.dgtreserach.com). The experiment was performed with the same inoculum as with the BMP test. The control sample contained only sludge with 2,52 g/L $NaHCO_3$, while others had additionally Co, Ni and Fe added with the following concentrations: Co: 25, 50 µM, Ni: 100, 350 µM and Fe: 200, 500 µM. The DGT devices (duplicates) were placed in 500ml of each sample for 4 and 8 hours, with constant mixing and temperature of 36,6 °C. After above mentioned deployment times, DGTs were taken out, the resin gel was taken from the device and eluted with 1ml of 1M HNO_3. The samples were measured by ICP-MS. Obtained concentrations were used to calculate masses of metals accumulated into the DGTs (for details on calculations look Davison and Zhang (1994)).

RESULTS AND DISCUSSION

The batch BMP experiment showed that none of the Co additions had a stimulating effect on methane production, but on the contrary, addition of 100 µM caused the inhibition of the methanogens. Similarly, Ni additions caused even stronger inhibitions, especially 350 and 500 µM, where methane production, after 15 days, was 80 % and 98 % lower than the control, respectively (Figure1a). The situation with Fe addition differed, where all the tested concentrations had a slight stimulating effect on the methane production, the highest having the sample with 1000 µM of Fe (Figure 1b).

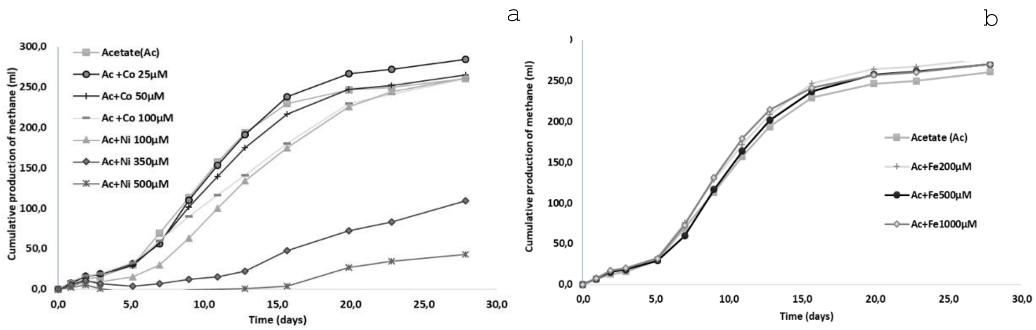

Figure 1. Methane production over time at different Co and Ni (a) and Fe (b) additions

To test linear accumulation of metals in the DGT devices over time, 4 and 8 hours were tested. In the samples where Ni was added, correlation was high ($R^2 \geq 0.91$), but the control sample showed no linearity. Linearity for Co measurement was even greater for all the samples, with $R^2 \geq 0.95$, while for Fe lower linearity was observed: $R^2 \geq 0.87$ for control and addition of 200 µM and no linearity for 500 µM addition. For comparison, masses accumulated after 4 h deployment time were chosen. Overall, addition of metals resulted in higher accumulation of metals compared to the control. Addition of 100 and 350 µM of Ni increased the DGT accumulated mass by 48 and 222 times, respectively. Interestingly, the accumulated masses of Co, where 25, 50 and 100 µM was added, were 166, 370 and 1019 times greater than mass in the control sample. Addition of Fe of 200 µM had only 3 times greater accumulated mass than the control. From the obtained results we can conclude that increases in the additions of Ni and Co led to disproportional mass accumulations. Furthermore, the same level of inhibition was induced by different metal concentrations, i.e. Ni showing higher toxicity than Co.

ACKNOWLEDGMENTS

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Toxicity Analysis of Wastewater from Full-Scale Municipal Wastewater Treatment Plants at Different Treatment Stages Using Microtox® Assay

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INTRODUCTION

There is a worldwide consensus about the need to develop effective wastewater treatment systems. Effective treatment systems include appropriate maintenance and efficiency in operation to guarantee that effluents receive adequate reduction in toxic residues. The qualitative and quantitative characteristics of pollutants present in samples is never sufficient for determination of their interaction with living forms. For this reason, only (eco)toxicological studies give an objective assessment of the degree of threat posed by pollutants to the water environment. Toxicity evaluations have been adopted for wastewater management in many WWTPs, where various test methods are used to characterize the wastewater toxicity (Power and Boumphrey, 2004; Zhao et al., 2014; Ma et al., 2016; Liang et al., 2018). One of the most widely used methods of biotesting is the Microtox Acute Toxicity Test, introduced by Beckman Instrument Co., which became the first microscale biomonitoring tool in environmental toxicology due to a number of advantages. This approach is rather simple - it is based on very few elements and there is no need for preculturing of test biota because the measurement of light emission begins immediately after bacteria enter the sample. Bacteria used in Microtox are stored in lyophilized state which makes the test cost-effective due to the elimination of maintenance costs and long term stability of the culture. Microtox tests are generally completed in 15 or 30 min. The short duration of Microtox analysis significantly increases the sampling throughput capability of this test (Zadorozhnaya et al., 2015).

The aim of the research was to assess the toxicity of wastewater from full-scale municipal wastewater treatment plants at different treatment stages using the Microtox® assay.

METHODS AND RESULTS

Wastewater and sludge samples were collected from two Polish WWTPs (named WWTP1 and WWTP2). The samples were transported and stored at 4 °C until chemical analysis and toxicity test were carried out within 48 h. The luminescence inhibition after 15 min exposure was taken as endpoint, measured by Microtox Model 500 Analyzer (AZUR Environmental), according to the recommended ISO Standard 11348:1998. This method utilizes the bioluminescent properties of *Vibrio fischeri*, in which a decrease in the luminescence of the bacterium in an experimental sample (*Vibrio fischeri* in solution with the sample wastewater) is compared to that of a control sample (*Vibrio fischeri* in a 2 % solution of NaCl). Toxic samples were defined as those in which the luminescence of the *Vibrio fischeri* decreased by 20 % or more. If initial screening showed that samples were toxic, then a further test was performed to determine the EC50 value. The EC50 was defined as the sample concentration producing a 50 % decrease in luminescence compared to the control sample. In some instances the initial screening result was not confirmed by the subsequent test; the samples in which a 20 % decrease in luminescence was initially observed were classified as non-toxic in the second test. The obtained results were evaluated according to the toxicity criteria, based on the EC50 value (15 minutes) as described by Persoone (2000). The toxicity of the sludge was evaluated with the Microtox® Solid Phase Test (SPT) according to the Microbics Corporation protocol (1995).

During the study, 19 samples collected at different treatment stages were assayed. The results indicate that the pollutants in the wastewater were gradually degraded, but some of them were collected in leachate and sewage sludge. The mean EC50 values were determined: 10.26 % and 18.05 % for the influent 1 and 2, respectively, which indicated that the samples were toxic. Also, the wastewater after mechanical treatment and sewage sludge collected from both WWTPs were toxic. High toxicity was also noted for the leachate samples from WWTP1 (EC50 = 4.8 %). The remaining samples, *e.g.* after chemical and biological treatments, and effluents from both WWTPs were non- toxic.

CONCLUSIONS

The Microtox® assay is recognized as a cheap and fast bioindicator method for evaluating toxicity in the natural environment and it was applied to assess toxicity in different situations. In this study, the toxicity of wastewater and sludge at different treatment stages from two WWTPs were tested. The change in the toxicity trends of the wastewater after different treatments was similar in both WWTPs. The raw and pretreatment wastewater samples showed greater toxicity than the treated samples. As far as the toxicity reduction estimated using Microtox is concerned, we can conclude that the reduction of effluent toxic load is quite effective, which can be contributed to the proper and efficient management of WWTPs. The treated wastewater do not pose any threat to the receiving surface water. The results presented above indicate that this test is sufficient for evaluating the toxicity from the WWTPs.

ACKNOWLEDGMENTS

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Fouling Behaviour of Ultrafiltration Membranes Modified by Nanoparticles During Ultrafiltration of WWTP Effluent Spiked with Micropollutants

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AIM

The aim of the study was to evaluate fouling tendency of polymer membranes modified with different nanoparticles during ultrafiltration of WWTP effluent.

INTRODUCTION

One of the major problems of membrane technologies is membrane-fouling, which leads to permeability loss of the membranes. Many efforts have been devoted to improving the permeability, rejection, and antifouling properties of the membranes. One approach is to modify polymer ultrafiltration membranes by means of nanoparticles (Adamczak et al., 2018). By adding nanoparticles, better performance, higher permeability, mechanical strength, fouling resistance, and contaminant elimination are achieved. Different types of nanoparticles such as nano-TiO_2, zeolite, silica, and graphene oxide can be used as modifiers of ultrafiltration membranes (Kamińska et al., 2015).

MATERIALS AND METHODS

Materials

Single-walled carbon nanotubes functionalized with carboxyl groups (Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Science), nanohalloysite (Sigma Aldrich, Poland) and nano-TiO2 (Sigma Aldrich, Poland) were used as modifiers of polymer membranes. Polyethersulfone (BASF Company, Poland) was the basic material for membrane preparation.

Membrane preparation

Membranes were prepared by phase-inversion method. Casting solution consisted of 15 wt.% of polyethersulfone and less than 84 wt.% of DMF. Content of modifiers in solution was kept at 0.1wt%. Proper amount of modifiers was added to the dimethylformamide. Casting solution was shaken for 20 h to obtain homogeneous solution. After that, membranes were cast using doctor blade with 0.25 mm thickness on glass plate and immediately immersed in deionized water at ± 20 °C. Precipitated membranes were stored in deionized water at temperature 7 °C for 24 h for their stabilization.

Filtration run and setup

Ultrafiltration process was carried out in cross-flow mode using GE Osmonics cross-flow filtration setup, presented in Fig. 1. Transmembrane pressure was 5 bar. As feed water was used effluent from local municipal WWTP spiked with organic micropollutants. Membrane filtration included three stages: (1) membrane conditioning with deionized water and (2) filtration of WWTP effluent (3) membrane flushing with deionized water.

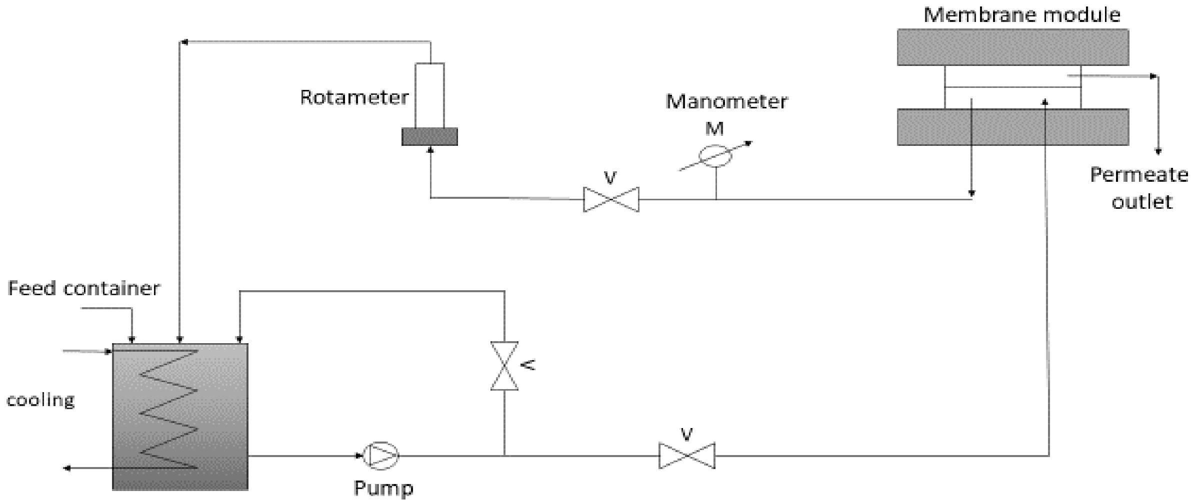

Figure 1. Cross-flow filtration set-up (GE Osmonics)

RESULTS

Figure 2 presents fouling tendency of studied membranes expressed as fouling index. It was found that there is much difference between fouling tendency of virgin PES membrane and modified PES membranes. It is due to different membrane surface properties which play an important role for fouling resistance of membranes. Modified membranes had stronger negative zeta potential and lower contact angle, suggesting higher hydrophilicity comparing to virgin PES membrane.

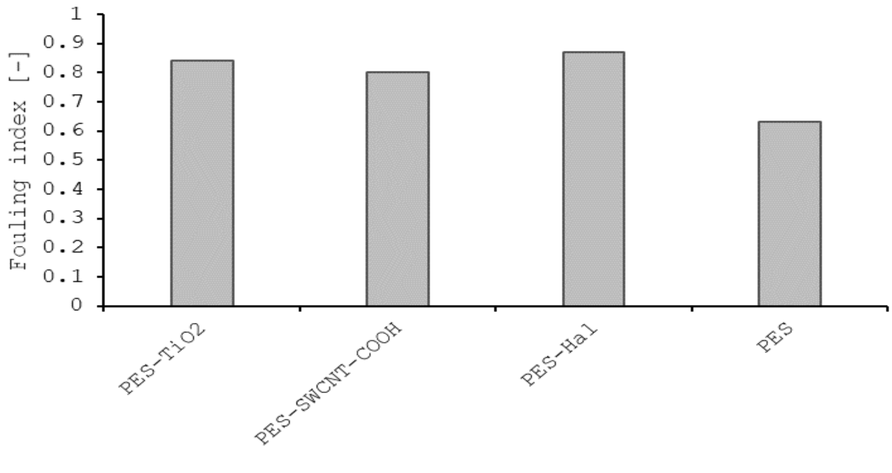

Figure 2. Fouling index for studied membranes

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Comparison of Start-up of High Efficiency Nitritation Reactor Using Synthetic and Real Reject Water

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INTRODUCTION

Alternative processes to standard nitrification and denitrification are either high efficient, approx. 90 % nitritation combined with denitritation or partial, approx. 50 % nitritation combined with Anammox process. These processes reduce mainly consumption of oxygen (O_2) for nitrification and COD for denitrification. Application of both processes is in recent years relatively often studied but the number of full-scale applications is still very limited (Lackner et al., 2014). Important condition for the processes is to keep nitritation (ammonia nitrogen N-(NH_4^++NH_3) is oxidized to nitrite nitrogen N-(HNO_2+NO_2)) while the nitrite oxidation to nitrates N-NO_3^- is limited. It means that ammonium-oxidizing bacteria (AOB) are active in the reactor while nitrite-oxidizing bacteria (NOB) are inhibited. NOB are inhibited especially by a low concentration of O_2, (less than 1 mg/L) and by a higher temperature (30-35 °C) in combination with a low sludge retention time (θ_X) (unis of days). The significant inhibitory effect has also a high concentration of substrate and product, particularly the concentration of non-dissociated forms of NH_3 and HNO_2. Inhibition with these forms can be achieved e.g. in sequencing batch reactor (SBR) with a concentration gradient of both compounds. Under these conditions, the effect of low O_2 concentration, θ_X and higher temperature is not so essential (De Asis et al., 2017; Svehla et al. 2015; Imreová et al., 2015). The aim of these experiments was to verify the start-up of a high – efficient (more than 90 %) nitritation in SBR with synthetic and real reject wastewater from dewatering of anaerobically digested sludge.

EXPERIMENT

The experiments were realized in SBR with volume (V) = 3 L and volumetric loading (B_v) = 0.16 kg N-(NH_4^++NH_3)/m^3.d. As an inoculum activated sludge from municipal WWTP with standard nitrogen removal was used. The duration of experiments was 2 months. Substrate was added 3 times per day (at 8 am, at 4 pm, at 24 pm) and the reactor feeding was interrupted during the weekends. Since the excess sludge was been discharged, the equilibrium concentration of activated sludge (X_c) was spontaneous. The substrate for model A (synthetic reject water) contained 500 mg/L N-(NH_4^++NH_3), 40 mg/L P-PO_4, 250 mg/L COD (in form of acetate). The substrate for model B (real reject water) contained in average 497 mg/L N-(NH_4^++NH_3), 28 mg/L P-PO_4 and 294 mg/L COD. In model A, the molar ratio of HCO_3^-: N-(NH_4^++NH_3) varied from 1.0 to 1.7 and was maintained by addition of $NaHCO_3$ into the wastewater. In model B, the average ratio of HCO_3^-: N-(NH_4^++NH_3) in real reject water was 1.2 and therefore it was varied from 1.2 to 1.7 by $NaHCO_3$ addition. All analyses were realized according to standard methods.

RESULTS AND DISCUSSION

In both experiments undiluted wastewater with approx. 500 mg/L of N-(NH_4^++NH_3) was added from the very first day. The immediate adaptation of the inoculum to high inflow concentrations of

N-(NH_4^++NH_3) was observed in both models A and B (low effluent N-(NH_4^++NH_3) during the first days; Fig. 1). Consequently, effluent concentration of N-(NH_4^++NH_3), both with pH, started to increase. In model A up to 280 mg/L on the 10th day. pH increased up to 9 – 9.2 and concentration of non-dissociated N-NH_3 increased up to 190 mg/L. These conditions reduced activity of both AOB and NOB. Subsequent decrease of pH to 6 – 6.5 (lower HCO_3^-: N-(NH_4^++NH_3) applied on 13th day restored the activity of only AOB and NOB remained inhibited. As a result, concentration of N-(NH_4^++NH_3) gradually decreased to less than 25 mg/L (more than 95 % efficiency of nitritation) and concentration of N-(HNO_2+NO_2) reached more than 400 mg/L (with N-NO_3^- less than 20 mg/L). pH was maintained at 6 – 6.5, i.e. concentration N-HNO_2 was high and NOB remained inactive till the end of the experiment. Start-up of nitritation SBR with synthetic reject water was successful.

Similar process was detected also in model B, just the regeneration of AOB after the pH decrease took longer time and nitritation efficiency was lower (only slow decrease of effluent N-(NH_4^++NH_3) concentration from 110 to 40 mg/L; 78 – 92 %). NOB remained inhibited (more than 400 mg/L N-(HNO_2+NO_2) in effluent). Start-up of nitritation with real reject water was longer but also successful. Possible reason for a longer start-up of B reactor was the foam formation which led to biomass loss. In model A, X_c during the experiment was approx. 0.7 g/L; in model B X_c decreased to 0.3 g/L (in the next experiment dosage of anti-foaming agent into the reactor will be tested).

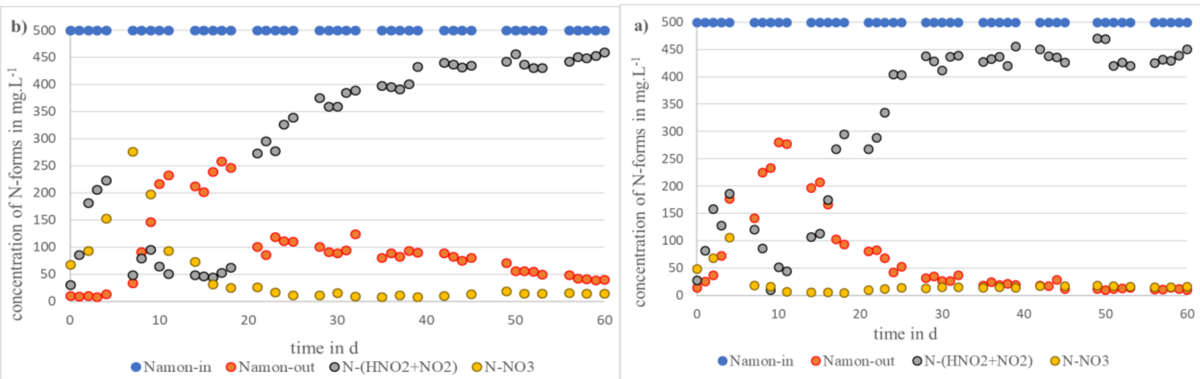

Figure 1. Concentration change of nitrogen forms during tests a) for model A, b) for model B

CONCLUSION

Start-up of nitritation SBR used for the treatment of reject wastewater containing approx. 500 mg/l N-(NH_4^++NH_3) was successful. Adaptation of inoculum from municipal WWTP was relatively rapid and after 25 – 35 days effluent concentration of N-(NH_4^++NH_3) was less than 100 mg/l and N-(HNO_2+NO_2) was more than 400 mg/l. Furthermore, it was also confirmed that undissociated forms of NH_3 HNO_2 were necessary for NOB inhibition. Free NH_3 with pH more than 9 the primary inhibition of NOB and further presence of free HNO_2 at pH lower than 6.5 kept NOB inactive.

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Separation and Concentration of Cationic Surfactant Solutions with the Use of Ceramic Modules

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INTRODUCTION

Cationic surfactants found applications in many areas of the industry due to numerous features resulting from their chemical structure. Cationic surfactants exhibit antistatic (ex. Benzlakonium chloride, Cetrimonium bromide LIT) or lubricating action (ex. Esterquats). Triethanolamine-based esterquats (TEAQ) has been the primary ingredient in European fabric softeners (Friedli et al., 2002). Biodegradation, coagulation, foaming, photocatalytic oxidation and membrane technologies may be effective in surfactant removal, however only membrane-based technics allow to recovery of the valuable wastewater ingredients. Fernández et al. (2005) reported anionic (SDS) and nonionic (Tergitol NP-9) surfactants removal in the range of 60-70 % with the use of ultrafiltration ceramic membrane Membralox®. Polak et al. (2019) examined tubular ceramic membranes (Mantec Technical Ceramics Ltd) for laundry wastewater treatment. The experiments conducted showed COD removal from initial concentration of 1024 mg/L to 200 mg/L after 90 minutes of membrane filtration.

MATERIALS AND METHODS

Commercially available UF and MF CéRAM INSIDE® modules purchased from Tami Industries have been chosen to the tests. The parameters of the membranes are given in Table 1.

Table 1. Characteristic of CéRAM INSIDE® (Tami Industries) modules

Parameter	**Value**		
Pore diameter, µm/ cut-off, kDa	0.45 µm	0.14 µm	150 kDa
Number of channels	7	7	1
Inner channel diameter, mm	2	2	6
Filtration area, m^2	0.0130	0.005	0.005
Distilled water flux, L/(m^2·h)	293.5	260.6	19.2

The experiments were performed in semi-pilot installation equipped with a membrane module, 10 L feed tank, cooling system and circulation pump (Grunfos). The tests were carried out under the temperature of 20 °C. Cationic surfactant Tequat LC90i, TEAQ solutions in concentration of 50, 100, 250, 500 and 1000 mg/L were prepared for the research. Surfactant critical micelle concentration (CMC) amounted to 0.026 ± 0.0067 g/m^3 and the micelle size distribution was 115.9 ± 6.9 nm (DLS method, Malvern Zetasizer Nano ZS, wavelength 532 nm). TEAQ concentration in the samples was monitored by TOC measurements (HACH IL550 TOC-TN).

RESULTS

Table 2 presents the TEAQ retention coefficients obtained during the 120-minutes purification processes with the use of three modules. High separation ratios (above 70 %) were noted for all tested modules, however a slight trend the smaller pore size, the bigger retention coefficient can be observed. The 150 kDa module allowed to obtain an averaged retention coefficient in the range from 82 to 95 %. It should also be noted that changes in the initial TEAQ concentration did not significantly affect the separation efficiency. Due to the very low value of CMC (0.026 mg/L) all of the tested solutions were the micellar ones. Taking into account the micelle size distribution (0.115 μm), relatively high separation ratios were noted for microfiltration modules, especially for 0.45 μm module – despite the pore size was fourfold greater than TEAQ micelle size, surfactant retention coefficients exceeded 70 %.

Table 2. Averaged TEAQ retention coefficients (R) versus concentration in the feed solution

Initial TEAQ concentration, mg/L	R, %		
	150 kDa	0.14 μm	0.45 μm
50	83.6	82.2	79.6
100	91.3	88.0	79.5
250	82.3	82.9	71.9
500	91.2	92.5	75.1
1000	95.2	94.9	85.2

Figure 1 shows relative flux values versus filtration time depending on module type and initial TEAQ concentration. As can be seen, the presence of the cationic surfactant in treated solutions negatively affects the transport properties of the modules. It was observed that depending on the feed solution concentration, the modules achieved various relative permeability – ex. for 0.45 μm module treatment of solutions in the concentration of 100-500 mg/L brought the relative flux in the range from 0.55 to 0.6, when for the highly concentrated solution, i.e. 1000 mg/L, the module was almost completely fouled – relative flux at the end of the filtration cycle amounted to 0.007. Fouling phenomenon was more pronounced for the module with the pore sizes close to the separated particles size (micelle 0.115 μm, monomer 0.058 μm), i.e. for the module 0.14 μm.

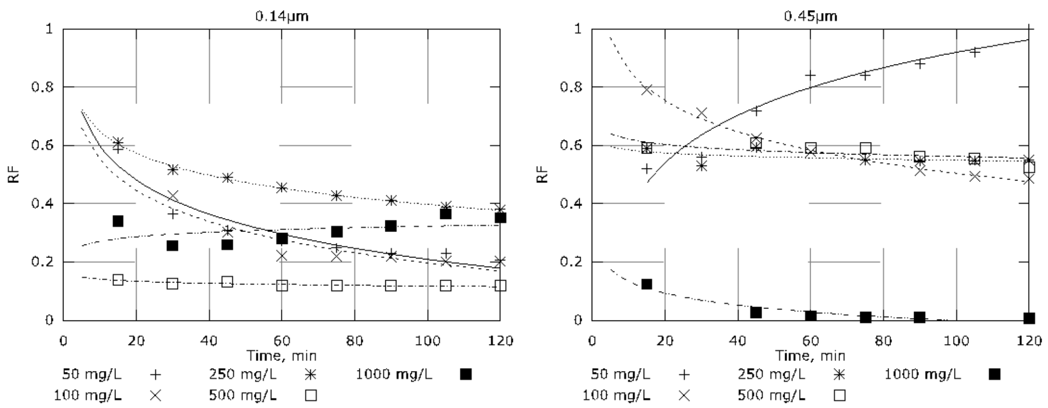

Figure 1. Relative flux (RF) versus filtration time and initial surfactant concentration

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The Dependency and Behaviour of Suspended and Immobilized Biomass in Activated Sludge

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INTRODUCTION

Hybrid bioreactor with combined, suspended and immobilized biomass is an innovative type of waste water treatment technology. Biomass immobilized on some type of carrier has lots of advantages (Masák et al., 2002). Immobilized biological material provides the easy of handling and prevention of its flush out from the system, thus keeping high biomass concentration in the bioreactor (Goswami et al., 2016). Many studies are focused on the various aspects of the immobilization process like the development of more effective carrier types etc (Leix et al., 2016; Zielińska et al., 2012). This research was focused on the relationship between immobilized and suspended biomass, especially the behaviour of the immobilized population and its dependence on the concentration of the suspended population. The particulate attention was paid to the subpopulation of nitrifying bacteria, which is a minority group involved in the naturally developed mixed microbial population as a part of the common nitrogen cycle.

MATERIALS AND METHODS

The relationship between biofilm and the suspension was tested on activated sludge from a waste water treatment plant Amazon (central Bohemia) and colonized carriers from the laboratory hybrid bioreactor. The various concentrations of both suspended biomass and the nitrogen concentration in feeding were tested and compared. For the evaluation of the dependency and behaviour of both biomass type's respirometry measurement of nitrification capacity was used.

The total volume of each sample was 200 ml and contained sludge of various concentrations (0.0 g/l, 0.5 g/l, 1.5 g/l, 3.0 g/l) and six carriers (samples 25-30 contained only sludge without carriers). A total of 10 ml of phosphate buffer (20 ml for the sample with an N concentration of 200 mg/l) and 50, 100 and 300 mg/l of NH_4-N were also added to the samples as the only substrate (electron donor) for the microorganisms. The NO_3^-N concentration in the sludge was about 25 g/l. Fifteen samples were prepared with different combinations of sludge concentrations (rate of suspended and immobilised biomass) and nitrogen concentrations. Each sample was prepared in duplicate to control the results. Therefore, the total number of samples was 30.

The prepared samples were used for respirometry measurement. Nitrification efficiency was tested by evaluation of the O_2 consumption rate (mg/l/h) and cumulative O_2 consumption - BOD (mg/l) using a Micro Oxymax respirometer. Thirty 200-ml flasks were placed into the respirometer and a magnetic stirrer was inserted into each flask for continuous mixing. During the measurement, the development of a graph of the O_2 consumption rate and cumulative O_2 consumption was observed. After about 137 h, the graph showed the end of the substrate nitrification and the measurement was stopped.

After the respirometry measurement, the samples were analysed for NH_4^+-N (mg/l), NO_3^-N (mg/l) and the pH values were determined. Two samples were analysed for NO_2^-N (mg/l) determination in order to evaluate whether the nitrification process was complete.

RESULTS

The experiment showed a significant effect of pH on nitrification rate and nitrification capacity. Particularly at higher nitrogen concentrations, the decrease in the pH value negatively affected the nitrification and when it fell below the critical value, it evidently led to the end of both phases of nitrification.

No effect on the total respiration rate at sludge concentrations (suspended population concentrations) of 0, 0.5 and 1.5 g/l was demonstrated. At a sludge concentration of 3 g/l, the respiration rate almost doubled, especially when comparing the maximum respiration rates. Furthermore, the advantage of the biofilm in increasing the respiration rate at a sludge concentration of 3 g/l was not demonstrated. No difference in the respiration rate with and without carriers was observed in these samples. The suspended biomass exhibited the same rates as the combination of suspended and immobilised biomass.

CONCLUSIONS

Before the start of the experiment, interaction of the immobilised and suspended populations was expected, manifested by an increase in nitrifying activity. However, this was not demonstrated in the case of the hybrid system with a sludge concentration of 3 g/l. The results of the experiment showed that the nitrification rates (measurement of respiration rate) of the suspended and immobilised populations are not cumulative.The results of the experiment showed that the nitrification rates (measurement of respiration rate) of the suspended and immobilised populations are not cumulative. The presence of a biofilm does not lead to the sum of the nitrification rates, which in the suspended population (sludge alone) is the same as in the combined population (suspended and immobilised). On the other hand, the test with non-activated sludge carriers and the tests with the addition of 0.5 and 1.5 g/l of sludge showed the same maximum respiration rates and similar analytical values at the end of the experiment.

The results showed uninfluenced nitrification capacity of immobilized biomass, independent on the concentration of suspended biomass in the system.

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Pilot-scale Experiences with Partial Nitritation Treating Anaerobically Pre-treated Sewage

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INTRODUCTION

Energy consumption of sewage treatment can be reduced by direct anaerobic pre-treatment and subsequent partial nitritation-anammox, but first, undesirable nitrite oxidizing bacteria in partial nitritation must be durably suppressed. In this study, pilot-scale partial nitritation SBR was fed with real sewage pre-treated in AnMBR. The SBR was seeded with fully nitrifying flocculent sludge, its start-up was accelerated by sulphide naturally present in AnMBR effluent and durable suppression of NOB was enabled by controlling the duration of aerobic SBR phase and keeping SRT at 4±2 days. At 24±4 °C (currently 15 °C) and two technical errors aside (biofilm development, electricity blackout), nitrite accumulation of 89±11 % indicated successful NOB suppression for 111 days at relevant nitrogen loading rate of 0.082±0.060 kg-N/m^3/d. This is a highly promising stepping-stone towards present testing at lower temperatures 10-15 °C.

Reducing costs for sewage treatment my main-stream partial nitritation/anammox

Direct anaerobic pre-treatment of sewage has been shown to be possible at pilot-scale, however several obstacles remain to using it in combination with partial nitritation/anammox (PN/A) for nitrogen removal under low wastewater temperatures of <15 °C. Such combination, in comparison to nitrification-denitrification, eliminates 60 % of the energy consumption for aeration, 100% of the organic carbon demand for denitrification and 80 % of the excess sludge produced (Daigger, 2014; Jetten et al., 1997; Wett, 2007). To achieve this combination at pilot-scale, it is crucial to ensure the lasting suppression of undesirable nitrite oxidizing bacteria (NOB) in PN/A in order to limit their competition for nitrite with anammox microorganisms (Cao et al., 2017). In this pilot-scale study, we seek to overcome NOB and integrate sulfide into an AnMBR and partial nitritation SBR for the treatment of municipal sewage. AnMBR effluent was pre-aerated in order to minimize the damaging effect of sulfide to AOB. To establish the process with a more widely used inoculum and to reduce costs, the SBR was started-up with fully nitrifying suspended sludge without FeCl3. Similarly to our previous lab-scale study, (i) NOB were initially washed out by kinetic out-selection using interactive aerobic cycle control, high DO (3 mg L-1) and biomass washout in the effluent. Further, (ii) applicability of sulfide to selectively inhibit NOB was evaluated in batch assays and in situ. Finally, (iii) NOB suppression by initially used aerobic cycle control and high DO 3 mg L-1 was augmented by a single sulfide dose and SRT limitation.

METHODOLOGY

Feed. The nitritation reactor was fed with real anaerobically pre-treated municipal wastewater. The raw municipal wastewater was obtained from a large municipal WWTP (Pilsen, Czechia) after screens and then treated in a psychrophilic AnMBR (hydraulic retention time 1-2 d, effective volume 2 m^3) equipped with parallel microfiltration and ultrafiltration membranes.

The pilot plant consisted of two 200 L tanks fed by peristaltic pump VERDERFLEX. In the first tank, anaerobically pre-treated sewage was accumulated and pre-aerated to eliminate sulfide in feed to nitritation. The first tank, the accumulation, was outfitted with aeration element connected to aerator (Aqua-Oxy 4800) and sludge pump (AL-KO DRAIN 12000) to feed nitritation reactor. Second tank used as nitritation reactor had effective volume 70-180 L and was outfitted with blade stirrer, aeration element connected to aerator (AirMac DBMX80) and probes for continuous measurement of dissolved oxygen (Hamilton VisiFerm DO Arc 120), pH and temperature.

RESULTS AND CONCLUSIONS

In the 1st phase, the combination of interactive aerobic cycle control, high DO 3 mg/L and biomass washout in effluent yielded only very slow accumulation of nitrite in effluent from partial nitritation (Figure 1) while stimulating the development of granular biomass. Simultaneously, in lab-scale batch assays, we determined that NOB can be selectively inhibited already by low concentrations of sulfide intrinsically present in anaerobically pre-treated sewage. In inoculum, fully nitrifying activated sludge, sulfides reduced the NOB (Nitrospira – probe Ntspa_mix) activity to 50 % at 4 mg-S/L, whereas ammonium oxidizing bacteria (AOB, betaproteobacteria AOB - probe Nso mix, halophilic and halotolerant AOB - NEU, genus Nitrosomonas oligotropha - Cluster6a) retained 65 % activity at 15 mg-S/L, with even more favourable results for culture in partial nitritation pilot.

Then, in the 2nd phase, augmenting the previous approach to partial nitritation with a single dose of sulfide (8.4 mg-S/L) in pre-treated sewage immediately accumulated nitrite, indicating successful NOB suppression.

Most importantly, in the 3rd phase, on top of interactive cycle control, high DO and initial sulfide dose, SRT was limited to 4±2 days. Consequently, two technical issues aside (biofilm development on the reactor walls, electricity black-out), <u>successful partial nitritation was maintained at 89±11 % nitrite accumulation and promising loading rate of 0.082±0.060 kg-N/m3/d for 111 days</u>. Although long-term operation at ≤15 °C is still currently tested, this study is a promising stepping stone towards full-scale partial nitritation-anammox treating anaerobically pre-treated sewage, thus opening the possibility towards substantial savings at WWTP.

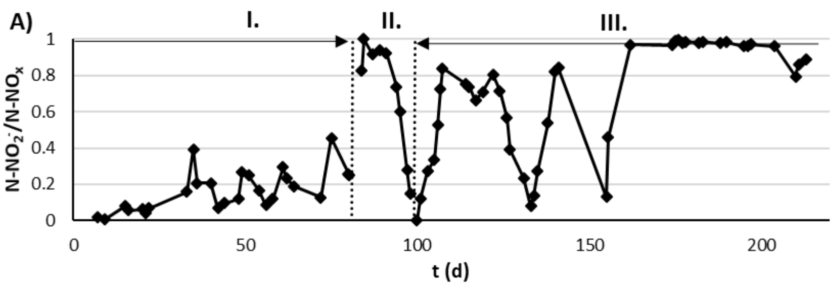

Figure 1. Accumulation of nitrite in the effluent from partial nitritation reactor

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Most Like it Hot: Impact of Temperature on Anammox Process Performance and Membrane Lipid Composition

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INTRODUCTION

The main-stream partial nitritation-anammox (PN/A) process will enable substantial savings at WWTPs. To reach suitable nitrogen loading rates even in mild climates, anammox microorganisms must be adapted to 10-15 °C, which remains a challenge. In this study, 5 psychrophilic and 9 mesophilic anammox cultures representative for the types of PN/A biomasses used in practice have been tested for (i) activities at 10-30 °C in batch assays, (ii) ladderane composition and (iii) microbial species. From the batch assays and an exhaustive literature survey, we show that anammox cultures involve an activation energy 83±18 kJ.mol^{-1} between 15-30 °C. The cold-adapted anammox cultures had the same activation energy as the mesophilic cultures. Therefore, only in certain cases does anammox activity break under 15 °C. Also, the susceptibility to ≤15 °C does not depend on biomass growth more (i.e. biofilm, granular or suspended biomass), whether the process is operated as one- or two-stage partial nitritation-anammox, or on most anammox genera and species. Furthermore, long-term operation in the psychrophilic regime may provide better activities in biofilm compared to suspension. Absolute values of anammox activities varied in an extraordinary manner (Figure 1), with only few promising parameters identified. We also describe in detail the effect of temperature on specific configuration of anammox membrane lipids, including the unique ladderane phospholipids. For the first time, we show that homeoviscous adaptation of anammox membranes to 20-37 °C involves a change in a phospholipid polar head group, specifically a change in the ratio between phosphatidylcholine, phosphatidylethylenamine and phosphatidylglycerol. These findings will enable more efficient introduction of anammox into the main stream of WWTP and elucidate the mystery of how anammox bacteria adapt to cold.

Reducing costs for sewage treatment my main-stream partial nitritation/anammox

Anaerobic ammonium oxidation (anammox) is an established process for nitrogen removal from reject water from sludge digestion and will unlock dramatic savings also in the main stream of municipal wastewater.

Currently, the main challenge in anammox research is its implementation to colder main-stream conditions, one of the main bottlenecks being the low activity of anammox bacteria at low temperatures. Anammox cultures activity as a function of temperature has yet to be reported in sufficient detail. One of the hypothetical mechanisms responsible for anammox adaptation to cold stress is the altered composition of ladderane phospholipids.

In this study, we assess the effect of temperature (10, 15, 20, 25, 30 °C) on the activity of anammox cultures ranging from those representative of full-scale reactors to simple enrichments. The activities and activation energies are correlated with the ladderane content of biomasses, anammox species and genera, and with either a psychrophilic or mesophilic temperature regime. We rebut the dogma that anammox cultures are exceedingly susceptible at less than 15 °C. Instead, we show the singular effect of temperature on all but one psychrophilic cultures and even on a mesophilic side-stream culture. We also show that ladderane phospholipid composition plays an important role in activity and effect of temperature on activity. Collectively, our findings not only identify the most suitable inocula and process conditions for side- and mainstream anammox, but also provide an essential basis for its modelling.

METHODOLOGY

Anammox activities were assessed in batch assays, 2 vessels of 1 L effective volume, controlled temperature and initial pH 7.4. *Anammox genera and species* were detected by Fluorescent *in situ* hybridization. *Membrane phospholipid composition* was determined on U-HPLC-Thermo Dionex UltiMate 3000 and MS(MS/MS)-TripleTOF^{TM} 6600 (Sciex).

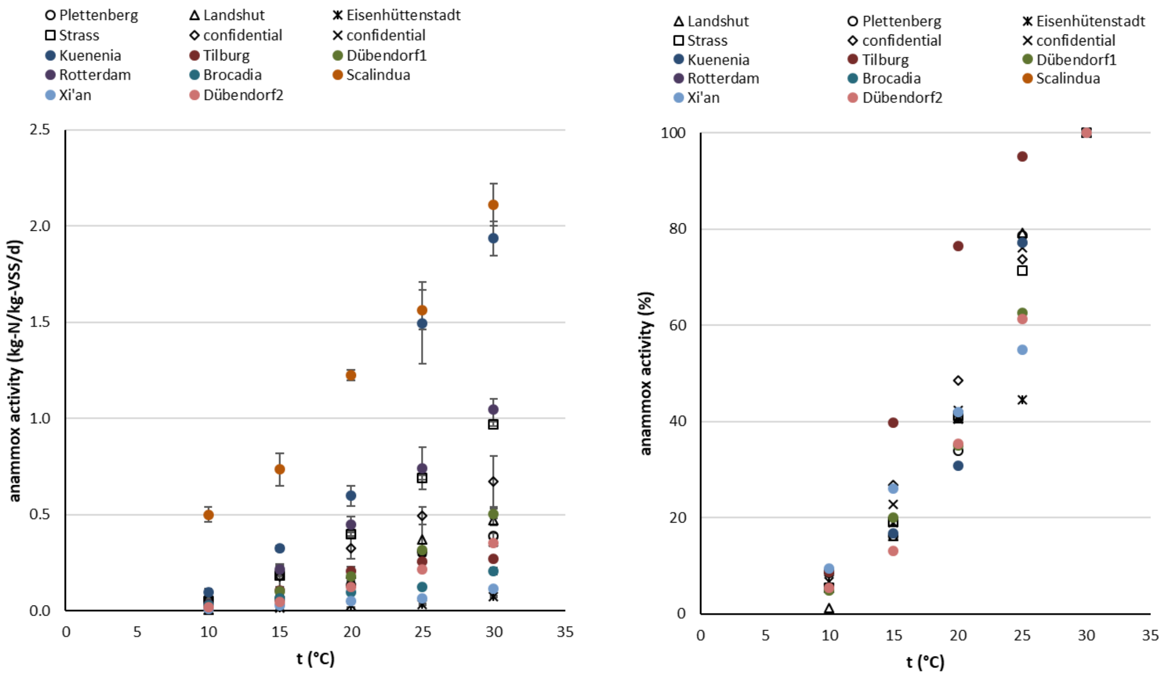

Figure 1. Specific anammox activity (SAA) in cultures from various mesophilic and psychrophilic installations in both absolute values (left) and normalized to 30 °C (right)

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Wastewater from Industrial Park and its Treatability

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INTRODUCTION

On the present industrial parks with manufacturing halls are built in many regions of Slovakia. Mostly they are situated out of municipalities and their own wastewater treatment (often with strict demands on water quality) is necessary. Wastewater from the parks is declared to be a sewage wastewater (separated from industrial wastewater) and so the treatment looks to be simple and easy (mostly biological treatment in activated sludge system with aerobic digestion). However, „sewage is not always a sewage“. In a case that the park involves only manufacturing halls, the main content of the wastewater is urine and wastewater contains very high concentration of ammonium and low ratio COD:ammonium (Henze, 2008). This paper introduces results from monitoring of such WWTP and from laboratory experiments realized with the aim to increase the treatment efficiency.
WWTP in industrial park contains: pumping station + screens + grit chamber + 2 parallel activated sludge reactors (2x50 m^3; SBR reactors feeded 4 times a day, with intermittent aeration 2 h aeration + 1 h mixing) + buffer tank for treated wastewater. Current demands on effluent are extremely strict: COD = 35 mg/l, BOD5 = 7 mg/l, SS = 30 mg/l. Average inflow is 53 m^3/d (39 – 64 m^3/d). Possibilities of biological treatment connected with post treatment (coagulation, filtration, adsorption) were tested in laboratory models feeded with real wastewater from industrial park.

Monitoring of WWTP

WWTP was monitored in 2 stages: stage I. (I - VIII/2018; treatment without continuous dosing of Fe) and stage II. (IX - XII/2018; treatment with continuous dosing of Fe into biological stage):

Table 1. Results from monitoring of WWTP

Influent		Design value	Stage I (average+range)	Stage II (average+range)
COD	mg/l	1000	1161 (296 – 4780)	1207 (894 – 2567)
SS	mg/l	500	456 (65 – 2190)	404 (277 – 600)
TKN	mg/l	120	247 (133 – 420)	289 (201 – 331)
P_{total}	mg/l	-	-	17 (4 – 27)
pH			7.6	6.5 (5.2 – 8.1)
Effluent		**Limit**	**Stage I (average+range)**	**Stage II (average+range)**
COD	mg/l	35	129 (41 – 326)	132 (42 – 180)
SS	mg/l	30	57 (8 – 199)	100 (13 – 340)
pH		6 – 9	6,3 (4.3 – 7.4)	5,8 (4,3 – 7)
NH_4-N	mg/l	-	34 (7 – 62)	60 (40 – 89)
NO_3-N	mg/l	-	67 (44 – 94)	77 (47 – 108)
NO_2-N	mg/l	-	0.2 (0.1 – 30)	0.5 (0.1 – 1)
PO_4-P	mg/l	-	-	0.4 (0.2 – 0.6)

Conclusion of monitoring and proposals of WWTP upgrade

TKN in influent is very high (more than 2x higher compared to the design value). This parameter was in design process underestimated (ratio BOD_5:TKN = 1,5 – 1,7): - organic pollution in influent corresponds with the design values, but concentration range is high; - nitrification with denitrification is running; however, as a result pH dropes to 5,8 – 6,3 (or lower). Dosing of lime was not designed (because the TKN was assuemd to be much lower): - in existing WWTP it is not possible to reach effluent limit for COD (35 mg/l is extremely low); - in stage II. Fe^{3+} (42 – 70 mg/l) was dosed into activated sludge reactor to improve COD removal by coagulation. Effect was negligible. Possible explanation is that Fe precipitated almost all PO_4-P and this nutrient was not available for biomass assimilation. In addition pH was further decreased. Following measures for WWTP upgrade were proposed: - re-evaluation of effluent limits; according to "BAT principle" in current slovak legislation COD = 90 mg/l, SS = 25 mg/l, NH_4-N = 15 mg/l is available; - to fulfill the limits improvement of COD removal and nitrification will be still necessary; - for more efficient COD removal tertiary (after biological treatment) coagulation with Fe + sand filtration, resp. adsorption with activated carbon + filtration were proposed. For more efficient nitrification dosing of lime directly into biological stage was proposed. Effect of the measures was verified in laboratory models with following results:

Table 2. Wastewater with peak concentration (produced mainly on Mondays) - average values

		Influent	Limit	Effluent $_{BS}$	Effluent $_{BSpH}$	Effluent $_{BSpH+TCF}$
COD	mg/l	1860	90	292 (281 – 309)	274 (243 – 306)	113 – 136
SS	mg/l	585	25	115 (76 – 150)	117 (83 – 160)	12 – 19
pH		8,0		4.4 (4.3 – 4.5)	7.5 (7.4 – 7.7)	6.5
TKN	mg/l	245				
NH_4-N	mg/l	172	15	25 (18 – 31)	3,3 (1.4 – 5)	3,0
NO_3-N	mg/l	-		128 (102 – 153)	129 (102 – 140)	125
PO_4-P	mg/l	-		5 (4.6 – 5.2)	4.8 (4.5 – 5.2)	0.1 – 0.3

Table 3. Wastewater with average conc. (produced mainly on Tuesday - Friday) - average values

		Influent	Limit	Effluent $_{BSpH}$	Effluent $_{BSpH+TCF}$	Effluent $_{BSpH+ACF}$
COD	mg/l	1200	90	157 (131 – 183)	113 – 136	41 – 67
SS	mg/l	335	20	62 (50 – 72)	12 – 19	10 – 14
pH		7,8		7.5 (7.4 – 7.7)	6.5	8
TKN	mg/l	155				
NH_4-N	mg/l	106	15	1.2 (1.1 – 1.3)	1.2	
NO_3-N	mg/l	-		83	80	
PO_4-P	mg/l	-		4.8 (4.5 – 5.2)	4.8	

BS - biological stage (continuous experiment in lab SBR); BSpH - biological stage with regulated pH; TCF - tertiary coagulation + filtration (40 % $Fe_2(SO_4)_3$ doses 0.3 – 0.6 ml/l; the best results reached at coagulation pH 6.5), ACF - tertiary adsorption with activated sludge + filtration (AC doses 166 g/l); TCF and ACF realized as batch tests; sludge conc. in SBR = 5.7 – 6.5 g/l

CONCLUSION

- upgrade of technology is necessary to reach effluent COD = 90 mg/l and NH_4-N = 15 mg/l
- tertiary coagulation with Fe^{3+} and sand filtration and dosing alkaline agent are proposed

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Combined VUV Photooxidation and Adsorption onto Granulated Activated Carbon as an Effective Technique for Post-treatment of Biologically Treated Effluent Wastewater

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INTRODUCTION

In the present work, some popular active pharmaceutical ingredients (APIs) that are known to be persistent micropollutants continuously detected worldwide in river and wastewater (WW) were selected as target analytes to assess the possible post-treatment of biologically treated effluent WW as follows: carbamazepine (CARB), diclofenac, metoprolol, naproxen, sitagliptin and tetracycline (TETR). Single component solutions of these APIs were prepared in ultra-pure water (UPW) in 5×10^{-6} M and were subjected to (V)UV photolysis and photooxidation (with O_2) in a batch scale reactor. Generally, good results were obtained except for CARB and TETR by UV irradiation at 254 nm. The VUV irradiation (also at 185 nm in 11 %) was capable of molecule degradation in <2 min. The degradation by-products could be identified by using liquid chromatography hyphenated to high resolution mass spectrometry after offline pre-concentration by solid phase extraction with Oasis HLB cartridges, and degradation pathways could also be proposed. Total organic carbon (TOC) content measurements of spiked UPW solutions revealed high mineralization rates for VUV+O_2 treatment only, decreasing the TOC by about 75 % in 15 min. In WW samples spiked to 5×10^{-6} M, efficient degradation of the selected APIs and their identified degradation products was achieved between 5 and 30 min. For further improvement of the proposed treatment, (V)UV irradiation was complemented with adsorption onto granulated activated carbon. Preliminary results showed almost complete removal of the residual API content and their respective degradation products in 5 min. This treatment is intended to be applied as a novel approach for WW treatment in the case of small/medium-sized settlements. The results on combination of these two procedures will be presented in detail during the presentation.

Persistent organic micropollutants (PMPs), such as active pharmaceutical ingredients (APIs) are detected worldwide in different water matrices, from ng/L to μg/L concentration (Paíga et al., 2017). Carbamazepine, diclofenac, metoprolol, naproxen, sitagliptin and tetracycline are frequently used compounds. Excessive intake of APIs and low removal rates in wastewater treatment plants (WWTPs) lead to their occurrence in detectable quantities in wastewater (WW). The benefit of using VUV irradiation compared to UV is the higher photon energy and capability of water photodissociation leading to a faster degradation via radical and molecule reactions. Adsorption onto granulated activated carbon (GAC) has been preferred for removal of PMPs from aqueous matrices due to its simplicity, cost effectiveness and avoidance of undesirable byproducts, etc.

The aim of this work was to assess removal rates of the selected APIs and their photodegradation products from biologically treated effluent WW after post-treatment through (V)UV irradiation and/or GAC adsorption paying special attention to the identification of their potential (V)UV degradation products. To achieve this, ultra-pure water (UPW) and biologically treated effluent

WW spiked with these compounds were irradiated. Relationship between the pore size of GAC and the chemical characteristics of pharmaceuticals was also investigated.

MATERIALS AND METHODS

The biologically treated effluent WW samples originated from the effluent stream of a WWTP in Hungary with a daily WW capacity of 800-1000 m^3. For adsorption, Organosorb10 AA GAC was used. Adsorption was conducted after (V)UV degradation in batch and flow systems. The spiked solutions prepared in UPW and WW contained APIs in 5×10^{-6} M. For the preconcentration of drugs, Oasis HLB solid phase extraction (SPE) cartridges were used. Identification of the degradation products was achieved on a Bruker Elute ultra-high performance liquid chromatograph coupled to a quadrupole–time of flight mass spectrometer. Mineralization was followed by total organic carbon (TOC) measurements in samples spiked to $2\text{-}5\times10^{-5}$ M levels for each drug.

RESULTS AND CONCLUSIONS

Photolytic and photooxidative degradation of the APIs were compared by a conventional low-pressure mercury lamp with λ_{max} = 254 nm and a VUV one, emitting also at 185 nm (in 11 %) in spiked UPW and biologically treated WW. For UPW, almost complete degradations were observed by VUV irradiation for all compounds within 2 min. About 75 % decrease in the TOC content was determined after 15 min. Effective degradation of the APIs was achieved in spiked WW by photolysis and photooxidation at 185 nm (11 %) within 10 min (Figure 1). Several aromatic degradation products were identified after preconcentration with offline SPE upon irradiation of the UPW matrix spiked with the selected drugs. The degradation products in WW spiked to 5×10^{-6} M were undetectable by VUV+O_2 in 5-30 min. However, the total organic content decreased by only 25 % in the WW sample.

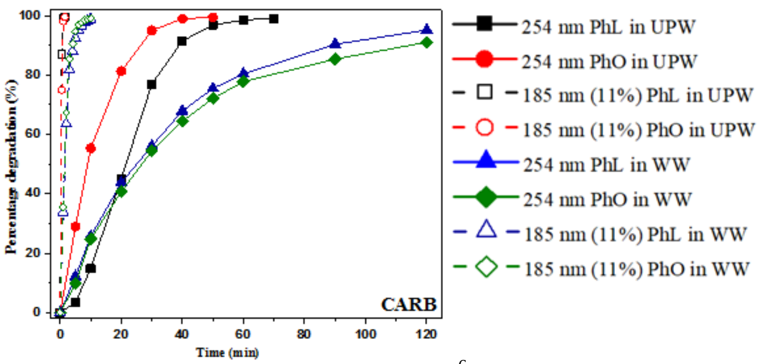

Figure 1. Percentage degradation of 5×10^{-6} M carbamazepine as a function of irradiation time by photolysis (PhL) and photoxodation (PhO) in ultra-pure water (UPW) and wastewater (WW)

The GAC was successfully applied as a second post-treatment step after irradiation to remove the residual degradation products from the spiked WW samples. On basis of the above presented results, combination of VUV+O_2 degradation with adsorption onto GAC is a promising tool for further cleaning of biologically treated WW originating from small settlements. Moreover, due to its disinfection potential, the proposed photooxidative procedure can be recommended even for irrigation water production.

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Determination of Some Popular Drug Residues of Diverse Therapeutic Use in Different Water Matrices in a Single Chromatographic Run by Means of LC-HRMS

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INTRODUCTION

In this study, an ultra-high performance liquid chromatographic high resolution mass spectrometric method preceded by offline sample preconcentration consisting of solid phase extraction was developed for the quantitative determination of 10 popular persistent active pharmaceutical ingredients (APIs) belonging to 5 different therapeutic classes in one chromatographic run as follows: atorvastatin, carbamazepine (CARB), ciprofloxacin (CIPR), clarithromycin (CLAR), diclofenac (DICL), metoprolol (METO), naproxen, sitagliptin (SITA), sulfamethoxazole (SULF) and tetracycline. The primary criterion for the selection of the target analytes was the compliance with regional trends within the EU according to the 2018 edition of the Eurostat yearbook on death rates from chronic diseases recorded in Eastern Europe and the Baltic Member States. Four of our target compounds were also involved into the European Commission's surface water Watch List enacted by Directive 2013/39/EU. Characterization of the performance of the proposed method was also performed and has been applied for drinking water (DW), Danube River water (RW) and biologically treated effluent wastewater (WW) matrices. Concentration of CARB in DW *per se* was about 0.025 μg/L, confirming the low removal rates during river bank filtration applied for drinking water production. Several compounds were detected in the RW usually in ≤50 ng/L. Eight out of 10 compounds were detected in WW, including CARB, DICL, NAPR and SITA in concentrations >1 μg/L. Seasonal changes were also investigated. The concentration of APIs used for chronic affections (CARB, DICL, METO, SITA) was almost constant during the monitored time period, the concentration of ingredients typically used for acute treatment of infections such as influenza (CIPR, CLAR, SULF) registered peak values in the cold season.

There are hundreds of different active pharmaceutical ingredients (APIs) that have been detected worldwide in wastewater (WW) (aus der Beek et al., 2016). As the conventional WW treatment plants are unable to remove APIs from the raw WW, the treated effluents still contain them, resulting in their discharge in quantifiable concentrations into natural water bodies. Information about their long-term, low-concentration effects on ecosystem and humans is scarce.

The primary aim of the present study was to develop a ultra-high performance liquid chromatographic quadrupole time-of-flight mass spectrometric (UHPLC-QTOF-MS) method for the quantitative analysis of several APIs in a single chromatographic run after preconcentration by solid phase extraction (SPE) suitable for different water matrices, such as drinking water (DW), Danube River water (RW) and biologically treated effluent WW. The key objective of the method development was the selection of targeted analytes based on different criteria as they should represent relevant pollutants for the local aquatic environment. Characterization of the performance of the proposed method was also a goal. Finally, study of the seasonal variability in the occurrence of selected compounds was also aimed.

MATERIALS AND METHODS

DW was sampled from a regularly used cold water faucet at our workplace. Danube RW samples were taken from a docking unit in Budapest, while the biologically treated effluent WW samples originated from the effluent stream of WW treatment plant in Hungary with a daily treatment capacity of 800-1000 m^3. For the preconcentration and purification, Waters Oasis HLB cartridges were used. Separation of the target analytes was achieved on a Bruker UHPLC-QTOF-MS.

RESULTS AND CONCLUSIONS

The primary selection criterion was based on sales figures in Central Hungary between 2014 and 2018 taking into consideration death rates from chronic diseases registered in Eastern Europe and the Baltic Member States (Eurostat, 2018). A further viewpoint was the inclusion of priority substances from the European Commission's surface water Watch List. Finally, 10 compounds, namely atorvastatin, carbamazepine (CARB), ciprofloxacin (CIPR), clarithromycin (CLAR), diclofenac (DICL), metoprolol (METO), naproxen (NAPR), sitagliptin (SITA), sulfamethoxazole (SULF) and tetracycline could be successfully determined by the developed off-line SPE-UHPLC-QTOF-MS method. Thus, lower limit of quantitation values resulted to be ≤0.025 µg/L, except for NAPR (i.e., 0.25 µg/L) enabling ultra-trace analysis. Good overall recovery between 80-120 % was observed for all the 10 target compounds in the three studied matrices. Generally, relatively high ion suppression was estimated (Figure 1). To eliminate matrix effect, internal standard calibration method was used with the corresponding isotopically labelled internal standards for each analyte.

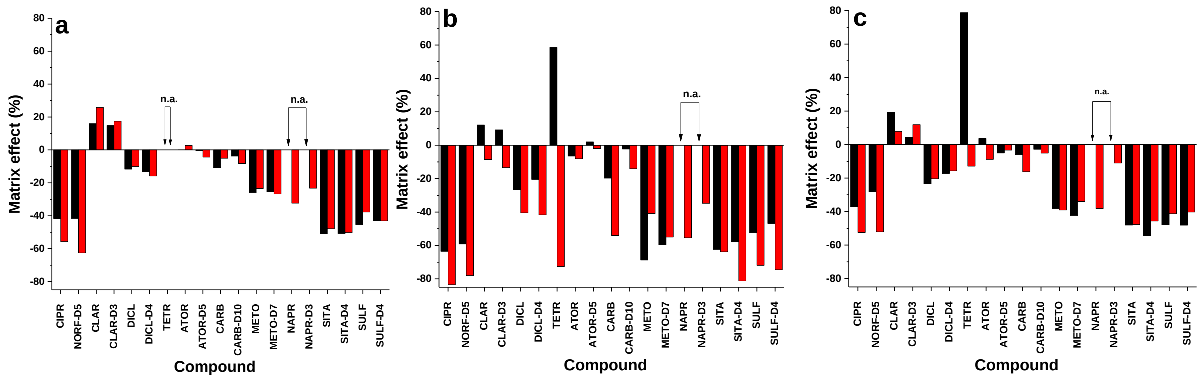

Figure 1. Matrix effect calculated for the target compounds and their isotopically labelled internal standards at two concentration levels in drinking water (a), river water (b) and wastewater (c)

The developed method was successfully applied for DW, RW and biologically treated WW samples. In the analyzed DW samples *per se*, carbamazepine was quantified in about 25 ng/L concentration. Several compounds were detected in the RW in ≤50 ng/L. Eight out of 10 compounds were detected in WW, including CARB, DICL, NAPR and SITA in >1 µg/L. The concentration of APIs used for chronic affections (CARB, DICL, METO, SITA) was almost constant during the monitored time period, while the concentration of ingredients typically used for acute infections such as influenza (CIPR, CLAR, SULF) registered peak values in the cold season.

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Techno-economic Feasibility of Diffused AD Implementation in Small Breweries in Friuli-Venezia Giulia Region and Effect of Biochar and Granular Activated Carbon on Methane Yield

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INTRODUCTION

The mountain area of Friuli-Venezia Giulia region is characterized by the diffused presence of Small to Medium Enterprises (SMEs). Brewing organic residues include end-of-fermentation beer, brewery spent yeast (BSY) and spent grain (BSG), as well as whirlpool residue, coming from hop and trub separation from wort (Mainardis et al., 2019). Biogas production from brewery waste through anaerobic digestion (AD) helps to reduce energy and disposal costs (Panjičko et al., 2017).

Biochemical methane potential (BMP) tests were extensively used to establish methane production potential of several substrates. BMP procedure involves adding small amounts of selected substrate and inoculum into serum bottles, creating anaerobic conditions and measuring gas production over time (Pearse et al., 2018). Biochar is a carbonaceous material formed under combustion of plant materials in low-zero oxygen conditions; BC has been tested to improve AD process (Fagbohungbe et al., 2017). There is a strong interest in using BC and granular activated carbon (GAC) in AD, to both increase process recovery rate and decrease the nutrient loss (Sunyoto et al., 2016).

This study was aimed at evaluating the technical and economic feasibility of AD implementation in small breweries located in the mountain area of Friuli-Venezia Giulia region (IT) to improve organic waste management, reducing energy costs. The possibility of installing simple AD reactors at brewery scale was investigated.

MATERIALS & METHODS

All the samples were withdrawn from local breweries. Physicochemical characterization was performed following Standard Methods (APHA, 2012). BMP tests were executed using AMPTS (Bioprocess) equipment at 35 °C; inoculum to substrate ratio was fixed at 6 for all substrates, except from BSG, where it was chosen as 3. Commercial GAC was purchased from Sigma-Aldrich. BC was produced in a downdraft gasifier (Neweng srl, Azzano Decimo) from red spruce woodchips.

RESULTS AND DISCUSSION

The results from BMP tests highlighted the high methane potential of BSY1 (up to 486.9 NL CH_4/kg VS_{added}), and BSG (306.4-356.2 NL CH_4/kg VS_{added}). Whirlpool residue produced a lower BMP value of 290.3 NL CH_4/kg VS_{added} and was digested with a slower kinetics. GAC and BC addition stimulated a substantial increase in BMP value on BSY. Whirlpool residue gave a higher BMP only when adding biochar (404.4 NL CH_4/kg VS_{added}), while granular carbon addition did not improve final methane yield (300.0 NL CH_4/kg VS_{added}). Conflicting effects appeared on BSG.

Biochar addition to end-beer produced acidification, with a low final CH_4 yield (151 NL CH_4/kg VS_{added}).

As for energy analysis, in brewery 1 produced beer was in the range of 2,940-4,628 hL/year, specific electricity (EE) consumption was 130.6-148.9 MJ/hL and thermal energy (TE) need was 116.4-147.0 MJ/hL. Total energy costs were estimated around 25,000 €/year for the years 2016 and 2017 while they were expected to arise up to 42,866 €/year in 2018. In the actual brewery BSG was the main organic residue (87 %, VS mass basis), BSY accounted for 10.4 %, while whirlpool and end-beer contributed for the residual 2.6 %. AD reactor implementation at brewery level could lead to significant energy cost reduction: biogas, if burned in a CHP unit, could provide up to 73.766 kWh_{el}/year and 105.380 kWh_{ter}/year. Net electricity production corresponded to 57.1 % of the total plant need, while net heat production was 65.3 % of the total thermal request.

CONCLUSIONS

Brewery residues investigation for anaerobic digestion implementation at plant level was carried out. BMP tests highlighted a good biodegradability of the analysed residues, in particular spent yeast and spent grain. The addition of granular activated carbon and biochar significantly increased methane yields, underlining a positive connection between thermal processes and anaerobic digestion. Reduction in transport and management costs of the produced waste could be successfully achieved with synergism between thermal processes and anaerobic digestion, together with a move towards circular economy. An energy analysis revealed that anaerobic digestion implementation at brewery level is sustainable and can provide most of the energy need of the plant.

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Modelling of NOB Wash-out in Nitrification Process at Low Temperature

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INTRODUCTION

Suppression of nitrate oxidizing bacteria (NOB) especially under low temperatures (10–15 °C) is one of major bottlenecks for the partial nitritation/anammox (PN/A) process (Ma et al., 2015). The NOB repression is achieved through the application of dissolved oxygen (DO) limitation, high free ammonia (FA) and free nitrous acid (FNA) inhibition of NOB, and short solids retention time (Wu et al., 2016). The major driving force behind the successful NOB washout is inhibition of those bacteria based on the difference in the growth rate between ammonia oxidizing bacteria (AOB) and NOB. However, inhibition of NOB activity undesirably affects AOB activity and leads to inefficient partial nitrification process and when used as pretreatment for anammox it can limit nitrite supply to anammox bacteria.

In this research, modelling and experimental design on NOB wash-out from the conventional activated sludge in low temperature was investigated.

MATERIALS AND METHODS

A sequencing batch reactors (SBR) was operated with a total liquid volume of 10 L, at 12C. Low DO (0.6 mg/l), and sequential reduction SRT (from 4 to around 1 day) was applied, during 60 days of SBR operation. The reactor had a total cycle time of 480 min, and sequence of mix and fill (10 min), mix only (455 min), mix and decant (10 min), and settle (5 min). Also, sufficient alkalinity for the process was provided and pH, DO, and N_2O were carried out by online data controller. Synthetic wastewater was used, and maximizing the AOB activity and washing-out of the NOB was the control strategy of the reactor.

RESULTS

In the SBR reactor, partial nitrification was accomplished based on NO_2 accumulation from about days 5 to 35. However, the observed concentrations of NO_3-N did not decrease to zero as expected and it was active in different operational condition and low biomass concentration, but it was stabilized at approximately 4-8 mgN dm^{-3} between days 20 and 40. Air diffusion based on high speed mixer and low biomass concentration caused to increase the DO from 0.6 to 1.2 and operational failure (feeding pomp) led to full nitrification.

According to Figure 1 (A), biomass concentration decreased based on reducing the SRT from 4 to around 1 day. Furthermore, two-step nitrification model predicted the trend of experimental data and full nitrification, but it failed to stimate the residual NO_3 as shown in Figure 1(B), but new developed and optimized model showing better estimation of AOB, NOB during long term SBR operation still needed.

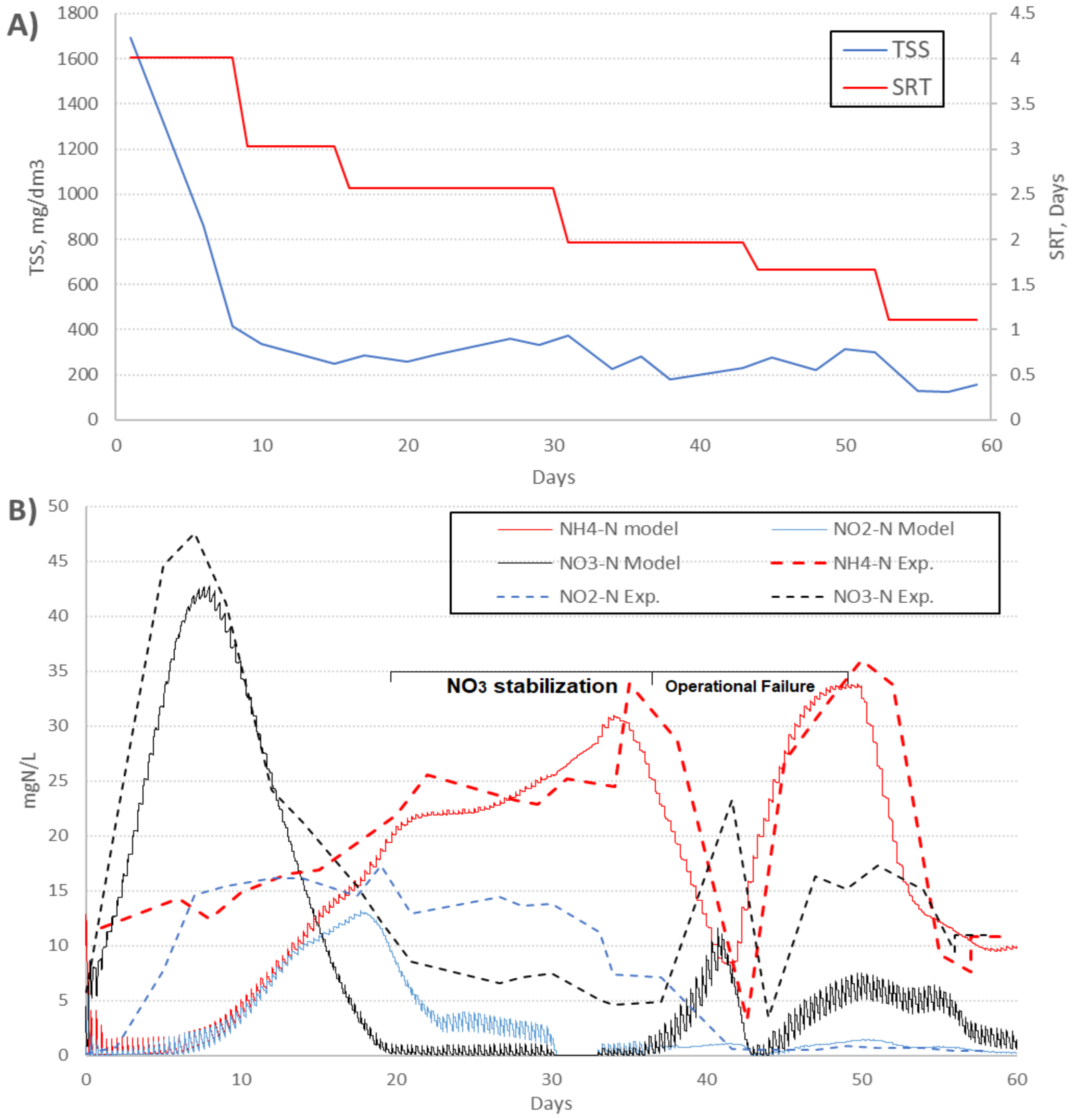

Figure 1. SRT and biomass concentration (A), predicted and experimental results of nitrogen concentration (B)

CONCLUSION

The simple two-step nitrification model (mantis 2) successfully simulated the experimental trend and full nitrification during the process, but failed in estimating the residual nitrate concentrations during complete wash-out of NOB. The calibrated and modified model needed to better simulation of NOB washout from system. However, further studies focused on model developing, and kinetic parameters is fundamental for better understanding of process control and estimation of kinetic parameters.

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NPHarvest – Innovative Nitrogen and Phosphorus Recovery Process

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INTRODUCTION

Phosphorus and nitrogen are crucial elements for supporting the human population through the use of fertilizers. Even though the motives for their recovery and reuse are different, in the interest of energy and resource efficiency they are equally important. Avoiding environmental problems similar to the climate change or politically unstable situations such as the control of global phosphorus reserves are few examples of nutrient-related challenges we are facing for the next few hundred years. Developing the technology to recover nutrients efficiently as valuable products is important for this purpose.

The objective for this study was to develop a new innovative process for recovery of nitrogen and phosphorus. The innovations are using ammonia specific hydrophobic membranes for chemisorption of ammonia originating from liquid waste streams while precipitating phosphorus with a calcium product to enhance the precipitation process and quality of the final product.

Several research groups have studied recovering nitrogen with membranes before (Boehler et al., 2014). The method is successful yet the method has not proven to be economically feasible due to the high level of expensive pre-treatment for removal of solids. The membrane contactor in this study was designed to withstand higher levels of irregularities and solids after testing a commercial membrane contactor, which proved to not function sustainably.

MATERIAL AND METHODS

The study is experimental by nature. The earlier phase of this study was focused on lab scale batch and continuous tests with both a custom built membrane contactor and pre-treatment methods. Pre-treatment is a ballasted sedimentation process, which utilizes poly aluminium chloride (PAX), a cationic polymer and lime kiln dust (LKD) to precipitate solids and phosphorus. LKD is a sandy by-product from Nordkalk’s lime production mainly composed of calcium carbonate. Its role in the process is to increase the weight of flocs in sedimentation and thus the efficiency of solids separation. It also enhances the quality of the final product.

The nitrogen separation process is based on ammonia specific membranes. Most of the nitrogen is in the form of ammonia, which can be stripped using an ammonia specific membrane. An acid reacting with ammonia on the other side of the membrane ensures that ammonia concentration, which is the driving force of diffusion through the membrane, stays constant.

The membrane contactor in this study was designed to be able to function with effluent containing some solids. This is not the case for commercial membrane contactors, which tend to be tightly packed with capabilities to withstand high pressure. As opposed to this, the contactor used was larger in volume and well mixed with a hyperbolic mixer. An efficient mixing ensured that water with high ammonia concentration was always in contact with the membrane surface.

RESULTS AND CONCLUSIONS

Solid separation with LKD aided ballasted sedimentation process removed over 80 % of the total suspended solids (TSS) and over 85 % of total phosphorus (TP) and 99 % of orthophosphate. The nitrogen recovery efficiency depends on the hydraulic retention time (HRT) and the tests showed 8 hours to be economically feasible. The effectiveness of the contactor was 80 %. The process functioned continuously and the effectiveness did not decrease even though the membranes gained some visible fouling.

Simplified mass balances are presented for the process through Figure 1 and Tables 1 and 2. It is clear that the recovery processes presented above are suitable for liquid waste streams containing high concentrations of nitrogen and phosphorus.

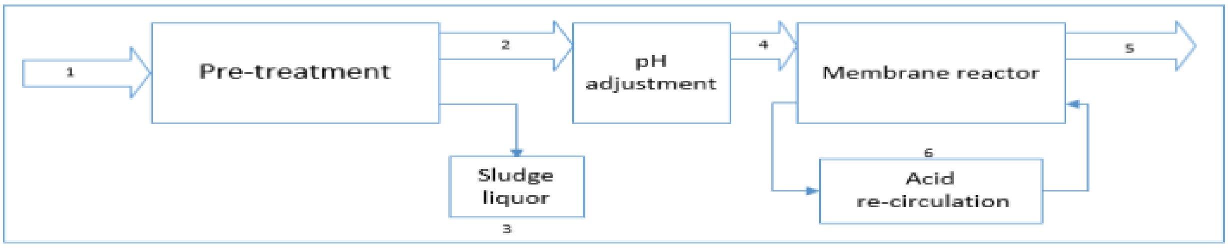

Figure 1. Schematic for the entire process

Table 1. Mass balances for pre-treatment

Number of flow	1	2	3
FLOW (ml/min)	1000	650	350
TSS (mg/min)	1500	120.9	1225
TP (mg/min)	13	1.7	11.1

Table 2. Mass balances for ammonia recovery

Number of flow	4	5	6
FLOW (ml/min)	650	650	
NH3-N (mg/min)	523	74	409.5

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Antibiotic Resistance Genes in Different DNA Fractions Sampled at Wastewater Treatment Plant

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INTRODUCTION

Extracellular DNA (eDNA) may mediate the horizontal gene transfer (Molin and Tolker-Nielsen, 2003). It has been already studied in soils and marine sediments (Torti et al., 2015) showing persistence up to few months, but still was neglected in most of the studies of hot spots of antibiotic resistance – wastewater treatment plants (WWTPs). Zhang et al. (2018) studied cell-associated and cell-free DNA fraction in WWTPs with qPCR, which was crucial as popular disinfection methods assure antibiotic resistant bacteria elimination, but do not eliminate antibiotic resistance genes (ARGs) in cell-free DNA. ARGs are often released from dead cells of antibiotic resistant bacteria during disinfection and PCR based techniques are unable to distinguish between DNA originating from active bacteria and the eDNA. Therefore, ARGs quantification in wastewater treatment samples containing considerable amounts of eDNA, may be biased in activity studies with qPCR (Dominiak et al., 2011).

METHODS

Samples of the influent, activated sludge and effluent were taken from a large WWTP in the Czech Republic. Differentiation of samples with diverse fraction of DNA was made by filtration as described by Zhang et al. (2018). Cell-associated (staying on 0.22 μm filter) and cell-free DNA fractions were distinguished. DNA extraction was achieved using the FastDNA™ Spin Kit for Soils (MP Biomedicals, Santa Ana, USA) according to manufacturer instructions. The amplification of eDNA was performed using multiplex reaction targeting resistance to sulfonamides and beta-lactamases according to Blahna et al. (2006) and Monstein et al. (2007), respectively.

RESULTS & DISCUSSION

The study screened the tested WWTP for two resistance mechanisms: antibiotic inactivation for beta-lactamase and antibiotic target replacement for sulfonamides. While the latter was present in most of the samples, only one sample was positive for class A beta-lactamases in example TEM genes (most common beta-lactamase in gram-negative bacteria). While genes *sul1* (linked to class 1 integrons) and *sul2* (often linked to small plasmids) giving resistance to sulfonamides, specifically coding enzymes dihydropteroate synthases, were encountered in total DNA and cell-free DNA (cfDNA) in all samples studied.

Even though eDNA is not completely separated from intracellular DNA, due to its absorption on free cells or on the flocs of activated sludge, the difference in resistance genes occurrence in cfDNA and cell-associated DNA (caDNA) were observed in the study. In a few cases (both influents and both effluents, *sul2* in both activated sludge samples) ARGs were found in cfDNA and total DNA, but not in caDNA. It is possible that ARGs in effluents have origins in bacteria that were destroyed in the treatment process and now are only part of cfDNA. This case need to be further investigated. Some inhibitors stopped during filtration to cell-fraction fraction may have also impair amplification of total DNA and caDNA.

Table 1. Positive results of screening different fractions of DNA (total, cell-associated, cell-free) in influent, effluent and activated sludge from Czech WWTP

	total DNA							cell-associated DNA							cell-free DNA						
	sulfonamides				beta-lactamases			sulfonamides				beta-lactamases			sulfonamides				beta-lactamases		
type of sample/ ARG	*sul2*	*sul2*	*sul1*	*sul1*	*bla*$_{SHV}$	CTX-M	TEM	*sul2*	*sul2*	*sul1*	*sul1*	bla-SHV	CTX-M	TEM	sul2	sul2	sul1	sul1	bla-SHV	CTX-M	TEM
influent 1/2			+	+											+	+	+				
influent 2/2			+	+			+								+	+					
activated sludge 1/2	+	+	+	+						+					+	+	+				
activated sludge 2/2			+	+						+					+	+	+	+			
effluent 1/2	+	+	+												+	+					
effluent 2/2															+	+					

CONCLUSIONS

Gene *sul2* was found in all tested compartments, while *sul1* was found in influent and activated sludge. In some cases, where ARGs were found in cfDNA, but not in caDNA, resistance in sample may be related only to cell-free DNA. For preliminary screening PCR is proper method, nevertheless it is advised to perform future analyses with quantitative techniques. It is also recommended to study more resistance mechanisms.

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Bubble Generation at Micro-Orifices under Variable Gas Flow Rate with Application to Wastewater Treatment

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INTRODUCTION

Gas bubble dispersion plays a significant role for mass transfer, mixing and product quality in a large number of chemical, biochemical, and other processes (Qu et al., 2017). Of particular importance is the dispersion of air bubbles, known as aeration process, in the activated sludge basins in biological wastewater treatment plants (WWTP). The aeration process takes the largest share of energy bill in the whole WWTP in the range of 45 % to 75 % (Zimmerman et al., 2011). Commonly used aerators are rubber membrane diffusers, which offer relatively low standard oxygen transfer efficiency (SOTE) in the range of 40 % to 60 % (Wang et al., 2010). Several factors affect the SOTE, e.g. the gas holdup, bubble size, bubble residence time, and the apparent viscosity. Mass transfer efficiency highly depends on the bubble size, which determines the surface area to volume ratio, and thus affects the volumetric oxygen transfer coefficient k_La and the oxygen absorption. The optimum diameter of bubbles in the typical aeration tanks is known to be between 0.75 and 1 mm to achieve 95 % oxygen absorption from the air bubbles (Motarjemi and Jameson, 1978). However, the bubble size of conventional fine-bubble aeration systems is between 2 and 5 mm (Hendricks, 2016).

One way to achieve finer gas dispersion is to scale-down the opening, at which the gas bubbles are generated. At very small openings, the bubble formation process is highly influenced by high capillary pressure, gas kinetic energy, and the volume of gas reservoir under the orifice. Previously, we reported on the current state of works on the bubble formation from submillimetre orifices (Mohseni et al., 2019). Moreover, we studied the initial gas dispersion performance of diffuser concepts based on micro-orifices, i.e. orifices smaller than 0.3 mm in diameter, and needles with very fine orifice diameters in the range from 37 μm to 225 μm. We investigated these openings under significantly small gas chamber volume, which leads of a constant gas flow rates during the bubble formation. Compared to commercially available membrane diffusers, micro-orifices generate significantly smaller bubbles (see Figure 1 left) at average of up to 22 % enhanced oxygen absorption rate (see Figure 1 right). Further potential of micro-orifices exists due to the smaller initial bubbles with diameters below 1 mm, which coalesce to a bigger final bubble. The latter is known as the bubble inrush and it is illustrated in Figure 2.

At moderate and high chamber volumes and at millimeter-scale orifices, it is known that the volume of the gas chamber influences the bubble volume. In millimeter rage openings, it is reported that, by increasing the volume of the gas chamber, the bubble volume increases as well (Clift et al., 2005). The latter hold for the case, at which bubbles are generated at similar orifices and under the same rate of gas flow. However, the underlying reasons behind this observation are not well understood. Especially this is the case at submillimeter orifices, where scarce data is available and yet, they offer a great potential towards enhancing the efficiency of the aeration process.

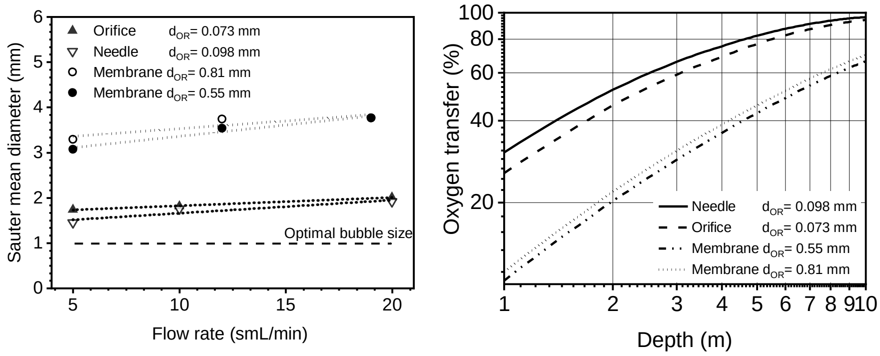

Figure 1. Performance indicator (left) bubble Sauter mean diameter, (right) rate of ratio of oxygen transferred from air bubbles at different depths at 5 smL/min (Mohseni et al., 2019)

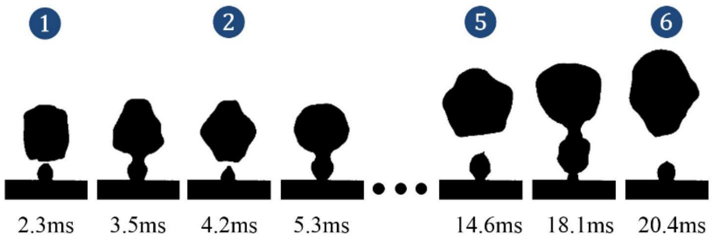

Figure 2. Image sequence of bubble in-rush at orifice dia. 0.1 mm with 6 times coalescence prior to final detachment

METHODOLOGY

In this work, we experimentally investigate the effect of the gas chamber volume on the bubble formation mechanism. The range of orifices vary between 0.1 mm to 1 mm. The gas chamber volume is varied according to its critical value as suggested by Tsuge (Tsuge, 1986). The latter refers to the volume of the gas chamber, at which bubbles start to generate under variable gas flow rate. We studied the formation process by means of high-speed shadowgraphy and corresponding image processing. The final bubble volume, as well as the evolution of bubble volume and the distance of the bubble's center of mass from the orifice plate during formation were measured with a high-speed camera and application of proprietary image processing algorithms.

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Treatment of Industrial Wastewater in a Continuous Two-phase Partitioning Bioreactor Operated with Effluent Recycle

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INTRODUCTION

Occurrence of toxic substrates strongly limits the feasibility of biological processes for industrial wastewater treatment: high levels of inhibitory compounds, extreme pH, high salinity and toxic inorganics cause “hostile” reaction environments, which can reduce and even interrupt microbial activity. The application of bio-treatments to these streams requires well-acclimated cultures combined with powerful technologies. Tubing two-phase partitioning bioreactors (tubing-TPPBs) have been recently proposed for the treatment of chlorophenolic (Tomei et al., 2016), saline wastewater (Tomei et al., 2018) and effluents coming from tannery industry (Mosca Angelucci et al., 2017). Tubing-TPPBs are operated with a polymeric tubing immersed into a conventional suspended biomass bioreactor: wastewater flows inside tubing which provides the simultaneous separation of the wastewater from the cell-containing bulk phase and the selective transport of toxic compounds trough tubing walls towards the bioreactor side, where the biodegradation occurs (Figure 1). Objective of this study is to investigate the application of the effluent recycle in the tubing-TPPB treating a high-strength phenolic wastewater and to evaluate its effect on the process performance. An increasing step organic loading and two different recycle ratios were applied. Target compound was 2,4-dichlorophenol (DCP) a typical halogenated contaminant found in many industrial, agricultural and pharmacological wastewater and it was selected because of its low biodegradability and high persistence in the environment.

MATERIAL AND METHODS

The tubing-TPPB (shown in Figure1) consisted of a glass vessel (3 L working volume, such as to completely submerge the tubing) equipped with a thermostatic probe (temperature at 28±0.5 °C), a magnetic stirrer and a cylindrical grid support connected to the bioreactor head on which the polymeric tubing (Hytrel G3548) was coiled in a spiral. Dissolved oxygen (DO) was controlled in the range of 3-4 mg/L, and continuously monitored so allowing the calculation of the specific oxygen uptake rate (SOUR). The bioreactor was connected to a computer through an interface to monitor and control DO and to manage mixing and pumps. Synthetic wastewater, constituted by a tap water solution of DCP (at increasing concentration in the range of 200–900 mg/L, corresponding to an organic loading rate (OLR) of 48-217 mg/(L day)) was pumped into the tubing at 0.032 L/h flowrate, corresponding to a hydraulic retention time (HRT) in the tubing of 3 h. The effluent recycle flow rates were 0.01 and 0.016 L/h corresponding to recycle ratios, defined as (recycle flow rate)/(influent flow rate), of 0.3 (R1) and 0.5 (R2), respectively. The bioreactor was inoculated with a biomass already acclimated to DCP. During the operation of tubing-TPPB, samples from the bioreactor liquid phase and of the tubing effluent were analysed for DCP concentration;

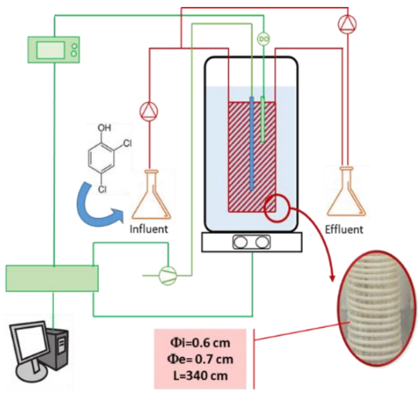

Figure 1. Scheme of a tubing-TPPB

furthermore, chloride evolution in the bioreactor liquid phase was also monitored to follow DCP biodegradation.

RESULTS

The operation of the tubing-TPPB under increasing dynamic DCP loading lasted 4 weeks: practically complete removal of DCP from the wastewater was achieved (despite the high level of influent concentrations) during the entire experimental period (DCP in the tubing effluent was always ≤5 mg/L). Figure 2 gives an overview of the observed results: applied OLR, biodegradation rate (BR) and polymer build-up rate (PBR) of DCP are shown in Figure 2a, while the fractions (with respect to the fed amount) of DCP biodegraded (Bio), discharged out of the system (Out), in the reactor liquid side (Rea) and retained by the polymer tubing (Pol) are reported in Figure 2b. The stepwise increased load reduced the tubing-TPPB performance in correspondence of 700 mg/L: at this point, the first effluent recycle ratio (R1=0.3) has been applied based on the simultaneous decrease of the biodegradation efficiency and correspondent increase of DCP retained by the polymer itself. After the first recycle application, the system clearly showed a performance recovery until 900 mg/L of influent DCP, BR maintained a constant level (437±10 mg/d) but PBR increased up to 170 mg/d, due to the increasing OLR (Figure 2a). To avoid an excess of DCP retained by the polymer, it has been necessary increasing the recycle flow rate to R2=0.5. Satisfactory biodegradation efficiencies (>80 %) and reduced polymer uptake percentages (<15 %) have been achieved at the end of the experimentation (Figure 2b).

Oxygen uptake trends demonstrated the absence of inhibitory conditions for the biomass, in spite of the high-strength and toxicity of influent wastewater. It is worth noting that DCP is a highly toxic substrate at the concentration levels applied in this study, which are prohibitive for conventional bioreactor systems. The effluent recycle application exerted a positive effect on biomass activity: SOUR values increased more than 30 and 80 % with R1 and R2 application in comparison to the operation without effluent recycle.

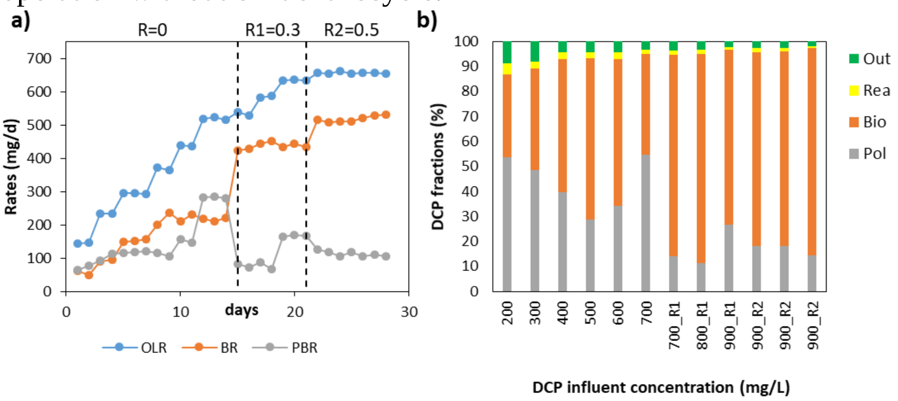

Figure 2. OLR, BR and PBR observed during the operation of tubing-TPPB (a) and distribution of the DCP fractions for all the tested influent levels (b)

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On-Line Titrimeter: Full Scale Biosensor for Control in Wastewater Treatment

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INTRODUCTION

Instrumentation, control and automation (ICA) in wastewater treatment systems intend to improve the efficiency and robustness of the process; moreover the increasing requirements in effluent quality standards and the need for processes more sustainable in terms of energy consumption/efficiency, costs and environmental performance are among the driving forces for the adoption of ICA in wastewater treatment plants (WWTPs). The core of WWTPs is biological treatment such as conventional activate sludge (CAS). ICA can improve the efficiency of the aeration system for CAS tanks, which is one of the higher features of the overall WWTP consumption. In fact, oxygen supply accounts for as much as 60 % in average and can reach up to 80 % of the energy consumed in wastewater treatment (Jonasson, 2007). In the perspective of more stringent law limits of nitrogen content in the final effluent, the nitrification process is a crucial step in CAS tanks due to the imposed conditions and set-points such as dissolved oxygen concentration (DO). Nitrifiers have lower growth kinetics and lower affinity for oxygen compare to the other microorganisms in CAS: this determines the need for higher DO and Sludge Retention Time (SRT) in the mixed liquor, in order to ensure a sufficient ammonia oxidation rate. In the last decades, control strategies for reducing the energy consumption needed for oxygen supply evolved in parallel with the state of the art of sensors and monitoring techniques (Olsson, 2012). In recent years' phosphate, nitrate and ammonia sensors are available on the market and especially ammonia probe showed high potential for energy savings; however, ammonia probes are either slow, expensive, not accurate and, above all, suffering from several chemical interferences. The applicability is restricted to domestic wastewater treatment, while the interferences do not allow its application in most of industrial wastewater. At the same time, monitoring instruments for measurement of biological activity were regarded with a great interest, that are respirometers and titrimeters that use DO and pH probes on activated sludge sampled from WWTP in controlled conditions (Gernaey et al., 2006). These instruments allow the measurement of oxygen uptake rate (OUR) and alkalinity production (or consumption) and acquiring information on kinetics and stoichiometry of the processes. The applicability of set-point titration for monitoring biological processes has been widely demonstrated in the literature. Based on published and on-going experiences, a full-scale on-line differential titrimeter has been specifically developed and installed at the industrial WWTP of Cuoio-Depur S.p.a. (Pisa, Italy) that treats vegetable tannery wastewater characterized by high salinity and COD loads.

MATERIALS AND METHODS

A schematic of the on-line sensor is reported in Figure 1, the titrimeter is composed by two identical jacked reactors of 2 L of effective volume (R1 and R2), each of them equipped with pH probe, LDO probe and temperature probe. Operational conditions in the reactors are maintained as follow: 1) Hydraulic Retention Time (HRT) in the reactor is maintained at 1 h, by continuously dosing the mixed liquor (ML) from the WWTP aerobic tank through peristaltic pumps; 2) not limiting conditions for nitrifiers growth for what concern ammonia and oxygen concentration are guaranteed by the continuous dosing of ammonia and the controlled dosing of H_2O_2; 3) the temperature is kept the same of the aeration tank, by mean of a thermostat; 4) pH is controlled at a given values identical in both reactors (within the range 7 to 8.5) and set according to the pH in the aerobic tank; 5) mixing in both reactors is continuous and ensured by mechanical mixers. The metabolic activity of nitrifiers is inhibited in R1, through allythiourea (ATU) dosing, while in R2 there are not-inhibited conditions for nitrifiers. The difference (differential titrimeter) between the dosing of NaOH and H_2O_2 in R1 and R2 allows to estimate the maximum ammonia and the nitrite oxidation rate based on the stoichiometry of both biological reactions. Moreover, the titrimeter provides real-time information about the process such as influent toxicity and nitrification capacity and it is connected to Cuoiodepur's ICA in order to provide in real-time the optimal DO set-point and to manage efficiently the biological process. Also, a plant-wide model has been developed by using SUMO® software. Three-year historical data regarding the performance of the biological unit has been processed in order to calibrate model stoichiometry and kinetic, with particular focus on influent characterization and nitrifier kinetics. Model results has been critically reviewed together with the ongoing outcomes from the online differential titrimeter.

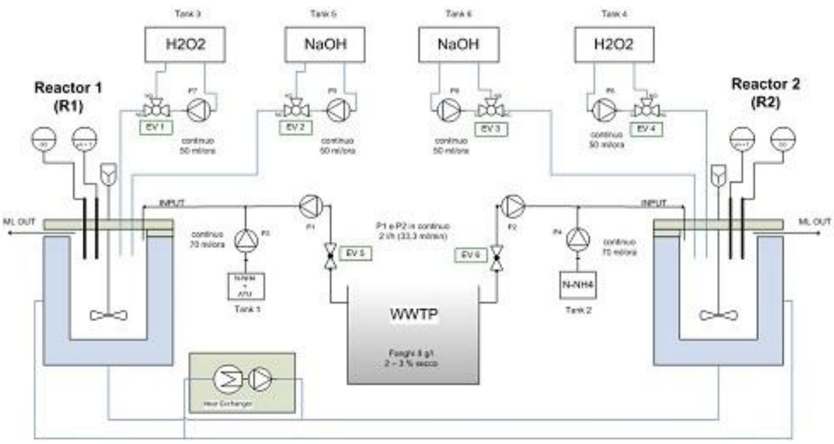

Figure 1. Schematic of differential titrimeter installed at Cuoiodepur WWTP

RESULTS AND DISCUSSION

The titrimeter was running for 6 months, and the actual maximum nitrification rates were validated through nitrogen compounds mass balance; a mean difference lower than 5 % was found. At the same time, the output of the model was consistent with the results provided with the titrimeter confirming the possibility to synergistically use titrimeter output and plant model to predict the nitrification process performance and support ICA as feedforward. Experimental actual maximum ammonia nitrification rate, provided by the titrimeter, varies in time (from 3 to 19 mg NH_4^+ L^{-1} h^{-1}) according to some fundamental operational and environmental conditions in Cuoiodepur WWTP as temperature, inhibiting compounds influent loads (tannins), and salinity. In some circumstances, registered ammonia oxidation rates resulted higher than those strictly needed for the production of a final effluent respecting ammonia low limit for discharge. This fact leads to evaluate the possibility to reduce the DO-set point to be maintained in aerated section of the WWTP and to reduce, as consequence, energy consumption. The new algorithm for the aeration control of the biological section of the Cuoiodepur WWTP, as the new mathematical model, are going to be definitely implemented.

ACKNOWLEDGEMENT

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Wastewater Reuse and Tertiary Treatment: Introduction of Research and Development Projects of the Company ENVI-PUR, Ltd.

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INTRODUCTION

This article introduces some of the recent research and development projects of the company ENVI-PUR, Ltd, which is one of the strongest Czech companies that deal with development, production and delivery of environmental technology and equipment, focused especially on wastewater treatment and water treatment. ENVI-PUR, Ltd works with a very strong research and development department and cooperates with universities and specialists from the environmental area.

The recent projects presented in this article involve water reuse and pharmaceutical and personal care products (PPCP) removal, using advanced technologies such as membrane separation or adsorption on activated carbon.

The AMAYA membrane technology

The AMAYA technology was developed by ENVI-PUR, Ltd. It is a mobile one-step filtration module used for water treatment and for reuse of wastewater. The module contains ceramic membrane with the pore size 0.1 μm. Coagulant is dosed into the raw water in front of the membrane. The process runs in dead-end mode. The membrane is backwashed by permeate every time the trans-membrane pressure increases to a certain value, which can be adjusted manually. In addition, the membrane is cleaned using chemical enhanced backwash (CEB) when needed, oxidation CEB and acidic CEB. The CEB is usually required once every couple of days.

Reuse of industrial wastewater

One of the projects presented is a water reuse of industrial wastewater from a factory producing collagen casings for food (meat, sausages etc.). The aim was to reuse the treated wastewater as service water in the factory. The wastewater was first treated together with municipal wastewater in a conventional activation process. The microfiltration membrane unit AMAYA was used to treat the effluent from the activation process. The parameters monitored in-situ using a mobile laboratory were A_{254}, A_{387} and A_{820}. A_{254} correlates with the organic pollution, A_{387} represents colour and A_{820} represents turbidity of the wastewater. Measuring these parameters allowed immediate reaction to any changes in the wastewater quality. In samples analysed in a regular laboratory more parameters were measured, such as COD, BOD_5, P_{total}, Ca+Mg or microbiological parameters.

The pilot testing showed that the technology was able to remove 50-70 % of the organic pollution, 100 % of suspended solids and nearly 100 % of total phosphorus and microbiological pollution. Furthermore, this experiment showed that the amount of water needed for backwash of the membrane represented only 2,46 % of the total treated water volume.

Reuse of wastewater from backwashing of filtration material

Other water reuse project the company is currently conducting is a pilot testing of a possible recycling of a wastewater from backwashing pool water filters. This pilot testing unit is located at one of the largest water parks in the Czech Republic. There are numerous swimming pools, both indoor and outdoor, with total water surface of 3000 m^2. Some of the pools contain thermal water from a local source. The pool water is filtered on sand filters. The wastewater which occurs during the backwash of the filtration material contains high amount of TOC (total organic carbon) and increased microbiological parameters. The wastewater can be reused for backwashing of the filtration material provided the TOC and microbiological pollutants are removed. To achieve this, the AMAYA membrane technology combined with activated carbon filtration is being tested.

Tertiary wastewater treatment – PPCP removal

Another project currently running is technical and economical optimization of tertiary treatment for PPCP removal from wastewater. The pilot testing plant constructed for this project compares three kinds of granulated activated carbon (GAC) from different suppliers, one of them had been used and reactivated before this experiment. The unit can be operated both in series and parallel. The technology is located at a wastewater treatment plant comprising of the membrane bioreactor (MBR) process. The location was chosen because the membrane process removes suspended solids, which might decrease the sorption capacity of the GAC. The removal of antibiotics, antihypertensives, antiepileptics, antidepressants, analgesics and other specific pollutants or their metabolites is being monitored.

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Purification of Emulsified Oil by Polyvinylidene Fluoride/Polyvinylpyrrolidone Membrane

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INTRODUCTION

Oil species in urban and industrial wastewater are harmful for ecological environment and show negative impact on human health (Cui et al., 2018). It is known that one litre of waste oil contaminates one million litre of pure water. Therefore, oil-water purification has become much attractive research subject for researchers. There are many techniques to separate oils from waters. The diversity of these techniques is varied according to the structure of oils (emulsified or not, and drop size) and the region where oils are (Eryılmaz, 2015). For example, oils spilled by a petroleum accident can be removed by in situ separation techniques such as adsorption and chemical methods. Biological, electrochemical treatment, coagulation, flocculation, vacuum evaporation, absorption, precipitation, and membrane filtration techniques are used for the treatment of emulsified oil wastewater. Among these technologies, membrane-based methods are promising without need a de-emulsification process. The technique has important advantages such as low energy consumption, high separation efficiency.

In this study, porous poly(vinylidene fluoride) (PVDF)/Polyvinylpyrrolidone (PVP) blend membranes were produced by phase inversion method for separation of oil-emulsion water mixtures. PVDF is a hydrophobic polymer which is used in membrane separation processes depending on its superior properties such as good mechanical strength, high heat resistance, good chemical resistance and good film formation. PVP acts as a pore forming polymer in membrane preparation during the phase inversion process. The molecular weight of PVP affects the surface morphology of the PVDF-PVP blend membrane. Therefore, the effect of PVP concentrations in PVDF matrix was studied.

EXPERIMENTAL

Membrane preparation. Blend membranes were prepared using phase inversion technique. A certain amount of PVDF was dissolved in dimethylformamide (DMF) solvent with the concentration of 10 wt.%. PVP was also added to polymer-DMF solution. The PVDF/PVP weight ratios were varied as 9/1, 8/2, 7/3, 6/4. The blend membrane solution was homogeneously mixed at 55 ºC for four hours. The mixture was allowed to remove bubbles at room temperature for 24 hours. The mixture was poured on a glass surface and a casting knife was used to homogenously disperse the mixture. Then, the glass plate was immersed in a water bath. After membranes dried at room temperature, they were cured at 200 ºC in Etuv.

Membrane characterization. The pore structure of the membrane was investigated using Scanning Electron Microscopy. The surface hydrophobicity of the membrane was characterized using Contact Angle Measurements. The chemical structure and crystallinity of the membrane was analysed by using Fourier Transform Infrared Spectroscopy and Differential Scanning Calorimetry.

Oil/Water Uptake. The water and oil affinity of the membrane was determined in terms of the swelling character of the membrane. Membranes were immersed in water and soybean oil, separately. The water/oil uptake was calculated by the weight of adsorbed water/oil.

Filtration test. Filtration test was carried out in a vacuum filtration test unit. The prepared membranes were settled on a porous glass support and the oil/water solution was fed onto prepared membrane. 670 mmHg vacuum was applied at the room temperature. The oil concentration of the permeate and retained solution was determined by UV/Visible spectrometer.

RESULTS

FTIR peaks at 1680 cm^{-1} are assigned to the carbonyl stretching in membranes. The characteristic –CH2– deformation peaks reveal at 1400 cm^{-1}. the peaks from 760 cm^{-1} to 1190 cm^{-1} are corresponding to CF and CF_2 stretching. The intensity of CF based peaks decreased due to the PVP addition.

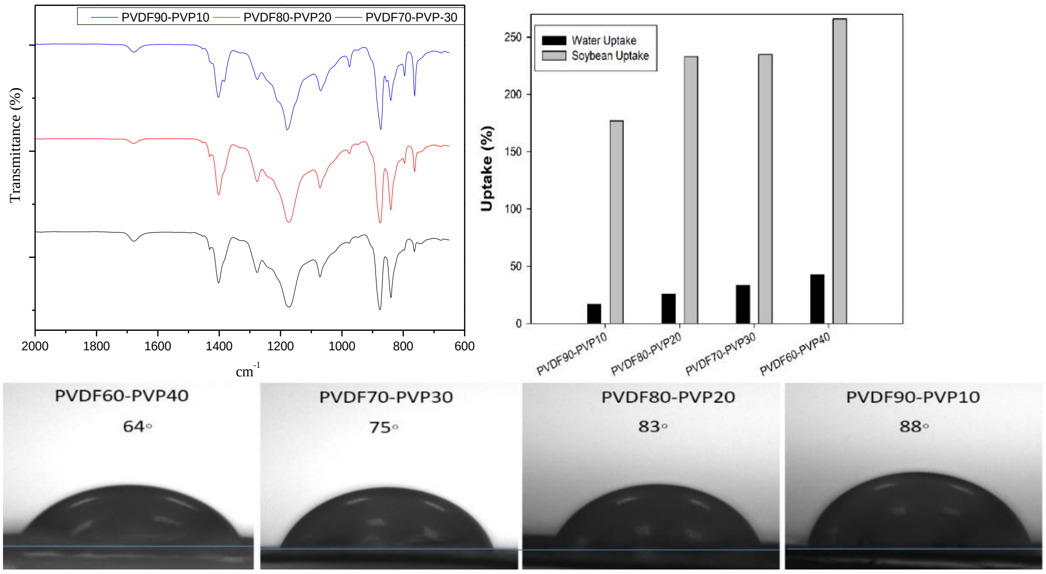

Figure 1. Characterization of membranes

The surface hydrophobicity of the membranes was determined using contact angle measurements. The contact angle of the surface decreased as the PVDF ratio in membrane increased. This is due to the hydrophobic character of the PVDF. It is also related to the PVP is hydrophilic. Moreover, during the phase inversion process, the porosity of the membrane increased by increasing PVD ratio. Thus, the water penetration on the surface of the membrane increased as expected.

Oil/water uptake capacity of the membranes having different ratios of PVP was determined by immersing water and soybean, separately. The increasing amount of PVP increased water uptake and decrease soybean uptake on the membrane's surface owing to the hydrophilicity of the membrane. The oil uptake results of the membranes confirmed the results of water uptake. The increase in PVDF ratio on membranes increased the water uptake from 177 % to % 266.

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Treatment of Textile Wastewater with Heterogeneous Fenton Oxidation

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INTRODUCTION

The textile industry produces large volumes of bleaching effluents that contain appreciable quantities of organic compounds which are not easily amenable to chemical or biological treatment. Furthermore, treatment cost of textile wastewaters has been scaling rapidly in recent years. Hence a search for more cost- effective treatment methods has practical application. In this study, 0.05-2 gr/L Fe-coated sepiolite, 10 mM H_2O_2 doses were performed in the range of pH 2.5-5.0. Heterogeneous Fenton process were pH of 3, catalyst dosage 10 mg/L, H_2O_2 dosage 10 mM. With these optimum conditions, the actual removal efficiency for COD, TOC and color are 72 %, 62 % and 95 % for heterogeneous process respectively.

METHODS

Using peroxide, the production of hydroxyl radicals is enhanced by the presence and action ferrous ion (Fe^{+2}), as a catalyst. In this case, hydrogen peroxide is decomposed to hydroxyl radical and hydroxyl ion, while ferrous ion is transformed into ferric ion. This reaction is known as Fenton's reaction. The optimal pH value for Fenton's reaction is about 3. At this pH, the formation of the free hydroxyl radicals is activated. In this study textile wastewater was collected from a textile factory situated in Tekirdağ, Turkey. The typical composition of raw wastewater is shown in Table 1. The biologically treated effluent taken to the laboratory, filtered from sand and stored at 4 ^oC. For the Fenton experiments optimal values of reagents such as concentration of Fe^{+2} and H_2O_2 pH were investigated to increase the removal of COD, TOC and color of raw wastewater by Fenton process.

Table 3. The typical composition of raw wastewater

pH	Color (Pt-Co)	EC (µs/cm)	TOC (ppmC)	COD (mg/L)
7.8 – 8.2	120 -250	1602 - 1720	30 - 45	90 – 110.5

DISCUSSION

Table 2. The % Removal Efficiency with the pH change

pH	Color (Pt-Co)	EC (µs/cm)	TOC (ppmC)	COD (mg/L)	COD (%)	TOC (%)	Color (%)
2.5	42	3844	10.1	29.81	67.4	59.5	80.9
3.0	31.5	3115	9.3	25.38	72.4	62.7	85.0
3.5	45	2908	10.7	27.14	70.6	56.8	79.9
4.0	33	3059	10.2	27.42	70.3	59.1	78.5
5.0	44.5	2703	10.5	29.48	68.0	57.9	81.0

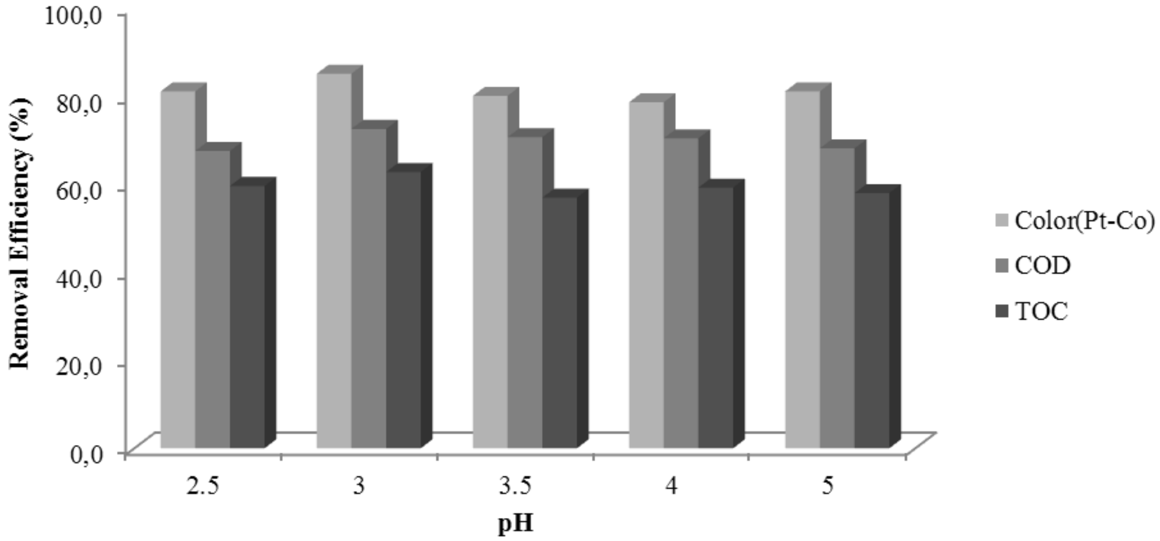

Figure 1. Effects of experimental parameters on COD, TOC and Color removal for pH

CONCLUSIONS

Thus, in heterogeneous Fenton process were studied and it was found that heterogeneous Fenton process is efficiently for COD removal, TOC removal and color removal. Also it is found that the sludge formation is less in heterogeneous Fenton process compared to homogeneous method.

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Performance Comparison of Three High Rate Anaerobic Bioreactors (EGSB, DEGBR & SGBR) for the Treatment of Poultry Slaughterhouse Wastewater (PSW)

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INTRODUCTION

The processing of birds in poultry slaughterhouses requires huge quantities of potable water in order to meet the hygienic requirements imposed by regulatory bodies and deliver safe products to a growing clientele. Rajakumar et al. (2011) reported that it requires 18.9 to 38 L of potable water, for an average of 26L/bird, to process a single bird in a poultry slaughterhouse. The blood, feces, carcass debris, suspended solids and floating materials collected by the used potable water results in the formation of poultry slaughterhouse wastewater (PSW). This waste is essentially organic and has a higher strength than domestic sewage (Baddour et al., 2016; Rajakumar et al., 2011).

MATERIALS AND METHODS

PSW sampling

The PSW used in this experiment was sampled during the processing operations in a 20L polystyrene container from a poultry slaughterhouse facility located in the Western Cape, South Africa. After collection, the sample was conserved in a refrigerator whose temperature was maintained below 4 ^{o}C to prevent PSW acidification.

Granular anaerobic inoculum collection and storage

The inoculum to three bioreactors (EGSB, SGBR and DEGBR) used in this study was collected from an UASB operated from the treatment brewery wastewater in a local brewery, SAB Miller, Newlands, Cape Town. The UASB was continuously operated at a mesophilic temperature range (29 – 36 ^{o}C). The inoculum was stored in a 20L polystyrene container and stored at 32 ^{o}C prior to being used to inoculate the three bioreactors.

RESULTS AND DISCUSSION

Comparison pf the performance of the SGBR, EGSB, and DEGBR

A comparison of the characteristics of the feed to the product of the three bioreactors (SGBR, DEGBR, and EGSB) provides an insight into the performance of these units for the treatment of poultry of PSW. A significant decrease of the average concentration of parameters such as the tCOD, TSS, FOG, BOD_5, turbidity was noticed for the three bioreactors. The significant of turbidity in the product of the three bioreactors translated to an effluent clearer, with a lighter coloration, as highlighted by the decrease of the concentration of TSS. This clarity of the effluent was also accompanied by the reduction of the smell of products as compared to the feeds, but parameter was not quantified. From the three bioreactors, the DEGBR product presented the lowest concentration of TSS, tCOD and BOD_5, with average concentrations of 51.64 ± 44.98, 264 ± 187.99, 45 ± 67.25, respectively. However, the lowest concentrations of FOG and turbidity were observed in the SGBR product, with average values of 51 ±22 and 14.7±24.6, respectively.

CONCLUSION

The performance of three bioreactors (EGSB, SGBR and DEGBR) was evaluated for the treatment of PSW under mesophilic conditions. Despite good results achieved by the SGBR and the EGSB, the DEGBR provided the best results in terms of organic matter removal, methane production and process stability. The process instability of the EGSB was more pronounced at the beginning of the process and culminated in a longer operating period for the assessment of its performance. Overall, the down-flow bioreactors (DEGBR and SGBR) displayed good performance despite changes of the OLR, suggesting that the import of the anaerobic granular sludge from an operational can significantly reduce the start-up of such bioreactors and reduces the operational costs required by up-flow configurations.

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Heterogenous Photocatalysis with Nano-zinc Oxide as a Possible Solution for Removal of *Bisphenol A* from Landfill Leachate

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INTRODUCTION

Bisphenol A (BPA) represents a endocrine disrupting compound which is widely used for production of polycarbonate plastic and epoxy resins. BPA is phenolic compound which is characterized with high persistence in the environment, chronic and acute toxicity and provokes adverse effects on human and wildlife (Reddy et al., 2018). BPA was frequently detected in different water systems in concentrations up to 0.37 mgL^{-1} and 17.2 mgL^{-1} in urban wastewater and landfill leachate, respectively (Zheng et al., 2019). Since it is estimated that BPA has half-life of 160 days in natural water, traditional wastewater treatment by using activated sludge is not efficient for its removal (Zhao et al., 2018). Because of this fact, some improvement in wastewater treatment needs to be applied. Photocatalysis relies on formation of highly reactive oxidative species with non-selective nature which can degrade a wide range of organic micropollutants. The objective of this study aimed to evaluate a possibility for destruction of Bisphenol A in landfill leachates samples with nano-zinc oxide (ZnO).

MATERIALS AND METHODS

Photocatalytic treatment of Bisphenol A with zinc oxide

Bisphenol A (purity ≥99 %) and zinc oxide (purity 99.999 %) were acquired from Sigma Aldrich. Zinc oxide was used without further purification. The photocatalytic activity of zinc oxide was examined for degradation of Bisphenol A under artificial UV light. In order to examine influence of catalyst loading, three different concentrations of zinc oxide were applied, from 0.2 to 0.8 mg mL^{-1}. Initial concentration of target pollutant was 5 mgL^{-1}. The samples were irradiated for one hour and aliquots were withdrawn at certain time intervals. Prior to HPLC analysis, all samples were filtrated through a 0, 45 μm syringe filters.

Analytical procedure

Detection and quantification of Bisphenol A was achieved using HPLC system with diode array detector. Isocratic elution of Bisphenol A was performed using reversed phase column, Eclipse XDB-C18 (150 x 4.6, particle size 5 μm). Mobile phases consist of binary mixture: acetonitrile (A) and 0.1 % acetic acid in ultrapure water (B).

RESULTS AND DISCUSSION

Figure 1. shows the changes in BPA concentration by using different zinc oxide loadings. As it is shown in Figure 1, lower concentration of ZnO provided the highest BPA removal, 94.9 % (remaining concentration of BPA was 0,05 mgL^{-1}) after one hour of UV exposure. With increasing a catalyst amount, removal efficiency decreased. This is explained by the fact that higher

concentration of catalyst causes dissipation of UV light and nanoparticles agglomerate which decreases a number of activate sites at a surface of nanomaterial (Kanakaraju et al., 2014).

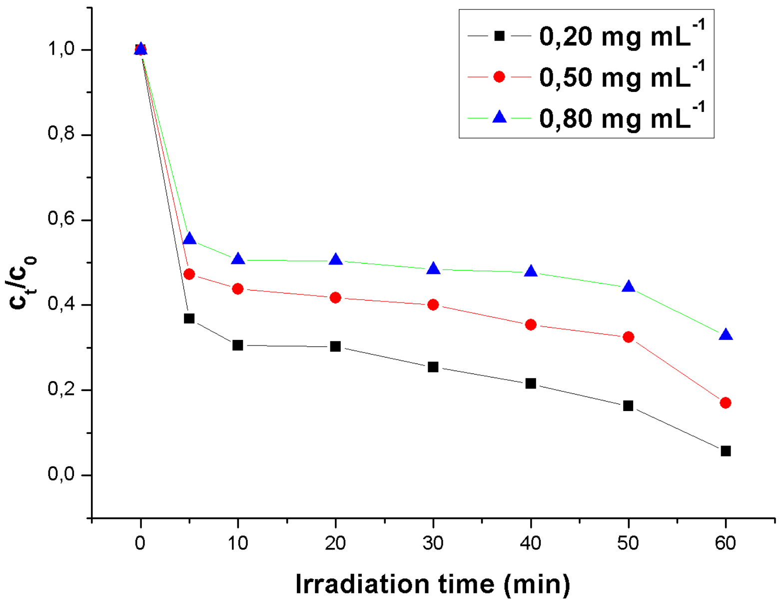

Figure 1. Influence of ZnO loading on photocatalytic degradation of BPA

CONCLUSIONS

According to preliminary results, influence of catalyst loading on BPA degradation has a great impact. Complete degradation of BPA was not achieved after one hour of UV exposure. For further investigation, UV irradiation time will be prolonged in order to achieve higher degradation of BPA in aqueous media.

ACKNOWLEDGMENTS

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Metagenomic Analysis as a Tool to Reveal the Changes in the Structural Biodiversity in Sludge and Wastewater Samples Taken From Full-Scale Municipal Wastewater Treatment Plants

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INTRODUCTION

Despite the advantages of culture dependent techniques, including low cost and the potential to combine with other methods, the availability of culture- based methods for studies of environmental microbes gives a highly restricted view of microbial community structure in environmental ecosystems (Heidrich et al., 2016). Culture-independent molecular methods based on 16S rRNA genes and on shotgun sequencing of total DNA (metagenomic sequencing) have been developed to characterize the phylogenetic and functional diversity of microbial communities. Recently, integrated “omics” analyses have provided an enhanced understanding of the species and their functions in wastewater microbial systems (Ibarbalz et al., 2016; Jiang et al., 2016; Sharma et al., 2012; Shchegolkova 2016; Yang et al., 2014; Schmieder and Edwards, 2012). However, there are still many gaps in our knowledge on the phylogenetic changes of the WWTP microbiome.

The aim of the study was to determine of the differences between microbiomes of the wastewater and sludge samples taken from the various steps of wastewater treatment process of the full-scale municipal wastewater treatment plants in Poland.

METHODS AND RESULTS

Wastewater and sludge samples were taken from the full-scale municipal wastewater treatment plants in Poland. The water samples were filtered through 0.22 μm micropore membrane and kept in −80 °C for further study. Genomic DNA was extracted by the commercial kits following to the manufacturer’s instruction. The Power Water kit (MoBio) and the Power Soil kit (MoBio) were used for wastewater and sludge samples, respectively. The quality of DNA was determined by running 1 % agarose gels and DNA concentration and potential RNA or protein contamination were determined by microspectrophotometry (BioSpectrometer, Eppendorf).

DNA quality determined as the ratio of absorbance at 260 to 230 nm should be in the range from 1.8 to 2.0. These values were obtained for all samples. The quality and quantity of DNA obtained was right for sequencing. Purified PCR products were subjected to DNA library preparation using TruSeq DNA PCR-free Kit (Illumina, San Diego, CA, USA). Libraries were normalized to 4 nM, pooled at equal volumes, and sequenced using Illumina technology at Macrogen (Korea). Taxonomic profiles were assigned against the SEED database using MG-RAST (Meyer et al., 2008) with specific parameters (>10 alignment lengths, >65% sequence identity to a subsystem, and E-value 10^{-5}). Statistical significance variation between analysed samples we conducted using two-sided Welch's t-test at 95 % confidence intervals with default parameters and then the results were visualized in an extended error plot using STAMP analytical software.

The obtained results of DNA sequencing showed that the number of reads for analysed metagenomes were in range between 75,463.282 and 201,866.924. The quality of Q20 was higher than 93,792 %, whereas Q30 quality was higher than 87,821 %. GC content was varied and was in the range from 43.092 to 61.349 %. Taxonomic analysis showed that there are difference in microbial communities structure both between different stages of wastewater processing and between different wastewater treatment plants.

CONCLUSIONS

Metagenomic tool is extremely useful in identifying the microbiome structure of various environments, including sludge and wastewater samples. An in-depth knowledge of microbial structure at biological treatment plants is very important and can be very helpful in improving the subsequent stages of biological treatment. The obtained results can be helpful in better understanding the function of microbiome in biological wastewater treatment technology.

ACKNOWLEDGMENTS

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Sequestering of Heavy Metal in Waste Water Using Polyaniline

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INTRODUCTION

Water is an essential ingredient for living organisms and the quality of water utilized is of great importance to the well-being of all creatures. Pollution of the environment increases with the increase in population growth and industrial activities. Technology advancement has led to the use, release and mobilization of the increase in metal ion concentration in the environment and this has been an issue of major concern in recent times. Toxic/heavy metal-contaminated waste may be generated from anthropogenic activities such as mining, smelting, electroplating and manufacturing operations among others (Ehrlich and Breirley, 1990; Volesky, 2001; Glazer and Nikaido, 1995). Generally in treating water, emphasis are made mostly on the major heavy metals due to its' high concentration.

Polyaniline (PANI) as a nanomaterial is a good conducting polymer and has variety of application. The adsorption properties of PANI include but not limited to acid dye removal (Noby et al 2018), removal of gaseous ammonia. Also, a polyaniline (PANI) prepared by chemical oxidation method was studied for Hg (II) removal from aqueous solution (Chen et al 2009).

(Noby et al., 2018) studied the preparation of PANI nano-structures via four preparation techniques which were sol-gel, rapid mixing, sonochemical and supercritical carbon dioxide (SC-CO2) assisted polymerization. The morphology of the prepared PANIs varied from nanoparticles, nanofibers (with low and high aspect ratio) and nanorods by changing the synthesis method from sol-gel, rapid mixing, sonochemical and SC-CO2 polymerization respectively (Abdelraheem et. al., 2018).

In this work, PANI was prepared by the sol-gel process using aniline, Potassium Persulphate (KPS) and HCL. In the second stage of the experiment, the PANI was characterized by FT-IR, SEM and XRD. Kinetic adsorption experiments with varying parameters will be carried out to confirm the best isotherm to fit in the adsorption work. Moreover, the study will also reveal what attributed to the sequestering process of the PANI in heavy metal removal.

EXPERIMENTAL WORK

Materials Needed. Aniline 99.8 % pure, Potassium Persulphate (KPS), hydrochloric acid (HCl) 35-38 % , and methanol were purchased from Acros Organics and used as received. All chemicals were of pure analytical grade and solutions were prepared with freshly distilled water.

Synthesis of PANI. PANI was prepared as stated by Abdelraheem method (Abdelraheem et al., 2016), with few modifications; 0.1M HCL was prepared and used as the dopant; aniline (20mL) was dissolved in 250 mL HCl (0.1 M) at room temperature. In another beaker, 45.6 g of KPS was dissolved at 250 mL of HCl (0.1 M). The KPS/HCl solution was promptly added to the preceding aniline/HCl mixture and mixed together for half an hour, pH was recorded as 1.2. The solution turned brownish precipitate, thus, polymerization begun. The polymerization process was terminated, the produced precipitate was washed several times using distilled water, methanol, and HCl (0.1M), then filtered with a vacuum pump filter and dried at 60 ^{o}C for 24h in an electrical oven. 15.87 g of PANI was produced. Samples were taken for characterization.

Characterization of PANI. A sample of the synthesized PANI was observed by SEM (JSM-7500F, JEOL, Japan) with 20,000-fold magnification and TEM (JEM-2100F, JEOL, Japan) to determine the morphology of the surface. The functional groups of the PANI were determined via FTIR analysis was was determined by a shimadzu IR Prestige-21(Bruker spectrometer model) spectrometer. X-ray diffraction was detected using shimadzu XRD-6100, Shimadzu, Japan.

Batch Adsorption Process. Heavy metal removal by PANI adsorption test will be carried out at varying conditions of heavy metal (20 – 75 mg/L), agitation speed (100 – 300 rpm), temperature (25 – 50 ºC), mass of PANI (75 – 150 mg/L).

RESULTS AND CONCLUSION

The adsorption of heavy metal will be studied at various conditions described above to obtain a sorption isotherm. The effect of different agitation speed, temperature and mass of adsorbent will also be studied to obtain the adsorption capacity.

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Wastewater Flow Conditions in a Hydroponic Lagoon in Terms of Quality of Treated Sewage

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INTRODUCTION

There are many dangerous substances in municipal sewage, which untreated introduced into the environment may disturb the natural balance of the receivers (Jin et al., 2017). One of the most important parameters related to the quality of sewage is organic matter, the presence of which limits the development of bacterial flora. Organic matter is determined by indicators such as BOD, COD, TOC, and total suspended solids (TSS) (Joshi, 2016). Ensuring appropriate flow rates of sewage through the treatment plant, significantly influences the organic matter content along with the wastewater stream.

RESEARCH AIM

The main objective of the research was to assess the conditions of sewage flow in the hydroponic lagoon in relation to the value of selected quality parameters. The observations were carried out in the hydroponic ditch, which was used as the third stage of treatment in the municipal sewage treatment plant. Municipal sewage after initial mechanical and biological purification is introduced into the hydroponic system constructed in the form of an artificial river with a length of 190.0 m, depth 1.4 m and a flow time of 9 hours. This lagoon simulates self-purifying processes occurring in river ecosystems (Figure 1).

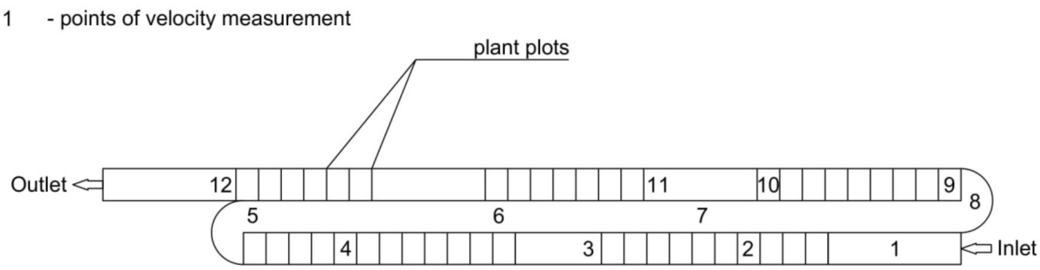

Figure 1. Scheme of the hydroponic lagoon with measurement points

METHODOLOGY

Measurements of the velocity of sewage flowing through the lagoon were made at 12 measuring points (Figure 1) using an electromagnetic flow meter (USGS, 2010) at depths of 0.1 m, 0.3 m, 0.5 m and 1.0 m. The content of organic matter in the wastewater was described by BOD, COD, TOC and TSS. In selected measuring points, the granulometric composition was tested using a laser granulometer.

RESULTS

The average value of organic matter in the sewage flowing in the hydroponic lagoon was respectively: BOD - 4.83 gO_2 m^{-3}, COD - 57.1 gO_2 m^{-3}, TOC 10.2 ppm, TSS 34.4 g m^{-3}. The measured flow velocity had a similar course for all given depths (Figure 2). The average value ranged in 0.07 - 0.073 m s^{-1} with the maximum value measured at a depth of 0.1 m at measurement point 1 (inlet to the lagoon). At the outlet of the lagoon, higher sewage flow rates were observed for deeper levels (0.5 - 1.0 m).

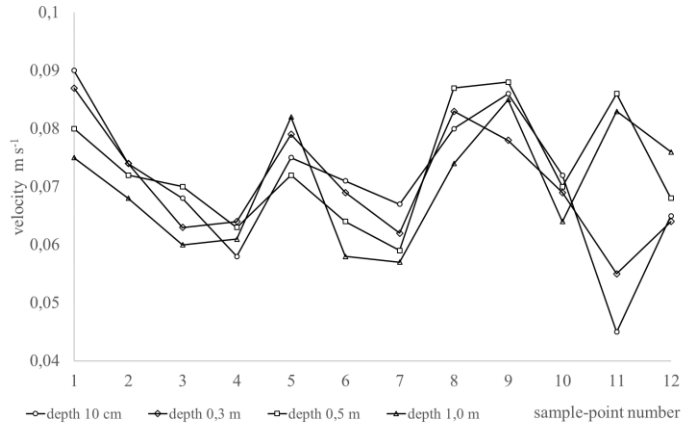

Figure 2. Changes in the flow velocity of the sewage in the hydroponic lagoon at different depths

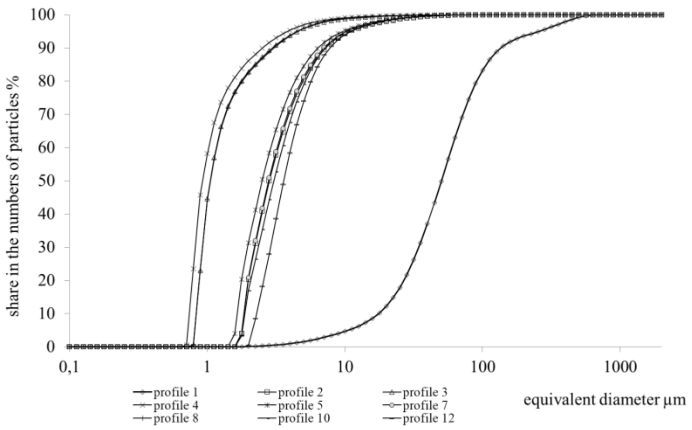

Figure 3. The granulometric composition of the suspended solids in the hydroponic lagoon

At the measurement points the particle diameters varied in the range of 0.8 - 800 μm (Figure 3), the particles with the largest equivalent diameters were measured in the profile 1 (inlet to the lagoon). Over 90 % of particles for this measurement were characterized by diameters above 178.5 μm, while in the rest profiles 90 % of the particles were in the range of 0.8 - 8.7 μm. Along with the flow of sewage through the hydroponic lagoon, the particle size decreased (disaggregation).

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Wastewater Recycling for Use in Water Management in the Cities of Future

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INTRODUCTION

The potential of treated wastewater increases with the climate change, industrialization, increasing drought and irregular torrential rains. Recycled wastewater is a reliable source of water that must be taken into a consideration. It could be used for agricultural and landscape irrigation, for watering of hotels gardens, parks, golf courses etc. Because of that, the regulations of wastewater recycling are needed to be settled. It is essential to protect public health and prevent negative effects on environment. All those reasons encourage the Czech Republic legislation process to treat the wastewater differently. Not only to discharge it into a recipient, but to reuse it where it is needed.

EXPERIMENT

The tested technologies were selected in line with standards used to treat drinking water. The coagulation was the first step of treatment. Optimal dose of coagulation agent was calculated and tested using coagulation experiments. Ferric sulfate was found to be more suitable as coagulating agents. The optimal time for fast and slow mixing and time for sedimentation was also chosen using the coagulation tests. Time for fast mixing was 30 seconds, time for slow mixing was 5 minutes and sedimentation time was 10 minutes. With these mixing and sedimentation times, tests were carried out. Another type of coagulation called "in-line" coagulation was tested as well. The ferric sulfate was diluted much more than during coagulation. There is no slow mixing phase and no time for sedimentation. The sample of water with the coagulating agent was immediately treated further. This type of coagulation will be used in the pilot plant. There will be no tanks for slow mixing phase and sedimentation due to lack of space in the container. After the coagulation, different types of filtration were tested. In the beginning, sand filtration was used after the coagulation. The filtration rate was 25 L/h. The size of sand grains was 1 - 2 mm. The volume of the column was 1.53 L. After approximately 25 L the sand needed to be replaced because of the biofilm growth. The microbiological pollution was removed with efficiency from 50 % to 99 %. The other type of filtration was membrane filtration. Hollow fiber membrane Zeeweed®10 (Zenon) was used, with pore size 0.04 μm, the useful membrane filtration area was 0.93 m^2. The device operated at a transmembrane pressure of max. 600 mbar (optimum 70-550 mbar), the optimal permeate flow was 42 L/h (working range 18-72 L/h). The membrane worked on the principle of ultrafiltration. It was "OUT-IN" type of membrane. After approximately 250 L of wastewater the membrane needed to be regenerated with citric acid solution and with distilled water. During the membrane filtration the microbiological pollution was removed by almost 100 %. The next type was filtration through granulated activated carbon. The filter was filled with activated carbon in size of 1.0 – 1.5 mm. This type of filtration could capture about 80 %. The residual pollution is eliminated after the disinfection. The disinfection was carried out with sodium hypochlorite, chlorine dioxide or UV radiation. The chlorine contact time during the disinfection was 90 minutes in line with the legislation and the dose was used so that the residual concentration was at most 0.3 mg / L. For the laboratory experiments the UVC lighting 1G lamp was chosen, the maximum flow was 2 L/min, the capacity was 22.4 J/m^2. An accumulation was the last treatment step. It took 90 minutes. The results showed that there is no deterioration in the quality of the treated water during this last stage.

RESULTS & DISCUSSIONS

All these technological stages were tested in the different configuration. As an example, one of the technological arrangements is explained as follow: Into the purified wastewater a coagulant was added and mixed. Then the water passed through the sand filter and the filter with the granulated activated carbon. Chlorination provided a disinfection of water. The last step was accumulation. Table 4 shows the results of this arrangement. The *Clostridium perfringens* does not occur in water at all. Intestinal enterococci are removed after the filtration through activated carbon. The treated water meets the requirements for water reuse after the chlorination.

Table 4. Microbiological parameters in the treated wastewater

Sample	Colony count 22 °C (CFU/100 mL)	Colony count 36 °C (CFU/100 mL)	Coliform bacterie (CFU/100 mL)	*E. coli* (CFU/100 mL)	Intestinal enterococci (CFU/100 mL)	*Clostridium perfringens* (CFU/100 mL)
Input	162 000	169 000	19 560	2 620	270	0
Coagulation	15 000	8 000	24 200	211	19	0
Sand filtration	3 234	1 080	1 733	33	3	0
Filtration GAC	1 727	0	51	4	0	0
Chlorination	52	20	0	0	0	0
Accumulation	1	0	0	0	0	0

CONCLUSIONS

The results of all laboratory testing showed that if all designed technological stages are included, treated water meets the legislation requirements for reuse of wastewater. Depending on the quality of treated wastewater or the way how it would be use, the dose of reagents and the contact time during the filtration will be chosen. There is a need for legislation for reuse of purified wastewater in the Czech Republic. The ideal way would be that such legislation is applied uniformly throughout Europe. A proposal for a regulation of the European Parliament and of the Council on minimum requirement of the reuse of water from May 2018 was filed. The aim of this document is to help with the threat of water scarcity and with “water stress”.

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Environmental Risk Assessment of Municipal Solid Waste Landfill in the Vicinity of Novi Sad - A Project Review

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INTRODUCTION

The most relevant problem caused by inadequate and uncontrolled waste disposal is pollution of all environmental compartments – water, air, soil and its effect on biota. Theoretical reflections, experimental research and experience-based datasets from EU have shown that it is necessary to monitor emissions of pollutants from unsanitary landfills and dumpsites using previously defined list of hazardous and toxic substances developed for specific location (Papadopoulou et al., 2007; Matejczyk et al., 2011). The growing number of toxic, hazardous and persistent substances that pose potential threat to safety and security of human health and environment, uncontrolled waste disposal on unsanitary landfills, as well as the need for development and implementation of methodologies for planning, sampling and quantification of toxic inorganic and organic components, are the major concerns surrounding waste sector. The main objective of the research within the project "Environmental risk assessment of municipal solid waste landfill in the vicinity of Novi Sad" is identification of key toxic substances in leachate and landfill gas of the municipal solid waste landfill in Novi Sad. The water that percolates through the landfill body dissolves the waste material, which can infiltrate ground water through horizontal and vertical migration processes.

OVERALL OBJECTIVES AND AIMS OF THE PROJECT

The main objective of the Project is identification of key toxic substances in leachate and landfill gas of the municipal solid waste (MSW) landfill in Novi Sad. This will lead to the expansion of the database on environmental quality in the vicinity of MSW landfill in Novi Sad. The secondary goal of the Project is identification of the type and the volume of impact of inadequate and uncontrolled long-term disposal of waste on the environmental compartments and human health. The realisation of the Project will lead to identification of the type of pressure on the environment and human health, selection of parameters for the obligatory monitoring programme at landfills and dumpsites, and calculation and prediction of negative effects on human health and environmental quality. The implementation of this research in the selected area will provide support for the implementation of the specific requirements defined in national regulation and EU directives, which explains in detail the need for extensive research in this field.

METHODOLOGY OF THE PROJECT

The concentration levels of key toxic pollutants will be used to assess the environmental risk of the MSW landfill in the Novi Sad area and its impact on human health. The laboratory analysis of key parameters from leachate samples and landfill gas will be carried out in the accredited Laboratory for environmental and occupational monitoring of landfills, wastewater and air, at the Faculty of Technical Sciences, University of Novi Sad. The Project will use the modern methodologies, proposed by the European Commission (EC), to calculate the pollution index in order to assess and predict the various negative effects of the selected toxic substances on the human population and the state of the environment of the city of Novi Sad (Petrović et al., 2018).

PREDICTED RESULTS

Based on experimental results, pollution index calculation and assessment of negative effects, project team will propose research and control monitoring of the heterogeneous media at the landfill based on the results from the landfill in Novi Sad. The research and control monitoring of the heterogeneous media at landfill around Novi Sad will contribute to the improvement of waste management system. Particular focus will be on management of toxic fractions of municipal waste that led to generation of hazardous substances with negative impact on human health and all environmental media (soil, water and air). Proper design of the monitoring system for the heterogeneous media is an imperative of a modern and developed society, and a leading factor in planning of environmental policies and legislation. Continuous monitoring of leachate and landfill gas with the application of innovative risk assessment methodologies at municipal solid waste landfills, is necessary for early detection of pollution, development of a contingency response plan and the sustainable management of environmental media.

CONCLUSIONS

Environmental risk assessments in the vicinity of unsanitary municipal solid waste dumpsites in countries of Central and Eastern Europe are not part of the regular waste management system practice. The available information on the quality of the environment around the landfill sites in Republic of Serbia is almost non-existent. The obtained results will represent the basis for implementation of the current EU methodology for calculation of the pollution index and risk assessment of eco-status of the environment and human health, as well as the basis for the development of modified models adapted to the conditions in Autonomous Province of Vojvodina.

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Evaluation of Working Characteristics and Calibration Strategies of the Ion Selective Electrode Measurements for Wastewater Treatment Plant Process Control and Monitoring.

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INTRODUCTION

Wastewater as a chemical medium is a very complex matrix. In ideal scenario, wastewater undergoes purification process at the wastewater treatment plants. For efficient performance of the wastewater treatment utility, reliable monitoring strategies and instrumentation are necessary. Various sensors are being developed for more sophisticated process control and monitoring. One of the key indicators to monitor is nitrogen. This study deals with the evaluation of working characteristics for the ion selective electrode measurements which are more and more often used to monitor or control the activated sludge process. For the practical use of ISE, we need to know the working range and the response characteristics of the sensor, influence of various interferences, and the stability of these characteristics over time.

Working characteristics

The ISE working range and response slope are determined directly from the calibration curve. The working range is characterized by the lower and the upper detection limits of the ISE. Traditionally, these limits were defined by IUPAC (IUPAC, 1976) as the values of the concentrations (activities) of the target analyte where the error of the analysis equals 100 %. This definition implies that the measured concentration (activity) is twice larger or twice lower than the target value (Mikhelson, 2013).

Membrane potential

The membrane potential EM is found to be a fundamental part since it clearly describes the whole performance of the ion – selective membrane electrode. For a membrane which is supposed to be ideally and exclusively selective for the one specific ion type I, the zero-current membrane potential is a direct and specific measure of the respective activities in the contacting solutions on either side:

$$E_M = \frac{RT}{z_i F} \ln \frac{a_i^{'}}{a_i^{''}} . \tag{1}$$

Where: $a_i^{'}$ refers to the activity (concentration) of I the external solution (sample) and $a_i^{''}$ to the internal solution; zi is the charge of the ion I, in units of the proton charge, R is the gas constant, T the absolute temperature [K], and F the Farady constant. In this case, we can expect a Nerstian response of the membrane of the electrode cell since the composition of the internal filling solution is kept constant:

$$E_M = E_i^0 + S \log a_i^{'} . \tag{2}$$

Where: E_i^0 is the standard potential and *S* is the Nernst slope

S = 2.303 RT/zi F = 59.16 mV/zi. (25°C) (3)

Experimental part

A set of experiments was carried out to determine the calibration curves for two differently old and used NH_4^+ selective electrodes. One was previously heavily used in different WWTP monitoring campaigns and the second one was brand new. The comparison of these 2 electrodes reveals the practical aspects and issues with usage of such instrumentation as well as suitability of application for different monitoring purposes.

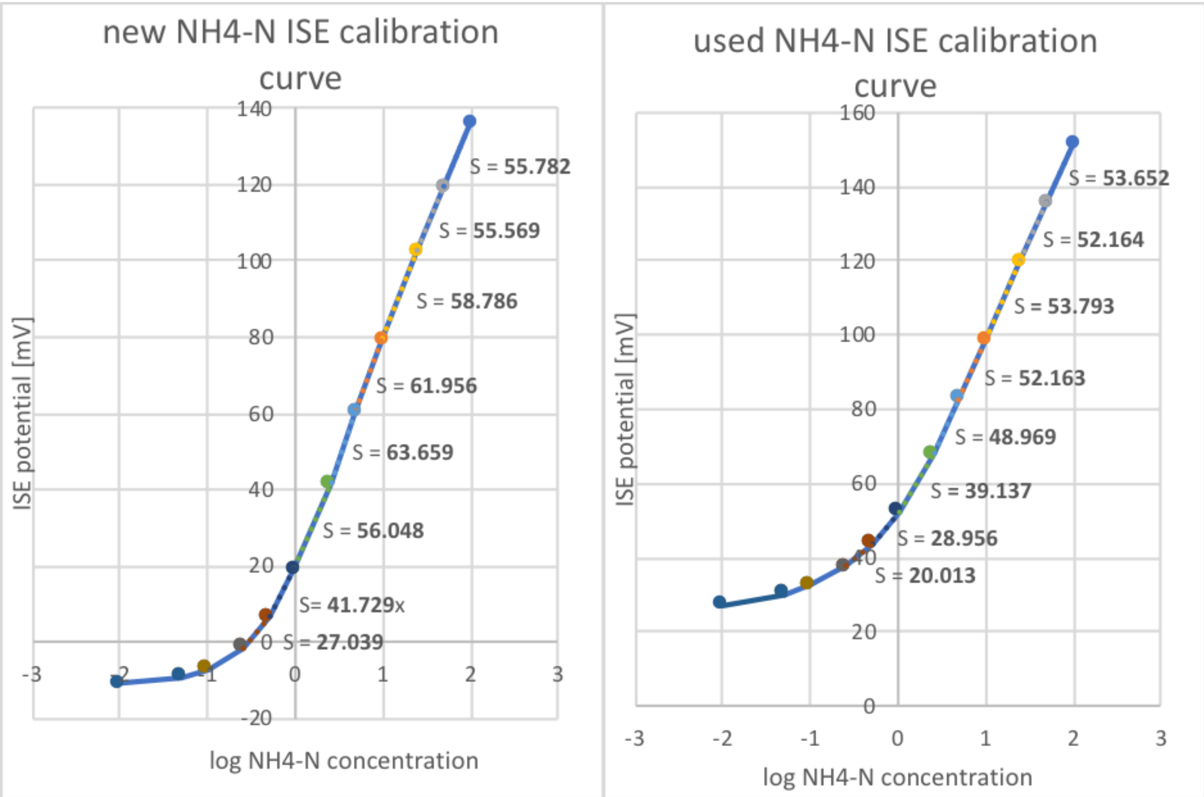

Figure 3. Calibration curves of different NH_4^+ ion sensitive electrodes with the calculated slopes of calibration curve sections. (Nernstian (theoretical) slope S value = 59.16 mV [eq.3])

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Conservation and Revival of Water bodies: A Delhi perspective

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INTRODUCTION

Inadequate water supply and contamination is associated with a large number of illnesses every year and affects one third of the world population. The major causes of water contamination in developing nations arise due to anthropogenic activities such as discharge of wastewater and surface run from agricultural lands. Domestic sewage accounts for a large portion of wastewater from different sources and if left untreated can pose a serious environmental hazard. The United Nations in its Sustainable Development Goals (SDG6) mentions providing clean drinking water and sanitation to all by 2030. This includes conservation, restoration and sustainable use of water ecosystems in addition to ensuring ways to improve water quality (United Nations, 2015).

Conservation of water bodies

Water is a limited natural renewable resource and overconsumption of water has affected countries all over the world. Conserving water bodies is essential to preserve the biodiversity and maintain the ecological balance. Destruction of the habitat by way of pollution or encroachments can disturb the fine balance of the ecosystem. Lakes or static waterbodies are susceptible to a number of stressors due to the low turnover of water, potential for the accumulation of toxins in the sediments and its dependence on the quality and quantity of the influent water (Giller, 2005). A healthy water body also contributes to the economy and ensures the livelihood of people in the surrounding areas. Involving community participation in water body restoration can positively lead to increased awareness and also instil a sense of responsibility towards maintaining the water body. Involving community participation has been the approach of the Delhi Govt. to work towards the revival of water bodies in the city.

EFFORT TOWARDS WATER BODY REVIVAL IN DELHI

There is an increased concern in recent years over the unchecked exploitation and degradation of wetland systems, particularly rivers and lakes. It is part of the Nation`s policy to conserve, revive water bodies and devise action plans towards environmental management. The Govt. of Delhi plans to revive 255 water bodies (159 through the Delhi Jal Board and 95 through the Department of Irrigation and Flood Control) in the city and aims to achieve a Biological Oxygen Demand (BOD) of 10 mg/L and Total Suspended Solids (TSS) of 10 mg/L in the revived water bodies. Three approaches to waterbody revival have been proposed to be used by the Govt. of Delhi depending on the conditions prevailing in the location. The approaches are namely:
1) Bringing treated water from existing Sewage Treatment Plant (STP) after polishing.
2) Constructing small STP at the site and use treated water as a perennial source of supply.
3) Diverting excess floodwater and rainwater into waterbody.

A case study of static water body revival at Rajokri in Delhi, India where decentralized wastewater treatment plant has been designed to feed the water body is analysed in the current study.

Water body revival at Rajokri

The water body is located at Rajokri village on the outskirts of Delhi and until recently was a dying water body affected by illegal encroachments and unchecked sewage dumping. The Govt. of Delhi started a project to convert the surrounding area into a mini-sewage treatment plant. The waterbody was brought back to life at a cost of INR 222 lakhs (~ € 28000) and the project was completed in 1.5 years. The technology adopted to treat the influent wastewater is SWAB (Scientific Wetland with Active Biodigester) and the system treats 0.6 MLD wastewater.

Steps in wastewater treatment

Sewage from surrounding areas is tapped to meet at a common collection point and this wastewater is treated before being fed into the desilted water body. The mesh filters out plastic waste and debris reaching the mini sewage treatment plant and the water then flows into an underground sedimentation tank. The BOD at the inlet is around 150 mg/L with a high Total Dissolved Solids (TDS) content of 2214 mg/L. The second stage after sedimentation is the bio-digestion where organic material is broken down into smaller simpler particles with the help of Mixed Liquor Suspended Solids (MLSS). The partially treated water is then pushed to artificial wetlands using energy from solar panels installed at the site. The artificial wetlands are constructed using gravel and hormonally treated wetland plants such as Cana and Phragmites which are capable of adsorbing trace pollutants such as heavy metals and toxins. The treated water with a BOD of 20 mg/L flows through a slope before finally reaching the waterbody. Additional filters can further reduce the BOD and TDS content (Gandhiok and Singh, 2019).

Figure 1. Rejuvenated water body at Rajokri

Aesthetic appeal and community participation

Landscaping of the surrounding areas to include an amphitheatre and walk way to involve community participation. This will help in maintenance of the water body as well hep in its rejuvenation. It is expected that the ecosystem will also develop with the presence of a clean water body and greenery attracting more birds. Community level Sewage Treatment Plants which treat water locally can go a long way in recharging groundwater as well as reviving water bodies.

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Batch Studies of Phosphonate Adsorption on Granular Ferric Hydroxides

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INTRODUCTION

The implementation of the European Water Framework Directive requires the reduction of nutrient discharges into surface waters (EU, 2000). With regard to phosphorus emission, in addition to ortho-phosphate, other quantitatively relevant phosphorus-containing compounds such as phosphonates should be considered. Phosphonates are used in various industries, such as in the textile industry as bleach stabilizers, in domestic and industrial detergents, but also as antiscalants in drinking water purification (Nowack and Stone, 1999; Boels et al., 2012). The phosphonate-containing wastewater is often discharged directly into a receiving watercourse without further treatment (Müller and Sacher, 2016). Phosphonates are suspected of contributing to the eutrophication of water bodies in the long term, as UV radiation can promote their degradation to readily available ortho-phosphate (Rott et al., 2018). The oversupply of phosphate is an essential feature of water bodies that are no longer in ecological equilibrium and thus phosphonates are important target substances with regard to the sustainable improvement of the ecological status of water bodies.

The use of UV lamps to eliminate phosphonates often fails due to high energy costs and large volume flows to be treated. When Fenton and flocculation processes are used, large quantities of sludge are produced which must then be separated and disposed of. In addition, in order to form sufficient amounts of flocks, a very high flocculant concentration is often necessary, as phosphonates have complex-forming properties (Rott, 2016). In addition to these possibilities, iron-containing adsorbents can also be used to remove the adsorption-affine phosphonates.

Possible adsorbents range from iron-coated sand (Boels, 2010) and commercially available granular ferric hydroxides (GFH) (Boels, 2012) to minerals such as goethite (Nowack and Stone, 1999). In order to be able to use filter materials in wastewater under real conditions in long-term technical applications, these adsorbents should have not only a good adsorption capacity but also a certain abrasion resistance and regenerability. So far, however, hardly any studies have been published on these properties with regard to iron-containing adsorbents.

METHODS

In order to close these knowledge gaps, within this study, a large number of batch experiments with four different GFH adsorbents, which seemed to be suitable for the elimination of phosphonates, were carried out using a vertical tube rotator. Firstly, different physicochemical properties of these materials were determined, including their specific surface area, density, bulk density, and grain size distribution. Following, adsorption experiments with nitrilotris(methylene phosphonic acid) (NTMP) were carried out under different conditions – varying parameters such as contact time, dosage of adsorbent and pH value – in order to evaluate their performance based on their adsorption kinetics and capacity. After this, the best performing GFH was chosen and its surface topography and composition was investigated by SEM and EDX analysis. In a next step, adsorption isotherms were generated for contact times of up to 7 days at different temperatures (5 °C, 20 °C, 35 °C) to find the maximum capacity of the GFH. Following, pH adsorption edge graphs were created for six different phosphonates – namely NTMP, diethylenetriamine penta(methylene phosphonic acid) (DTPMP), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), 2-hydroxy phosphonoacetic acid (HPAA), 1-hydroxyethane-1,1-diphosphonic acid (HEDP) and ethylenediamine tetra(methylene phosphonic acid) (EDTMP). Lastly, five adsorption-desorption cycles were carried out with a synthetic NTMP solution and 1 M NaOH to prove the regenerability of the GFH adsorbent.

RESULTS

The highest achieved capacity of approx. 38 mg/g NTMP with the most efficient of the four GFHs studied was found at 35 °C and 20 °C at 7 d contact time (Figure 1). The most efficient adsorption was achieved at pH 6, since the adsorption affinity decreased at higher pH values and the GFH disintegrated at lower pH values. Furthermore, adsorption correlated with the size of the phosphonate: the more phosphonic acid groups a phosphonate had, the lower the capacity was. The regeneration experiments proved that GFH can be reused several times.

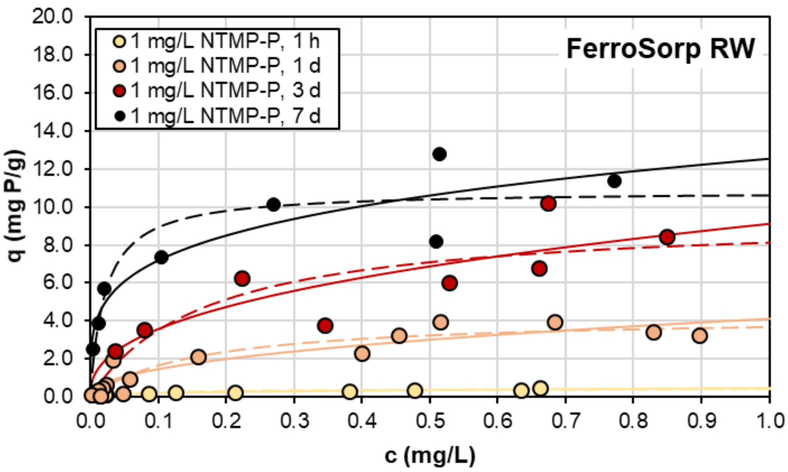

Figure 1. Adsorption isotherms of GFH. Initial pH: 6 (buffer: 0.01 M MES), room temperature (20 °C), 20 rpm, solid lines: Freundlich model, dashed lines: Langmuir model

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Deammonification Recovery Strategy: A Pilot Scale Study

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INTRODUCTION

Stable and efficient nitrogen removal is one of main goals of wastewater treatment. Applying deammonification, beyond many advantages, results in the risk of the WWTP effluent quality violation in case of the failure of the process (Janiak et al., 2018). In deammonification systems failures are caused by three main factors: (i) sensitive for disturbance of the external factors (e.g. DO, temperature, pH), (ii) the presence of organic compounds inhibits the activity of AOB and AAOB, (iii) high concentration of NO_2-N (Feng et al., 2017).

The main aim of this study was to recovery deammonification process in a pilot sequencing batch reactor (SBR) after failure in the first days of SBR operation at the WWTP.

MATERIALS AND METHODS

Initial biomass and pilot reactor

Initial biomass originated from a deammonification full scale side-stream treatment system in a wastewater treatment plant in Duisburg-Kasslerfeld, Germany. Initial biomass concentration during experiment was 0.8 g m^{-3}.

Full scale experiment was carried out in a SBR with a maximum volume of 500 m^3. Full scale installation was equipped with set of pumps for feeding and draining the SBR, a measuring system including probes for continuous monitoring of ammonia and nitrate, pH, DO and temperature. In addition, the SBR was equipped with a heating system and an automatic pH correction system.

Start-up of deammonification process was carried out in a laboratory conditions at Gdańsk University of Technology, using a synthetic wastewater. Full scale research was carried out at the WWTP in Swarzewo (North Poland, PE:130 000 – summer, 45 000 – winter). The initial SBR operation cycle lasted 8 hours. The operational temperature was 30 ˚C.

RESULTS

Reactor failure was observed from the first day of operation at WWTP in Swarzewo. Ammonia utilization rate (AUR), NPR and ratio of NO_3-N produced to NH_4-N oxidized during SBR cycle are presented in the Figure 1. From the first day of operation full nitrification was observed in the pilot SBR. Almost all ammonia was oxidized to nitrate (98-100 %). Probably, the sudden failure resulted from the change of synthetic wastewater into the real sludge digester liquors. The development strategy, presented in the Table 1, has allowed the recovery deammonification process after 18 days. During next 14 days AUR increase from 0,7 to 9,85 mg NH_4-N dm^{-3} h^{-1} and NO_3-N production was constantly below 20 %. Obtained results indicates a continuous increase in the rate of nitrogen removal in the deammonification process.

Table 1. Steps of deammonification recovery process

Steps	Problem	Solution
1	High nitrate production rate (NPR) and high concentration of nitrate (>150 mg dm^{-3})	HRT: decrease from 35 to 18 DO: decrease from 0,5 to 0,4 mg O_2 dm^{-3}
2	Decrease of AOB activity. Low nitrite production rate (NiPR).	DO: increase from 0,4 to 1,2 mg O_2 dm^{-3}. Change in the length of the aeration and mixing phases from 5/10 minutes to 3/6 minutes.
3	Decrease of anammox activity.	DO: decrease from 1,2 to 0,5 mgO_2 dm^{-3}. Extending the mixing phase from 6 to 12 minutes.

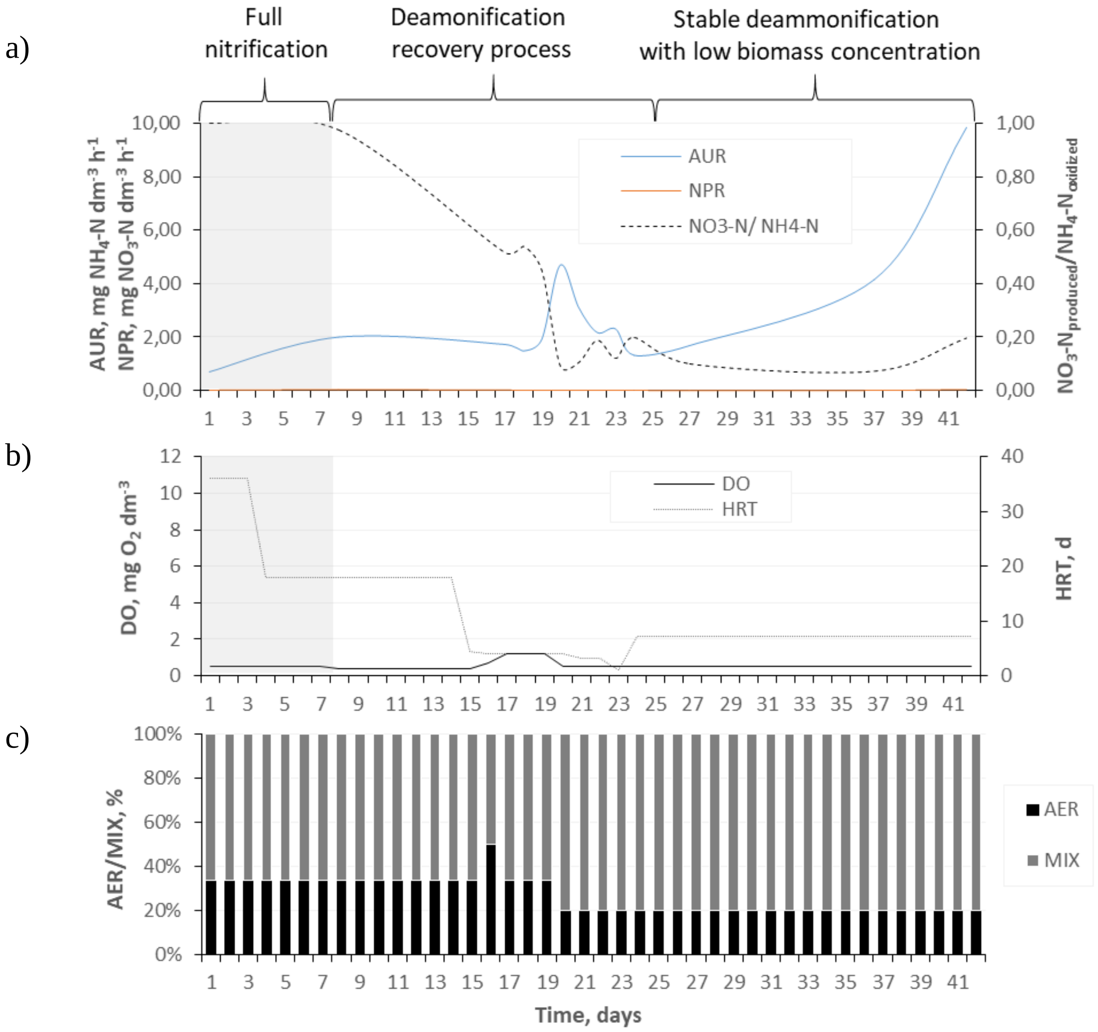

Figure 1. a) AUR, NPR and NO_3-N/NH_4-N ratio; b) HRT and DO concentrations and c) percentage of the aeration and mixing phases in the operational cycle during pilot SBR operation

ACKNOWLEDGEMENTS

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Preliminary Studies on COMAMMOX Process under Different Aeration Conditions during Wastewater Treatment

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INTRODUCTION

The complete nitrification process, i.e. complete oxidation of ammonia to nitrate (COMAMMOX), by only one microorganism belonging to *Nitrospira* sp. was experimentally confirmed only three years ago (Daims et al., 2015; van Kessel et al., 2015). This discovery adds a new dimension to the current understanding of the nitrogen cycle (especially nitrification).

Although the “comammox” *Nitrospira* has already been found in wastewater treatment systems (especially in biofilms), their importance for nitrogen removal has not been investigated yet. The presented data are preliminary results of the research aimed at estimation of the role of *Nitrospira* in the first step of nitrification and their competitiveness compare to the other nitrifiers. The main objective of this series of studies was to determine optimal oxygen conditions for long-term nitrite oxidizing bacteria (NOB) wash-out experiment at low temperature (sequencing batch reactor -SBR started in a separate series of tests), i.e. dissolved oxygen concentration, at which the NOB activity will be the lowest.

MATERIALS AND METHODS

Initial biomass

The biomass originated from the full-scale mainstream bioreactor in Swarzewo WWTP (North Poland, PE: 130 000 - summer, 45 000 - winter) performing the conventional nitrification-denitrification process.

Experimental set-up and laboratory experiments

Batch tests were carried out in two parallel reactors (V= 4 dm^3) at temperature of 11 °C. During tests six different DO concentrations (0.5, 0.7, 1.0, 1.5, 2.0 and 2.5 mg O_2 dm^{-3}) were analysed. The nitrifiers activity was monitored by supplying a synthetic mixture of NH_4-N and HCO_3. The measurements of pH, DO, temperature and N_2O were monitored on-line. Based on results of nitrification tests the ammonia utilization rate (AUR), nitrate production rate (NPR), nitrite production rate (NiPR) and nitrous oxide production rate (N_2OPR) were calculated.

Microbiology

A relative abundances of the ammonium oxidizing bacteria (AOB) and NOB in applied activated sludge were analysed by quantitative PCR, with primers pairs CTO-654R & CTO-189F and NSR1113F & NSR1264R respectively, in relation to 16S rDNA of the total bacterial population (primers 341F & 515R). Additionally comammox *Nitrospira* clades A and B were investigated with primers F1norA & R2norA, comaA-244F & comaA-659R and comaB-244F & comaB-659R respectively.

RESULTS

Results obtained during batch tests are presented in the Figure 1A. The AUR was in the range from 0.58 to 0.74 mg NH_4-N dm^{-3} h^{-1}. The minimum AURs were observed for the extreme DO set points i.e. 0.5 and 2.5 mg O_2 dm^{-3}, while highest at 1.5 and 2 mg O_2 dm^{-3}. The lowest NPR versus AUR was observed at a DO concentration equal to 0.7 mg O_2 dm^{-3} (0.35 mg NO_3-N dm^{-3} h^{-1}). In DO concentrations higher than 1.0 mg O_2 dm^{-3} NPR was almost equal to the value of AUR. The highest NiPR (0.02 mg NO_2-N dm^{-3} h^{-1}) was observed at 1.5 mg O_2 dm^{-3}. Higher N_2OPR was favored by DO set point limitation, however the relation was not linear and the highest values was gained at 1.0 mg O_2 dm^{-3}.

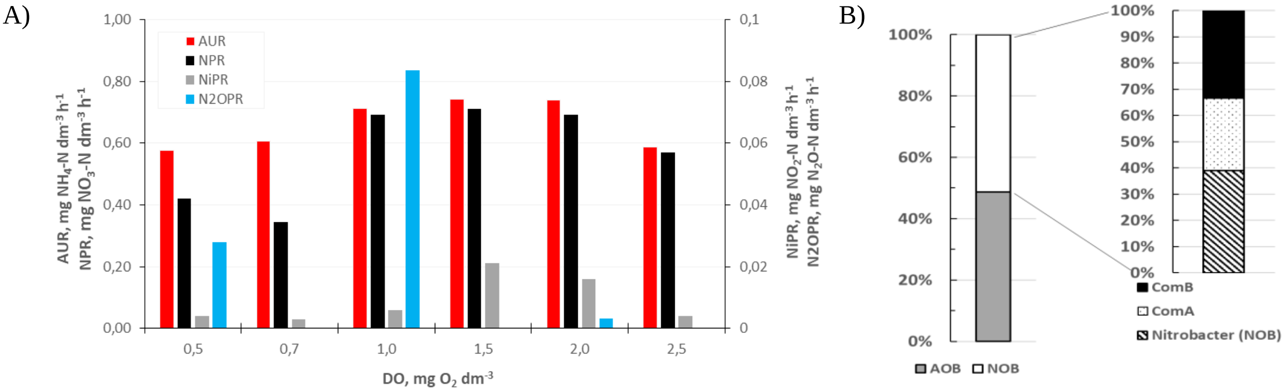

Figure 1. AUR, NPR, NiPR and N_2OPR during nitrification in low temperature (A), relative abundances of the main nitrifying bacteria groups (B)

Microbiological analysis revealed similar abundances of AOB and NOB in analyzed activated sludge samples. NOBs were represented basically by members of comammox *Nitrospira* from both clades (A and B), which constituted about 60 % of the mentioned group. Remaining 40 % attributed to *Nitrobacter* genera (Figure 1B).

FURTHER PROCEEDINGS

Obtained results will be applied during design of the long term experiment directed at NOB wash out from the system. Based on data from the batch tests, DO set point at 0.7 mg O_2 dm^{-3} was selected for further experiment due to favoured AUR/NPR ratio. Moreover N_2O measurements reflected relatively high production of mentioned gas within range of such value, which was potentially connected with nitrite accumulation during operational cycle. Microbial analysis conducted with qPCR, reflects applicability of such approach for comammox *Nitrospira* detection and abundance control during long term experiments.

ACKNOWLEDGEMENTS

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Characterization and Modelling of Fungal and Bacterial Tannin-degrading Biofilms with Respirometric Techniques

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INTRODUCTION

In environmental biotechnology applications for wastewater treatment, fungi tend to be outcompeted by bacteria. The application of fungal-based bioreactors, with similar performance under sterile and non-sterile conditions, for a long-term operation is still challenging. However, an engineered ecosystem, based on fungal and bacterial tannin biodegradation, has been recently and successfully tested in lab-scale bioreactors under non-sterile conditions by Spennati et al. (2019). In that previous study, the bioreactors (rotating submerged packed bed reactors) were inoculated with a pure culture of *Aspergillus tubingensis* immobilized in PUF cubes and fed with two different tannins (Quebracho and Tara). Promising results were obtained from the bioreactor fed with Quebracho Tannin (QT), which showed a steady fungal biofilm development and satisfactory performance. However, dedicated experiments were still required to characterize the fungal biofilm in terms of kinetics and stoichiometry. To this aim, in the present study the set-up of specifically designed respirometric tests, to characterize tannin-degrading fungal and bacterial biofilms developed under non-sterile conditions, was performed. Afterwards, a mathematical model was developed and applied.

MATERIALS AND METHODS

Respirometric tests were performed in an LFS-type respirometer under controlled conditions. The respirometric vessel had a volume of 0.3 L and was provided with a gas diffuser. The respirometer was jacketed with temperature control via the recirculation of a thermostatic water bath (Polystat24, Fisher Scientific, Spain). Vessel mixing was ensured by magnetic stirrers. Temperature and pH probes (SenTix82, WTW, Germany) and a DO probe (CellOx 325, WTW, Germany) were connected to a benchtop meter (Inolab Multi 740, WTW, Germany) and a computer for data acquisition and process monitoring. The pH was controlled trough the addition of NaOH and HCl solutions with a microburette (Multi-Burette 2-SD, Crison Instruments, Spain). The biofilm to be characterized in the respirometer was obtained from the bioreactors mentioned above (see Spennatti et al., 2019 for detailed information) which contained the inoculated PUF cubes in a rotating cage and were provided of a pH control system and continuous aeration. Each respirometric test required withdrawing 5 of the PUF cubes from the bioreactors, a pre-wash of the biofilm with phosphate buffer and an abiotic stage in the respirometric vessel. Aquasim software was used to simulate the experimental profiles, substrate limitation (Monod-type equation) and inhibition (Haldane) were considered besides biomass decay and hydrolysis of particulate matter.

RESULTS AND DISCUSSION

The outcomes of the respirometric tests as reported in figure performed with the biomass sampled from the bioreactors were coupled with the results of the long-term operation of the bioreactors to construct the overall biomass activity model. The growth of the tannin-degrading fungal biofilm was described by using a specific tool (biofilm compartment) provided with Aquasim software which allowed obtaining the biofilm features and transport parameters that could not be either measured directly or estimated from the literature (as shown in the table below). A part from the experimental tests and process modelling presented herein, the same approach was successfully performed with tannin-degrading bacterial biofilms sampled from the bioreactor fed with Tara tannin. The results obtained in this study represent the first step for modelling a future real-scale application of fungal and bacterial biofilms for tannin biodegration.

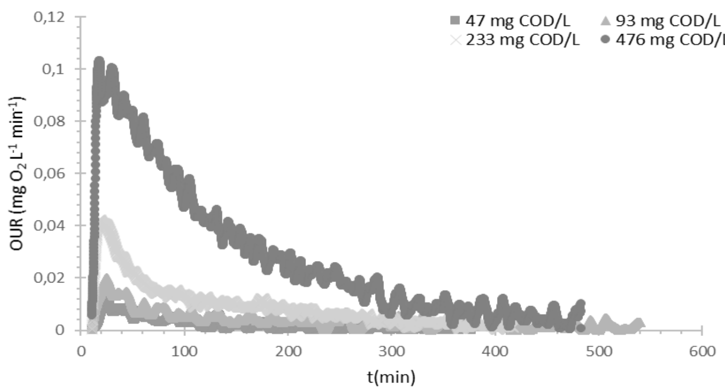

Figure 1. Exogenous Oxygen Uptake Rate (OUR_{ex}) respirograms of immobilised fungi of of QT pulses

Table 1. Estimated and chosen microbial kinetic coefficients

Symbol	Characterisation	Value	Units	Reference
Y_f	Yield coeff. for fungi in aerobic growth	0.45	g COD g COD^{-1}	This study
b_f	Decay coefficient for heterotrophic biomass	0.22	d^{-1}	(Wang et al., 2008).
f_P	Fraction of inert COD generated in b. decay	0.08	g COD g COD^{-1}	(Andreottola et al., 2001)
K_{iq}	Inhibition constant	13	g COD m^{-3}	This study
K_{sf}	Half-saturation coefficient	993	g COD m^{-3}	This study
μ_f	Maximum growth rate on substrate	5.39	d^{-1}	This study

ACKNOWLEDGEMENT

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Treatment of Olive Mill Effluent Wastewater Using Some Advanced Processes and Reuse of the Treated Wastewater

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INTRODUCTION

The olive mill wastewater (OMW) has a high relation in the Mediterranean countries. Although olive oil is a useful product its production gave high several adverse effects to the ecosystem, primarily due to its high chemical oxygen demand (COD), color and polyphenol content. OMW is defined by a high suspended solids content (e.g. TSS between 6 and 70 g/L), dark brown color, characteristic unpleasant odor, low pH, high turbidity and high organic load (e.g. COD between 30 and 318 g/L) (Yalılı Kılıç et al., 2013; Amor et al., 2015). In addition, OMW include many complex organic substances [e.g. phenolic compounds (TPh between 0.5 and 24 g/L), polysaccharides, tannins, pectin, organic acids, etc.], which are generally resistant to biodegradation. The aim of this study was to investigate some sequential treatment processes to determine the optimum operational conditions for the treatment of OMW using sequential anaerobic-aerobic reactors, sonacation, sunligth photocatalysıs and reverse osmosis (RO) in an economical and feasible way. Furthermore the recovery of treated wastewater as irrigation purpose was evaluated.

MATERIALS AND METHODS

Dark colored glass reactors sealed with rubber lids having volumes of 1,5 liter was used for the anaerobic treatment 300 ml of granulated anaerobic sludge taken from a yeast factory anaerobic digestor was used as seed and put to the glass reactor (Figure 1a). The effluent of the aerobic reactor was given to a sonicator (Bandelin sonorex) at a frequency of 5 Hz at a power of 18 W/m^2 (Figure 1b).

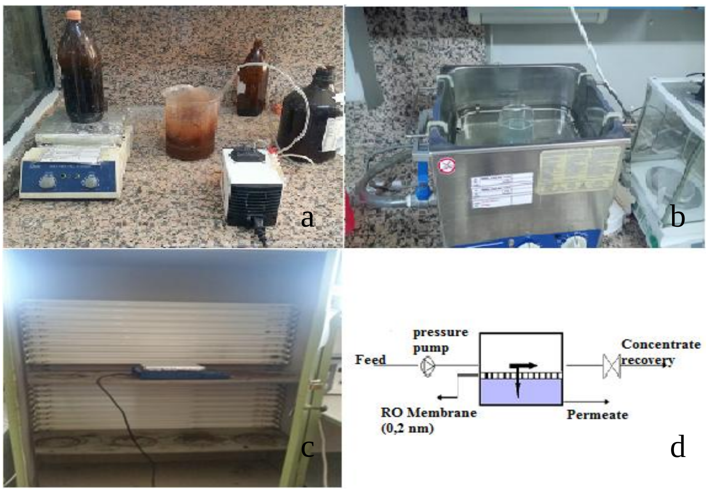

Figure 1. a) Anaerobic and aerobic reactors in laboratory, b) sonication reactor system, c) Photocatalitic reactors, d) Reverse Osmosis flow rate

The effluent of the sonicator was taken in dark for 24 hours to detect the removal with adsorption. Then the effluent of sonication was photodegraded using nano-SiO_2 under sun ligth (Figure 1c). Reverse Osmosis (RO) stage remove all the microoorganism, salinity, magnesium, calsium and all metals and heavy metals (Figure 1d).

RESULTS

The maximum COD removal in anaerobic reactor was 60 % while the maximum COD removal in aerobic reactor was 66 %. The total yield of sequential biological reactor was found to be as 86 %. The maximum sonication yield was observed as 53 % for a 45 min retention time in the sonicator. The effluent of sonication reactor was taken under sunligth between 10 and 70 minutes. No significand COD losses was detected (data not shown).

In the same time the effluent of the sonication reactor was taken in dark conditions for 24 and 48 hours. No COD removal was observed. The effluent of photolizis process was processed with 0,5 mg/l Nano SiO_2 under sunligth in times between 12.00 a.m morning and 15.30 p.m afternoon. The maximum COD yield was obtained after 45 min photodegradation time. In the effluent of the RO; the COD yield reached 100 %. The yields of Phenol, TN, TP Dissolved COD reached approximately to 99.7 %.

CONCLUSIONS

The textile industry wastewater can be treated successively and recovered as irrigation water by using sequential biolagical, sonication, photocatalyzis and RO processes. The maximum COD removal in anaerobic reactor was 60 % while the maximum COD removal in aerobic reactor was 66 %. The total yield of sequential biological reactor was found to be 86 %. In the sonication reactor the yield was observed as 53 % for a 45 min retention time in the sonicator. No removal of COD was observed via photolysis and adsorption.

The maximum photo catalytic removal of COD was 40 % at a nano SO_2 concentration of 0,5 mg/l after 10-60 min. In the effluent of the RO; the COD yield reached 100 %. The yields of phenol, TN, TP Dissolved COD reached approximately to 99.7 %. In order to treat 1 m^3 OMW wastewater the total cost was calculated as 1.033 €.

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Evironmental Risk Assessment of Toxic and Emerging Pollutants in Waste and Surface Water of Novi Sad – A Project Review

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INTRODUCTION

Increasing urban population and industrial development cause a concern for the quality of aquatic environment. Surface water is very often the direct recipient of industrial and domestic waste, since the wastewater in many developing countries is directly discharged into river without any treatment. Emerging pollutants (EmP) enter the environment throught many natural, but mostly antropogenic pathways. NORMAN list of EmP (https://www.norman-network.net/?q=node/19) comprises of substances that are suspected or proven to be toxic and/or hazardous for environment and/or human health. EmP can be persistent, pseudo-persistnet, toxic with chronic or acute effects even in low concentration levels (ppb, ppt and lower), hazardous, iritant, carcinogenic, teratogenic, mutanogenic and other. The supstances that are listed as EmP and investigated belong to the groups of illicit drugs, bacteria, wood preservatives, pesticides, pesticide precoursors and metabolites, phthalates, metal cations and other. Metal cations as the conservative pollutants were detected in water bodies and have high potential risks to aquatic organisms (Chow et al., 2005). Toxic, pseudo-persistent species have tendency to bioaccumulate in tissues of aquatic organisms (fish, algae, etc.) which introduces the pathway to the human body that can cause a diversity of harmful effects. Henceforth, metal cations could cause negative impact to environment and human health via processes of bioaccumulation and biomagnification (Sremački et al., 2017; Bhuvaneshwari et al., 2016; Čavić et al., 2018).

MATERIALS AND METHODS

Sample analyses

For detection of all metal ions the atomic absorption spectrophotometer (AAS) was used. Prior to analyses the water samples were digested with 5 ml of the acid mixture (HNO_3:$HClO_4$ = 9:4) and filtered through Whatman No. 42 filter paper. For the other EmS the HPLC-MS^2 or equivalent was used. Analyses were carried out in Accredited Laboratory for environmental and occupational monitoring on Faculty of Technical Sciences, University of Novi Sad. using standard and validated methods.

Environmental risk assessment method

The stressor-response relationship represents the main toll for the risk evaluation. The Environmental risk assessment was performed with the estimation of the Risk Quotients (RQs). The RQs are obtained by calculation of ratios of the measured environmental concentrations and predicted no effect concentrations (Sremački et al., 2017; Su et al., 2013). This method of ERA calculation is provided by the EU guidelines. If the RQ is calculated via MEC values it represents real risk quotient for selected and observed location.

Statistical methods

The large data set was statistically processed by the DART 2.05 software. DART software applies the following ranking techniques: Desirability, Utility, Dominance, Concordance, SAR (Simple additive ranking), HAR (Hasse average ranking) and Absolute reference ranking. The applied ranking techniques allow direct evaluation of metal cations concentrations and RQs, and the visualisation in form of HDs. The ranking of metal cations in HDs is performed according to the all variables, acquiring a valuable overview of the whole dataset (Sremački et al., 2017).

EXPECTED RESULTS

The preliminary results indicate that EmP with high RQs can originate from the four sources of pollution - the direct discharge of communal and industrial wastewater without any treatment, the high agricultural activity in surrounding areas along the rivers, the runoff of the atmospheric water and the historical input of contamination from the neighbouring countries and accidental events.

ACKNOWLEDGMENTS

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Effect of Morphological Properties of Modified Biogenic Sorbents: A Diversification of Phosphates Removal Technologies

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INTRODUCTION

The environmental significance of phosphorus (P) arises from its role as an essential nutrient for both plants and microorganisms. The combination of greatly increased nutrient input and a wide range of other potentially ecotoxic pollutants that reach the water have serious impact on the aquatic ecosystem. Eutrophication is the most significant effect of water pollution that not only causes environmental (Smith, 2009), but also economic costs (Withers, 2014). Recently, much attention has been paid to the use of different waste products for the adsorption of nutrients from water. Eggshells are cheap, easily accessible waste product with porous structure and low water solubility. Both eggshells and sorbents derived from them could be effectively used to remove various pollutants from water and wastewater (Guru, 2014; Carvalho, 2011; Smirnova, 2017). This study explores the phosphate sorption by varying untreated and treated (calcined) eggshell powders.

MATERIALS AND METHODS

Eggshells were rinsed with distilled water several times and then dried at room temperature. Dried eggshells were crushed and sieved. A fraction of 0.25 to 0.50 mm was used for further experiments. To obtain calcinated eggshells the raw powder was heated in the furnace at 300 °C for 1 h. Then the temperature was raised to 800 °C and the powder was held for 4 h.

Phosphate sorption experiments were studied at room temperature in static conditions and sorption kinetics was investigated at various phosphate concentrations prepared of KH_2PO_4 and various dosage of adsorbents. Phase composition, FTIR, specific surface area and porosity (BET) of obtained bio sorbents were determined before and after heating.

RESULTS

The XRD pattern and FTIR spectra of the raw eggshell powder indicate that the given material is a crystalline compound corresponding to calcite, but thermal treatment of eggshell promotes the decomposition of $CaCO_3$ to CaO. BET results show that after heating specific surface area of egg shells increases about 4 times (from 0.41 to 1.67 m^2/g), total pore volume 2.4 times (from 1.28 to 3.10 mm^3/g) and micropore volume – 2.7 times (from 0.26 to 0.70 mm^3/g). SEM images (Figure 1) present the pore size distribution of raw and calcined eggshells.

After phosphate binding FTIR spectra of calcined eggshells has changed significantly (Figure 2.). The Ca-O absorption peak has completely disappeared, and new absorption bands of carbonate and phosphate functional groups appear. Phosphate-specific absorbance peak was observed also in FTIR spectra of raw eggshell powder, indicating that the phosphate adsorption onto eggshell surface is a result of chemical adsorption that occurs during formation of poorly soluble compounds that could be calcium carbonates and calcium phosphates.

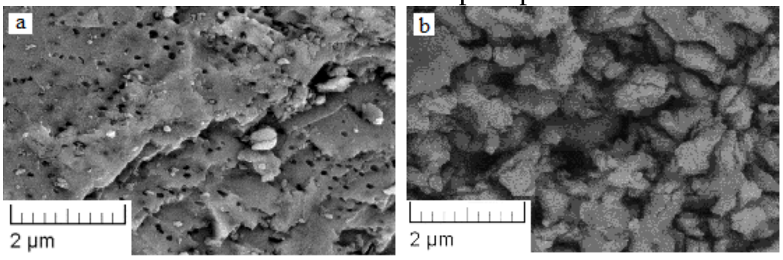

Figure 1. SEM images of a) raw and b) calcined eggshells

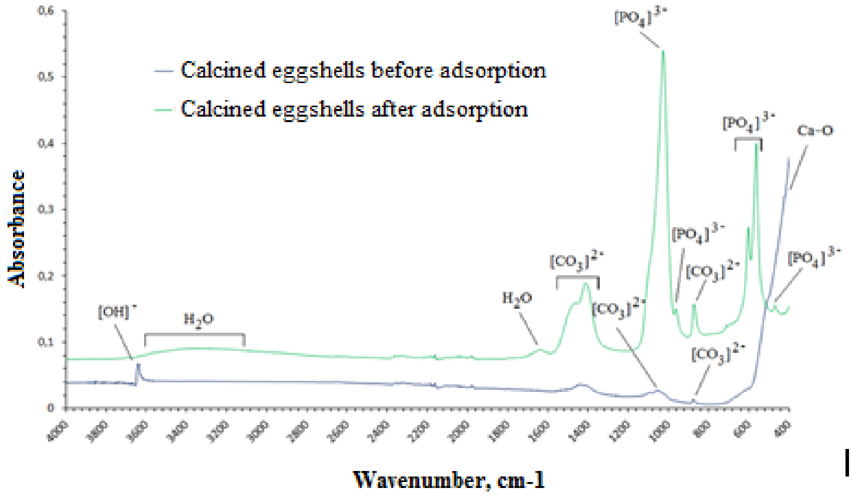

Figure 2. FTIR spectra of calcined eggshells before and after adsorption (c_0 = 150 mg/L PO_4-P)

Experimental results show that even slight changes in the amount of sorbent added, can greatly impact phosphate adsorption efficiency on eggshell powders. Furthermore, in the case of calcined eggshells, almost complete removal of the phosphate was achieved by adding a very small amount of this biosorbent (98 % P removal rate when 0.025 g of sorbent was added at initial phosphate concentration C_0=100 mg/L PO_4-P).

CONCLUSIONS

The affinity of egg shells to bind P may be increased by calcination process and reaches maximum value of approximately 11 mg/g. High phosphate adsorption efficiency of calcined eggshells demonstrates the ability of this waste material to be used as precipitation reagent for phosphorus removal from aqueous solutions. Adsorption capacity of the raw eggshells reaches the maximum value of approximately 5 mg/g, which is comparable with adsorption capacities of other low-cost adsorbents. Phosphate adsorption on egg shells occurs as a result of specific chemical adsorption by formation of poorly soluble compound on the surface of the adsorbent.

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Aerobic Granular Sludge Process Performance Analysis under Increasing Phenol Loading Rates

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INTRODUCTION

Aerobic granular sludge (AGS) is a relatively new and very promising wastewater treatment technology (Sarma et al., 2016). The use of granular biomass presents significant advantages over the classical activated sludge (AS) wastewater treatment process (Dulekgurgen et al., 2003). The objectives of the research are to investigate treatment efficiency and morphological change of AGS treatment system under increasing phenol loading rates.

MATERIALS AND METHODS

A 3 liter laboratory scale sequencing batch reactor was used with the following operational parameters, initial OLR 2.84 (kgCOD/m^3·d), volumetric exchange ratio 49.85 (%), SAV 96.31 (m^3/m^2·h), H/D ratio 9.5, cycle time of 4 (h), feed 10 (min), aeration 3.6 (h), settling 2.5 (min) and drawn 20 (sec). Acetatebased synthetic wastewater was used (Mosquera-Corral et al., 2004) with initial 950 mg/L COD the phenol tolerance of the system was investigated by stepwise increase of phenol loading rates between 0.34 and 2.4 gPhenol/L·d. For each phenol concentration scenario the reactor was operated for minimum 16 cycles. Dissolved oxygen, ammonia, nitrate and pH were continuously monitored (WTW sensors, XT2020 data logger), reactor operation was controlled by PLC. Biomass concentration, COD, ammonium and nitrate, phenol were determined according to standard methods (APHA, 2005).

RESULTS AND DISCUSSION

Stable granules and efficient treatment performance was observed after four weeks of operation (Figure 1) confirming the conclusion of Pan (2003) that at least 20 days of operation are necessary for granule formation. COD removal and ammonia nitrification rates were 96 % and 88 %, the low nitrate concentrations indicated the occurrence of simultaneous nitrogen removal. Table 1 presents the effluent values without phenol and at different phenol loading rates. Treatment performance was unaltered at the smallest phenol load, however further increase of phenol negatively influenced the COD and phenol removal. Nitrification was stable up to 1.8 gPhenol/L·d phenol loading, supported by the low ammonia values (influent ammonia was 37 mg/L). The denitrification capacity significantly decreased at loading rates above 0.69 gPhenol/L·d. Increasing phenol concentration primary influenced the activity of heterotrophic microorganisms supported by the higher values of organic matter and nitrate.

Optical microscopy images of granules at different phenol concentration scenarios showed gradual disintegration of granular structure with increasing phenol loading rate. In non-phenolic environment regular granules were observed. Visible structural changes occurred also at low phenol loading rate, however significant granule disintegration was observed at 1.38 (gPhenol/L·d) and above. At the highest loading rate the granular structure can’t be identified and total disintegration of granules has been observed.

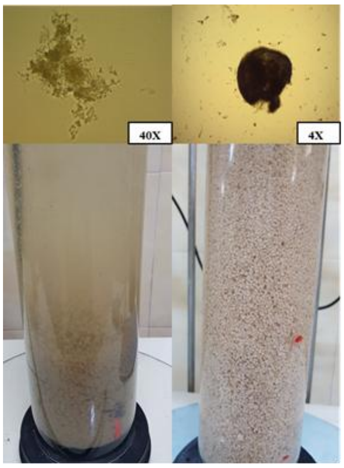

Figure 1. Sludge sample and reactor images at stratup and after granule formation

Table 1. Effluent parameters at different phenol concentration scenarios

Phenol concentration (mg/L)	No phenol	115	230	460	600	800
NH_4^+ (mg/L)	4.3	4.4	4.6	1.8	4.3	12.0
NO_3^- (mg/L)	0.5	0.5	1.5	28.0	82.0	158.5
COD (mg/L)	24.0	55.0	217.0	420.0	1290.0	2012.0
Phenol (mg/L)	-	0.6	11.3	155	514	810
Phenol loading rate (gPhenol/L·d)	0	0.345	0.69	1.38	1.8	2.4

CONCLUSIONS

Aerobic granules were obtained from fluffy inoculum after 4 weeks of operation, and highly efficient COD and simultaneous nitrogen removal were observed. The aerobic granular sequencing batch reactor phenol organic load tolerance was 0.69 gPhenol/L·d (230 mg/L influent) in terms of treatment efficiency; starting with 0.345 gPhenol/L·d (115 mg/L) structural changes of granules was observed in parallel with the decrease of treatment efficiency. Nitrifier microorganisms tolerated higher phenol loads, significant nitrification decrease was observed at 1.8 gPhenol/L·d load (600 mg/L). Denitrification was seriously affected already at phenol loading rate of 1.38 most probably due to the loosening of the granular structure and the consequent decrease of anoxic environment.

ACKNOWLEDGEMENTS

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Cost Effective Improvement of the Performance of an SBR System Using a Floating Seal

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INTRODUCTION

In a Sequencing Batch Reactor (SBR) according to the sequenced operation utilization of oxygen having been blown into the system is typically undesirably low during the early periods of the cycles due to the relatively low water level. On the other hand, oxygen that can penetrate into the reactors through the open water surface may cause both metabolic and kinetic inhibition in the non-aerated parts or phases of the operation (Plósz et al. 2003; Wanner and Jobbágy 2014; Jobbágy et al. 2015) hindering efficient denitrification and biological P-removal. Since the water level is relatively low compared to those of common activated sludge basins, oxygen penetration through the same surface area can result in considerably higher oxygen amounts hitting the biomass of the reactors. This reaction is especially dangerous when the influent is in lack of readily biodegradable carbon source having been experienced worldwide. Purpose of the research has been to verify the use of a floating seal on the mooving surface of an SBR reactor.

EXPERIMENTAL PROCESS AND RESULTS

The experiment was carried out by using an SBR system with two trains designed by UTB Envirotec Co in Hungary. This system has a staged reactor including originally a temporarily aerated selector and a main reactor. The experiment was started by converting the selector of the Test train into a non-aerated basin and covering the whole surface of this system by a floating seal. There was no technological change executed in the Reference train. On the basis of the influent data, marginal C-source availability, even carbon deficiency could be assumed in the system.

The experimental results confirmed the presumed advantages appropriately. In the winter period, with ~ 7-8 ºC influent temperature 1-1.5 °C higher values could be measured in the effluent of the seal-covered system. Also at highly increasing temperature the Test train could keep a relative stability. The most significant advantage of the insulation potential was the higher nitrification efficiency under cold conditions, seen in (Figure 1)**,** despite the decreased aeration capacity.

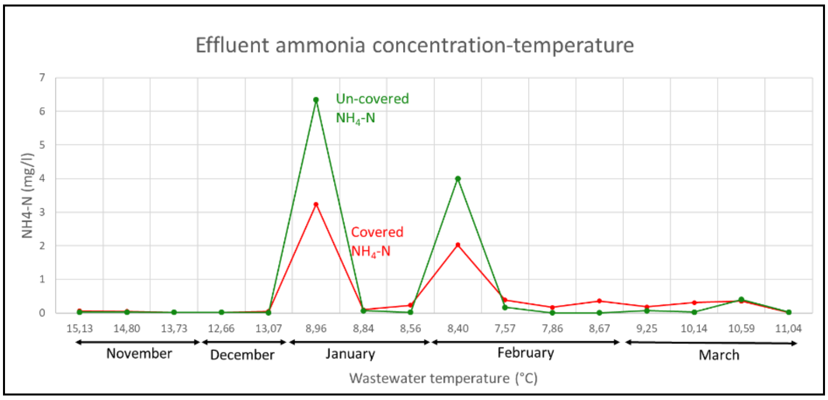

Figure 1. Effluent ammonia concentrations measured during the experiment

Efficiency of denitrification proved to be also higher in the Test (seal-covered) train. Therefore, despite the higher nitrification efficiency, 1-5 mg/l lower values could be detected in the effluent TIN (Total Inorganic Nitrogen) concentrations of the experimental system.

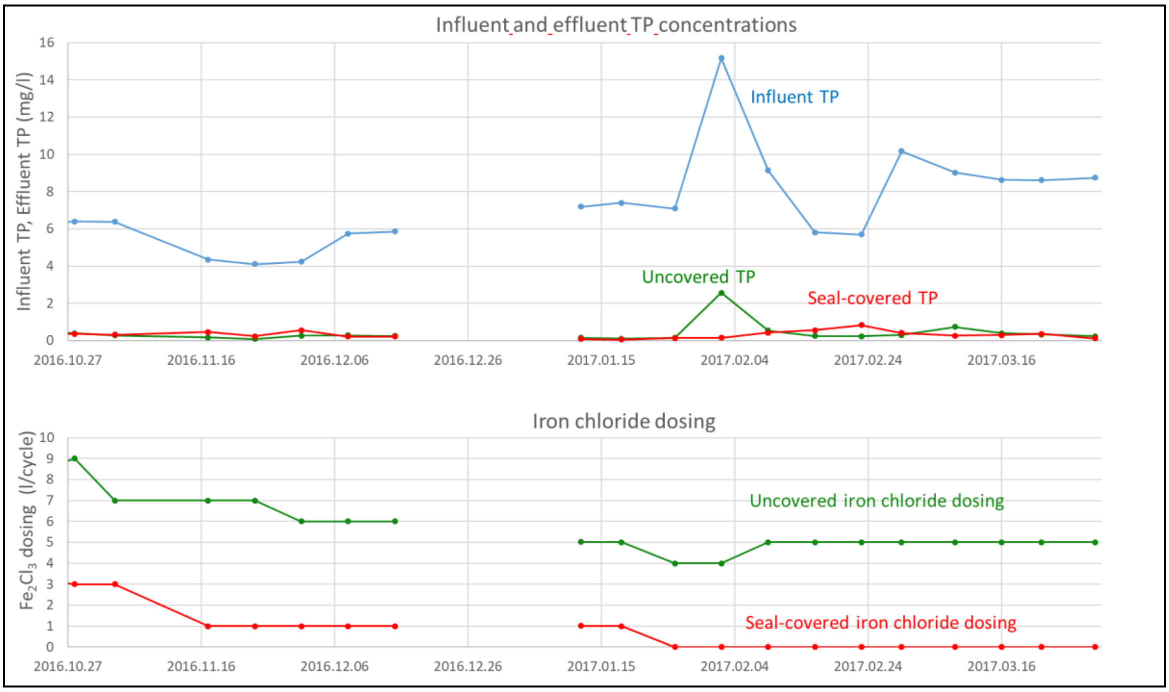

Figure 2. Influent and effluent TP concentrations, chemical dosing measured during the experiment

Maintaining PAOs (Phosphorous Accumulating Organisms) in an activated sludge system is extremely useful for a good floc structure and settleability, since these organisms are floc-formers. Creating a non-aerated selector may obviously help in this respect. However, growth of PAOs may generally have difficulties in winter. Figure 2 shows that in the seal-covered system a stable and continuous growth of PAOs could be observed even in wintertime. The iron chloride dosing could be lowered progressively in the experimental train down to zero, and still the effluent total phosphorus concentrations of the seal-covered system were significantly lower than those of the uncovered train. When the influent TP concentration increased suddenly, the seal-covered train was able to remove the excess phosphorous biologically, while the reference train could not appropriately handle it despite the chemical addition. The sludge volume indexes in the two trains proved to be close to each other, despite the high difference in chemical dosing.

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Ecotoxicity Effects of Carbon Nanomaterials on the Activated Sludge Microorganisms

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INTRODUCTION

The development of new technologies in industry and science, entails the growing production of advanced materials, including engineered nanomaterials. Nanotechnology has become one of the fastest growing fields of science and the widespread use of nanomaterials increases the emission of nano-pollutants into the environment (Bundschuh et al., 2018). Carbon nanoparticles are a particularly interesting group. Their relatively stable structure makes them able to migrate in the environment over long distances and enter wastewater treatment plants (WWTP) (Flores-Cervantes et al., 2014). Therefore, the aim of this study was to determine the potential toxicity on the activated sludge microorganisms, of four selected carbon nanostructures: graphene oxide (GO), reduced graphene oxide (rGO), carbon nanotubes (CNTs) and oxidized carbon nanotubes (oCNTs).

MATERIALS AND METHODS

Fresh activated sludge originated from the municipal WWTP, located in the Silesia region (Poland). Carbon nanoparticles influence on the activated sludge microorganisms has been investigated using two acute ecotoxicity tests. Growth inhibition was determined after 5 hours of exposure, based on standard method (ISO 15522:1999), using optical density (530 nm), at 22 ± 2 °C, pH 7.0 and with an average total suspended solids concentration (TSS) 2.2 ± 0.1 g/L. Respiratory activity was measured based on oxygen uptake rate (OUR), according to the standard method (PN-EN ISO 8192:2007), at 22 ± 2 °C, pH 7.5 and with an average TSS concentration 4.5 ± 0.9 g/L. All tests were performed in triplicate, the difference between means was tested using the t-test.

RESULTS

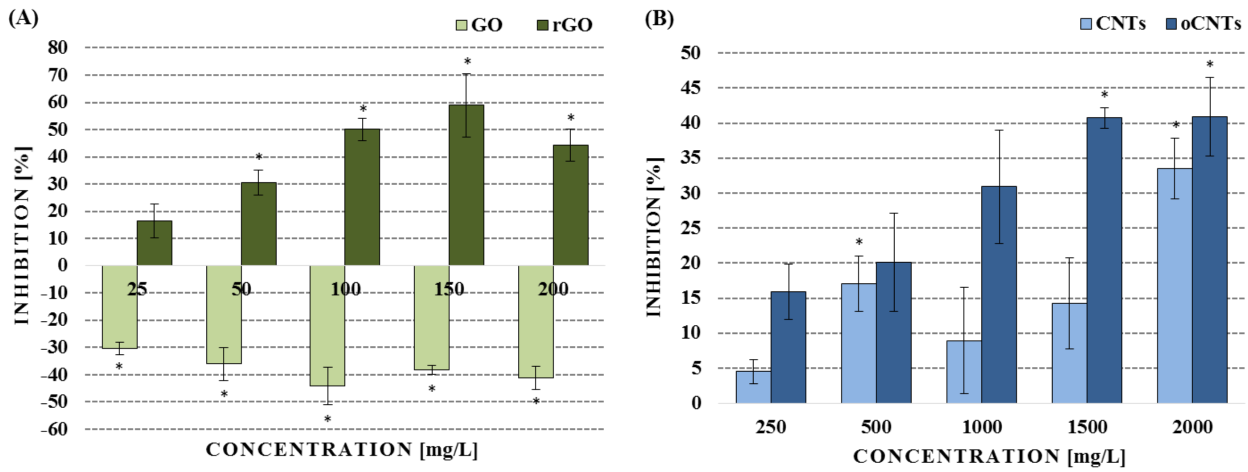

Figure 1. Growth inhibition test results after 5 hours of exposure on GO, rGO (A) and CNTs, oCNTs (B). Bars - standard error; '*' - statistically significant difference with control at $p < 0.05$

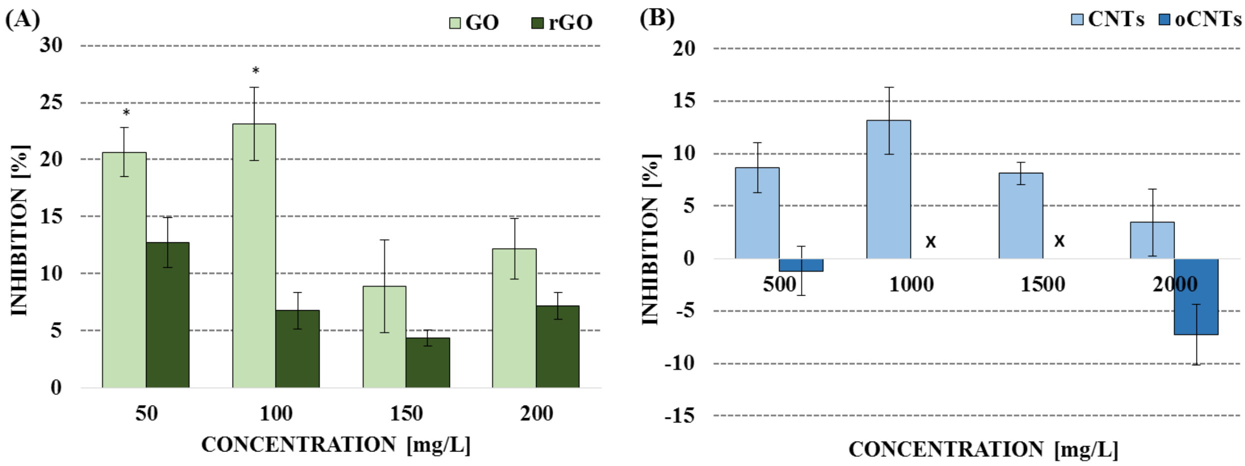

Figure 2. OUR test results underexposure on GO, rGO (A) and CNTs, oCNTs (B). 'X' – no data for oCNTs; bars - standard error; '*' - statistically significant difference with control at $p < 0.05$

CONCLUSIONS

Results of the growth inhibition test, after 5 hours of exposure, revealed the toxicity of three nanomaterials: rGO, oCNTs and CNTs. The highest 59 % inhibition was observed for rGO in concentration equal to 150 mg/L (68 mg/g TSS). 41 % and 34 % inhibitions were indicated for 2000 mg/L (909 mg/g VSS) of oCNTs and CNTs, respectively. In the case of GO, statistically significant stimulation of the activated sludge microorganisms was noted, up to 44 % with 100 mg/L (45 mg/ g TSS) of GO. It is not a new phenomenon, because several previous studies revealed that bacterial growth rate and activity can be accelerated by this kind of nanomaterial (Ruiz et al., 2011). Definitely, different results were observed for the aerobic activated sludge microorganisms in the respiratory activity test, where the effects of nanomaterials were determined immediately after addition. 100 mg/L (22 mg/g TSS) of GO caused the highest 23% inhibition, while toxic effects of all others materials were much lower than in growth inhibition test. It can be explained by shorter exposure time, higher TSS concentration and limitation to aerobic organisms. Moreover, results suggest that oCNTs and CNTs could be used as a carbon source by heterotrophic microorganisms, increasing oxygen uptake rate.

ACKNOWLEDGMENT

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Respiratory Activity of Nitrifying Bacteria Exposed to the Nanoparticles of Zero Valent Iron, MnO_2, Reduced Graphene Oxide and Activated Carbon

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INTRODUCTION

An anammox (anaerobic ammonia oxidation) process combined with partial nitrification is assumed to be an efficient and beneficial alternative for conventional nitrification-denitrification technology. The implementation of this technology in mainstream municipal wastewater treatment plant (WWTP) has to face several challenges. One of them is a decrease in the anammox bacteria growth rate and activity at temperatures below 20 °C, typical for the municipal wastewater in eastern Europe. Recently, several studies revealed that the growth rate and activity of the anammox bacteria can be accelerated by a few kinds of nanoparticles, including zero valent iron (ZVI), MnO_2 and reduced graphene oxide (RGO) (Erdim et al., 2019; Qiao et al., 2012; Tomaszewski et al., 2019).

However, during single stage partial nitrification – anammox process operation, attention is directed not only on the anammox bacteria but also to promote ammonia oxidizers instead of nitrite oxidizers. Moreover, processes being a part of the nitrogen biogeochemical cycle do not exist separately and anammox bacteria coexist in the complex community (Langone et al., 2014), but the role of nitrifying bacteria was omitted in the previous works, regarding anammox process supported by nanomaterials. For these reasons, the influence of the nanoparticles of ZVI, MnO_2, RGO and activated carbon (AC) on the respiratory activity of the nitrifying bacteria was investigated in this study.

MATERIALS AND METHODS

Suspended activated sludge from the municipal WWTP, located in Southern Poland, was used in the experiment. Nitrifying bacteria activity was measured based on the oxygen uptake rate (OUR) measurements, with $NaClO_3$ and allylthiourea (ATU) as specific inhibitors of nitrite and ammonia oxidizers, respectively. pH was adjusted at 7.5 using 10 % HCl or 10 % NaOH. Samples were placed in vessels (volume of 120 mL), with an oxygen sensor (N5221 Elwro) connected with oxygen level recorder (Line Recorder T2 4620). Tests were performed in triplicate, at two temperatures (10 and 20 ˚C), with three concentrations of each nanoparticle. An average total suspended solids concentration (TSS) was 4.6 ± 0.5 g/L. The difference between means was tested using the t-test.

RESULTS AND CONCLUSIONS

Respiratory activity of the nitrifying bacteria at two temperatures, with three concentrations of the four nanoparticles, was shown in Figure 1. The influence of the nanoparticles was evaluated as a percentage of activity in relation to the control without their addition. In most cases, bacterial respiration was not affected significantly or was inhibited, up to 56 % of relative activity at 20 °C, with 20 mg/L (4.3 mg/g TSS) of ZVI addition.

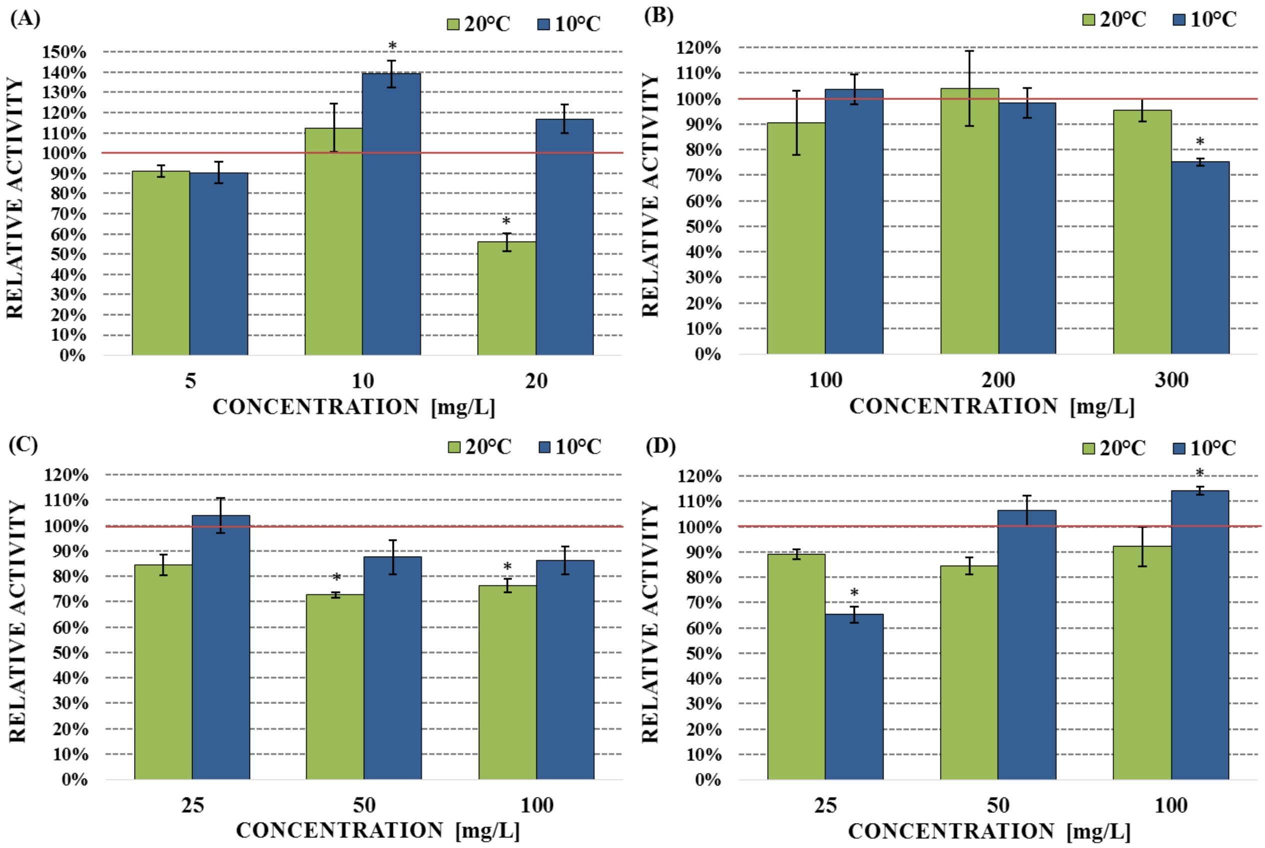

Figure 1. Relative respiratory activity of the nitrifying bacteria at different temperatures underexposure on the ZVI (A), MnO_2 (B), RGO (C) and AC (D) nanoparticles
(bars - standard error; * - statistically significant difference with control at $p < 0.05$)

Fluctuations of activity during exposition on MnO_2, RGO, and AC show that the nanoparticles influence strongly depends on the temperature, indicating greater susceptibility of activated sludge at 10 °C. The most extreme difference was observed for ZVI at concentration 20 mg/L. However, 10 mg/L (2.2 mg/g TSS) of this nanoparticle enhanced the activity of nitrifying bacteria to about 112 % and 139 %, at 20 and 10 °C, respectively. These results coupled with the other research (Erdim et al., 2019), suggest that ZVI is one of the most promising nanoparticles in the field of low temperature partial nitrification-anammox process.

ACKNOWLEDGMENT

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Investigation of Tetrahydrofuran Removal Technology from Process Wastewater

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INTRODUCTION

The work is motivated by an industrial problem, which is tetrahydrofuran removal from pharmaceutical process wastewater with extractive distillation. The goal of the research is to rigorously model and optimize this operation in professional flowsheet simulator environment. The number of minimal theoretical plates of distillation columns, binary mixture feed stage, solvent feed stage location and optimal reflux ratios are determined. Dimethyl sulfoxide (DMSO) is used as extractive agent.

Considering the results, it can be concluded that, the extractive distillation process is suitable for separation tetrahydrofuran and water in 99.9 weight percent (m/m%) purity of water and 99.5 m/m% tetrahydrofuran.

METHODS AND RESULTS

Tetrahydrofuran (THF) forms heterogeneous azeotropic mixture with water, which means separation problem. THF content above 93.3 weight% can not be achieved with conventional distillation techniques (Marsden, 1954).

It can be mentioned, extractive distillation is capable for separation of tetrahydrofuran-water mixture (Deorukhkar et al., 2016; Ghuge et al., 2017; Xu and Wang, 2006; Zhang et al., 2014). This technique has been widespread in the chemical and environmental industries, but it is not economical in many cases in the reason of its high operation cost.
The aim of this study is to remove of tetrahydrofuran from process wastewater (PWW) with extractive distillation in professional flowsheet environment. PWW from pharmaceutical industry has to be separated with the following initial composition: 5 m/m% THF and 95 m/m% Water. The product purity is min. 99.5 m/m% in both cases and 1000 kg/h PWW must be treated. The ChemCAD flowsheet of extractive distillation can be seen in Figure 1.

The first column is the extractive column, where the heterogeneous azeotropic mixture can be separated with dimethyl sulfoxide as entrainer. The second column treats the water-dimethyl sulfoxide mixture, the entrainer can be recycled and mixed into the feed stream. The optimal reflux ratio, the mass- and bottom flow rates, heating and cooling requirements, number of theoretical plates (N) and feed plate have to be optimized. As an equilibrium model for the calculation of the non-ideal vapour-liquid equilibria (VLE) the UNIQUAC model is applied. The optimized results of simulations with extractive distillation process is listed in Table 1.

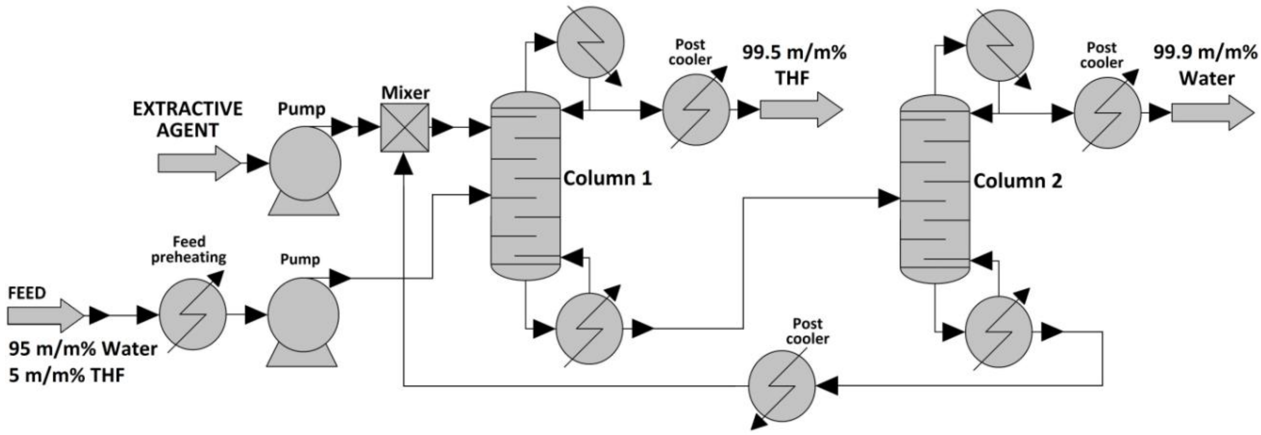

Figure 1. Flowsheet of tetrahydrofuran-water separation with extractive distillation

Table 1. Optimized results of tetrahydrofuran-water separation

		Extractive column	Recovery column
N [-]		15	20
Feed stage (PWW)		7	8
Feed stage (DMSO)		2	-
Reflux ratio [-]		3	1
	THF [m/m%]	99.5	0.05
D	Water [m/m%]	0.3	99.9
	DMSO [m/m%]	0.2	0.05

SUMMARY

The extractive distillation is investigated in professional flowsheet environment. It can be concluded tetrahydrofuran-water mixture can be separated into pure components with this operation. The goal composition, which is min. 99.5 m/m% in both product case can be reached.

This work was supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences, ÚNKP-18-4-BME-209 New National Excellence Program of the Ministry of Human Capacities, OTKA 112699 and 128543. This research was supported by the European Union and the Hungarian State, co-financed by the European Regional Development Fund in the framework of the GINOP-2.3.4-15-2016-00004 project, aimed to promote the cooperation between the higher education and the industry. The author thanks the members of Environmental and Process Engineering Research Group (http://www.envproceng.eu/en/home-en/) for their help.

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Hybrid Treatment for Sequential Removal of Phenol and Cyanide from Coke Oven Wastewater by Nanoscale Zero-valent Iron Mediated Adsorption and Biological Degradation

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CYANIDE AND PHENOL REMOVAL USING NANO ZERO-VALENT IRON

Batch studies were conducted for sequential removal of cyanide and phenol from synthetic coke oven waste water. Adsorption of phenol and cyanide using nanoscale zero-valent iron (nZVI) was employed as a pretreatment step before biological degradation to enhance the treatment efficiency. Response surface methodology using central composite design was employed for optimization of process parameters and to examine the effect of independent variables such as dose of nZVI, pH and time on removal efficiency of contaminants. Toxicity analysis of zero valent iron treated samples were carried out to select the combination of optimized factors which imparts minimum toxicity to facilitate enhanced efficiency for the subsequent biodegradation step.

RESULTS

Optimization study using Central Composite Design (CCD)

In our previous study, it was shown that Zero-valent iron can effectively degrade cyanide from synthetic coke oven wastewater with removal efficiency of 98.98 % (Tyagi et al., 2018). In this study, results obtained after optimization demonstrated that 1.75 g/L dose of nZVI removes up to 42.52 % of 1500 ppm phenol along with 97.67 % of 100 ppm cyanide in a contact time of 50 minutes at pH 9.

Adsorption study

Adsorption studies were conducted for adsorption of cyanide on nZVI at the optimized values of process parameters and most commonly used adsorption isotherms models such as Langmuir isotherm and Fruendlich isotherm were applied. Adsorption data was found to fit with the Langmuir isotherm model with adsorption capacity of 277 mg/g and R^2 value of 0.99.

Characterization

FE-SEM (Field Emission Scanning Electron Microscopy), XRD (X-Ray Diffraction) and FTIR (Fourier-transform infrared spectroscopy) analysis were carried out to confirm the adsorption of phenol and cyanide on surface and pores of zero-valent iron. FE- SEM shows the morphological changes in nZVI after treatment process. Shape of nZVI changes from being smooth and spherical to rough and elongated after treatment process which indicates the adsorption of phenol and cyanide on the surface of nZVI.

Biodegradation

For biodegradation of remaining phenol, bacteria was isolated from coke oven wastewater, which was identified as *Pseudomonas* sp. *Pseudomonas* was found to effectively degrade remaining phenol concentration, thus achieving an overall 97.67 % degradation of cyanide by nZVI and 98.2 % degradation of phenol by employing the hybrid treatment.

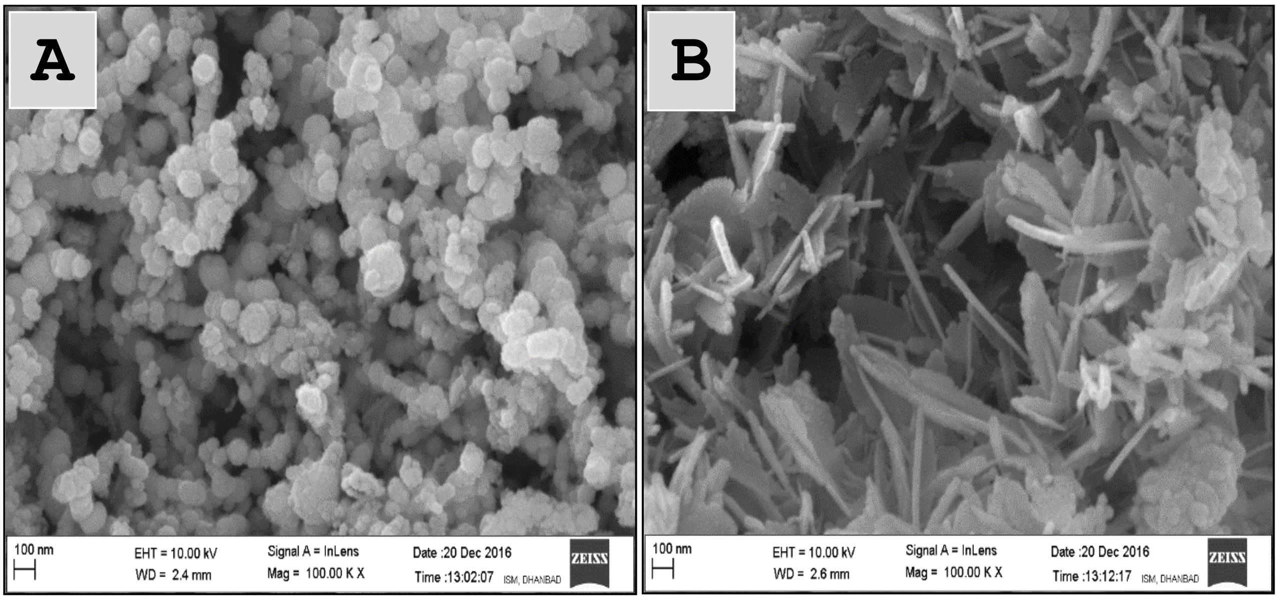

Figure 1. FE-SEM micrographs of nZVI (A) Before phenol and cyanide treatment (B) After phenol and cyanide treatment

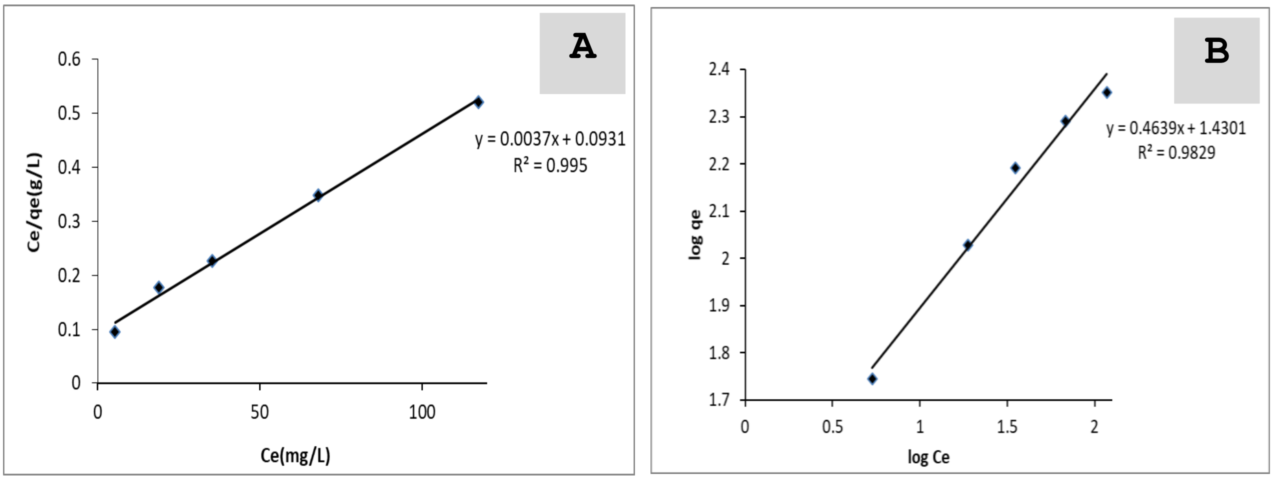

Figure 2. Linear plot of (A) Langmuir isotherm and (B) Freundlich isotherm for cyanide at adsorbent dosage of 1.75g/L, pH 9 and contact time of 50 min at 30 °C

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Recovery of Cutting Oil from Wastewater by Pervaporation Process Using Natural Clay Modified PVA Membrane

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INTRODUCTION

The solar energy and semiconductor sectors need more and better wafers. The general cutting process cannot satisfy these demands, so the wire saw process was enhanced. In the wire saw process, material called cutting oil is used in the wire saw instrument. The cutting oil is consisting of SiC particles, solvent, and additives. The used solvent must have two properties: it is easily cleaned using water and viscosity must cause the abrasive to be suspended in the solvent. Ethylene glycol (EG), diethylene glycol (DEG), and polyethylene glycol (PEG) are often used as solvents for cutting oil. DEG has the necessary characteristic properties of cutting oil. Only disadvantage of DEG is high boiling point of 245.3 °C. This point and its miscibility with water increase difficulty of its recycle. Tons of waste cutting oil is produced by wafer slicing. The waste cutting oil contains the original cutting oil, water, and Si particles. SiC and Si particles will be recovered by solid-liquid technique, but the solvent recovery is possible with dehydration method. The conventional method for dehydration is distillation. Distillation requires high energy and cost and the obtainment of high purity of DEG is not possible. Therefore, a new process must be developed. Pervaporation is a good alternative to distillation process in treatment the waste cutting oil (Chen and Huang,2018). In this study, a synthetic wastewater DEG-water was tested in pervaporation system. Natural clay modified Poly(vinyl alcohol) (PVA) membrane was used in the process. PVA is a well-known hydrophilic polymer that is used in the pervaporation process.This study has a new development in using a natural clay additive hydrophilic membrane for pervaporative dehydration of cutting oil. Clay improved the dehydration performance of membrane. The optimum clay amount and optimal operation temperature were investigated. According to the author's knowledge, this is the first study on pervaporative dehydration that deals with the effect of the different ratios of clay/PVA membranes on dehydration of cutting oil performance.

EXPERIMENTAL METHODS

Membrane Preparation

A 6 wt% Poly(vinyl alcohol) (PVA) aqueous solution was prepared at 90 °C. Certain amount of natural clay was dispersed in 10 ml of deionized water by sonication for 2 h. Clay amount was defined as the respect to the dry polymer weight. After mixing for 24 h, membrane was cross-linked by using glutaraldehyde and hydrochloric acid solution. Then final solutions were cast onto glass plate and dried.

Waste cutting oil pervaporation experiment

Pervaporation experiments were carried out by using the pervaporation system which is shown in Figure 1.

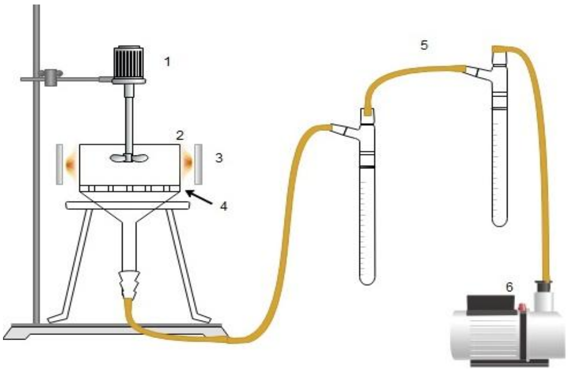

Figure 1. PV configuration. (1) agitator thermocouple (2) membrane cell (3) heating jacket, (4) membrane, (5) Dewar flasks (6) vacuum pump

The partial flux and separation factor were calculated by analysis of the compositions of both the feed and permeate streams with the gas chromatography. The flux and selectivity values were determined as the following equations:

$$J = \frac{m}{A.t}, \tag{1}$$

$$\alpha = \frac{(y_a / y_b)_{permeate}}{(x_a / x_b)_{feed}}, \tag{2}$$

where J is the flux, m is the permeation mass, t is the time in Equation 1; y_a and x_a is the weight fraction of water in the permeate and feed streams, and y_b and x_b is the weight fraction of DEG in the permeate and feed streams in Equation 2.

RESULTS AND DISCUSSION

The effect of clay/PVA ratio on flux and separation factor

The effect of the nanoclay amount on pervaporation performance was investigated. It is observed that separation factor increases, and then decreases with clay amount. This result can be related to the aggregation of clay nanoparticles. When the clay amount is greater than 3 wt %, the compatibility of the additive and the polymeric matrix decreases. This situation is resulted in microphase separation. It is also found that all nanocomposite membranes showed a higher separation factor than the neat membrane (Anilkumar et al., 2008).

CONCLUSIONS

PVA-clay nanocomposites containing different clay amounts have been prepared, and application of separation performance was investigated in pervaporation system. Pervaporation experiments showed a far excellent performance in solvent selectivity in the case of the clay loaded membrane compared to the pristine membrane. Membranes containing 3 wt% clay showed maximum separation performance. However, an increase in flux and a decrease in separation factor were observed when the clay amount became higher than 3 wt %.

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Purification of Copper Metal Using Carbonized Mandarin Peel

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INTRODUCTION

Heavy metals in industrial wastewaters pose a great threat to ecosystem. Inorganic and organic pollutants discharge from the effluent of many industrial plant such as mining, paint, leather and textile industry. Especially, heavy metal pollution is an important problem both for the environment and human health. Heavy metals are non-biodegradable inorganic pollutants that contaminate in air, water, and soil. Various methods such as precipitation, coagulation and flocculation, reverse osmosis, membrane filtration, ion exchange, adsorption have been developed for treatment of heavy metals from waste waters (Barakat, 2011). Among these methods, adsorption is the most commonly used due to the ease of processing.

The adsorbent is the key factor of adsorption process. Activated carbon is the most effective material used for effective adsorption. However, the reusability of activated carbon is low and the production cost is high. In recent years, bio-based and agricultural wastes have been used as adsorbent by converting into activated carbon. Therefore, both the cost and structural properties of activated carbon have been improved. Adsorbent fabrication from bio-based waste provides high efficiency by increasing the adsorption capacity, the surface area and porous structure of adsorbent. It is possible to provide functional chemical groups into adsorbent by surface modification. Therefore, adsorption efficiency is improved (Azimi et al., 2017; Salam et al., 2011).

In this study mandarin peel activated carbon (CMP) was prepared, characterized. The adsorption behavior of the activated carbon for copper removal was investigated. According to the data of the United Nations Food and Agriculture Organization (FAO) 2013, 21 million tons of mandarin has been produced in the world. A great part of the mandarin (872 thousand tons) is supplied from Turkey. Mandarin contains of 8-14 % peel residual. Due to its lignocellulose and phenolic content, it provides high adsorption efficiency when is fabricated as activated carbon [4].

Therefore, this study mainly focuses on the active carbon synthesising. Copper adsorption studies have been carried out at the elevated temperature and neutral pH conditions. The effects of initial metal concentration, solution pH, adsorbent dosage and contact time on copper removal were investigated. Additionally, adsorption isotherms, kinetics and adsorption thermodynamic were studied.

EXPERIMENTAL

Adsorbent preparation

Activated carbon was synthesized by means of hydrothermal carbonization under high temperature and pressure conditions. Mandarin peels were washed with distilled water and dried in oven (Santez SE-45F) at 100 °C for 24 hours. The peel carbonization was carried out four hours at 105 °C with 1M of H_2SO_4 solution in hydrothermal reactor. The carbonized mandarin peels (CMP) were dried in oven at 70 ºC for one day. Following the drying process, CMP was neutralized with 2M NaOH solution. After the neutralization, CMP were dried in oven at 70 °C for 2 hours.

Adsorbent characterization

The thermal degradation behavior of the adsorbent was characterized by means of thermal gravimetric analyses (TGA). The chemical structure was characterized using Fourier transform infrared spectroscopy (FTIR).

Ion removal

Batch adsorption experiments were carried out at elevated temperature. The effects of metal concentration, adsorbent dosage, pH, and the adsorption time. The experiments were carried out in 100 ml Erlenmeyer with a total solution of 20 mL in a fixed mixer. Absorbance were measured by UV/visible spectrophotometer (Thermo Spectronic).

RESULTS

The highest removal of 100 % was obtained when copper concentration was 5 mg/L, adsorbent dosage was 3.75 g/L, pH value was 6.9 within 150 minutes operating time. The Langmuir and Freundlich isotherms were investigated. The appropriate isotherm was defined as Freundlich isotherm. The kinetic of the copper adsorption onto CMP was obtained as pseudo-second order. As a result, it can be evaluated that the adsorbent synthesized from the waste mandarin peels is an effective candidate to be used as a low-cost adsorbent.

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Process Performance Optimization for Mainstream MBBR Partial Nitritation-Anammox Systems: The Use of Model Predictive DO Control

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INTRODUCTION

In a deammonification MBBR, the conversion of NH_4^+ −N takes place in the biofilm in which OHO and AOB exist on the exterior of the biofilm, while AAO exist deeper within the biofilm in an anoxic environment (Lackner et al., 2014). Single reactor is operated with intermittent aeration to provide both oxic and anoxic conditions in the same reactor. Selected time and DO of the oxic period should be enough for the conversion of NH_4^+ −N during partial nitration and should be less enough to not harm the Anammox activity in the following unaerated period. A model can help fast forward the process, and put to the test hypotheses difficult to practically test in reality. Therefore, using modeling in the start-up and operation of Anammox process is crucial. In order to accelerate the progress and receiving the results from the mathematical models, some computer based simulation programs are used. This study aims to simulate different scenarios evaluating the effect of aeration pattern on process performance in single stage deammonification systems.

METHODS AND MATERIALS

Steady-state simulations were carried out for the influent data (COD=599,4 mg/l, TKN=56 mg/l, NH_4^+-N=37 mg/l) collected from Bursa Dogu STP Mainstream Deammonification MBBR pilot system(550 m²/m³ specific area of media, 35 % filling ratio) in Turkey using BioWin6 simulator. The BioWin configuration of the plant is shown in Figure 1. To study the effect of intermittent aeration (i.e., transient anoxia) duration and DO level during oxic period of operation under minimum, average and maximum wastewater temperature conditions different scenarios were run with Biowin simulator. The results of simulations were evaluated in terms of effluent values from the plant together with changes in microbial population distribution of AOB, AAO, NOB, OHO on the carriers.

RESULTS AND DISCUSSIONS

The simulations demonstrated that in the operation of mainstream deammonification MBBR systems the dominance of partial nitritation over full nitrification and Anammox over denitrification is heavily dependent on bulk DO level, seasonal wastewater T changes, oxic-anoxic operation pattern and HRT of the system. Based on the simulations performed under constant HRT and T (Figure 2), summer season (Tmax) requires adjustment of DO level by making no significant changes in short oxic- long anoxic aeration pattern while winter season (Tmin) requires optimization of DO level by keeping oxic periods longer than anoxic periods. However, the simulations performed under various HRT conditions (data not shown) showed that HRT is the main factor limiting partial nitritation and Anammox efficiency during winter months. If HRT is adjusted properly at design stage based on Tmin (Figure 3), the system can perform partial nitritation and Anammox by making proper adjustments at DO level and oxic-anoxic periods.

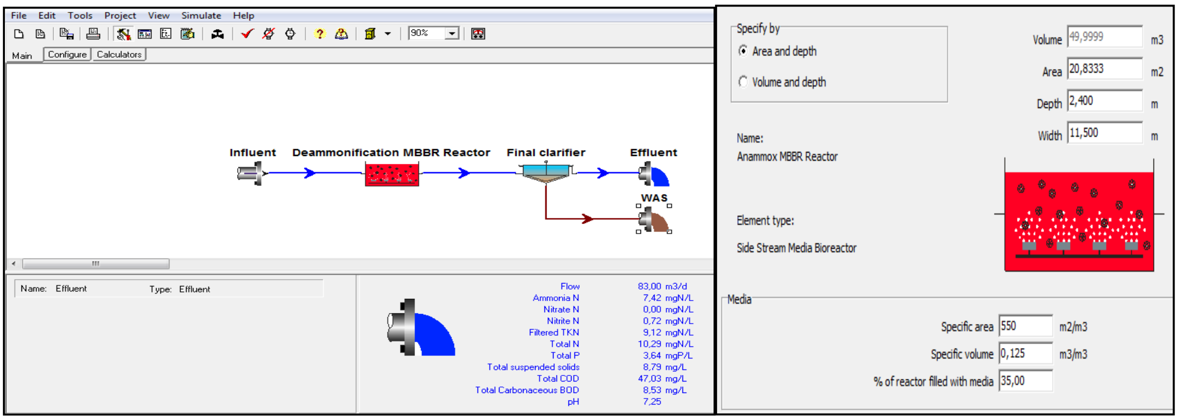

Figure 1. Schematic flow diagram and design input page of mainstream deammonification MBBRin BioWin software

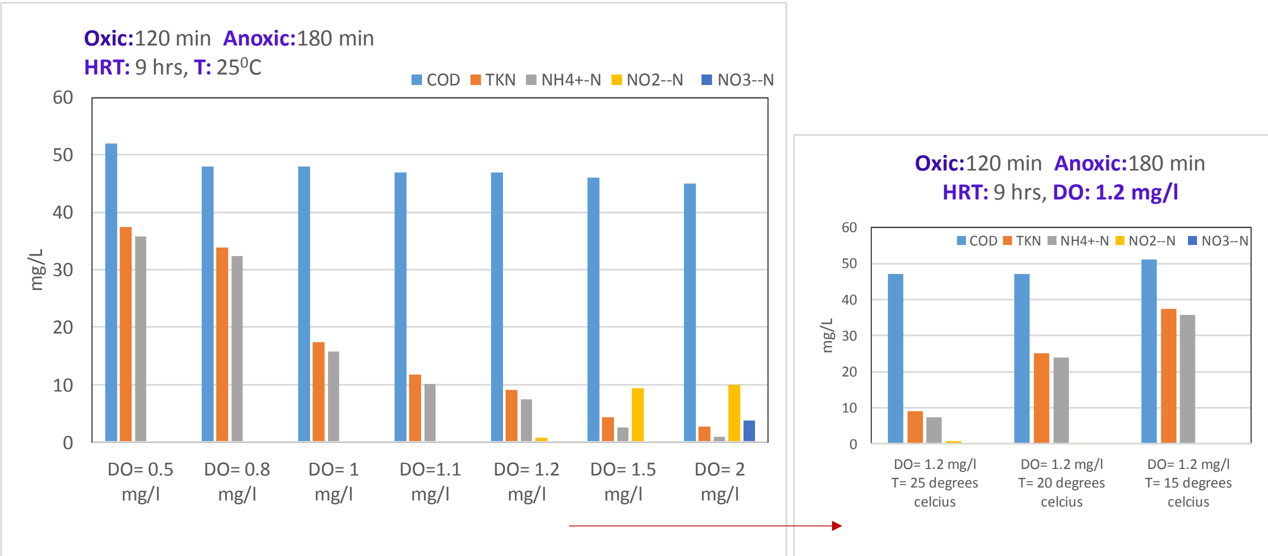

Figure 2. The effect of DO level under constant oxic-anoxic aeration pattern @ T max

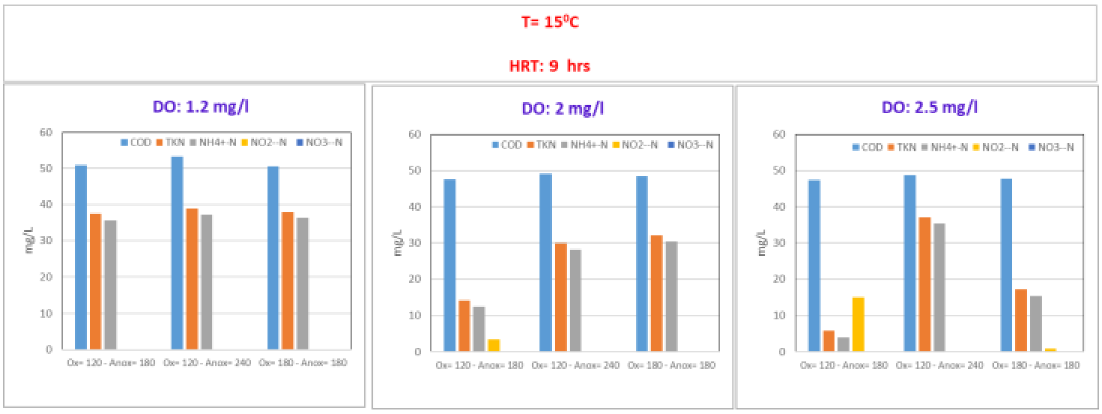

Figure 3. The effect of DO level under various oxic-anoxic aeration pattern @ Tmin

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Purification of Real Car Wash Wastewater with Complex Coagulation/Flocculation Methods Using Polyaluminum Chloride, Polyelectrolyte, Clay Mineral and Cationic Surfactant

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INTRODUCTION

Car wash stations produce large- and increasing amount of strongly polluted wastewaters, since the number of registered vehicles exceeded 1.2 billion in 2014 (worldwide), and it is estimated to be 2 billion until 2035 (Currie, 2018). Efficient purification and reclamation of these waters are highly recommended both from environmental and economic reasons (Kiran et al., 2015). Moreover, the utilization of fresh water has already been limited in some countries (e.g. Netherland, Scandinavian countries, Australia, etc.), which makes it compulsory to reclaim the used waters (Kiran et al., 2015; Pinto et al., 2017). Membrane separation is a suitable technique to achieve the reclamation, however the efficient pre-treatment of carwash-wastewaters is necessary to protect the membrane and to slow down its fouling, achieving lower costs and higher available fluxes. Among the contaminants of these wastewaters, oily pollutants have a major responsibility for membrane fouling and flux reduction, since the oil droplets can form blocks in the pores and/or a hydrophobic cake layer on the surface (Veréb et al., 2017). Conventional floatation as a first stage of a complex purification system is able to eliminate free- and dispersed oil, but emulsified oils require more effective methods (Souza et al., 2016). Although the common coagulants (Fe- and Al-chlorides/sulfates) are not able to eliminate the emulsified oil, but as it was proved in our previous study (Veréb et al., 2017), the combination of polyaluminum chloride and ionic polyelectrolytes can be effective for the destabilization of micro-sized oil droplets of oil-in-water emulsions. Therefore, these materials might be useful for the effective purification of carwash wastewaters as pre-treatment before membrane separation.

MATERIALS AND METHODS

In the present study, purification of pre-floated real car wash wastewater was investigated in a Jar Test flocculator (VELP Scientifica) by the addition of polyaluminum chloride (named as "Bopac", Unichem Kft.), different flocculants, such as non-ionic and anionic polyelectrolytes (named as "Unifloc-M20" and "Unifloc-LT27", Unichem Kft.) and different clay minerals (sodium bentonites, named as "Deriton" and "Kunipia-F", produced by Unikén Kft. and Kunimine Industries). Utilization of cationic surfactant - hexadecyltrimethylammonium bromide (Sigma-Aldrich) – addition was also investigated, since organophilized clay minerals can be able to adsorb different type non-polar contaminants, such as hydrocarbons and polycyclic aromatic hydrocarbons. Aggregation-, sedimentation properties and purification efficiencies were compared in case of different combinations and concentrations.

Purification efficiencies were determined by measuring turbidity (Hach 2100N) chemical oxygen demand (COD) and extractable oil content (TOG/TPH). COD values were measured by the standard potassium dichromate oxidation method using standard test tubes (Hanna Instruments) and applying digestions for 120 min at 150 °C in a Lovibond ET 108 type COD digester. The COD values were measured with a Lovibond COD Vario type COD photometer. Extractable oil content was measured by a Wilks InfraCal TOG/TPH type analyzer, using hexane as extracting solvent.

RESULTS

Utilization of Bopac alone (without any clay mineral or polyelectrolyte) was not effective enough to decrease efficiently the turbidity and COD of the wastewater. In case of extra clay mineral addition, the utilization of Hungarian type bentonite was more beneficial than Japanese Kunipia in relation both with the volume of the sediment and the sedimentation time. Addition of polyelectrolyte (LT27) significantly increased the size of the produced clusters and decreased the necessary sedimentation time. Simultaneous addition of the cationic surfactant (hexadecyltrimethylammonium bromide - HTABr) significantly affected the color removal by the successful in-situ production of organophilic clay minerals from Na-bentonite.

In summary, 20 ppm Bopac, 500 ppm bentonite, 0.5 mL HTAB and 0.5 ppm polyelectrolyte resulted the best purification efficiency in relation with turbidity-, COD-, extractable oil content and color removing.

ACKNOWLEDGEMENTS

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Potential Soil Quality Improvement from Digested Sludge Supernatant Liquor

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INTRODUCTION

Phosphorus removal in wastewater treatment is an important step in protecting our recipient water bodies. Phosphorus is a crucial element in plant cultivation throughout the world. The quantity of the easily available phosphate rock is depleting year after year (The Phosphate File, 1997); however the amount available in the sewage is almost constant.

Wastewater treatment plants with complemented sludge digestion produce sludge supernatant liquor in the final dewatering stage with high concentration of phosphorus (+50 mg/L). In this level of magnitude, reclaiming is a promising option.

If we remove phosphorus from the sludge supernatant entirely, then it will not re-pollute the treatment line. Therefore, we can achieve indirectly lower operational costs. As a consequence, this means phosphorus removal from the sludge supernatant has hidden benefits.

The sludge supernatant liquor can be treated with calcium (Ma et al., 2018). With this step we can remove phosphorus from the supernatant, and yield a material with beneficial attributes. In the agriculture, calcium is used to increase soil pH, thus the adsorbed phosphorus grants secondary ‘side-effect’, which is greatly welcomed.

MATERIALS & METHODS

We wanted to check if the chosen burnt lime dissolves with sludge supernatant. Fortunately, the adsorption process engaged in a positive sense. The phosphorus content formed with calcium, and some negligible amount of calcium went into the solution. The precipitant has a quick settling ability which is ideal for further phase separation. The burnt lime itself has a roughly 50 % of calcium content.

We have further investigated the possible ion exchange rates in order to realize the amount of calcium required to remove all the available phosphorus content. This was important to determinate the overfeed phenomena, where adding more calcium does not contribute effectively to phosphorus removal. Regarding the initial phosphorus content (30-60 mg/L), the ideal calcium and phosphorus ratio was found to be 10 : 1, with this supersaturation we could achieve solid removal efficiencies.

The intensity of mixing was investigated to determine how much rotational pressure is required to homogenize the solution after dosing with calcium, and whether it has any kind of effect on it. The burnt lime is not a uniformly homogenous material. It contains very small blocks beside dusty portions, which can be easily fractured with finger, however these blocks reduce the potential surface for phosphorus adsorption. Evidently, the type of mixing was not influential.

Theoretically, it is possible the increase a material solubility by increasing the solution temperature. This case was tested, because at the sludge treatment facility we can find high amount of waste heat around the biogas engines, hence it would have been a possible alternative. Unfortunately, heat exchange only increased the effectiveness of phosphorus removal with 1 % for every 10 °C increment.

RESULTS

In laboratory we have set up an experimental device to simulate the ongoing process in continuous flow design. The core method was similar to a vertical flow ion-exchange bed, such as used in labs to produce low salinity water. In practice, the supernatant was injected at the bottom, and the clarified water was collected from a drain pipe at the top. This technic required no pumping, moving parts, electricity, to reduce any possible cost.

In the modified bed, we have put the burnt lime as an adsorbent material. After and before the influent and effluent pipe, we have also inserted a patch of sponge to increase homogeneity of flow at the former, and to limit solids washing out at the later. This particular set was then regulated with manual height adjusted water pressure. The calcium mixed up at the beginning, but after the initial burst it settled down. During the experiment the flow speed could be regulated with a tap, which is suspected to be an important driving force to yield good phosphorus removal efficiencies.

PROSPECTS

At the wastewater treatment plant of Nyíregyháza no.I. we have 200 m^3 of sludge supernatant liquor from dewatering the digested sludge. This supernatant is recirculated back to the front end of the plant to treat it again. This process again has cost. With the above calculated amounts and phosphorus content, we have roughly 10 kg of phosphorus a day in a concentrated stream, which is 3.65 ton/year. This has a predicted treatment cost of circa three thousand Euros via ferric chloride, while the phosphorus content itself worth another five thousand Euros.

Our goal is to implement the mechanism of phosphorus adsorption into calcium in a bigger scale. The produced material is then easily mixable with the already existing sludge compost product, enhancing its properties superiorly to deliver a refined product for agricultural purposes.

This approach is in harmony with the recent National Sewage Waste Sludge Strategy in Hungary, which aimed to strengthen regional sludge treatment centres throughout the country (Szennyvíziszap kezelési és hasznosítási stratégia 2018-2023, 2017). The possible production costs are still under evaluation in order to meet PE unit ranges of the targeted centres.

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Ultrafiltration as a Promising Technology for Laundry Wastewater Reuse

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INTRODUCTION

Membrane performance is influenced by many factors. Especially the decrease in concentration of silica (Si) is very important issue. High concentration of Si cause a steep increase of the transmembrane pressure (TMP) resulting in higher consumption of treated water, used chemicals in chemically enhanced backwash and higher operating costs. An earlier solution for laundry wastewater recycling is predominantly focused on the use of ceramic membrane units (Sostar-Turk et al., 2005). Our vision and effort is to reduce high investment costs by the use of low-cost solution - polymeric membranes. The main advantages of these membranes are not only the low cost but also the lower built-in layout.

MATERIALS AND METHODS

Wastewater samples

Samples of wastewater were collected in three laundries in the Czech Republic (designed A, B, C). Main characteristic is given in Table 1. While the wastewaters didn't differ much in the concentration of organic pollutants, they did differ in the Si concentration. This difference is caused by the form of detergents - powdered or liquid. If the powdered one is used, the Si concentration in the wastewater is higher.

Table 1. The most important parameters of tested wastewaters

Parameter	Laundry A	Laundry B	Laundry C
pH	10.2	10.0	11.7
COD [$mg \cdot L^{-1}$l]	780	803	684
TOC [$mg \cdot L^{-1}$l]	230	226	210
ρ(Al) [$mg \cdot L^{-1}$l]	0.53	0.29	4.20
ρ(Si) [$mg \cdot L^{-1}$]	15.0	5.80	14.3

Coagulation batch tests

In coagulation batch test, aluminium sulphate, aluminium chloride and sodium aluminate were applied as coagulation agents. The pH was adjusted to the required value by adding 40 % solution of sodium hydroxide or 40 % solution of sulphuric acid. Fast stirring was carried out for 30 s at 200 rpm and slow stirring for 10 min at 20 rpm. Then 60 min of sedimentation followed.

Continuous tests

In continuous tests, an ultrafiltration unit equipped with membranes with a 20 nm pore size made of PES-PVP (polyethersulfone-polyvinylpyrrolidone) was used. For well-filtered wastewater, the flux was increased from 60 $L \cdot m^{-2} \cdot h^{-1}$ up to 80 $L \cdot m^{-2} \cdot h^{-1}$. The basic filtration time was 10 min, followed by a 30 s backwash with flux of 230 $L \cdot m^{-2} \cdot h^{-1}$.

RESULTS AND DISCUSSION

Coagulation batch tests

At the beginning, it was necessary to find the optimal coagulant and pH value. A dose of coagulant corresponding to Al concentration from 50 to 300 mg·L^{-1} and pH value from 4 to 8 were tested.

After several sets of coagulation batch tests, aluminium chloride was chosen as the optimal coagulant. The amount of sludge after sedimentation increased with increasing Al dose. As the pH value increased, the concentration of residual Si decreased but the TOC slowly increased and the filterability of the supernatant deteriorated. Al dose of 150 mg·L^{-1} and pH value of 6 were were chosen as optimal. Although the wastewaters B nad C have different characteristics (Table 1), similar trends were observed. It must be pointed out that the residual concetration of Al was negligible.

Continuous tests

After the optimal conditions were found in coagulation batch tests, the continuous tests using UF unit were performed. In these tests, 3-10 L of laundry wastewater and appropriate dose of coagulation and adjusting agent were used.

In the continuous tests with laundy A wastewater, the effect of pH on the filterability was examined. It was observed that increase of pH value causes higher TMP and the filterability worsens. Therefore, these results correspond with results of coagulation batch tests with the same wastewater.

Due to the long distance of laundry B and C, the continuous tests were performed right in there. Since the laundry B applies liquid detergents, the UF unit showed very stable parameters and very low TMP (about 0.2 bars). In the laundry C, similar results were obtained, except high TMP caused by high concentration of Si. The best results of batch tests and average results of continuous tests are given in Table 2.

Table 2. Results of batch and continuous tests

	Laundry A		Laundry B		Laundry C	
Parameter	Batch	Continuous	Batch	Continuous	Batch	Continuous
COD [mg·L^{-1}]	217	230	329	298	214	266
TOC [mg·L^{-1}l]	52.0	57.0	91.0	95.0	67.0	73.0
ρ(Al) [mg·L^{-1}]	0.44	0.67	0.027	0.22	0.19	0.61
ρ(Si) [mg·L^{-1}]	8.30	7.60	1.20	2.15	5.10	9.80

CONCLUSIONS

We have shown that, after the effective preparation of suspension by coagulation, it is possible to operate the UF unit with stable TMP throughout filtration and significantly decrease the concentration of COD and Si. These findings make the UF system with polymeric membranes a good solution for pre-treatment or re-use of laundry wastewater.

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Sulfadiazine Degradation Performance of a Fe^{3+}/CaO_2 Fenton-like System in the Presence of L-cysteine

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INTRODUCTION

Nearly 6000 tons sulfonamides were used on livestock industries in 2013 according to the report from China, and among them, sulfadiazine (SDZ), one of typical sulfonamides, accounted for more than 15 % (Wang et al., 2019). Unfortunately, up to 70-90 % of sulfonamides including SDZ were released into environment without effective treatment, and gradually accumulated in soil, groundwater or surface water on account of their recalcitrant and high-mobile property (Zhu et al., 2016). The undesirable existence of SDZ could result in the acute or chronic toxicity on organisms and the emergence of antimicrobial–resistant bacteria pathogens and related genes (Yang et al., 2018). These perniciousness and characteristics of non-biodegradability exerted potential threat on human, animals and ecosystem. Fenton-like reaction one of promising advanced oxidation process, has been widely applied in degradation of SDZ (Batista and Nogueira, 2012). Although the Fenton-like reaction was verified to be effective in removal of organic pollutants, the narrow pH operating range of Fenton reaction, the slow reduction of Fe^{3+} to Fe^{2+} and instability characteristics of H_2O_2 (Zhang et al., 2018) were limited to application in wastewater treatment.

Hence, we have proposed a Fe^{3+}-L-cys/CaO_2 system for SDZ degradation efficiency. The results indicated that L-cys could effectively promote the SDZ removal in Fe^{3+}/CaO_2 system. With the addition of 0.5 mM L-cys, the SDZ degradation increased from 2.14 % by blank to 66.43 % in Fe^{3+}/CaO_2 system. Then, it was noticed that partial ferric iron was converted to ferrous iron in the presence of L-cys. In addition, electron paramagnetic resonance (EPR) analysis and radicals scavenge tests affirmed the generation of •OH and O_2^-• in L-cys/Fe^{3+}/CaO_2 system. Possible degradation pathways of SDZ were speculated and the toxicity of SDZ intermediates was further evaluated. High concentration of HCO_3^- could obviously inhibit the degradation of SDZ and slightly negative effects on SDZ degradation were observed in the presence of Cl^- or humic acid (HA) in L-cys/Fe^{3+}/CaO_2 system.

RESULTS

More than 65 % SDZ were eliminated in the presence of 0.25 or 0.50 mM L-cys, while 0.75 mM and 1.00 mM L-cys could remove 51.47 % and 39.90 %, respectively. It could be deduced that the restriction on SDZ degradation might be thanks to competition of chelating agents as L-cys with SDZ for Fenton oxidation.

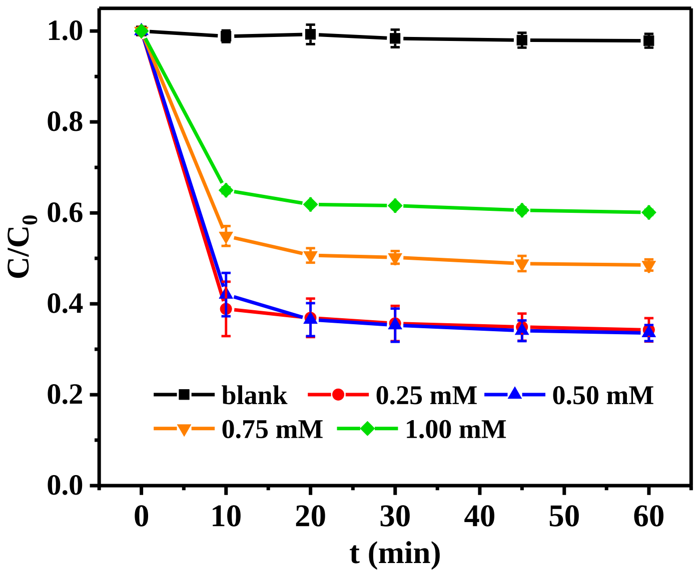

Figure 1. Effects of different L-cys concentration on SDZ degradation in Fe^{3+}/CaO_2 system. [SDZ] = 50 mg/L, $[Fe^{3+}]$ = 1.5 mM, $[CaO_2]$ = 2.0 mM, T = 20 °C

CONCLUSIONS

The performance of a Fenton-like system applying Fe3+ and calcium peroxide (CaO2) in the presence of L-cysteine (L-cys) for sulfadiazine (SDZ) degradation was investigated in this study. The results indicated that L-cys could effectively promote the SDZ removal in Fe3+/CaO2 system, compared with other chelating agents such as citric acid (CA), butyric acid (BA) and Ethylenediaminetetraacetic acid (EDTA). With the addition of 0.5 mM L-cys, the SDZ degradation increased from 2.14 % by blank to 66.43 % in Fe3+/CaO2 system.

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Anaerobic–aerobic Treatment DEHP and PCP from Real Textile Wastewater in a Sequencing Batch Biofilm (SBBR) Reactor: Effect of Aeration Time

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INTRODUCTION

Conventional parameters from textile industry have treated with general treatment methods. But another pollutant as named micropollutant is a problem for many treatment facilities. From the raw material manufacturing to end product wastewater containing these micropollutants discharge the environment. DEHP which originates from generally plastic production industries is endocrine disorder character and very harmful mainly aquatic environment (Gao and Wen, 2016). PCP which generally used as a biocide in agriculture is toxic.

SBBR process is constituted by adding bio carrier to the SBR process. The process is commonly used for some micropollutant removal with or without other treatment processes (Gonzalez et al., 2009; Muhamad et al., 2012).

The aim of this study is to investigate the treatability of PCP encountered in cotton textile wastewater and DEHP, which is one of the plasticizers used in synthetic textile production which are selected as model micropollutant from real textile industrial zone wastewater, and to determine the effect of bio-carriers addition and anaerobic/aerobic cycle time on system performance.

METHODOLOGY & RESEARCH

Experiments were carried out different anaerobic/aerobic (A/O) sequence (SET 1: 4/16, SET 2: 8/12, SET 3: 12/8, SET 4: 16/4 h) and hydraulic retention time (HRT) and solid retention time (SRT) were kept constant as 36 h and 15 d, respectively. During the study period, SBR (sequencing batch reactor) and SBBR (sequencing batch biofilm reactor), which is acclimatized K3 kaldness bio-carrier with 50 % filling ratio, were fed by real textile wastewater and their performance were monitored via not only micro-pollutants as PCP and DEHP but also macro pollutants as COD, TOC, TN and TP. SBR and SBBR were operated in 24 h cycle (0.5 h filling, 20 h (A/O) reaction, 2 h settling, 1 h withdraw and 0.5 h idle) in same sequential operation mode.

DEHP and PCP concentrations in collected samples were analyzed with GC-MS. Total DEHP and PCP removal was found from initial and effluent concentrations also removals of selected micropollutants via sorption to sludge, biodegradation and volatilization mechanisms were calculated separately.

$$C_{\text{Influent}} = C_{\text{biodegradation}} + C_{\text{sorption}} + C_{\text{volatilization}} + C_{\text{effluent}} \quad (1)$$

RESULTS & CONCLUSION

The maximum DEHP removal efficiency was 72.2 % for SBBR at 4h/16h (A/O) and 42.1 % for SBR at 8h/12h (A/O) sequence. The PCP removal efficiency was not affected significantly by the change of aeration times and the removal efficiency was between 51.1 % to 56.5 % for SBBR and 35.0 % to 43.2 % for SBR. It was determined that the addition of biocarrier resulted in 30% increase in removal efficiency for DEHP and only 13 % for PCP. Mass balances for DEHP and PCP were calculated to determine investigated micropollutants removal mechanisms. Main removal mechanism was found to be biodegradation for DEHP and PCP. According to our results, the removal mechanism was dependent on the type of biomass and aeration time.

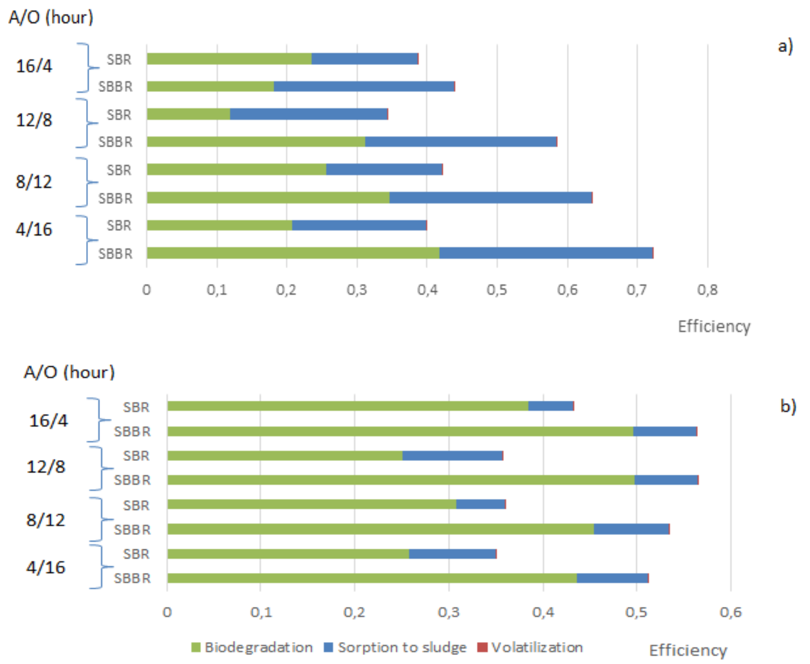

Figure 4. The fate of DEHP (a) and PCP (b) for SBBR and SBR in different aeration times

Aeration time cycle is important operation conditions for removal of the micropollutant in biological wastewater treatment plants (Grandclement et al., 2017). Adding biocarrier to the wastewater treatment system increase the same micropollutant removal rates (Toressi et al., 2007).

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Performance of Retention Soil Filters for the Reduction of Antibiotic-resistant Bacteria and Other Pathogenic Microorganisms in Raw and Treated Wastewater before Being Discharged into Surface Waters

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INTRODUCTION

Environmental quality standards for surface water bodies have been significantly expanded through the recent amendments to German regulations (OgewVO, 2016). The newly introduced substances comprise mainly anthropogenic trace elements. Limit values for hygienic-microbiological parameters are only established in currently applicable regulations, if the water is indicated for certain uses, e.g. abstraction of irrigation water for agricultural use (AGA, 1991). Nevertheless, surface water bodies are often used for hygiene-sensitive purposes such as water sports.New to the water quality and management discussion is the presence of antibiotic-resistant bacteria (ARB) in surface waters and the resulting risk to the population. Thus, the minimization of microbial inputs in all streams is sensible at least from the point of view of precautionary health protection.

In the course of climate change, precipitation patterns are expected to change in terms of quantity, incidence and frequency. Consequently, more storm and severe precipitation events will occur, which may lead to more frequent load and discharge of combined sewage overflow (CSO) and higher release from the landscape. In order to reduce the pollution of surface waters, a treatment of the discharged water by the construction of retention soil filters (RSFs), a special vertical type of constructed wetlands, has been increasingly carried out on rain overflow basins for several years. Improvement of the cleaning performance of waste water treatment plants by a fourth purification stage is subject of technical discussion in Germany. Processes such as UV disinfection, ozonation and membrane bioreactors are in the focus of interest. The limited effect of these methods on chemical trace elements is substance-specific (Rudolph et al., 1993).

MATERIALS AND METHODS

In order to investigate the effectiveness of RSFs as an additional purification stage for sewage treatment plants, an RSF test facility was established at a municipal wastewater treatment plant (WWTP) in Germany, as part of the EU-funded project (TAPES, 2016). This facility consists of three semi-technical RSFs, each with a 1.5 m² filter area. Two of those test facilities contain original material from large-scale RSFs (RSF A and RSF B) which were already in operation for several years. The filters were fed exclusively with treated waste water from the WWTP. The samples taken from the RSFs were investigated for human-pathogenic microorganisms by cultural detection. The difference of the concentrations in log units between the effluent and influent from the RSFs or WWTP was used to measure the reduction performance.

RESULTS AND CONCLUSIONS

For most of the hygienic-microbiological parameters, an additional reduction of about 1 to 2 log units was reduced by passage through the RSFs. The results of the "HyReKA" project indicate RSFs diminished ARB: there was a 2.26-log-unit (median) reduction by the filters at the semi-technical facility (Table 1). The process achieves similar or even better reduction performances than other methods discussed as a fourth purification step. Results on combined sewage overflow are described in the final reports of the research projects "SWIST IV" (SWIST IV, 2012) and "ReSMo" (ReSMo, 2016). The efficiency in bacterial reduction was different between the two large-scale RSFs, which provided the filter material for the semi-technical filters. Reduction performance was much higher in RSF A, which had an effective throttled flow rate of 0.015 L/(s * m^2) compared to RSF B at 0.03 L/(s * m^2).Influences like filter structure and influent composition can be eliminated as reasons for the disparate reduction performances by examining the individual CSO compositions in the large-scale experiments and the use of the same operation conditions in the experiments with the semi-technical filters. Both filters in the semi-technical facility operated at same flow rate (0.03 L/(s * m^2)) and did not show any significant differences. Thus, the rate of throttle drainage, based on the structural parameters discussed herein, appears to be the deciding factor in the effectiveness of the RSF hygienic-microbiological reduction performance.

Table 1. Reduction performances of the large-scale filters (A and B) and the corresponding semi-technical test facilities (1 and 2). RSF A corresponds to material from filter 1 and RSF 2 to filter 2

			Reduction in log units			
			RSF A	Test facility (1)	RSF B	Test facility (2)
Somatic coliphages	[pfu/100 ml]	*n*	24	14	24	14
		Min	1.47	1.08	0.31	1.08
		Median	3.15	2.46	1.12	2.53
		Max	4.68	3.3	1.84	3.3
E. coli	[cfu/100 ml]	*n*	25	6	23	6
		Min	1.27	1.25	0.64	0.92
		Median	2.66	2.02	1.24	1.76
		Max	4.7	3.81	4.95	3.33
ESBL-*E. coli*	[cfu/100 ml]	*n*	9	5	-	5
		Min	0.50	1.26	-	-0.07
		Median	1.08	2.26	-	2.26
		Max	3.50	3.69	-	3.69

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Purification and Improved Biogas Production from Real Dairy Wastewaters by Combining Membrane Separation with Fenton-reaction and Ozone as Pre-treatments

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INTRODUCTION

There are several investigations to reuse of dairy wastewaters, and membrane processes are promising methods to treat such wastewaters. Earlier works proved that an appropriate retention can be achieved by membrane filtration and permeates can be reused. However, membrane fouling is a limiting factor in these processes. Proteins of the dairy wastewater were found to be severe foulants for the existing membrane materials (Ng et al., 2017; Vrijenhoek et al., 2001). Membrane separation is also good for reducing the amount of the wastewater, by concentrating it. With the appropriate choice of the membranes, the purification efficiency can be high, but the concentrate needs further treatments. Fortunately the concentrated dairy wastewaters don't contain any toxic materials or dangerous compounds, but contain high amount of organic materials like proteins and lactose. This concentration mixed with proper anaerobic sludge can be used to produce biogas.

Advanced oxidation processes (AOPs), like Fenton-reaction are widely used in the fields of water and wastewater treatments and are known for their capability to mineralise a wide range of organic compounds. AOPs also have some other effects on the filtration procedure, e.g. the micro-flocculation effect (László et al., 2009). Ozone as pre-treatment also has similar effects like AOP-s, and it's also can increase the biodegradability of food waste, and can increase the production of biogas. (Beszédes et al., 2009).

In the present study the effect of the Fenton-reaction and ozone as pre-treatments of real dairy waste waters were investigated. Fluxes, filtration resistances and pollutant retentions were determined and compared. We also investigated the biogas production from the wastewater's concentration mixing with municipal sludge.

EXPERIMENTAL

The raw dairy wastewaters are coming from a mozzarella producing company in Hungary, Szarvas. Fenton reaction was carried out in a stirred vessel with 1.5 mmol/dm^3 $FeSO_4 \times 7H_2O$ (pure 99 %, VWR International, EU) adjusted to pH 3 with 1 M H_2SO_4 (pure 96 %, Farmitalia Carlo Erba, Italy), and H_2O_2 (30 %) (pure 99 %, VWR International, EU) solution, the [H_2O_2]:[Fe] ratio was 5:1 (Fenton (5:1). The UF experiments were carried out in a batch stirred ultrafiltration cell (Millipore, SN:XFUF04701, USA) with a capacity of 250 cm^3, and the filtrations were performed at 0.3 MPa transmembrane pressure and the feed solutions were stirred at 350 rpm. For filtration experiments flat-sheet PES membranes (PES6 series, New Logic, USA) MWCO (10 kDa) were used with effective membrane area of 0.00173 m^2. The initial feed volume was 250 cm^3, the UF experiments were carried out until 50 cm^3 of the total sample was filtered, where the volume reduction ratio VRR=5.

Biogas production tests were performed in triplicate in batch mode under mesophilic conditions, at 40 °C for 40 days, in an anaerobic laboratory digester with a pressure measuring head (Oxitop Control AN12 measurement system, WTW Gmbh, Germany). The capacity of digesters was 1000 mL, the volume of the concentrated wastewater was 50 mL mixed with 20 mL anaerobic sludge from the municipal wastewater treatment factory. The digester was inoculated with acclimated sludge from a municipal wastewater treatment plant in order to eliminate the possible lag-phase of anaerobic biological degradation process. The pressure values were automatically stored by barometrical heads in every 2 hours. After inoculation nitrogen gas was flowed through the reactor to prevent exposure to air. The pH was adjusted to pH 7 with 1M NaOH.

RESULTS

The Fenton-reaction and the ozone as pre-treatments both reduced the filtration resistance, thereby increased the available flux. The analysis of filtration mechanisms and models showed that the irreversible resistances causing permanent blockage of the membrane were reduced, while the reversible resistances increased probably due to the flocculating effect of $FeSO_4$ in the Fenton-reaction and the microflocculating effect of ozone. Due to the formation of large particles, after filtering, the contamination can be more easily removed from the membrane surface. The purification was effective, the combination of membrane filtration and the pre-treatments provided at least 67 % COD elimination efficiency. The biogas production from the pre-treated concentrations increased, also the methane content of the biogas was higher than in the case of untreated samples.

ACKNOWLEDGEMENT

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Assessment of Polypyrrole Nanoparticles Prepared in Presence and Absence of Surfactant for Heavy Metals Decontamination

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INTRODUCTION

Industries producing heavy metals, such as Ni, Cr, Cu, Cd, As, Pb, and Mn, are the most hazardous among the chemical-intensive industries, because heavy metals are highly soluble in the aquatic environments and can easily be absorbed by organisms (Babel and Kurniawan, 2004).

Polypyrrole black powder nanoparticles (PPy NPs) have been synthesized in the absence and presence of surfactant and tested as an adsorbent for heavy metals removal such as copper, iron, and manganese ions from aqueous solution. PPy NPs were chemically prepared by chemical oxidation using ferric chloride ($FeCl_3$) as an oxidant, distillate water as a solvent, and polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA) as surfactants. The prepared PPy adsorbents were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared spectroscopy (FTIR) and Burnauer-Emmett-Teller (BET) surface analysis. The adsorption process was conducted by varying different parameters as contact time and adsorbent dosage. The results show that copper, iron and manganese removal was 90 %, 78 %, and 70 % after 2 hours respectively, also PPy prepared without or with surfactant acts as an effective adsorbent for the removal of copper, manganese and iron ions from aqueous solution, particularly copper in wastewater treatment.

MATERIALS AND METHODS

PPy NPs synthesis without a surfactant

Typically, to synthesize PPy NPs, 2 g of $FeCl_3$ was dissolved in 100 mL DI water with vigorous magnetic stirring for one hour. Then, 1 mL pyrrole was added dropwise at room temperature. After stirring at 500 rpm for three hours, the color of solution changed from brown to dark black indicating the successful polymerization of Py. Finally, the product was centrifuged and washed with ethanol five times until the supernatant became transparent and the sample was dried in vacuum oven for 24 hr at 60 ℃. (Aliabadi and Mahmoodi, 2018)

RESULTS AND DISCUSSION

Characterization of Polypyrrole

X-Ray Diffraction (XRD) analysis. Figure 1 shows XRD pattern of PPy, PPy/PVP, and PPy/PVA. *Scanning Electron Microscopy (SEM).* The morphology of PPy, PPy/PVP, and PPy/PVA is shown in Figure 2.

Effect of time Figure 3 illustrates the effect of time on the removal efficiency of copper, iron and manganese ions from wastewater stream using 0.2 g of PPy/PVP.

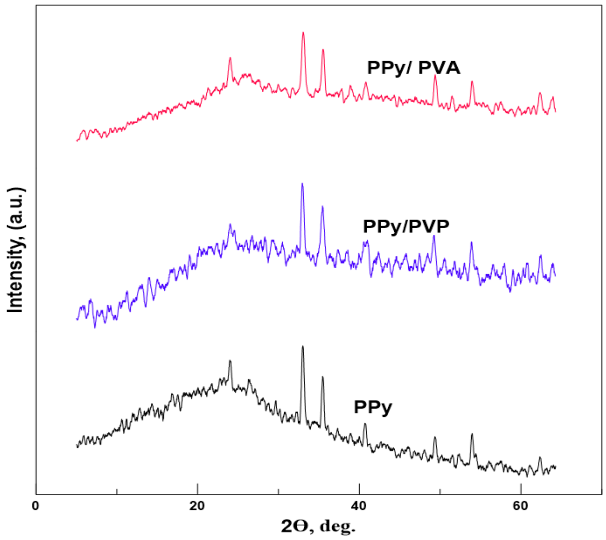

Figure 1. XRD of PPy, PPy/PVP, and PPy/PVA

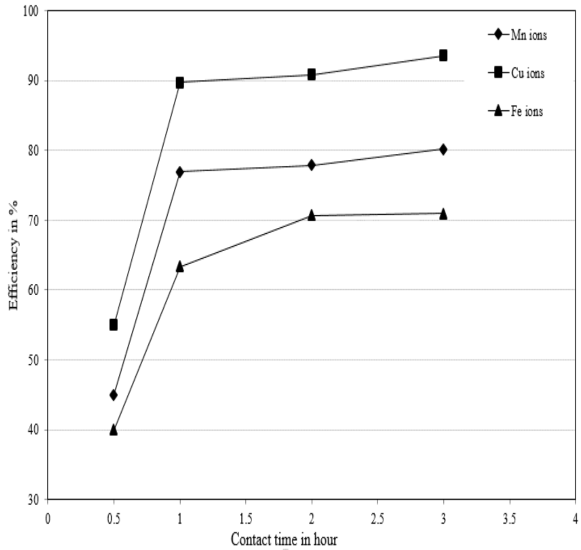

Figure 3. Effect of contact time on adsorption efficiency for 0.2 g PPy/PVP

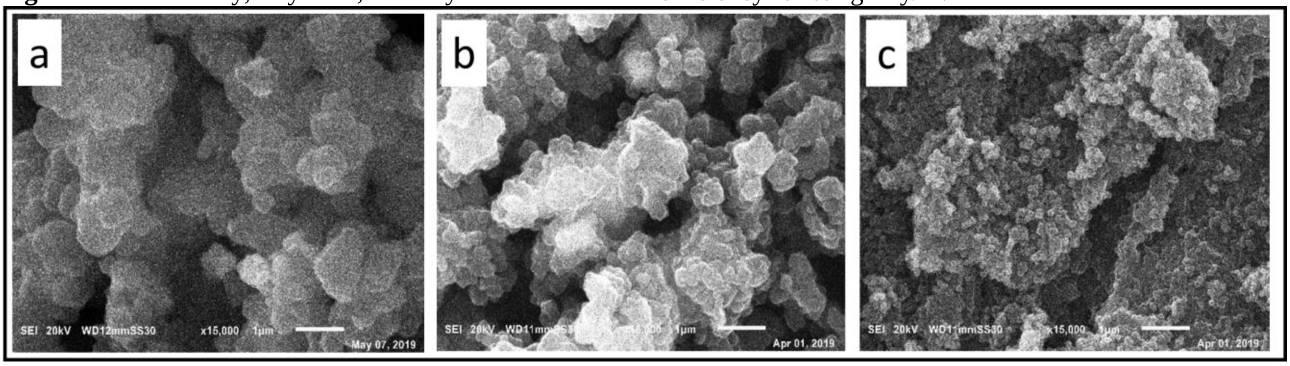

Figure 5. SEM (a) PPy, (b) PPy/PVP, and (c) PPy/PVA

CONCLUSION

PPy NPs have been prepared by chemical oxidation reaction in the absence and presence of surfactant. It worth mentioning that the amount of oxidant and surfactant was the same for PPy NPs produced. The adsorption results show that PPy NPs, PPy/PVP, and PPy/PVA are super-adsorbents for heavy metals like copper, iron and manganese, especially the copper ions with more than 90 % removal in 1 hour.

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Long-term Effects of CeO_2 Nanoparticles on Granulation of Aerobic Granular Sludge: Extracellular Polymeric Substances and the Microbial Community

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SUMMARY OF KEY FINDINGS

The average removal efficiencies of COD and NH_4^+–N were less influenced by the CeO_2 NPs, whereas the removal of TN and TP were more sensitive and decreased with the increase of CeO_2 NPs concentrations. More production and broader distribution of EPS were observed when exposed to different concentrations of CeO_2 NPs. Meanwhile, the percentage of the PN in TB-EPS increased after exposure to CeO_2 NPs. These responses are likely to promote the formation of strong biofilm architecture to resist CeO_2 NPs. The ROS and LDH levels indicated that a high CeO_2 NPs concentration was biotoxic to AGS that decreased cell viability. Long-term exposure to CeO_2 NPs increased microbial diversity, shifted the microbial community structure, and reduced the representative abundance of genera involved in nitrogen and phosphorus removal.

BACKGROUND AND RELEVANCE

With the accelerating application of CeO_2 nanoparticles (NPs), municipal wastewater treatment plants will increasingly accumulate CeO_2 NPs, thus inevitably causing potential environmental toxicity (You et al., 2017). Aerobic granular sludge (AGS) is one of the microbial aggregates, with high energy effectiveness, limited nutrients requirements and low sludge production (Jiang et al., 2019). Extracellular polymeric substances (EPS), produced by microbes, act as a gel-like matrix that twines the cells together to form bigger aggregates and provide protection for microorganisms against the harsh external environment.

The major purposes of this study were as follows: (i) to investigate the long- term (140 d) effects of CeO_2 NPs (at concentrations of 0, 1, 5 mg/L) on the removal efficiencies of nitrogen and phosphorus during the granulation and stable operation periods of AGS; (ii) to explore the effects of different concentrations of CeO_2 NPs on the contents of LB-EPS and TB-EPS, as well as PS and PN in them , in order to understand how EPS protect AGS from the toxicity of CeO_2 NPs; (iii) to elucidate the variations in the richness and diversity of bacteria related to nitrogen and phosphorus removal, and evaluate the potential impact of CeO_2 NPs on the microbial community.

RESULTS AND DISCUSSION

The LB-EPS content gradually increased from 56.46 ± 3.12 to 64.42 ± 3.06 mg/g VSS, while the TB-EPS content, which were much higher than that of LB-EPS, increased from 80.69 ± 3.74 to 136.64 ±3.96 mg/g VSS as the CeO_2 NPs concentration increased. The production of EPS (expressed as the sum of LB-EPS and TB-EPS) increased by 5.92 % (R1) and 46.60 % (R5) after exposure to 1 and 5 mg/L CeO_2 NPs, respectively. This result suggested that long-term exposure to CeO_2 NPs positively affected the production of EPS. Specifically, enhanced EPSs production prevented CeO_2 NPs toxicity to maintain the stability of granular sludge.

The relative abundances of *Comamonadaceae* and *Rhodocyclaceae*, which have been considered involved in conventional biological phosphorus removal, slightly decreased from 8.16 % and 4.95 % in R0 to 7.46 % and 4.53 % in R5, respectively. Furthermore, the relative abundances of *Burkholderia* and *Acinetobacter*, including predominant bacteria in enhanced biological phosphorus removal, significantly decreased from 15.86 % and 9.33 % in R0 to 10.63 % and 5.97 % in R1, 9.08 % and 3.18 % in R5, respectively, which were corresponded to the abovementioned decreased phosphorus removal efficiencies in R1 and R5. Owing to the dense 3-D structure of AGS, there are not only oxic zones but also anoxic and anaerobic zones in the granular sludge because of the limited oxygen penetration depth inside the granular sludge (Zheng et al., 2018). These results indicated that aerobic *Burkholderia* and *Acinetobacter* mostly occurred in the outer AGS layer, so they were more sensitive to damage when exposed directly to the NPs. However, the facultative anaerobic genus of *Comamonadaceae* and *Rhodocyclaceae*, located deeper in the sludge layer, were less influenced by the CeO_2 NPs.

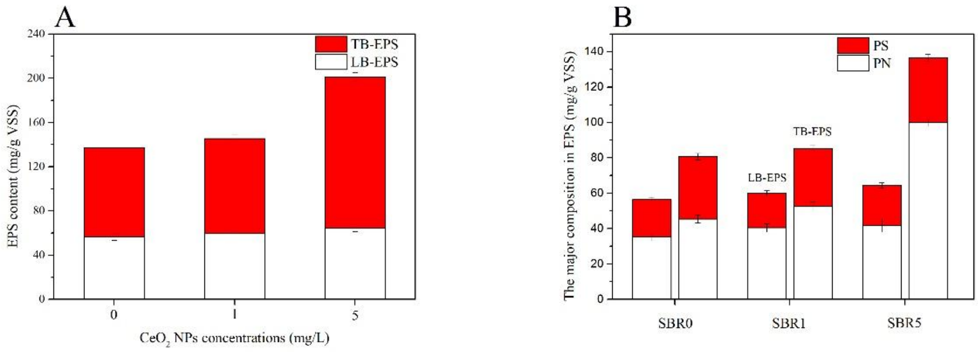

Figure 1. Effects of CeO_2 NPs on (a) EPS production and (b) the composition of stratified EPS in AGS (140 d)

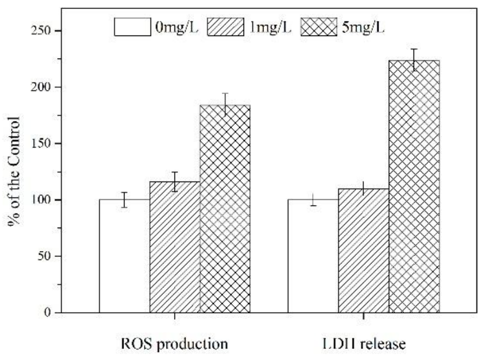

Figure 2. Relative ROS production and LDH release for AGS at different CeO_2 NPs concentration (140 d). 0 mg L^{-1} CeO_2 NPs was marked as the control (100 %)

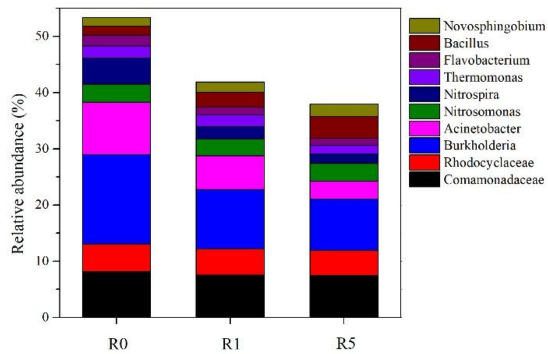

Figure 3. Microbial community analysis in R0 (0 mg L^{-1}), R1 (1 mg L^{-1}) and R5 (5 mg L^{-1}). Percentage of representative abundance of genera (nitrogen and phosphorus removal related bacteria) in AGS samples

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Cultivation of the *Nannochloropsis Oculata* during Treatment of the Reject Water from the Anammox Process

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INTRODUCTION

Innovative methods of removing nitrogen compounds from post-fermentation reject water by the use of the anammox process are currently intensively studied. Despite this, a certain charge of nitrogen and phosphorus remains in the dissolved and colloidal form after the treatment. Common practice in cases, where maximum removal of nutrients is required, is introduction of additional treatment step based on microalgae cultivation. Moreover microalgae biomass seems to be valuable substrate for the biogas production, which is an interesting approach of closed-circuit bioenergy (Jankowska et al., 2017). Marine mesophilic *Nannochloropsis oculata* seems to be very attractive for such application due to elevated temperatures of the reject water obtained after anammox process. Moreover, based on previous studies, this species reflects faster growth and lipid production rates compare to other species (Cabello et al., 2015).

The aim of this study was to select optimal conditions for microalgae *Nannochloropsis oculata* cultivation during treatment of the reject water derived from the anammox process. For this purpose, long term experiment at the different lightening and mixing condition was designed.

MATERIALS AND METHODS

Biomass origination and characteristics

The microalgae applied in the experiment was marine *Nannochloropsis oculata*, obtained from the Ugo Plankton Shop (https://ugoplanktonshop.blogspot.com).

Microalgae cultivation

Cultivation of microalgae was performed in a lab scale system consisting of two non-flow batch reactors with a volume of 4 dm^3 each, made of transparent plexiglass. The reactors operation was monitored by the use of on-line system for pH and dissolved oxygen (DO) measurements. Constant temperature of 25 °C ± 2°C was ensured during all experiments. The artificial light was provided by 6W Leddy Tube Plant with the light intensity at 400 luxes. The microalgae reactors were fed with the synthetic reject water obtained after treatment with the anammox process, in a volume which ensured initial ammonium concentration at 15 mg N-NH_4/L. Cultivation was divided into 2 periods based on the purpose of each test (Table 1). In order to control the process performance, mixed liquor samples were withdrawn from the batch reactors with a set frequency to establish NH_4-N, NO_3-N, NO_2-N concentrations. The activity of the microalgae was evaluated based on the oxygen production and utilization rates (OPR and OUR).

Table 1. The operational conditions and the goal of the experiments

	Period	Operational condition
.	Selection of the light supply strategy	▪ Ambient sunlight (june) vs 24h/0h on/off vs 14h/10h on/off ratio
2.	Selection of the of mixing conditions	▪ Continuous vs Intermediate vs No mixing

RESULTS

Effect of the light supply and mixing condtions

Among all the experiments, the lightening on/off ratio (14h/10h) has the highest value of oxygen production rate and also oxygen utilization rate, 1±0.3 mgL-1 and 1±0.2 mgL-1, respectively (Figures 1.A and B). However, based on a comparison between OPR and OUR, the ambient sunlight produced more oxygen (0.7±0.6 mgL-1h-1) than it consumed (0.2±0.2 mgL-1h-1).

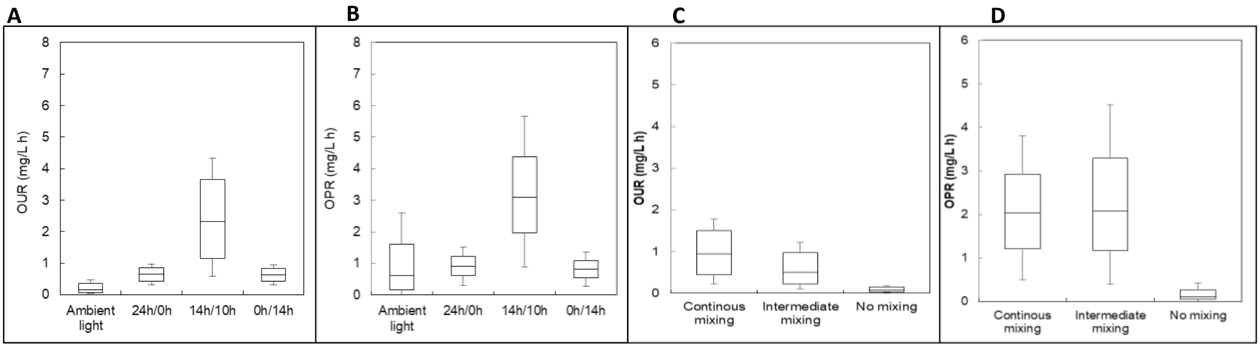

Figure 1. Box plot of (A, C) oxygen production rates (OPR) and (B, D) oxygen utilization rates (OUR) across all for the treatments. Boxes encompass the upper and lower quartiles, while the line indicates the median

Figures 1.C and D shows the slope comparison between all the obtained results. The intermediate mixing has ensured the highest values of OPR while in the case of OUR, the continuous mixing has the widest range. There is no substantial difference between the continuous mixing condition and intermediate mixing condition. A sharp decrease of microalgae acctivity was obtained when the stirring was completely stopped.

CONCLUSIONS

Continuous lightening supply does not benefit overall microalgae activity, which was improved by the division of the operational cycle into dark and light phase. What reveals importance of application of the lag phase during microalgae cultivation. Lack of the substantial differences between the continuous and intermediate mixing conditions in terms of microalgae activity, promotes second strategy due to potential savings of the energy that has to be supplied to run the system.

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The microalgae were obtained with the financial aid of the Universitas Syiah Kuala, Indonesia.

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Occurrence of Microplastics during Washing Processes

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INTRODUCTION

Every day we meet with a large amount of various plastic materials (synthetic/natural). These materials are daily distributed widely through out to the freshwaters, seas, oceans including sediments. Microplastics are defined like particles in the size range 1 nm to < 5 mm (Hernandez et al., 2017).

The major source of microplastics in wastewater treatment is from various industrial companies but also from household from washing processes. The not small source of microplastics is also from industrial laundry (Dris et al., 2017).

The wastewater treatment plants (WWTPs) is in many studies defined like the source of releasing microplastics to the environment. Here is the question, is WWTPs really like source or just barrier from companies, household and environment (Gatidou et al., 2018).

In our study we detected synthetic materials, released during washing. Subsequently was analyses also water (effluent) from WWTPs.

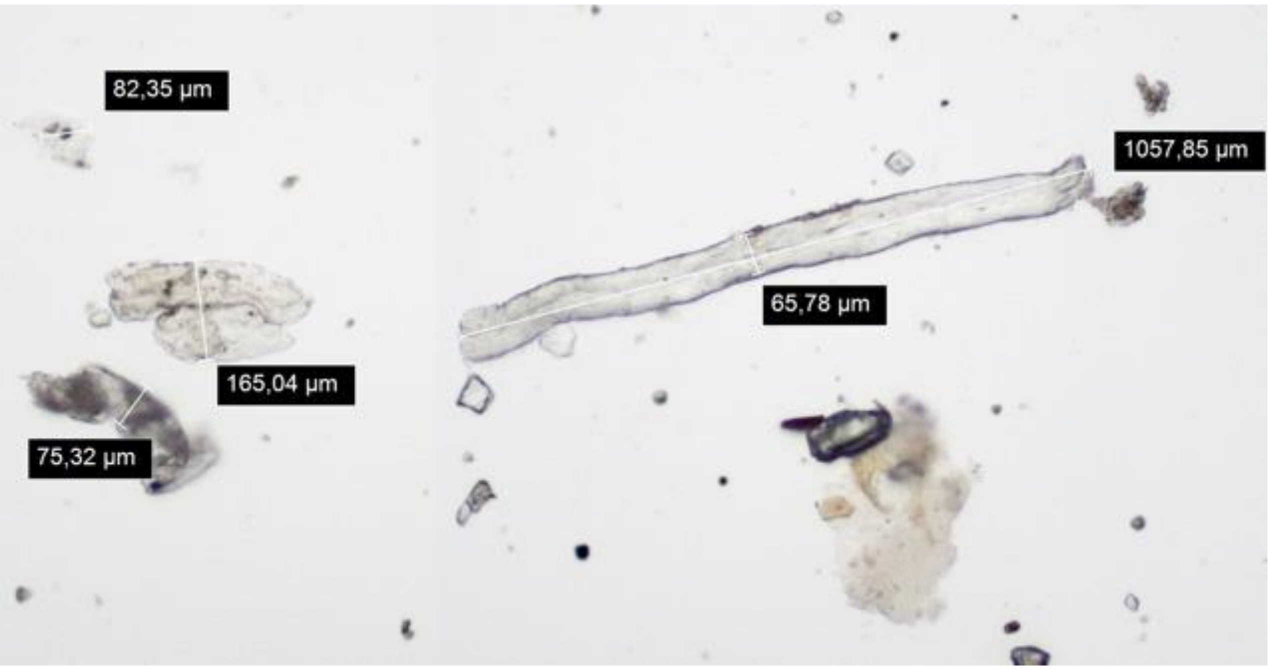

Figure 1. Captured water (without washing powder) after 45 minutes washing, used filter 100 µm under fluorescence microscopy in water after washing. Size of plastic (polyester) fragments or fibers is in range from 9 µm to 1000 µm

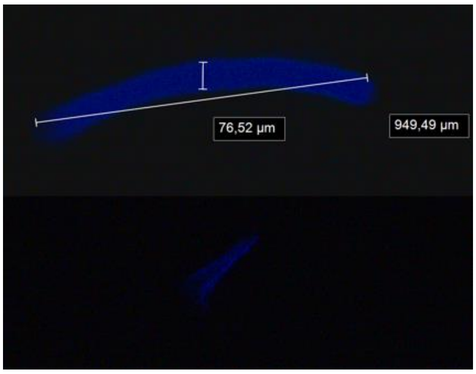

Figure 2. Captured water under blue fluorescence after used filter 100 µm. Size of plastic (polyester) fibers is in range from 80 µm to 1000 µm

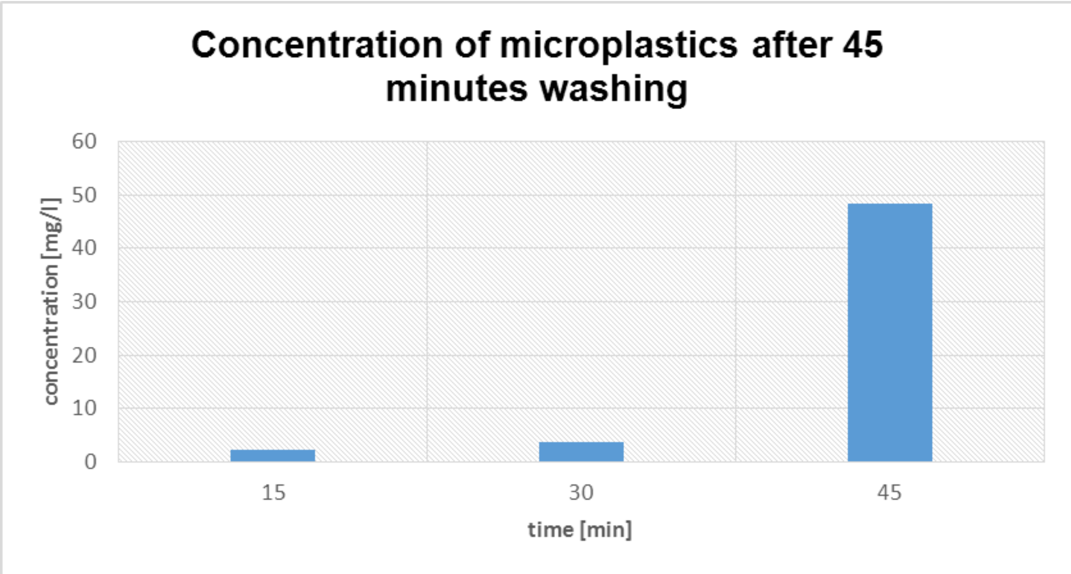

Figure 3. Graphical representation of captured microplastics on the filter, used filter 100 µm. After 45 minutes was capture 48 mg/l microplastics (PET)

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Physico-chemical Analysis of Soil in Cultivated Land in Flood Control Area

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INTRODUCTION

Daecheong dam in South Korea is a multipurpose dam with a height of 72 m, a storage capacity of 1,234,000 m^3 and a flood plain elevation of 80 m. This dam was constructed to be used for various purposes including domestic use, industrial use, agricultural use and others. Daecheong has allowed various agricultural activities in flood control areas greater than 76.5 m but less than 80m elevation to reduce increasing concern of the residents in submerged areas from the time of construction. However, nutrient leaching from different artificial sources such as fertilizers, composts, and pesticides is occurring, and nutrients flow into surface waters along with stormwater runoff during rainfall that lead to eutrophication (Burt, et al., 2008; Jarvie et al., 2013). Recently, agricultural activities in the watershed area of the multipurpose dam have been identified as the main pollutant source of the reservoir water pollution. These findings led to managing the agricultural activities in the watershed area which has been under discussion since 2006 to protect the water quality of the multipurpose reservoir. However, difficulties managing arose due to lacking proper survey and studies about water quality effects. Therefore, this study analyzed the physico-chemical properties of soil in the watershed area of Daecheong Dam and the changes of pollutant concentration in the soil for each crop to investigate the necessary data for the derivation of effective management measures.

MATERIAL AND METHODS

Hyeonri, Okcheon-gun was considered as representative of the Daecheong area where agricultural activities were concentrated and was selected as the study area in the watershed area. The main crops in Hyeonri, Okcheon-gun were corn, soybean, perilla, red pepper, Chinese cabbage, garlic, tobacco, barley and rice. Monthly monitoring from May 2018 was performed by collecting soil samples from agricultural areas and in situ soil samples around the watershed area. The collected soil samples were analytically analyzed for physical and chemical characteristics based on soil standard method and agricultural soil analysis method.

RESULT AND DISCUSSION

The pH was the highest in aralia field, while the lowest concentration was found in potato field. Electric conductivity showed high concentrations in aralia, soybeans, rice, sweet potatoes, and tobacco, and slightly lower prices in the alday, bulky feed, red pepper, and chinese cabbage arable land. Rice was found to have the highest ignition loss followed by pepper, perilla, bean, chili, cabbage, potato, bulky feed, sweet potato, tobacco, barley, corn, and alday, respectively. The average TN concentration of in situ soil was found to be 4.700 mg/kg, while alday, barley, red pepper and sweet potato cultivated land were analyzed to have greater TN concentration compared to the in-situ soil. Among the soils sampled, TN concentration in sweet potato cultivation was found to be the highest at 7.800 mg/kg, while the lowest TN concentration of about 1.800 mg/kg was found in Aralia field. Rice, aralia, corn, tobacco and potato showed low TN concentration compared to in-situ soil which was found to be 0.2-1.8 times higher concentration than the other crops.

Higher TN concentration in cultivated soils compared to in-situ soil was due to the continuous drainage of surplus nitrogen to the acidification of the soil thereby changing its structure. TP concentration was lowest in Aralia cultivated area and highest in garlic field. In the field of bean, Chinese cabbage, corn, garlic, potatoes, and tobacco, the concentration deviation was higher than the average TP concentration, and in most crops there was a variation of concentration compared to the in-situ soil. Considering Ca, a substitute cation, the cultivated soil was lower than that of in-situ soil and the lowest in potato field. The substitution cations were the highest in garlic and red pepper, which is due to the accumulation of soil in large amounts of compost and fertilizer application.

Table 1. Phyical – Chemical Characteristics of soil

	pH	EC ug/cm	Ignition loss (%)	TN	TP	SiO2	Ca (mg/kg)	K	Mg	Na
In-situ soil	6.2	136.8	14.0	4663.6	707.6	817.5	1824.0	151.2	158.4	23.9
Alday	6.0	90.3	15.3	3775.0	923.7	229.5	878.3	130.6	150.3	13.1
Aralia	6.7	180.1	6.3	2753.5	564.9	-	-	-	-	-
Barley	6.1	135.7	16.7	6814.2	873.9	424.1	737.7	194.2	156.1	20.3
Bean	6.2	159.5	25.9	4983.3	1179.8	697.6	1593.7	169.4	327.3	57.9
Bulky feed	6.0	97.9	21.8	5170.2	721.3	232.1	728.3	110.1	125.6	12.7
Chili	6.3	102.7	26.9	6531.7	969.7	174.2	937.0	276.8	168.0	29.5
Chinese cabbage	5.9	106.9	23.7	4550.6	1135.4	230.8	1090.0	97.9	158.8	26.7
Corn	6.2	127.8	15.2	4435.1	1267.3	306.3	1182.8	169.0	198.9	21.5
Garilic	5.6	139.3	10.0	4692.0	1725.7	207.9	1000.0	280.0	212.0	43.8
Rice	5.8	172.3	33.1	3972.5	708.9	354.2	1066.8	193.2	161.8	34.6
Sweet potato	6.0	172.5	19.2	7803.6	818.1	493.0	1273.2	210.9	349.9	8.9
Perilla	5.9	118.7	31.1	4698.3	956.0	315.8	1001.3	135.3	172.9	22.9
Potato	5.2	134.7	22.3	2926.0	1063.2	159.9	753.8	190.5	104.1	23.0
Tobacco	6.2	150.7	18.8	3001.4	1445.3	425.9	1728.7	69.4	266.3	43.5

CONCLUSIONS

Soil concentrations of cultivated crops were higher than those of wet field. It was also found that soybean, Chinese cabbage, corn, garlic, potato, and tobacco cultivated area showed high pollutant concentrations. It is assumed that the cultivation in the reservoir may affect the pollutant concentration of water flowing to nearby water bodies during the rainfall and should therefore be monitored continuously in the future.

ACKNOWLEDGEMENT

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Numerical Modelling of Hydraulic Transients Considering Dynamics Effects in a Water Pumping System

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INTRODUCTION

Hydraulic transient modelling is important in the design of pressurized piping systems to ensure their safety, reliability and good performance under various normal operating conditions. Several causes can originate transient phenomena such as valve maneuvers, pump trips or start-up, or by the occurrence of sudden pipe ruptures (Soares et al., 2013). Checking the minimum permitted pressures is important to prevent pipeline collapse by avoiding air release, cavitation and separation of the water column. Calculation of the maximum transient pressures is usually performed to verify if materials and characteristics of the pipe are sufficient to withstand the expected pressure loads to avoid tube rupture or damage to the system (Covas et al., 2006).

In this context, hydraulic models are useful tools whose purpose is to reproduce with accuracy the actual behavior of the physical system by means of mathematical equations. In this study, transient pressurized pipe flows caused by pump trips have been analyzed. Numerical results obtained from hydraulic modelling of a hypothetical system with similar characteristics to existing systems have been used to evaluate the performance of the transient solver.

METHODOLOGY

The case study consists of a hypothetical pipe-rising main between two storage tanks. The application of transient analysis concepts is directed to the development of a hydraulic model of pumping systems, operating during the transient regime and equipped with an air valve to protect the high point of the line *(x = 400 m)* and considering unsteady friction effects. Figure 1 presents the simplified scheme of the water pipeline profile.

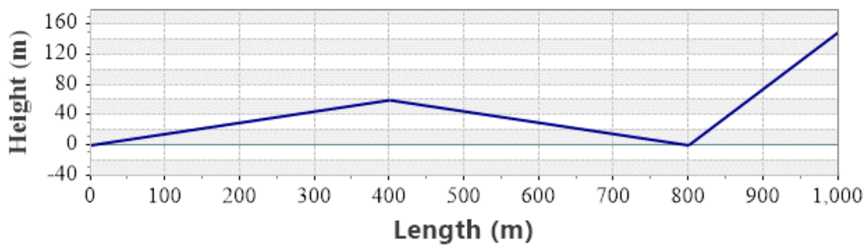

Figure 1. Water pipeline profile

In the analysis of hydraulic transients in pressurized conduits, it is possible to consider the elastic model, which takes into account the compressibility of the fluid and the mechanical characteristics of the conduit walls, used for the analysis of rapid transients with high frequencies (water hammer) (Soares, 2007).

The modelling of the flows using the elastic model can be represented by a pair of differential equations, obtained from the application of the Momentum Equation (1) and the Continuity Equation (2). The solution of the equations is usually obtained through the Method of Characteristics (MOC), which transforms the original pair of hyperbolic equations into two pairs of simple differential equations (Chaudhry, 2014; Wylie and Streeter, 1993).

$$\frac{\partial Q}{\partial t}+gA\frac{\partial H}{\partial x}+h_f=0, \tag{1}$$

$$\frac{\partial H}{\partial t}+\frac{a^2}{gA}\frac{\partial Q}{\partial x}=0, \tag{2}$$

where x = coordinate along the pipe axis; t = time; H = piezometric head; Q = flow rate; a = celerity or elastic wave speed (dependent on the fluid compressibility, and on the physical properties and external constraints of the pipe); g = gravity acceleration; A = pipe cross-sectional area; h_f = head loss per unit length.

To take into account unsteady friction effects, the friction losses, h_f, have been separated into two components (Equation 3):

$$h_f=h_{fs}+h_{fu}=\frac{fQ|Q|}{2gDA^2}+h_{fu}, \tag{3}$$

where h_{fs} = head loss for steady-state conditions (expressed in terms of square flow rate for turbulent flows); h_{fu} = head loss for unsteady-state conditions; and f = Darcy-Weisbach friction factor calculated for turbulent and laminar flow (Swamee, 1993).

With regard to the head loss for unsteady-state conditions, a one-dimensional model developed by Vardy and Brown (2007) is considered.

PRELIMINARY RESULTS

The hydraulic model for the hydraulic transients analysis in the pipe-rising system equipped with an air valve was implemented in C++ programming language. The initial tests were performed with the support of a hypothetical system, but with similar characteristics to existing systems. Comparisons of the results of the simulations of the hydraulic model developed are being carried out with a commercial software for the validation of the proposed model.

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Environmental Sustainability Evaluation under the Impact of Urbanization on the Basis of Water–Energy–Food Nexus

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INTRODUCTION

The water–energy–food (WEF) nexus attracts much attention due to the elevated public concern regarding environmental conservation and sustainability. As we head into a new era of civilization, population increase and modernized lifestyles have led to an increasing need for water, energy, and food. In the present study, an integrated evaluation of the WEF nexus was conducted for two areas with different levels of urbanization using empirical multiple linear regression in a simultaneous equation model (SEM). By incorporating the collected data into the SEM, the weighing coefficient of each identified variable was obtained, and the nexus implication was assessed in model simulation at different scenarios considering the population growth, agro-technology advancement, energy structure improvement and available water resources.

METHOD

Two areas (i.e., Taoyuan and Yunlin) with different levels of urbanization were selected to investigate the WEF nexus using the data collected from 2005 to 2015 (Ministry of Interior, 2005-2015; National Council for Sustainable Development, 2012). Ten parameters were selected in the present study. All the data were collected between 2002 and 2016. The models of sustainable water (SW), sustainable energy (SE), sustainable food (SF) and sustainable-WEF index (SI) were established considering the influence of population density (PD), as shown in Figure 1.

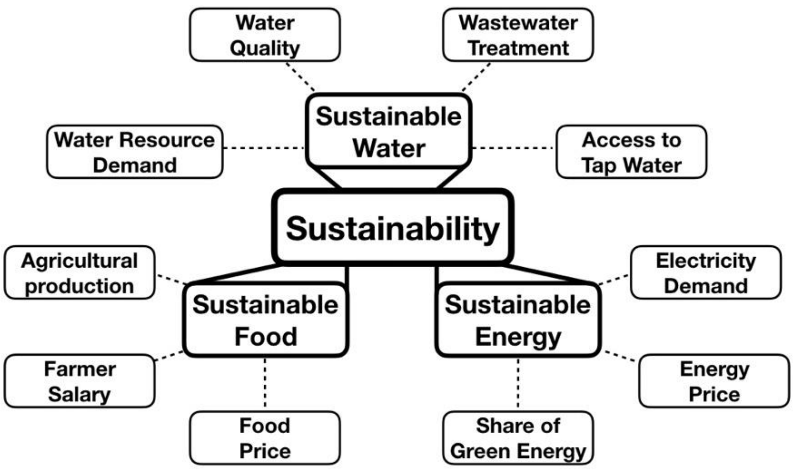

Figure 1. Sustainable water–energy–food (WEF) nexus

$$SW = \beta_0 + \beta_1 SE + \beta_2 AT + \beta_3 WQ + \beta_4 WT + \varepsilon_2 , \quad (1)$$

$$SE = \gamma_0 + \gamma_1 SW + \gamma_2 RE + \gamma_3 EP + \varepsilon_3 , \quad (2)$$

$$SF = \alpha_0 + \alpha_1 SW + \alpha_2 SE + \alpha_3 FS + \alpha_4 FP + \alpha_5 WQ + \varepsilon_1 , \quad (3)$$

$$SI = \ln(PD)^{SW+SE-SF} . \quad (4)$$

RESULT

The SI model was applied to calculating and comparing the sustainability of the two investigated areas with the consideration of population density. In 2002, the Yunlin area is considered more sustainable than the Taoyuan area, but the difference in between is not as apparent as that in 2015. The sustainability is considered to be achieved if the following criteria are met: (1) doubling the agricultural production and (2) farmer salary, (3) maintaining stable food prices, (4) increasing the ratio of tap water access more than 90 %, (5) improving the water quality to meet the requirements of the clean water category, (6) increasing the ratio of the appropriate wastewater treatment more than 90 %, (7) maintaining stable energy price, and (8) increasing the power supply of renewable energy by more than 50 %. Three scenarios of current practice, sustainable practice (the UN standards), and unsustainable practice (opposite implementation of the UN standards) were simulated using the data in 2016 as the basis. For the variation of the population, the estimation for a population density decrease of 20 % in 2050 for the two areas was adopted. In 2016, the SI in Taoyuan and Yunlin are 940.52 and 782.34. If the resource-consuming behaviors remain the same, the SIs would decrease 3.0 % and 3.5 % in Taoyuan and Yunlin in 2050, respectively. With the efforts to achieve the sustainable goals in 2050, the SIs decrease by 5.4 % and 13.8 % in Taoyuan and Yunlin in 2050, respectively. If an unsustainable development occurs in 2050, the SIs will increase by 30.7 % and 15.2 % in Taoyuan and Yunlin, respectively.

Table 1. Results of the sustainable WEF index

Year	Taoyuan				Yunlin				Sustainable WEF Index	
	PD_T	SW_T	SE_T	SF_T	PD_Y	SW_Y	SE_Y	SF_Y	Taoyuan	Yunlin
2002	1468.20	96.02	19.31	−6.13	575.44	167.46	22.17	58.28	885.66	834.75
2003	1492.34	95.27	19.73	−5.89	573.66	168.10	23.20	53.20	883.48	877.22
2004	1517.69	95.39	19.55	−7.18	570.77	168.00	23.34	56.19	894.52	857.80
2005	1540.04	95.83	19.98	−7.00	568.11	168.23	23.39	58.92	901.37	841.63
2006	1565.30	96.09	20.07	−7.60	564.36	168.42	23.53	58.12	910.36	847.91
2007	1584.80	96.39	20.17	−7.54	562.17	168.50	23.59	57.14	914.40	854.48
2008	1604.23	97.10	19.99	−6.53	560.63	168.36	23.61	62.79	912.36	817.59
2009	1620.69	96.25	20.21	−6.71	559.94	168.35	23.58	64.18	910.30	808.38
2010	1639.75	95.90	19.87	−8.05	555.96	168.27	23.52	62.69	916.55	816.00
2011	1648.96	95.76	19.99	−8.31	552.79	168.23	22.58	62.98	919.02	807.24
2012	1662.77	96.23	20.50	−8.08	550.80	168.09	24.06	64.74	925.62	804.13
2013	1674.12	95.76	20.91	−8.19	548.32	167.96	23.62	65.23	926.84	796.87
2014	1685.84	95.60	22.92	−4.04	546.43	168.19	23.45	66.84	910.62	786.67
2015	1724.70	95.89	20.18	−9.00	542.00	168.21	23.60	65.58	932.12	794.65
2016	1759.09	96.35	20.80	−8.72	538.31	168.27	23.88	67.74	940.57	782.34
Avg.	1612.57	95.99	20.28	−7.26	557.98	168.18	23.41	61.64	912.25	821.84

Table 2. Scenario simulation results

Trends	SI Taoyuan	SI Yunlin
2016	940.52	782.34
Maintaining in 2050	912.43	754.58
Sustainable in 2050	725.47	614.35
Unsustainable in 2050	1229.25	901.45

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Exploring the Distribution of Pesticides and Their Ecological Tisk for *Prionailurus Bengalensis*

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INTRODUCTION

Risk assessment has been widely used for environmental management, but their application to wild mammal health risk analysis has not been reported before. In order to establish a method to assess the risk caused by environmental pollution to local species, this study aims to establish a risk assessment model for wild mammals. The target species of this study is *Prionailurus bengalensis* (leopard cat), an endangered species that is at the top notch in the food-web structure in Taiwan and their existence is significant for ecological stability and biodiversity (Pei and Chen, 2011). The habitat of leopard cats is mostly located in the low elevation mountain regions, where is highly developed (Chen et al., 2016). To investigate the harmful factors affecting their survival, the ecological stability of leopard cats was evaluated in the context of the distribution/residual of environmental agents applied in agricultural activities. The research area was selected in the low elevation mountains of Miaoli where leopard cats survived. The risk assessment model was established and factors that threaten the survival of them were explored to determine the direct correlation of environmental pollutions caused by economic growth and the existence of leopard cats.

METHOD

Soil samples and parameter setting

The study area is at low-elevation mountainous townships of Tongsiao, Tonglu, Yuanli, Sanyi, Gongguan, Houlong, Sihu, Dahu, and Jhuolan in Miaoli County, Taiwan. Parameters including toxicological information and leopard cats' food data were collected. Reference dose (RfD) was used to measure the toxicity of compounds. The average activity range of a leopard cat is 5 km^2. The food of leopard cats was divided into five types: grasses and cereal shoots, arthropods, soil invertebrates, mammal and bird.

Risk assessment

The food intake rate (FIR (g/day) of leopard cats was calculated based on the individual's daily energy expenditure (DEE (kJ/day)) and total food energy (FE (kJ/(dry g))). HQ is assessed to represent the degree of influence of a harmful chemical on the organism (EFSA, 2009).

$$FE_{total,\,fresh} = \sum_{i=0}^{n}\left(PD_i \times FE_i \times (1 - \frac{MC_i}{100}) \times \frac{AE_i}{100} \right),\ DEE = 6.52 \times 10^{0.715 \times \log BW}\ , \tag{1}$$

$$FIR = \frac{DEE}{FE_{total,\,fresh}}\ ,\ DDD = \frac{C \times FIR}{BW} \times PT\ ,\ HQ = \frac{DDD}{RfD}\ ,\ HI = \sum HQ\ , \tag{2}$$

where PD_i is the weight ratio of a given intake food to the total food (PD=0~1). FE_i is the energy contained in the dry weight of a single food type (kJ/(dry-g)). MC_i is the percentage of moisture in food (%). AE_i is the percentage of the assimilation efficiency of a species to a particular food (%). BW is the average weight of the leopard cat. DDD is the hazardous material dose in daily dietary (mg/kg-day). C is the concentration of hazardous material (mg/kg, ppm). PT is the fraction of the diet within the treated area (0~1). HQ is the hazard quotient by a single pesticide residual in a single type of diet. HI is the total risk of all pesticide residues in the total diet, which is the sum of HQ.

RESULT

The average body weight of the leopard cat is 5 kg and we obtained the DEE of 2875.8 (kJ/day). The total FE is 4.37 (kJ/dry-g) and the FIR is 657.8 (g/day). Daily food intakes for grasses and cereal shoots, arthropods, soil invertebrates, mammals and birds are 65.78 g, 65.78 g, 65.78 g, 361.8 g and 131.56 g, respectively. As can be seen from the results, sundry pesticides residue in agricultural areas resulted in an acuity decline of leopard cats and an increase in the probability of poisoning, which reduces the survival chance of the leopard cat indirectly. Although the concentration of each prevailing pesticide is below the “Pesticide Residue Allowance Standard” proposed by the Ministry of Health and Welfare, their locations of application have a significant overlap with leopard cats’ activity zone. With the effect of bioaccumulation, pesticide residuals would cause considerable harm to leopard cats. The distribution of HI values is closely related to land use patterns and HI values in major agriculture activity areas such as Yuanli and Zhuolan are significantly higher than those in other areas. This study confirmed that this method can be used to assess the ecological risk for the leopard cat.

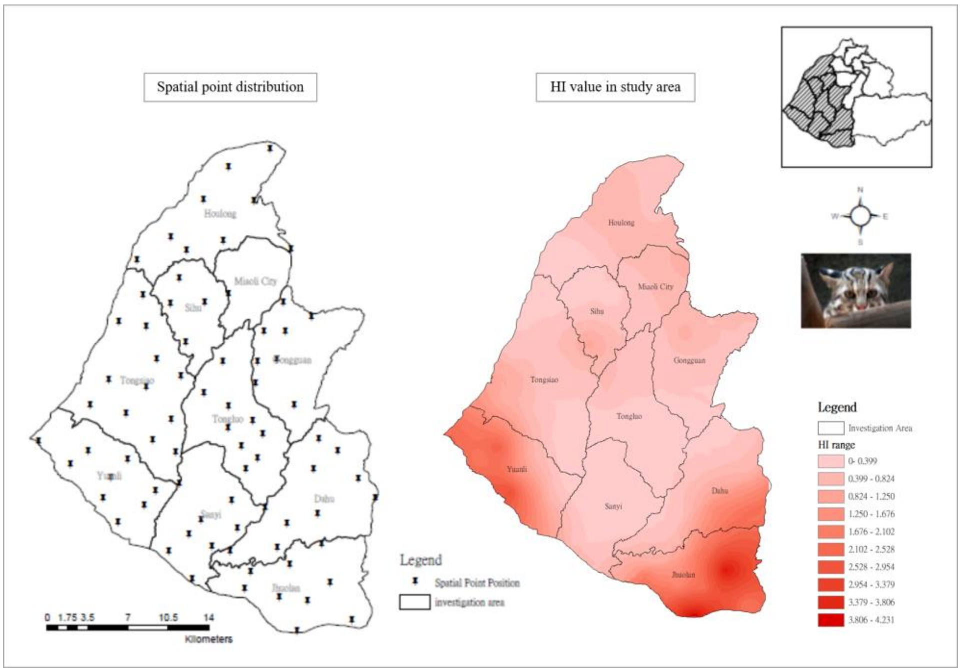

Figure 1. Sampling point distribution and hazard index analysis

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Calculating of the Wave Length of Undular Jump

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FORMATION OF UNDULAR JUMP

Undular jump is one of the types of hydraulic jump and characterised by a series of waves gradually diminishing in size that stretch out over a long length. It may occur in irrigation and water supply channels, flow under the vertical sluice gate, in estuaries during some period of the tides, in narrow or shallow straights subjected to strong currents, at the downstream of low drop structures or in a transitional region from steep to mild sloping channels, etc. (Chanson, 1995). This kind of jump occurs at low supercritical inflow Froude numbers (Fr_1): traditional hydraulic books (e.g. Chow, 1959) report its occurrence for $Fr_1<1.7$. However, there is disagreement as to the upper Fr_1 value for undular jumps: some scientists think it is 1.6 (Reinauer, 1995), or around 1.7 (Ohtsu et al., 2001) for fully developed flows. Other scientists consider that undular jump can formation, when Froude number is more than 1.7, e.g. $Fr_1< 2.1$ (Riabenko, 2004), $Fr_1<2.9$ (Chanson, 1995) and $Fr_1<3.6$ (Montes, 1986), etc.

It is very important to know, when undular jump can formation it influences of hydraulic structures and environment. The propagation of the downstream waves must be taken into account for the design of canals and for the maintenance of natural channels. The wave height is an important design parameter that determines the required height of the canal sidewalls (Chanson, 1995).

CALCULATING THE WAVE LENGTH OF UNDULAR JUMP

One of the main parameters of undular jump, which should be defined, is wave length. Analysis of undular jump issue showed that majority of scientists give large attention to defining the depths of this phenomenon. However, the determination of wave length of undular jump is important as well. There are not many formulas for calculating this parameter due to many scientists have used formula of other kinds of wave, that does not always give correct results. The aim of this paper is to compare some existed equations for calculating the wave length of undular jump with experimental data.

Andersen's formula for calculating wave length of undular jump

One of existed formula was suggested by Andersen (Andersen, 1978)

$$\lambda = h_2\left(\frac{1{,}79}{\left(1-\sqrt{Fr_2}\right)^{0.614}}\right), \tag{1}$$

here h_2 is second conjugated depth of undular jump and Fr_2 is Froude number in cross-section with h_2.

Reinauer's & Hager's formula for calculating wave length of undular jump

This formula depends on depth h_1 and Froude number Fr_1 in the initial cross-section of undular jump (Reinauer, 1995).

$$\lambda = h_1[6.5(1 + 0.5(Fr_1 - 1))] \quad (2)$$

Suggested formula for calculating wave length of undular jump

During theoretical investigation of undular jump it was confirmed the relation between wave length of undular jump λ parameter of cnoidal waves Δ. Based on this hypothesis, the next formula was suggested to calculate the wave length.

$$\lambda = 3{,}95\Delta + 3{,}0a \quad (3)$$

where a is height of first wave of undular jump.

NUMERICAL COMPARISON OF CONSIDERED FORMULAS OF WAVE LENGTH

To define which formula is the most proximate, we used experimental data of different scientists (Chanson, 1995, Riabenko, 2004) and compared with obtained data by different formulas (Figure 1).

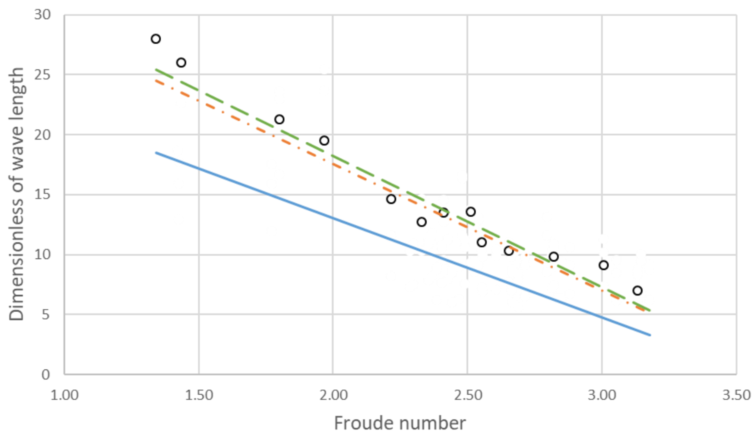

Figure 1. Comparison the experimental data with data which were obtained by formulas (1)-(3): —– – data by formula (1), -·- – data by formula (2), – – – data by formula (3), ○ – experimental data

CONCLUSIONS

It is necessary to calculate wave length of undular jump together with other important parameters of this phenomenon, i.e. maximum depth and second conjugated depth.

For calculating wave length, the formulas (2) and (3) can be used. They showed good convergence with experimental data (fig. 1).

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Detection of Polycyclic Aromatic Hydrocarbons at Black Sea Region with Using Semipermeable Membrane Devices (SPMDs)

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are large aromatic planar compounds formed by a variety of combustion processes (Baird et al., 2005). Within the scope of this study Polycyclic Aromatic Hydrocarbons have been determined with Semi-Permeable Membrane Devices (SPMDs).

PAHs are ubiquitous environmental contaminants, deriving mainly from anthropogenic inputs with a small contribution from events such as forest fires (Compaan et al., 1992). As a result of combustion; PAHs can make contamination to the air, from air to surface water, groundwater and soil. PAHs are cancinogenic and toxic compounds. The ability of PAH-containing mixtures to induce human cancer has been known since 1775. They have low solubility at water but high solubility at tissue; which explains why that pollutants called hydrophobic. Because of their low solubility at aquatic systems PAHs are difficult to determine. In that point making sampling with Semi-permeable membrane devices is a good solution.

Semi-permeable Membrane systems are passive samplers which were formed in 1990 in order to detect metals in water. As a result of the development work carried out on SPMD, it is possible to use it for micropollutant analysis. SPMDs consist of a thin-walled membrane tube made of low density polyethylene with triolein. Triolein basically works like fatty issues. SPMDs are taken from the aquatic environment after being left in the water until it is saturated by the pollutants.

In the study, aim of using SPMDs is determinate 16 priority PAHs at low concentrations which cannot be determinated by within standart methods. Sampling stations were chosen as Amasya province and the Turhal point at Tokat province. This stations at Yeşilırmak Basin in the Black Sea Region at Turkey.

Figure 1. Yeşilırmak basin sea stations

MATERIAL AND METHODS

Two SPMDs were placed to the selected points, with the sampling times being 3 and 6 days. The first SPMDs taken at the end of 3 days, second SPMDs were taken from the sampling points at the end of 6 days. One of other aim is in the study is to see the pollutants in SPMDs after 3 and 6 days. At all of the analyses GC-MSMS (Thermo TSQ 8000 Triple Quadrupole) is preferred for the analyses of semipermeable membrane devices because of the results can be smaller than ppt level.

RESULTS AND DISCUSSION

At the end of three days sapling pollutant quantities for Amasya point, the lowest pollutant level 4,5161 * 10-9 pg / Benzo [a] pyrene with SPMD; For Turhal, Benzo [b] fluoranthene is 1.32284 * 10-9 pg / SPMD. As a result of the 3-day sampling, the highest level of pollutants for Amasya is 0.001280685 pg / SPMD as Phenanthrene; For Turhal, Phenanthrene is 0.000507 pg / SPMD.

At the end of the sixth day the highest level for Amasya point is 0.001229 pg / SPMD. Phenanthrene as SPMD; Dibenzo [a, h] anthracene was the lowest of 4.96 * 10-9 pg / SPMD. The lowest level for Turhal is 1.73598 * 10-9 pg / Benzo [b] fluoranthene as SPMD, and the highest level is Phenanthrene with 0.000633056 pg / SPMD.

ACKNOWLEDGEMENT

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DARE-TU Project: Co-creation of Affordable and Clean Pumped Irrigation for Smallholders

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INTRODUCTION

Given the substantial amount of smallholder farms worldwide (Lowder et al., 2016), intensification of their crop production is crucial for increasing local and global food security (Tscharntke et al., 2012). Although irrigation water is not the only influencing factor in agriculture, improving (or enabling) its access and control is a major option to secure smallholder production as well as improving their livelihoods (Burney and Naylor, 2012). A way to achieve this goal is to provide intensified irrigation by using pumping technologies to water farmlands that will remain otherwise unirrigated. However, many current irrigation systems operate on electricity- or diesel-based pumping technologies. On one hand, this means high operation and maintenance costs due to the continuous use of electricity and expensive fossil fuels, respectively (Aliyu et al., 2018; Chandel et al., 2015), thereby becoming (too) cost-intensive for smallholder farming. On the other hand, these systems are strongly linked to air pollution due to their gaseous emissions and noise, hence affecting the local environmental quality as well.

A more environmentally sound and at times less expensive alternative for smallholders would be pumped irrigation systems that operate on renewable energies, i.e. solar power, wind power, biomass/biogas, hydropower (Gopal et al., 2013). From these, hydro-powered pumping (HPP) technologies, namely those hydro-mechanically driven by the water they lift, pose further advantages over their other RE-based counterparts. (i) Their energy source is, in general, locally available 24/7, relatively concentrated and more predictable; (ii) they have a higher power-to-size ratio, thus are more cost-effective; (iii) they are mechanically less complex and more robust, hence less maintenance-demanding and long-lasting; and, (iv) they are typically more efficient (up to 85 %) (Fraenkel, 1986). Despite these obvious advantages, most HPP technologies have not been used steadily over time, and are largely ignored nowadays. Moreover, their pitfalls lie beyond their mere technical performance: failures and misuse, thus eventual phasing out of HPP technologies, have found their roots in lack of proper management systems and business models (Intriago Zambrano et al., 2019).

RESEARCH APPROACH

In this context, the DARE-TU project aims to study a more robust, empowered, and sustained integration between the Integrated Turbine Pump (ITP) – an innovative HPP device that operates simultaneously as pump and turbine – and smallholder irrigation schemes, by means of an iteratively co-created Sustainable Product Service-System (SPSS). The latter, built by the bottom-up inputs of stakeholders (e.g. smallholders, businesses/organizations), does not focus in merely selling potentially unaffordable pumps but in providing ITP-based irrigation services to the community. In this way, the SPSS is able to cope with financial restrictions, management issues and environmental concerns, while at the same time creating social value for the smallholders and profit for the businesses (Boukhris et al., 2017). Furthermore, this process is conducted under the light of the innovative Context Variation by Design (CVD) approach, through which proposed SPSS designs are intentionally and systematically exposed to different contexts in early stages, so richer and more-satisfying solutions can be achieved (Kersten et al., 2017). In particular, this paper will focus on the co-creation process of the ITP-based SPSS in two different smallholder irrigation schemes (i.e. contexts), located in Nepal and Indonesia, respectively.

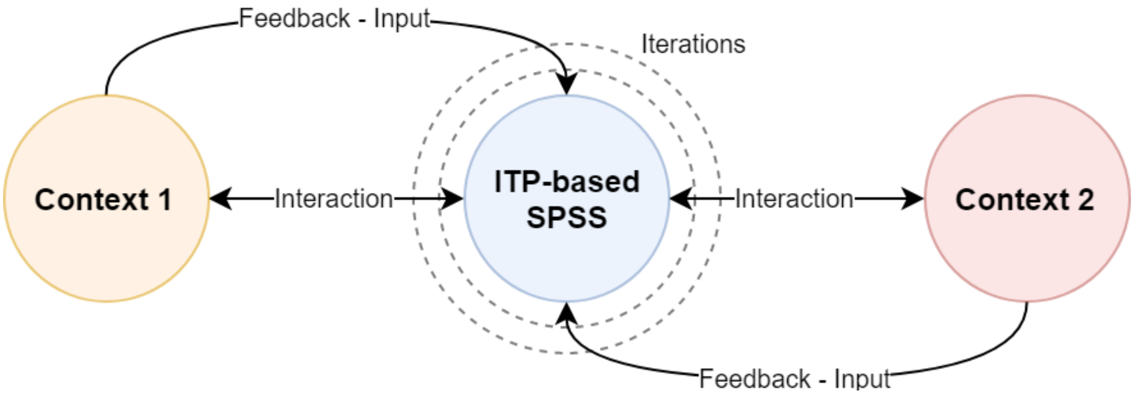

Figure 1. Co-creation of ITP-based SPSS. An early SPSS model, comprising both product (ITP, infrastructure) and service (irrigation water, others) is exposed to two different contexts; the reaction of (non)human agents (i.e. smallholders, other stakeholders, landscapes) in each of them, serves as feedback to co-create a second iteration of the SPSS that will be then re-exposed, thus repeating the cycle

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Assessment of the Reliability of a Hydraulic Model of the Topolnitza River with a Limited Number of Data

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STUDY AREA

The present study examines the upper reaches of the River Topolnitsa and three of its tributaries. The river is located in western Bulgaria and springs from Sredna Gora. The total length of the river is 129 km. In this case are considered 42 km from the river - from the mouth of the first tributary to the Topolnitsa dam. The displacement in the area under consideration is 580 m altitude at the mouth of the first inflow until 398 m altitude before the dam. The width of the river is 10 to 15 m long and the river bed has a depth of about 0.40-0.60 m. The right slopes of the valley in the section are sloping (10-15 degrees), and the left - steep. The slope of the river is 3 – 4 %. /(Varlev et. al., 1998).

HYDRAULIC MODEL

Used software

The software used for the model is MIKE Hydro River. This model allows a complete modelling of the hydraulic dynamics of the river (MIKE Hydro River User Guide). In the case under consideration, the water level over the period does not exceed the maximum cross-sectional height so the tributaries are inputs to the model as point sources.

Impute data

For the construction of the hydraulic model, the DEM (digital elevation model) and data on the water discharge in the river for the period 2016-2017 provided by Bulgarian National Institut of Meteorology and Hydrology were used.
The model is composed as set:
• Cross sections of 200 m spacing
• Manning roughness ratio 0.035
• Simulation period from 01.01.2016 to 31.12.2017
• Time step - 10 seconds
• Grid spacing - 50 m
• Boundary conditions - discharge at the beginning of the model, discharge after each of the tributaries, Q-H relation at the last point of the modelled area.

Modelling of the water flow is based on the solution of the one-dimensional equation for shallow streams (Saint Venan equation). The computational scheme is applicable to vertically homogeneous flow conditions.

RESULTS

At the last point of the model there is a hydrometric station. A comparison was made between the results from the model at the last point of the river and the observed ones (Figure 1). It is obvious that the data obtained discharge very little deviations from the actual measurement results.

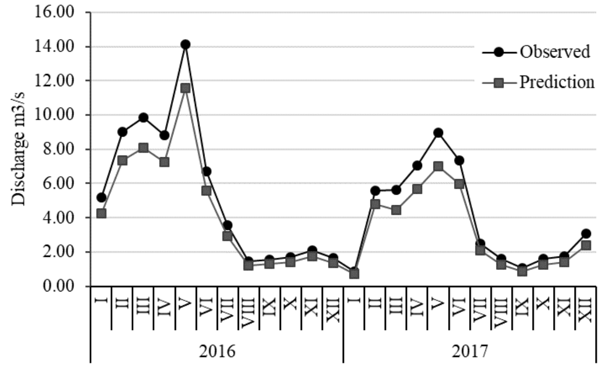

Figure 1. Comparison between observed data and prediction from the model

In order to evaluate convergence between observed and estimated results, Nash Sutcliffe Criterion Model was used (Figure 2). The Nash-Sutcliffe efficiency (NSE) is a normalized statistic that determines the relative magnitude of the residual variance compared to the measured data variance (Nash and Sutcliffe, 1970). Nash-Sutcliffe efficiency indicates how well the plot of observed versus simulated data fits the 1: 1 line. NSE = 1, corresponds to a perfect match of the model to the observed data. NSE = 0 indicates that predictions are as accurate as the mean of observed data, Inf <NSE <0 indicates that the observed mean is a better predictor than the model. In this case NSE is 0.904.

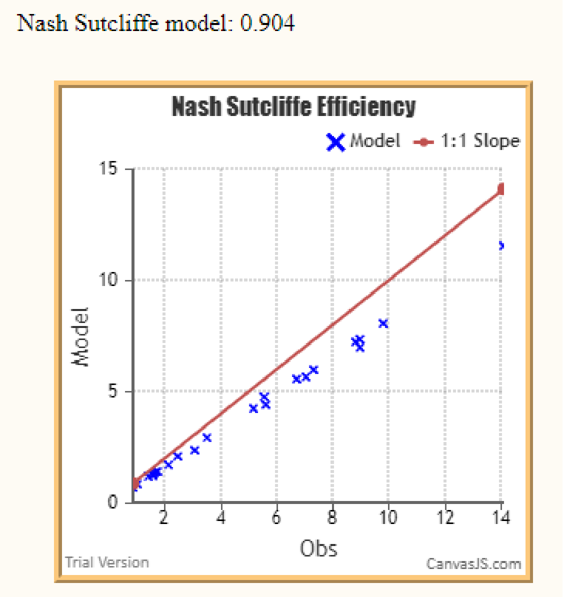

Figure 2. Nash-Sutcliffe efficiency coefficient

CONCLUSIONS

The results obtained correspond with the fact, that the river model thus created is sufficiently accurate. Based on this, it is possible to design various tasks related to river hydraulics, water quality, floods and forecasting of different processes.

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The Ecological Risk of Deterioration in the Water Flow of the Udy River Basin

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INTRODUCTION

The current state of surface waters requires the development of new scientific tools to prioritize the implementation of environmental protection measures. One of the most effective and efficient methods for determining the level of environmental hazard are environmental risk assessments. The method for assessing the environmental risk of disturbing the well-being of an aquatic ecosystem, presented in this paper, is based on the determination of environmental standards. The Udi River basin has a transboundary significance and flows through the territory of a large industrial center of Ukraine, characterized by high anthropogenic pressures. Therefore, prioritizing the implementation of environmental measures based on the assessment of the environmental risk of disturbing the well-being of the aquatic ecosystem of the watercourses of the Udi River Basin in the Kharkiv region is a very urgent task.

RESEARCH METHODS

There is proposed a methodology for assessing the environmental risk of deterioration of the aquatic ecosystem based on the determination of environmental standards, taking into account the landscape and geographical features of river basins (Rybalova and Artemiev, 2017). In the absence of environmental standards, it is proposed to use the upper limit of the 3rd category of surface water quality classification as a threshold value, corresponds to Class II with good condition according to the method. It is considered that if the ecological standard is exceeded, there is a probability of disturbing the well-being of the aquatic ecosystem (Vasenko et al., 2016). We propose to use the methodology of environmental assessment of the quality of surface waters in the relevant categories (Romanenko et al., 1998). In article (Rybalova and Artemiev, 2017) it was proposed to limit the number of indicators to five. We consider this restriction as incorrect, since the analysis of the ecological state of the Siversky Donets River in the Kharkiv region showed an excess of the environmental standard by 8-10 indicators. According to the presented methodology, an environmental risk assessment of the disturbance of the well-being of the aquatic ecosystem for the watercourses of the Udi River basin in the Kharkiv region is given. At the first stage, (Romanenko et al., 1998) determines the degree of pollution of the Udi river watercourses. The value of the ecological index of water quality is determined by the formula:

$$I_e = \frac{(I_1 + I_2 + I_3)}{3}, \tag{1}$$

where I_1 - the index of pollution components of the salt composition; I_2 - the index of trophic-saprobiological (ecological and sanitary) indicators; I_3 - index of specific indicators of toxic and radiation exposure. The assessment of the ecological status of the Udi River according to the values of the environmental index showed a deterioration in the long-term period. The qualitative state of the Udi River in the Kharkiv region is worsening from the border with Russia (v.Okop) to the mouth (v.Eschar). At the second stage, environmental standards are determined according to the method that is presented in (Vasenko et al., 2016). Then the risk of disturbing the well-being of the aquatic ecosystem (ER) is determined by definition (Rybalova et al., 2018):

$$\mathrm{Pr}ob = -2{,}3 + 2{,}21 \lg \sum \left(\frac{C_i}{C_{EHi}} \right), \tag{2}$$

where Ci - concentration of i-th substance in the water object, mg / dm^3; C_{EHi} - ecological norm for i-th substance in a water object, mg / dm^3. An environmental risk assessment of the deterioration of the aquatic ecosystems of the Udi River Basin in the Kharkiv region showed that the risk value of watercourses located in the city of Kharkiv corresponds to 4 classes (high risk), and the Lopan and Kharkiv rivers are the most polluted.

Table 1. Characteristics of the Udi River Basin in the Kharkiv region in terms of the environmental risk of deterioration of aquatic ecosystems

The name of the river, the post of observation	ER	Class	Qualitative assessment of ecological risk
Lopan River, the mouth, Kharkiv city	0,66	4	High risk
Kharkiv River, mouth, Kharkiv city	0,66	4	High risk
Udi River, village Horoshevo	0,64	4	High risk
Udi River, village Peresichna	0,63	4	High risk
Udi River, smt.Eskhar	0,60	4	High risk
Lopan River, village Kazacha Lopan	0,53	3	Significant risk
Udi River, village Okop	0,39	2	Increased risk

FINDINGS

For the first time, an assessment of the environmental risk of disturbing the well-being of the aquatic ecosystem for the watercourses of the Udi River Basin in the Kharkiv region was made on the basis of the determination of environmental standards. An environmental risk assessment of the deterioration of the aquatic ecosystems of the Udi River Basin in the Kharkiv region showed that the risk value of watercourses located in the city of Kharkiv corresponds to 4 class (high risk), and the Lopan and Kharkiv rivers are the most polluted.

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Anaerobic Digestion: Mixing Efficiency in Single- and Two-Stage Systems

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INTRODUCTION

In this work the main attention was paid to the efficiency of stirring process on anaerobic digestion (AD) of waste activated sludge produced at wastewater treatment plant of 1.4 million PE. There were three groups of reactors arranged and evaluated according two aspects: 1. Mixing efficiency in different temperature conditions: thermophilic (T), mesophilic (M) and temperature-phased (TPAD); 2. Mixing efficiency in single- (T and M) and two-stage systems (TPAD). A lot of standard analyses were performed to assess AD systems, besides which biogas quality and quantity was monitored and digestate studied in two ways. It was found that TPAD shows better results in both aspects.

Anaerobic digestion (AD) processes have been studied for decades (Riau, 2010; Lv, 2016). It has been already proved that mixing efficiency has a straight and proportional influence on the common efficiency of AD itself. It was decided to have a look at the stirring efficiency of single- and two-stage systems in terms of methane production, volatile solids destruction, digestate quality and such operational parameters as temperature stratification and microbiological variety over a full volume of single-stage thermophilic, mesophilic reactors and two-stage temperature-phased system. The obtained data were also evaluated as regard to the potential source of energy and products that can be recovered at WWTP and reused (Fagerstroem, 2018).

MATERIALS AND METHODS

For that, two different stirrers in four reactors were installed and two three-month periods run.

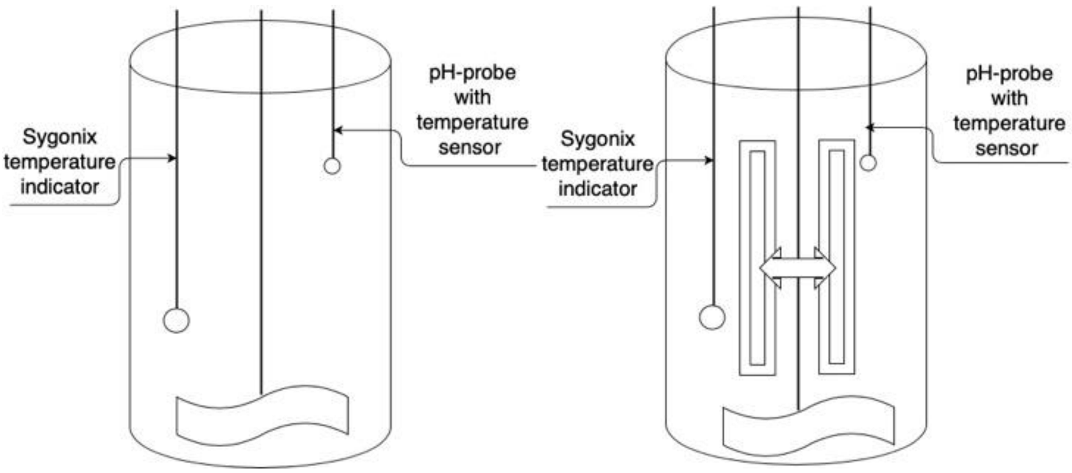

Figure 1. The scheme of two type mixing (N1 – on the left; N2 – on the right)

Figure 2. The lab installation: a – a new mixing system in all four reactors; b – the whole lab installation of three AD systems

Table 1. The main parameters of AD systems

Type of reactor	Abbreviation	Hydraulic retention time (HRT), days		Mixing speed, rpm	
		Mixing system N1	Mixing system N2	Mixing system N1	Mixing system N2
Single, mesophilic	M	15	15	110±1	50±1
Single, thermophilic	T	15	15	110±1	50±1
Two-stage, thermophilic (55°C, the first stage)	TPAD1	3.1	3.1	95±1	35±1
Two-stage, mesophilic (37°C, the first stage)	TPAD2	10.6	10.6	110±1	50±1

RESULTS AND CONCLUSIONS

In terms of mixing efficiency in different temperature conditions, it is important to mention that some interesting issues in reactor operation were observed after the change from N1 to N2 stirring:

1) Calorific value difference of substrate and digestate increased from 12% to 16%;
2) Total FVA production in all systems started be more balanced: the reactors working under thermophilic conditions stopped experiencing VFA accumulation: in TPAD1, the amounts of VFA increased twice, in T, it decreased three times and kept at the safe level;
3) Biogas production in TPAD was moved mostly from TPAD2 to TPAD1: in three-day retention time around half of methane started to be produced in the first step of TPAD;
4) In general, the content of methane raised up in all systems after the mixing system change;
5) Temperature stratification, noticed when exploiting the mixing system N1, dissapeared.

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Evaluation of the Migration of Paints Used in Flexographic Printing to the Aqueous Environment from Selected Plastics

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INTRODUCTION

The presence of plastics in the natural environment is currently one of the most pressing problems (Lv et. al., 2019; Niaounakis et. al., 2019; Alassali et. al., 2018). The issue is not only the ubiquitous microplastics, but also micro-pollutions derived from additives, plasticizers, and printing inks (Haned et. al., 2018). Migration of these types of pollutants into the environment, their transformations, and subsequent impact on living organisms is an important issue. For this reason, the subject of these studies has been the evaluation of the migration potential of compounds found in polyethylene foils used for flexographic printing. The possibility of migration of pollutants to various water matrices was analysed together with evaluation of the phytotoxic effects of the contaminated aqueous solutions.

MATERIALS AND METHODS

The subject of the research is LDPE polyethylene films (about 50 microns) with printing (water-based printing inks and Nitrocellulose printing inks). The influence of printing samples on water matrices with different compositions being deionized water (DW), tap water (TW), surface water (SW), and brine (BW) was analysed and, in addition, each of the samples was analysed in terms of the interaction of light conditions on the process (24 - hour light system (100%UV), no light (0%UV), day/night system - natural conditions (50%UV)). On each occasion, a sample of the film was also analysed in terms of the print colour, printing field, and the type of printing technique. Analysis of changes in the physicochemical parameters of water matrices was carried out for 90 days with measurements made once a week.

Total carbon (TC), TOC, and DOC in samples and matrices (after 0.45 μm filtration, PVDF syringe filter) were measured using a TOC-L series analyser by catalytic oxidation combustion at 680°C (Shimadzu). The UV254 values were measured using the UV VIS Cecil 1000 from Analytik Jena AG, with an optical path length of the cuvette d equal to 1 cm. Turbidity was measured using a EUTECH Instruments model Turbidimeter TN-100. The pH and redox potential in the samples and matrices were measured with a multi-parameter inoLab® 740 meter (WTW, Measuring and Analytical Technical Equipment).

The assessment of the phytotoxicity of liquid samples taken from foil solutions and matrices was made according to the author's methodology based on the US EPA (Sims et. al., 1999) recommendations and Phytotoxkit® (Microbiotest, 2004) using *Lemna minor*, garden cress (*Lepidium sativum*), and white mustard (*Sinapis alba*) as the indicator organism. Phyto-testing began in the third week of analysis. The assessment of sample phytotoxicity with *Lemna minor* was made based on the observation of either stimulation or inhibition of the growth in the number of fronds in a 7-day test using the coefficient of frond growth Rf and the coefficient of frond growth inhibition IRf (%). The examined effects of phytotoxicity with Lepidium sativum and *Sinapis alba* included root growth inhibition (%IR) and plant germination inhibition (%IG). Plant growth inhibition (phytotoxicity) indicator and growth inhibition coefficient values >0% were deemed positive, while growth stimulation was indicated by negative values (<0%).

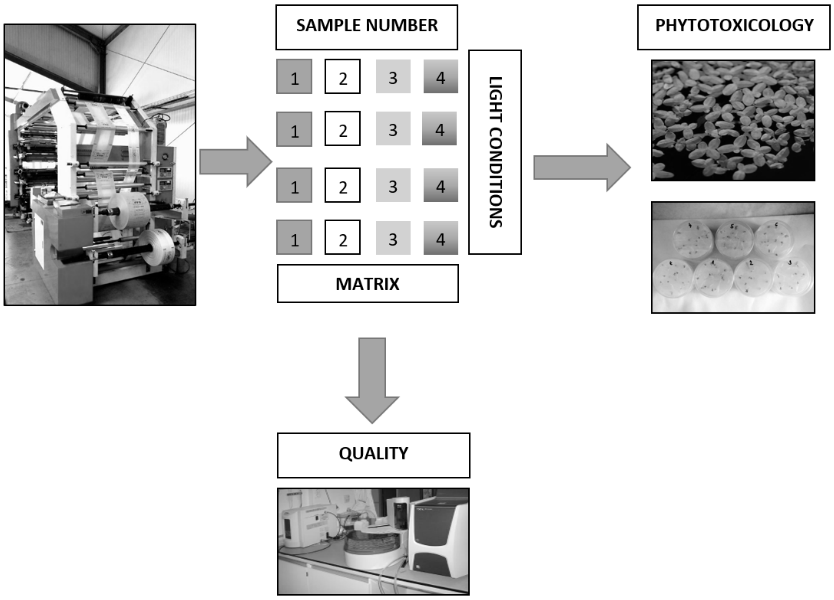

Figure 1. Methodology of conducted research

CONCLUSIONS

The influence of foil samples with printing on the quality of the analysed matrices was noted with equations shown for the release of impurities in various matrices. An increased ability to migrate pollutants in brine solution was observed. In this analysis, no phytotoxic effects from the released components were demonstrated on the test organisms. There were changes observed in the film's structure and size of the printable area, depending on the impact of light.

ACKNOWLEDGMENTS

The work was created in cooperation conducted as part of an industrial internship.

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Analysis of Pollution Degree According to Soil Depth of Cultivated Land

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INTRODUCTION

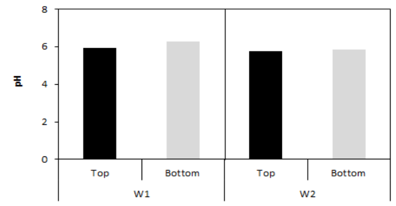
In agricultural activity, various kinds of fertilizer, compost and pesticides are used to enhance the growth and harvest of crops. However, a large amount of chemical and organic matter produced in various agricultural activities are leached and infiltrated to the soil through soil erosion, or discharged to nearby water systems through surface runoff during rainfall events. These substances cause incubation and algal bloom affecting the aquatic ecosystem. In addition, chemical fertilizers generated from cultivation activities are deposited with various receptors, which directly and indirectly affect human life (Lee and Koh, 2003). In particular, the leakage of contaminants due to the cultivation activities in watershed areas affects groundwater and surface water quality. As such, agricultural activities at the reservoir with multiple use were prohibited. However, for living sustenance, nearby residents illegally operate light crops and use various chemicals and organic fertilizer in agricultural activities. This study evaluated the effect of cultivation activities in the watershed area of Daecheong Lake by analyzing the contamination and comparing it with in situ soil.

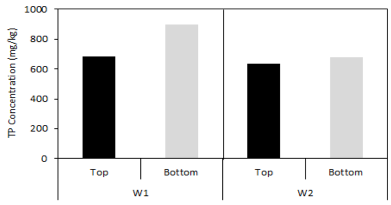
MATERIALS AND METHODS

Daecheong reservoir which is one of the main sources of water for several cities was selected as the monitoring site to survey the soil characteristics and soil nutrients of agricultural areas in its watershed. The monitoring location is located in Hyeon-ri, Annae-myeon, Okcheon-gun, and is currently being planted with barley (W1) and rice (W2). Monitoring was carried out in consideration of the timing of spraying of organic fertilizer and mineral fertilizer and the time of crop change in the cultivation process. To analyze the soil characteristics and status of the in situ soil according to the depth, the soil was divided into top soil (20 cm) and bottom soil (collected beyond 20cm depth) and collected. The collected soil was subjected to physical and chemical analysis of pH, TP, heavy metals based on the soil environment conservation method (Kim, 2005).

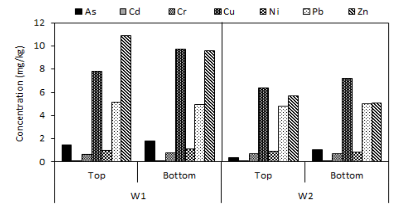
RESULTS AND DISCUSSION

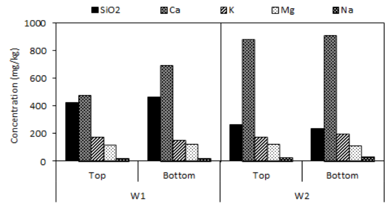
Figure 1 shows the results of the physical and chemical properties of the top and bottom soils collected in the monitoring site. For pH, the top soil was found to have a range of 5.7 to 6.0, and for bottom soil, it was analyzed to have a range of 5.8 to 6.3. It was analyzed that the pH range of upper soil could easily be moved to lower soil if surplus dissolved nutrients were present. Phosphorus components generally have a strong adsorption to the soil particles because of that, high TP concentration is expected in W1. Exchangeable cation are adsorbed on soil particles and are determined by the external environment such as temperature, pH, and DO. Ca was found to be the most abundant cation followed by K, Mg and Na in the cultivated soils of the reservoir. Apparently, higher cation concentrations were found in the bottom soil than in the upper soil. It was analyzed that the in situ soil of the watershed existed had similar order of abundance which were Ca, K, Mg and Na and also showed higher concentrations in the bottom soil compared to the top soil. It was analyzed that Ca concentration at point W1 was 1.8 times higher than that of W2. This finding is due to the natural compost organic matter w applied which were completely fermented thereby increasing the inorganic content of soil (Choi et al., 2003).





(a) pH (b) TP





(C) Heavy Metal (d) Mineral

Figure 1. Physical and chemical analysis of top and bottom layers of soil

CONCLUSION

In this study, soil pollution was analyzed according to soil depth in agricultural area, and the following conclusions were drawn.

(1) Considering that the difference between pH and TP concentration in the upper and lower part is not large, it is considered that the excess dissolved nutrients in the upper soil move easily to the lower soil.

(2) The upper layer was found to have a high concentration of exchangeable cation, which is estimated to have resulted from large amount of fertilizer application during cultivation. Based on these findings, it can be inferred that stormwater runoff may transport the excess nutrients to nearby water bodies.

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Concentrations of Emerging Organic Contaminants in Swimming Pools

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INTRODUCTION

The dynamic development of analytical techniques, which nowadays enable the identification of micropollutants present in the water environment in trace concentrations, causes the growing concern about the presence of emerging chemical contaminants in swimming pool. The assessment of occurrence in the pool water of anthropogenic organic micropollutants is not obligatory according to the applicable regulations. Thus, information on the occurrence of these compounds in the swimming pools is very limited.

This study presents the concentrations of organic micropollutants in fifty swimming pools located in Silesia, Poland, including publics and privates, outdoors and indoors, sports basins, hot tubes, water slides, paddling pools and recreational pools.

METHODOLOGY

Due to the lack of reference methods for the determination of micropollutants in the swimming pool water environment, authors have developed their own procedure, based on the method presented in paper (Lempart et al., 2018). It enables the quantitative determination of trace contaminants with satisfactory repeatability and accuracy, which guarantees full quantitative control of selected compounds in samples from swimming pools. The isolation of micropollutants from swimming pool water matrix was carried out by solid phase extraction (SPE) in Supelclean^{TM} ENVI-18 tubes. The bed was firstly conditioned in sequence with 5 mL of methanol and 5 mL of acetonitrile. Then it was washed with 5 mL of deionized water. Afterwards 1 L of water sample was applied. The extracts were analyzed using a Gas Chromatograph coupled to Mass Spectrometry (GC/MS) with Electronic Ionization, model 7890B by Perlan Technologies.

Human Risk Assessment (HRA) was conducted based on the methodology by Fantuzzi et al. (2018), considering both the exposure to each single contaminant and the co-exposure to all contaminants. Concentrations were compared with Drinking Water Guideline Levels (DWGLs). The ratios between the concentrations measured and the DWGLs are called Hazard Quotients (HQs). HRA assessed for co-exposure to all contaminants was measured following the Hazard Index (HI) approach, in which the HQs of single contaminants are summed to obtain a single risk value.

RESULTS AND DISCUSSION

Previous authors' study (Lempart et al., 2019) showed that from among 26 tested compounds, the most commonly occurred in tested swimming pools (> 50 % frequency of occurrence) are ibuprofen, N-Butylbenzenesulfonamide, nonylphenol, caffeine, butylated hydroxytoluene, diclofenac, pentachlorophenol, triclosan, triallate and benzocaine. Authors focused on the concentrations of these compounds in the presented study. Of them, the occurrence of butylated hydroxytoluene (BHT), pentachlorophenol (PCP) and N-butylbenzenesulfonamide (BMB) has not been studied so far in swimming pools by other researchers.

The concentrations of most tested compounds in Polish swimming pools are higher in outdoors than in indoors. Similar results were obtained by Ekowati et al. (2016) in Spain in the case of pharmaceuticals but the reverse was the case with UV filters. It was also observed that application of any method supporting water disinfection, ozonation or UV lamp, significantly reduces the concentrations of tested compounds in pools. Unfortunately, the analysis of post-processed water solutions in research (Kudlek, 2018) pointed that as a result of ozonation or UV lamp, endocrine-disrupting intermediates are formed.

Human Risk Assessment for the single substances and for co-exposure show negligible risks for swimmers of any age or sex. However, it is not allowed to disregard the occurrence of micro-pollutants in swimming pools. These compounds and their impact on human health are not yet well known, moreover they can be precursors of very dangerous disinfection by-products (DBPs).

CONCLUSIONS

This study demonstrated the environmental concentrations of emerging organic contaminants of several categories in Polish swimming pool waters at levels up to the hundreds of ng/L. In general, concentrations were in accordance with the reports in the available literature. The human risk assessment indicated that the health risk from exposure to tested compounds in swimming pools is generally low. However, further research is needed to check effects of the disinfection.

ACKNOWLEDGMENT

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Stimulating Effect of Magnesium Hydroxide on Aqueous Characteristics of Iron Nanocomposites

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INTRODUCTION

Nanotechnology has been emerged recently in several environmental remediation aspects owing to the excellent functional characteristics of the nanomaterials (Ghasemzadeh, 2014;Zhao, 2016). There is no longer any doubts that nanoscale zero-valent iron (nFe^0) is one of the most promising nanomaterials in water treatment technologies. Owing to its particular core-shell structure in addition to the dual redox potential, nFe^0 has the ability to react with most of the soluble contaminants in water (Wen, 2014). Furthermore, it has a high performance as an efficient adsorbent comparing with other adsorbents because of the relatively large surface/volume ratio of the nanoparticles (Maamoun, 2018). Despite all the formerly mentioned features, nFe^0 particles have some serious drawbacks in terms of the aqueous characteristics when it comes to the water treatment applications including the tendency of aggregation and the rapid settlement due to the strong magnetic attraction force between the particles (Tosco, 2014). Hence, in this study iron nanoparticles were modified by magnesium hydroxide ($Mg(OH)_2$) addition with different coating ratios in order to form a nanocomposite with superior aqueous characteristics. Optimization process of the iron-magnesium nanocomposite (nFe^0-Mg) was conducted through different approaches including; settlement tests, morphology and crystallinity investigations and particle size estimation.

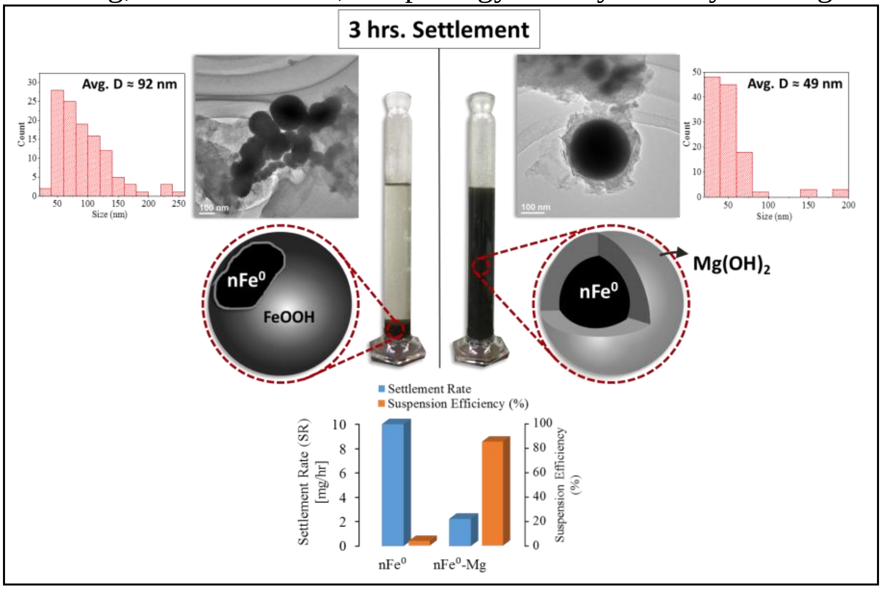

Figure 1. Graphical abstract; aqueous characteristics of nanoscale zero-valent iron (nFe^0), and iron-magnesium nanocomposite (nFe^0-Mg [Mg/Fe: 100 %]) after 3 hrs. settlement time

Table 1. Enhancement features of nFe^0-Mg composites comparing with nFe^0 particles

	nFe^0	nFe^0-Mg				
		Mg/Fe: 20 %	Mg/Fe: 40 %	Mg/Fe: 60 %	Mg/Fe: 80 %	Mg/Fe: 100 %
SR-Settlement Rate (mg/min)	0.167	0.126	0.131	0.082	0.061	0.038
SE-Suspension Efficiency (%)	4.2	14.67	13.33	47.62	86.67	87.77
Average particle size (nm)	92.4	70.84	61.32	73.97	75.94	49.25
Degree of crystallinity	60.63	35.56	41.32	54.34	63.49	70.82

FINDINGS AND CONCLUSIONS

Stability

The addition of $Mg(OH)_2$ to nFe^0 with coating ratio of (Mg/Fe: 100 %) resulted in stimulated stability of the particles in aqueous suspension with lower settlement rate (SR) than that of unmodified iron particles. The increase in the Mg/Fe coating ratio resulted in a higher suspension efficiency (SE) up to around 88 % for the fully coated nFe^0-Mg particles.

Characterization

Transmission electron microscopy (TEM) and X-ray diffraction (XRD) analyses showed an obvious enhanced features of the modified nFe^0 particles in terms of structure stability and degree of crystallinity respectively. Anti-aggregation effect was achieved corresponding to the smaller average particle size of the nFe^0-Mg particles which was confirmed by the morphological observation. Additionally, the iron core of the synthesized nFe^0 was adequately protected from aqueous corrosion with lower iron oxides leachates after the optimal modification with $Mg(OH)_2$.

Conclusions

Iron-magnesium nanocomposite with better aqueous characteristics was successfully synthesized. The current work suggests the potential applicability of the proposed iron-based nanocomposites towards sustainable effectiveness in water treatment applications.

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The Smart-Water Project: Smart Metering in the City of Thessaloniki

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INTRODUCTION

Smart-Water project is about smart infrastructure of telemetry systems for water consumption and management of drinking water demand. The water utility company involved in the project is EYATH SA, the water supply company of Thessaloniki. Smart-Water is co-financed by the European Union, Greek national funds as well as by partners' own funds. Among the objectives of the project are: (a) to design an original infrastructure which will exploit the latest technologies in order to give the opportunity to EYATH SA offer innovative services to its consumers and (b) develop and pilot test of a management, display and data analysis water consumption system.

Project Partners

Project partners of Smart-Water are: (a) APIFON, (b) EYATH and (c) Information Technology Institute (ITI)/CEntre of Research and Technology Hellas (CERTH). APIFON is an awarded small innovative company with specialization in cloud-based messaging, Machine-to-Machine (M2M) & Application-to-Person (A2P) communication. EYATH is the second biggest water supply and sewerage company in Greece. EYATH is a pioneer in testing innovative technologies for upgrading customer services and improving processes. ITI/CERTH is an institute with deep knowledge in techniques for the analysis, retrieval and visualization of data, complex event processing, interpretation and decision making algorithms.

WATER MANAGEMENT

The aim of urban water management is to provide a safe and reliable water supply to consumers. Nowadays, maintaining the sustainability of this water supply has become equally important, with the adverse effects of the projected climate change on water scarcity already manifesting themselves in many countries around the world. Water Demand Management (WDM), i.e. the management approach aiming to conserve water by influencing demand, is used by water utility companies and policymakers in order to manage water supply, enact water conservation and design water safety plans. WDM consists of activities ranging from engineering/infrastructure maintenance and upgrading to economics analyses, and from sustainable consumption incentives to consumers' education. The availability of reliable information on water use is the basis for the successful design and implementation of WDM strategies and, in this context, water metering is essential for acquiring the data needed. The transition from traditional water metering methods/tools to the technology known today as Smart Water Metering (SWM), as well as the added value SWM brings to water management as a whole, is the subject of this work and will be discussed in brief in the following (Randall and Koech, 2019).

SMART METERING

Smart water meters provide a new measurement technology. Application of smart water meters allows continuous collection of consumption data, without requiring natural person access in site. The most important benefit of this new measurement technology is the real-time control of water consumption with help of suitable telecommunication devices. Additional benefits are the detection of losses due to leak or unauthorized use of water network, protection of the environment by reducing the wastage of water resources, and customer service upgrade with modern information services. In addition to consumption information, smart meters, can provide instantaneous water supply information, water temperature, pressure values, reverse flow measurement, leakage notification, water meter alarm, etc.

Along with smart meters, smart valve regulates, drives and controls the flow of a water, by opening, closing or partially blocking its passage. Smart valves use the actuators to operate. Actuators require control signal and power source to operate. The control signal is a low power signal. It can be caused by electrical voltage or power supply. When the actuator receives the control signal, it reacts by converting the signal energy into mechanical motion. Remote management of smart valve is surely an important benefit of this new technology.

INTERNET OF THINGS (IoT)

The Internet-of-Things (IoT) has recently gained more attention due to the technological advancement of wireless technology. It is based on the integration of different technologies (Shah and Yaqoob, 2016). Low Power Wide Area Networks (LPWAN) are best suited for IoT applications which require the transmission of very small amounts of data over long distances· as in the case of recording and transmitting measurement data (Xu et al., 2018). IoT technology is applied in Smart-Water project through the installation of a fixed LoRa network of antennas with Radiofrequency of 868 MHz for the transmission of the water measurement data.

CASE STUDIES

Two areas have been selected for installing the smart equipment: (a) the centre of Thessaloniki and (b) Kalamaria, which is situated in the southeastern part of the city. They were selected due to their different urban structure, their water consumption habits and their geomorphology.

ACKNOWLEDGMENTS

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Towards Smart Infrastructure: A Case Study in the Water Supply System of Thessaloniki

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INTRODUCTION

Fulfilling total water use demands is a prerequisite for normal function of a water utility company. Efficient managing and operating the water supply network are affected and significantly aided by detailed water demand patterns, which provide a better description of the consumption needs (Herrera et al., 2010; Zhou et al., 2002). Smart metering technology provides (a) the proper data for creating such profiles, (b) opportunity of creating new products for the consumers.

Thessaloniki Water Supply and Sewerage Company S.A. (EYATH S.A.)

EYATH S.A. provides water supply and sewerage services to the broader urban area of Thessaloniki, which is situated in Northern Greece, Central Macedonia. Among its strategic targets is the implementation of smart metering infrastructure in order to: (a) reduce Unaccounted-For Water (UFR), (b) enhance customer service by creating new products and (c) contribute in developing water culture and in strengthening water-consciousness of the customers.

Challenge

Addressing the challenge of smart infrastructure by integrating smart technology in the existing water supply system requires a well-designed implementation plan. Studying this integration in the current city's infrastructure on a pilot research level makes its further financing on a wider scale more viable and robust.

In this paper, the study conducted for designing telecommunication parts of the smart water infrastructure is presented and analyzed. The developed scientific approach is Geographic Information System (GIS) based. In developing this approach, the GIS of the Utility has been used.

MATERIALS AND METHODS

The study area is the city of Thessaloniki, where EYATH provides its services. Two subareas in Thessaloniki were selected to take part in the pilot research project. The first subarea under study is situated in the urban centre of Thessaloniki and the second one in Kalamaria, which is an eastern extension of the older, central, urban tissue of the city. These subareas were selected in order to evaluate the new, available communication technologies in relation to the existing urban tissue and its geomorphology.

Smart water infrastructure requires the integration of a reliable telecommunication network to the existing city's infrastructure for (a) transferring measurement data from the smart metering system to a system of data storage and data processing, as well as (b) provision of smart services to the end-users (consumers & EYATH S.A.). The approach of a fixed network of telecommunication antennas (Radiofrequency 868 MHz) is to be applied and it was scheduled to be constructed especially for this project. The fixed network will work in combination with smart water meters and smart valves, which are to be installed -in the frame of the study- in households situated in Thessaloniki’s centre and Kalamaria. The project supports financially the installation of 100 smart water meters and 100 smart water valves.

Positioning of the antennas is a crucial step in the implementation of the project. Possible locations for the antennas were studied in the GIS environment utilizing the visibility analysis tool of the software. The aim of the visibility analysis was to detect locations, from which antennas are visible to an adequate extent in the study area.

Apart from running the visibility analysis, a selection of possible candidate consumers to take part in the pilot study was implemented. After that, a geocoding process was implemented, in order to geolocate the previously selected data of possible candidate consumers. The geocoding process was applied in the GIS environment.

RESULTS & CONCLUSION

The geocoding and the visibility results were superimposed as is illustrated in Figure 1 (indicative of the results). The visibility analysis allowed a better study of the positioning of the antennas. The product maps provided better overview of the geographic distribution of the consumers and the visibility coverage of the antennas.

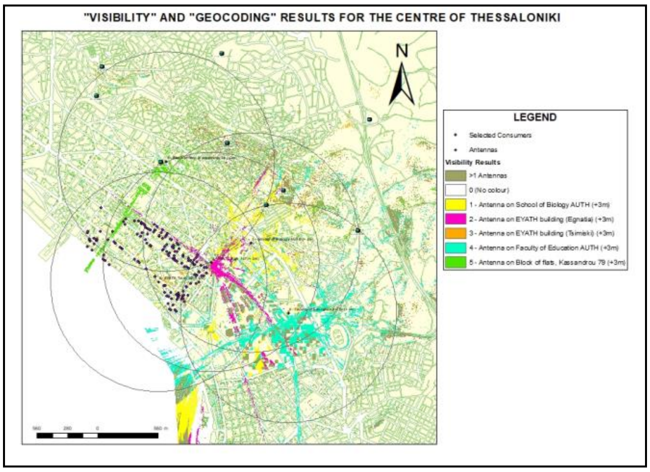

Figure 1. Product map depicting the visibility analysis and geolocating results for the centre of Thessaloniki. It is indicative of the results of this study

ACKNOWLEDGMENTS

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Microbial Diversity in Extreme Aquatic Environments from Transylvania

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INTRODUCTION

Analysis of microbial communities of extreme environments like low-pH lakes or heavily contaminated slurry lakes offers significant insight into the molecular mechanisms for acidophilic survival of microorganisms, or survival under high concentrations of toxic metals. Due to these findings, metabolic pathways characteristic to special habitats can be highlighted, and microbial/bacterial consortia or even bacterial species for the treatment of specific industrial wastewater or other bioremediation applications can be further suggested (Dalmaso et al., 2015).

Recent advances in high-throughput molecular methods, especially DNA sequencing have gathered an extensive body of omics data which reveal intriguing microbial diversity in some of the harshest environments on our planet (Tighe et al., 2016). A number of adaptive mechanisms help extremophiles to colonize the most acidic, saline, cold, hot or even the most polluted habitats, while their metagenomics and functional genomic characterization could reveal the genetic base of their adaptability (Rampelotto, 2013).

Recently, coordinated international efforts are being carried out by metagenome-based methods to offer comprehensive large-scale data on different microbiomes, from the human tissue and organ-specific microbiomes to microbiomes of the built environment, as well as that of extreme habitats. The latter are joined in two main projects, the Earth Microbiome Project (Thompson et al., 2017), and the Extreme Microbiome Project (Tighe et al., 2016).

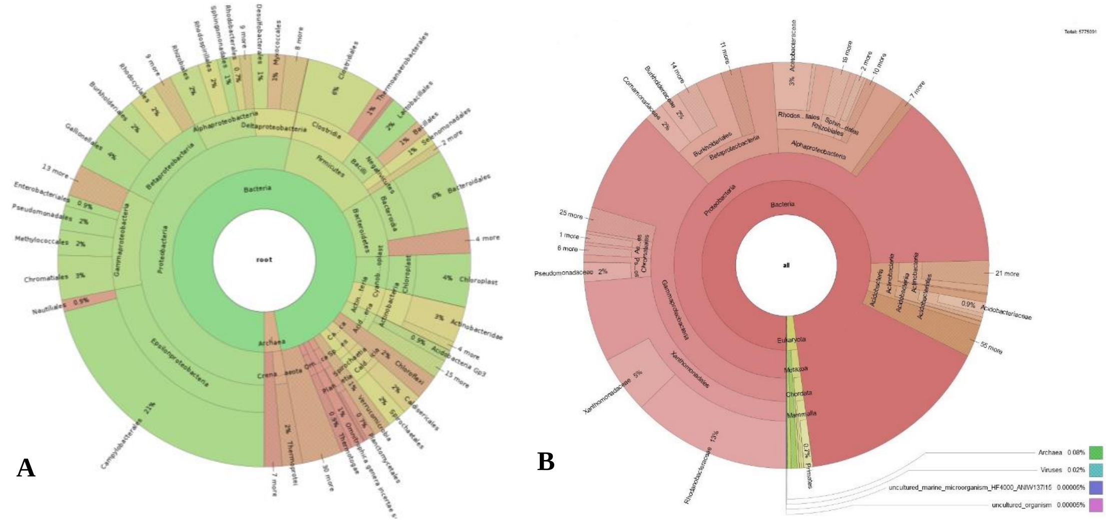
Thus, our main goal was to introduce specific habitats from regions of Transylvania on the map of extreme microbiome research. During our work, we investigated the microbial diversity of 3 quarry lakes and 1 extreme acidic lake of Transylvania by 16S rDNA and shotgun metagenome sequencing together with analytical methods. Similar studies had been conducted in different regions (Sanchez-Andrea et al., 2011; Chen et al., 2018), but to our knowledge, we are the first group to try to map these interesting habitats from Transylvania using a metagenomics approach.

METHODS

DNA Extraction: DNA was isolated from the sediments using the FastSpin Kit for Soil (MP Biomedicals), according to the manufacturer's instructions. DNA Quality/Quantification: Agarose gel electrophoresis was used to determine the quality of the extracted DNA, concentration of DNA was determined using the Qubit fluorimeter (Thermo Scientific) with the Qubit ™ dsDNA Assay Kit (Thermo Scientific). Sequencing: For high-resolution shotgun sequencing, 500 ng - 1 µg of RNase-treated DNA samples were used, sequencing was performed at least 1x75 bp, 200 000 reads/sample resolutions (GenXPro, Germany). Data visualization was carried out with the Krona Toolbox (Ondov et al., 2011).

RESULTS

Being at the beginning of our endeavour to map microbial diversity of Transylvania's most interesting habitats, firstly we investigated the microbial diversity of 3 quarry lakes and 1 extreme acidic lake. As shown in Figure 1, the exotic microbial community of the low pH lake includes sulphate-reducing and methanotrophic bacteria (Part A), while in the case of one studied copper slop, microbial diversity has been found lower (Part B and C). For comparative analysis of ecologies, a database is constructed, while analysis of other samples from interesting regional habitats is in progress (hypersaline lake, kaolin mine). We are confident that our data can contribute to the global effort of mapping extreme microbiomes.



C

Fe	14.70%
Al	3.90%
S	2.10%
Si	3900 ppm
P	1200 ppm
Pd	420 ppm
Rh	290 ppm
Ca	1600 ppm
K	160 ppm
Cu	450 ppm
As	45 ppm
Mo	24 ppm
Zn	49 ppm

Figure 1. Part A. Metagenome map of Bálványos pH≈2 lake with volcanic sulphuric acid. Part B. Metagenome map of a copper slop with metal concentrations presented in Part C

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Antibiotic Resistant Bacteria in Stormwater

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INTRODUCTION

Urban runoff water is often neglected in antibiotic resistance studies. Even though not many studies investigated dissemination of antibiotic resistant bacteria (ARB) and antibiotic resistance genes (ARGs) in urban runoffs, their distressing results are alarming. Anthropogenic pressure together with storms creates a new hot-spot and at the same time vehicle for creation and dissemination of ARGs and ARB. Selection of resistance is highly probable in stormwater due to faecal contamination as well as presence of heavy metals and antibiotics. Especially that low concentration of those contaminants stimulate creation of ARGs and their spread via horizontal gene transfer. That is also important as potential route of ARGs transfer from environmental bacteria to pathogens (Almakki et al., 2019).

METHODS

In presented study long-reads generated by Oxford Nanopore MinION shotgun metagenomic sequencing during examination of Swedish urban stormwater systems for faecal indicator bacteria and deposited in the Sequence Read Archive (SRA), under the accession number PRJEB20562 (Hu et al., 2018) were analyzed. The previously generated fastq from NanoPore sequencing were converted to fasta files using SRA toolkit (Leinonen et al., 2011). ARGpore (Xia et al., 2017) was used to investigate antibiotic resistance in stormwater. ARGpore uses Resistome prediction Algorithm (fasta was searched against nt-version SARG database (v1.0)) and Taxa Algorithm (searched against clade specific marker gene database - MetaPhlan 2). Additional classification of species was made based on MiDAS 2.0.

RESULTS

Antibiotic resistant bacteria

Seven main resistance types and ARB carrying them were found in tested samples. ARB were additionally classified to species encountered in wastewater treatment plants (marked with*), opportunistic pathogen (marked with ✶) and pathogens (marked with ☆). In sample 1: *Polymorphum gilvum*, *Rhizobium etli*, *Sphingomonas sp.** resistant to aminoclygoside and multidrag resistant *Pseudomonas sp.**. In samples 2 and 3: *Azospirillum lipoferum*, *Acidovorax delafieldii**; *Limnohabitans sp.*; *Rubrivivax benzoatilyticus* resistant to aminoglycoside; *Bacteroides stercoris*, *Anaerostipes hadrus** resistant to beta-lactam, fosmidomycin resistant *Acinetobacter tandoii**; multidrug resistant *Acinetobacter tandoii*; *Propionibacterium avidum*☆, *Slackia sp.**. In samples 4 and 5: *Sphingomonas sp.**; *Leifsonia xyli* resistant to aminoclygoside; *Limnohabitans sp.* resistant to beta-lactam, fosmidomycin resistant *Mycobacterium parascrofulaceum* ✶ , *Alicycliphilus denitrificans**, *Leptothrix cholodnii**; *Pseudomonas sp.**; *Sphingomonas sp.**;

Sandarakinorhabdus limnophila resistant to macrolide-lincosamide-streptogramin. Ten of found ARBs are usually encountered in activated sludge in wastewater treatment plants. One identified ARB is biofilm forming pathogen previously found responsible for prosthetic hip joint infections (Wildeman et al., 2016).

Resistance mechanisms

In studied samples, 11 resistance types with 26 resistance mechanisms were found: aminoglycoside - aac(3)-X, aac(6')-I, aph(3')-I, aph(3')-IIb; bacitracin bacA; beta-lactam – class, GES-23, mecI; chloramphenicol chloramphenicol; fosmidomycin rosA; macrolide-lincosamide-streptogramin ermO; multidrug – abeS, major facilitator superfamily transporter, mexE, mexX, ompR, opcM, oprA, oprN, qacG; puromycin puromycin; rifamycin ADP-ribosylating; trimethoprim dfrA12; vancomycin - vanH, vanR, vanS.

CONCLUSIONS

In presented study of five stormwater samples ARB were connected with defined resistance type. Coexistence of environmental and pathogenic bacteria in same niches in stormwater and detail investigated regarding horizontal gene transfer of extracellular ARGs between those groups should be further studied. At this point the possibility of identifying not only pathogens but also resistance encoding genetic material that may be integrated by pathogens is crucial. MinION sequencing and workframe presented in the study allows not only identification of ARGs (resistance mechanism), but also ARB carrying them.

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Environmental Risk Assessment of PhACs in the Largest Shallow Lake in Central Europe

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INTRODUCTION

The presence of pharmacologically active compounds (PhACs) in the aquatic environment is a well-founded issue nowadays, which causes concern worldwide (Daughton and Temes, 1999; Ginebreda et al., 2010). In the last decades, amount of consumed medicines increased and many new types of substances appeared in the pharmaceutical market (Guzel et al., 2018). However, despite of that wastewater treatment technique constantly improved, many active pharmaceutical residues appear in the cleaned effluents, therefore, in the surface waters as well. Nevertheless, the release of PhACs into aquatic ecosystems poses a serious environmental risk resulting in a chronic contamination of non-target organisms (Ginebreda et al., 2010; Mendoza et al., 2015; Carlsson et al., 2006). It should also be mentioned that, evaluation of concentration data is a very complex task, because the environmental level of PhACs are depend on many factors such as efficient of applied waste water treatment technology, resistance of biodegradation, dosage of medicine and weather conditions.

Our aim was to determine the ecological risk of PhACs concentrations in the waters of an important touristic region, the largest shallow lake in Central Europe, Lake Balaton (Hungary) and to explore a possible correlation between magnitude of actual hazard and impacts of seasonal changes. Earlier, the presence of 134 PhACs was examined at 10 different sites in Lake Balaton and its catchment area from June 2017 to August 2018 with seasonal frequency. Taking the complete studied period and all sampled sites account, 72 PhACs were detected and quantitative measured in environment. Based on their biologically activity, the detected PhACs were classified among others into the following groups: antiepileptics, cardiovascular agents, antipsychotics, and hormone modulators. Seemingly, according to our results, the impact of summer touristic season on number and concentration of PhACs is remarkable (Maasz, 2019).

METHOD

Measurement of PhACs concentrations from water samples was accomplished by supercritical fluid chromatography tandem mass spectrometry (SFC-MS/MS). (Maasz et al., 2019) To calculate of ecological risk assessment of investigated PhACs, it was also required collection of ecotoxicology data (e.g. EC50, LC50 or NOEC) and determination of the Predicted No Effect Concentrations (PNEC). Using a risk quotient (RQ), which is defined as the ratio of the Maximal Environmental Concentration (MEC) to the PNEC, the ecosystem risk from pollutants can be estimated. In general, $RQ<0.1$ reveals a low risk, $0.1<RQ<1$ represents a medium risk, and RQ above 1 indicates a high ecological risk to aquatic organism (Deo, 2014).

RESULTS

Taking into account the whole investigation PhACs with the highest environmental risk level (RQ>0.1) were tramadol, estrone (E1), beta estradiol (bE2), propranolol, caffeine, haloperidol, carbamazepine and MDMA (3,4-methylenedioxy-methamphetamine), however fortunately approximately 60 % of PhACs had negligible risk. The risk analysis was performed separately for the Lake Balaton and its catchment area, as well. It can be stated that aquatic organisms living in the catchment area are exposed to bigger hazard than those populating in the lake. The reason is likely the pollution of nearby city and the surrounding treated wastewater effluents into River Zala, the main inflow river of Lake Balaton. In addition, it has been examined how the risk level changes in each measured season in water of Lake Balaton. Based on our results summer tourist season increased the RQ (independent of compound) in investigated period.

CONCUSION

Overall, the results definitely show that the ecological risk is negligible in case of most of the investigated PhACs, however there were 8 compounds with at least medium risk in the largest shallow lake in Central Europe and its catchment area. The harmful effect of summer tourist season were detectable in Lake Balaton. Furthermore, the impact of urban pollution and wastewater load on water quality in the catchment area was also measurable. It is very important to pay attention the level of pharmaceutical ingredients in our surface water and to protect the ecosystem from possible future damages.

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UV-assisted Desalination of Seawater Using Titanium Dioxide Nanotube Doped Polyether Block Amide Membrane

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INTRODUCTION

Membrane technology is emerging science for advanced water treatment. Membranes are mostly used for water purification, waste-water treatment, and desalination purposes. The productivity and overall performances of membrane-based processes are directly related to the physicochemical properties of membranes. Therefore, scientific studies have been focused on the development of high-performance membrane materials. Especially for water treatment, it is important to produce superior membranes having high water permeability, high rejection capacity, biofouling resistance, and process stability. For this purpose, new generation composite membranes have been developed.

Photocatalytic membrane has been recently developed for a wide range of application. Biological treatment of organic content water, seawater desalination, and waste water treatments are most know application areas of photocatalytic membranes. Mechanical properties and selective separation capability of membranes can be destroyed by the cumulation of organic pollutants in seawater. Therefore, photocatalytically eliminating of organic pollutants may improved both structural properties and separation performance of membranes (Yacou et al., 2015).

In this study, it is aimed to develop a new material for UV-assisted desalination of seawater. For this purpose, titanium dioxide nanotube (TiO_2) doped polyether block amide (PEBA-Pebax1657(commercial name)) membrane has been produced. TiO_2 is a semiconducting material that destroy the organic contaminant in the water by assistance of UV-light (Mayyahi, 2018; Yacou et al., 2015, Salcova et al., 2016). The structural property of the composite membrane has been investigated by means of Fourier Transform Infrared Spectroscopy and X-Ray Diffraction. The distribution of TiO_2 particles within the membrane has been analysed using Polarized Electron Microscopy. Swelling experiments have been performed to determine the water-uptake capacity of the TiO_2 filled and unfilled Pebax1657 membrane. The separation performance of membranes with/without TiO2 nanotube was investigated to separate water from NaCl, $MgCl_2$, Na_2SO_4 and $MgSO_4$ -water solution. Desalination test has been conducted at the room temperature with/without UV light. The effect of TiO_2 concentration, UV light, and solid content in water were investigated.

EXPERIMENTAL

Titanium dioxide nanotube preparation

1 gram of commercial titanium dioxide powder (ACROS) was mixed with 10 M sodium hydroxide solution. The mixture was subjected in an ultrasonic bath for 30 minutes. The mixture was left for hydrothermal treatment at 130 °C for 24 hours in a Teflon lined autoclave. After filtration, the nanotube titanium dioxide was washed with hydrochloric acid and water. Nanotube titanium dioxide was dried at 110 °C for 16 hours and calcined at 500 °C for 2 hours.

Membrane Preparation

Polyether block amide was kindly supplied from Arkema, France. 10 wt.% of PEBA-acetic acid solution was prepared and stirred until the solution became homogeneous. The determined amount of TiO_2 particles were added to PEBA solution according to the weight of the dry PEBA polymer. According to the PEBA content, TiO_2 concentration in the membrane solvent was changed from 0 to 10wt.%. Membrane solutions were cast onto a Teflon plate and allowed to dry at the room temperature. Then, membranes were cured in a vacuum.

Desalination

Desalination test were carried out at the ambient condition. Prior to desalinate a seawater, separation capabilities of membranes were tested to separate water from NaCl-water, $MgCl_2$-water, Na_2SO_4-water, and $MgSO_4$ -water solution. Water removal was calculated from Equation 1 shown as follow;

$$R(\%) = \frac{c_i - c_f}{c_i} * 100, \quad (1)$$

where C_i and C_f represent the initial and final concentration of solid concentration.

Simulated seawater containing NaCl, $MgCl_2$, Na_2SO_4 and $MgSO_4$ solids were desalinated without UV light. The seawater desalination test was conducted under UV light and effect of UV on desalination was investigated. Total dissolved solids and ion concentrations were analysed using Multi-Functional Conductometry (Seven Compact-Mettler Toledo).

Characterization

The crystalline phases were characterized with X-ray diffraction (XRD) (Rigakku, Miniflex 2, Japan). 2θ values were selected from 10^o to 80^o with a step size of 0.02 using Cu Kα radiation (λ = 0.15418 nm) at 45 kV/40 mA. Fourier Transform Infrared Spectroscopy was used to determine chemical structure of the membrane in the wavelength range from 650 cm^{-1} to 4000 cm^{-1} (Perkin Elmer-ATS). Mechanical test of membranes before and after desalination was performed using Instron 3341 Universal Testing Machine. Surface hydrophilicity properties of membranes were determined using contact angle measurements (Attension).

RESULTS

Desalination test has been conducted at the room temperature. In conclusion, TiO2 and PEBA showed good compatibility owing to the homogenous dispersion of the particles in the polymeric matrix. Greater than 99 % salt rejection has been achieved.

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Role of Coagulation Kinetics in Water and Waste Water Technology Design

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INTRODUCTION

Kinetics of water treatment processes is one of the crucial factors in technology design. In this paper there is demonstrated how jar or coagulation tests could be beneficial in design of water treatment plant and in waste water treatment technology.

Surface water treatment

In the first case study the test objective was to define process parameters for water treatment plant technology renewal. There was a water treatment plant with obsolete technology with low and unstable efficiency of removing natural organic matter (NOM) from surface water. The primary intention was to simply replace the old device with coagulation filtration with very short hydraulic retention time by the same one. In pre-project preparation type and dose of coagulant (PACl), influence of pH and reaction time were tested. Furthermore the importance of reaction time was known also from experience with old device. Strong dependency of residual Al and NOM removal (measured as absorbance at 254 nm) on reaction time was also observed in tests. It was found out that it is necessary to keep reaction time about 8 minutes or higher for achieving of Czech national standard (Vyhláška 252/2004 Sb.) for Al concentration in drinking water (0.2 mg/l). Based on these tests couple of reaction tanks were added into project and built as a part of new technology in this water treatment plant.

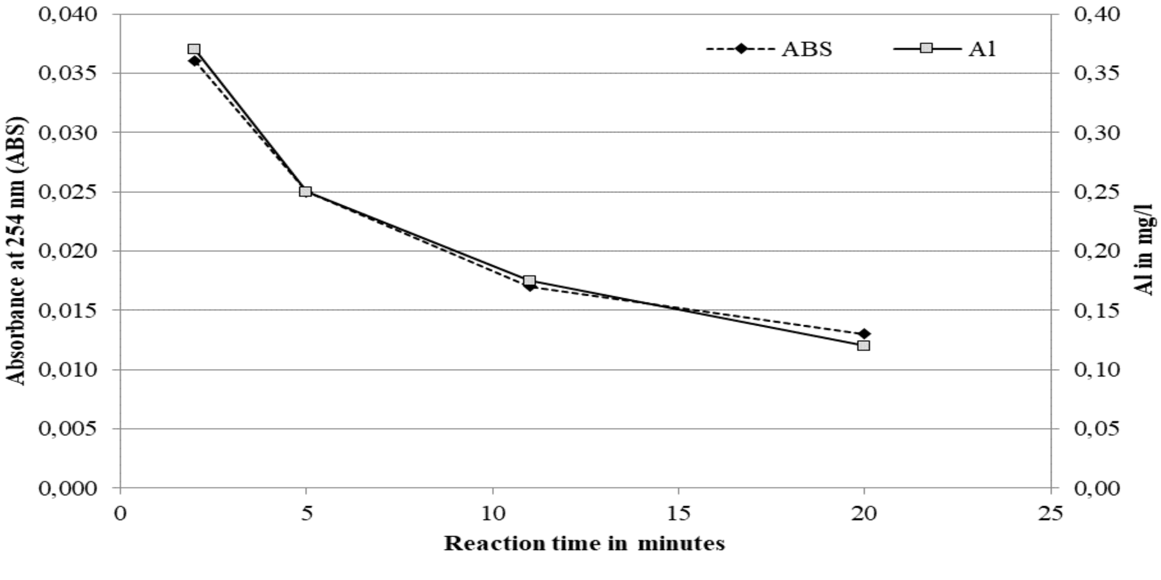

Figure 1. Effect of reaction time on effluent quality

Table 1. Average values of COD and turbidity in drinking water. Technology was replaced during second half of 2017. *- in 2019 there are data only from first 4 months

Year	2016	2017	2018	2019*
COD (mg/l)	1,72	1,75	1,41	0,96
turbidity (NTU)	0,62	0,61	0,16	0,09

Meat industry waste water pre-treatment

Second presented case is coagulation test of waste water from meat industry. Water is very rich in organic carbon and must be pre-treated before it is finally cleaned in municipal waste water treatment plant. There is very robust and good working flotation technology treating waste water from chicken slaughter and meat processing. This flotation unit is almost 30 years old and it is planned to replace it with new one. A project designer suggested to build up new flotation unit with tube mixer with retention time in minutes (or tens of seconds) as a replacement of current couple of tanks with HRTs 15 minutes for coagulation and 15 minutes for flocculation. Because there were some doubts about efficiency of technology with so much shorter HRT, coagulation tests were conducted. The first test was designed as similar with current technology as possible: in the beginning dose of coagulant ($Fe_2(SO_4)_3$) was added, then was solution slowly mixed. After 14.5 minutes flocculant (polymer) was added and another 15.5 minutes solution was slowly mixed. Second test was very similar, the only difference was in time of addition of flocculant which was dosed after 30 seconds since coagulant was added. During test samples were taken and it was found out that one minute is enough for formation of suspension and organic carbon removal. Long mixing time is not important for final effluent quality. Much more important is dose of coagulant and dose and type of flocculant. The only important difference is in size of flocs. With longer time of reaction flocs are bigger. If flocculant is added early, flocs are small and not even after next 30 minutes are as big as in the former test. On the base of these observation tube mixer was kept in the project and sludge dewatering unit was added into the project. There are no full-scale operational data because unit is now under construction.

Table 2. Results of coagulation tests. In both test $Fe_2(SO_4)_3$ was added in time 0. In test 1 polymer for flocculation was added in time 14.5 minute and in test 2 in time 0.5 minute

time [min]	0	1	5	15	30
	COD (mg/l)				
test 1 - current technology design	3510	960	670	578	573
test 2 - project technology design	3510	585	581	572	571

CONCLUSION

Coagulation tests, or generally verification of designed technology by laboratory simulation or half-scale testing, is very important. Tests are important especially in the case of lack of data, experience, or in case of complex water matrix (pollution). In two case studies presented above tests led us into project changes which improved efficiency of technology or dispel our fears. Both are important if high costs should be paid for technology.

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Success Factors for Citizen Science Projects in Water Quality Monitoring

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BACKGROUND AND GOAL OF THE STUDY

Attempts to monitor the quality (and quantity) of water resources on a global scale unveil huge data lacks. To address this data gap, researchers and practitioners increasingly call for the involvement of citizens in water quality monitoring. The idea is that citizens hold immense potential in terms of increased temporal and spatial data collection and therefore could bridge the data gap that the scientific and practical community faces at present time (Ballard et al., 2016; Buytaert et al., 2014; Carlson and Cohen, 2018). Research increasingly discusses here factors that support or hinder the success of citizen science projects, amongst them the motivation of citizens, supporting material, and the funding. However, these success factors are scattered across institutions and programmes, as well as several regional contexts (e.g., Europe, Asia, Africa) or dimensions of water quality monitoring (e.g., parameters, specific water quality goals). Moreover, studies generally focus on a small set of design principles rather than providing a systematic review in light of various success criteria such as the amount of reliable data across temporal and spatial scales (e.g., Buytaert et al., 2014; Weeser et al., 2018; Storey et al., 2018). Against this background, this study aims at identifying and synthesizing a comprehensive list of success factors for citizen science projects in water quality monitoring. The focus here is on the monitoring of freshwaters, including both surface and ground water, using different water quality parameters such as physical, chemical, and biological indicators.

METHODS

To identify success factors for citizen science projects on a global scale, we conducted a systematic literature review. Google Scholar, Scopus and Web of Science were used as web-based scientific platforms for the research. To identify relevant literature, we applied a set of key words; representing water-related terms (i.e. water, water quality, water monitoring) as well as specific terms indicating types of water and water bodies (aquifer, groundwater, watershed, surface water). Moreover, we matched the different water-related key words both with the term ‘citizen science’ and the closely related term ‘community-based monitoring’. Based on the application of these key words, we identified a particularly large body of potentially relevant literature. We further reduced the total number of articles, based on the date of publication (1999-2019), the impact factor of the journal (higher than 2), as well as the main content of the scientific article (based on titles and abstracts of the articles), resulting in a total of about 80 articles for further analysis. To extract relevant information from these articles, attention was payed to both positive and negative descriptions of factors. In this way, we could diagnose a broader variety of factors that contribute to the success of citizen science projects than by focusing on ‘success stories’ alone. Relevant text segments with success factors were then extracted and pasted to a separate excel sheet, being the starting point for further synthesis.

RESULTS

We identified three sets of success factors for citizen science projects in water quality monitoring, relating to (i) Attributes of Citizens that are involved in citizen science activities (ii) Attributes of Institutions that typically initiate citizen science activities, and (iii) Processes and Mechanisms of citizen science activities, which link citizens and institutions, see Figure 1. **Attributes of Citizens** relate to (i) Citizen knowledge and experience on data collection (e.g., scientific background of citizens, prior experience in citizen science projects), (ii) Citizens awareness of environmental issues (e.g., before and during the project), (iii) Citizens motivation (e.g, personal interests, monetary incentives, social commitment), and (iv) Socio-economic background of citizens (e.g, age, education, gender, economic background). **Attributes of Institutions** refer to (i) The type of organization (e.g, NGOs, research entities, governmental agencies, private organizations), as well as (ii) Funding (e.g., permanent funding over a project, financial support of volunteers). **Processes and Mechanisms** refer to (i) General aspects (e.g., institutional barriers, admission rules), (ii) supporting structures (e.g., data sampling protocols, sampling equipment, training, data management through applications and websites), (iii) Communication (e.g., between citizens as well as between citizens and researchers), and (iv) The feedback culture (e.g, applied by researchers). These three sets of factors may potentially influence both quantity and quality of data gathered by citizens. Their comparative role and effects in citizen science projects will be addressed in future research.

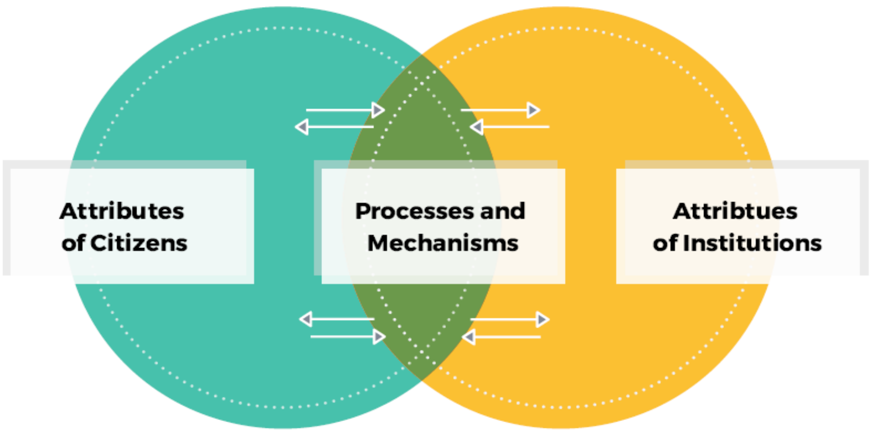

Figure 1. Three sets of success factors for citizens science projects in water quality monitoring

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Clean Water Production from High Salinity Water Using Pervaporation Membranes

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INTRODUCTION

Fresh water scarcity has materialized a serious threat to human livings and social developments. Due to the spectacular increase in the population and water pollution, it is necessary to find engineering solutions to provide fresh water in many water-limited areas (Subramani and Jacangelo, 2015; Mcginnis and Elimelech, 2008). One of the most effective methods to produce fresh water from salt water such as brackish water and seawater is the desalination technology (Zhu et al., 2013). Nowadays, membrane technology is considered as an attractive desalination way, counting on of their high efficiency, potential energy savings, high operational stability, low chemical costs, ease of integration and scale-up compared with traditional distillation techniques. In recent years, membrane distillation (MD) and pervaporation (PV) have become an appealing alternative for dealing with high-saline water and having the ability to resist certain type of fouling (Wang et al., 2016; Drioli et al., 2011). Although MD shows a promising way for high-salinity water desalination, membrane fouling and wetting are recognized as challenging problems leading to crucial disadvantage and result in increasing the costs of the process essentially for operating over long-term. Alternatively, PV is another membrane process which has been reported as a prospective process for desalination due to its potential in energy efficiency and feasibility in handling high salinity water. This work reports about a new MMMs of Laponite XLG clay / PVA for desalination by pervaporation. Laponite is a synthetic nanoclay consisting of a layered structure with 30 nm diameter and 1 nm in thickness with empirical formula $Na^{+0.7}[(Mg_{5.5}\,Li_{0.3})\,Si_8\,O_{20}\,(OH)_4]^{-0.7}$ and considered as belonging to semetic clay family (Selim et al., 2019).

MATERIALS AND METHODS

The mixed matrix membranes have been prepared by simple exfoliation process of the laponite clay in the solvent followed by mixing with the PVA solution to obtain 5 % PVA casting solution with different concentration of Laponite XLG of Laponite with respect to the dry polymer weight. After being stirred for 24 h in situ cross-linking was done using glutaraldehyde. After casting and annealing, the PVA membrane and the PVA-Laponite membranes were picked up and were designed as PVA, PVA-Lap_x, where x is the Laponite XLG content. A simple scheme showing the steps used for preparing PVA-Laponite XLG MMMs can be seen on Figure 1.

The surface morphology and hydrophilicity of the membranes was investigated. The pervaporation desalination performance of the PVA and PVA-Lap MMMs was studied using a lab-scale P-28 membrane unit from CM-Celfa Membranetechnik AG vacuum Pervaporation apparatus. Effect of NaCl % concentration in the feed solution as well as the effect of operating temperature were observed using 2 wt% laponite content and compared with the version PVA membrane.

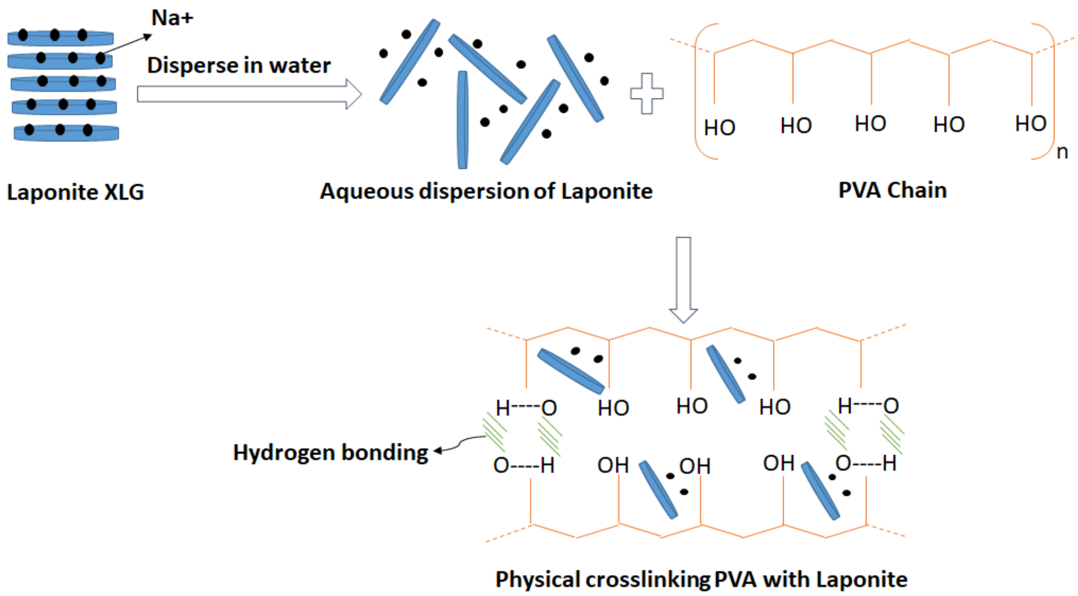

Figure 1. Graphical presentation of the Laponite XLG-PVA MMMs preparation

RESULTS

- Increasing the feed concentration (NaCl %) from 0 to 10 wt. % results in declining in the flux from 42.7 to 26.4 kg/m^2.h using 2 wt% laponite XLG MMM.
- However, the salt rejection show a modest increase from 99.90 % to ~ 99.95 % at the same conditions.
- The water flux increases with increasing the temperature by around 70 % for the pure water and 3 wt% NaCl solution in the temperature range of 40–70 ° C.
- The higher water flux of 58.6 kg/m2.h with a salt rejection over 99.9 % was achieved at 70 °C and feed solution of 3wt% NaCl.

CONCLUSIONS

Mixed matrix crosslinked membranes based on laponite nanoclay, PVA and GA were fabricated via exfoliation method. Pervaporation desalination performance of different NaCl solution was investigated using 2 wt% laponite XLG MMM. The feed concentration and feed temperature had a significant effect on the flux permeation of water through the membrane, where increasing the operating temperature from 30 °C to 70 °C led to remarkably increase in the water flux by approximately 44 %, while the salt rejection remained >99.9 %.

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Understanding Runoff Processes Using Hydrograph Separation in a Pasture Sub-catchment of UK

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INTRODUCTION

Hydrograph separation with natural tracers have become a popular method in identifying runoff components and their characteristics with respect to quality and quantity (Uhlenbrook and Leibundgut, 2002; Klaus and McDonnell, 2013; Hrachowitz et al., 2009; Weiler et al., 2003). The electrical conductivity (EC) is considered to be an easily monitored and inexpensive proxy for total dissolved solids and a signature for different water components, when the monitoring system is supported by an effective hydro-geomorphological conceptual model (Cuomo and Guida, 2016). The understanding of runoff generation mechanisms is important issue in the prediction of floods and droughts or in the case of the allocation of water resources or nutrient export. The study took place in the sub-catchment (0.09 km^2) located in the Upper Eden basin, Cumbria, UK. The results of this paper aim to answer the following questions: What are the major hydrological pathways in the sub-catchment? The research question is expressed as a testable hypothesis: Hydrochemical flow separation using continuous measurement of variables (electrical conductivity) at the catchment outlet can provide quantitative estimates of surface and subsurface components of flow.

MATERIALS AND METHODS

The electrical conductivity (EC) was used to distinguish between event water (overland flow) and pre-event water (baseflow/subsurface flow) according to the procedure of Hugenschmidt et al. (2010). During the sampling period, samples of baseflow/subsurface flow (pre-event water; water in the stream during periods without rainfall), overland flow and rainfall (both constituents of event water; from a tipping bucket set up on the hillslope) were collected and measured. The main discharge data that have been used in this work was provided by the existing runoff gauge and a V-notch weir at the Hollow sub-catchment. Stream discharge collected from CTD Diver (water levels converted to stream discharge using the rating curve) were retrieved from the outlet with a frequency of 15 min. In this study, electrical conductivity values were obtained by continuous measurements with a CTD Diver and by direct field measurements at the outlet of the sub-catchment.

Chemistry-based hydrochemical separation relies on the principle of mixing where the equations of continuity and mass balance govern the quantity of tracer flow (Ogunkoya and Jenkins, 1993). An example of a two-component separation is:

$$Q_t = Q_o + Q_n$$
$$Q_t C_t = Q_o C_o + Q_n C_n, \tag{1}$$

where Q_t, Q_o and Q_n (Q in m^{3}s^{-1}) represent volumes of current stream flow, pre-event water (old water - subsurface water including soil water and/or groundwater) and event water (new water - rainfall, overland flow), respectively, and C_t, C_o and C_n (C in mgl^{-1} or μScm^{-1}) are the corresponding tracer concentrations.

RESULTS AND DISCUSSION

In this paper, the two end-member compositions (event water and pre-event water) were considered from two initial sources: rainwater and baseflow/subsurface flow. The end-members chosen for the two-component hydrograph separation for each storm event are given in Table 1. The baseflow/subsurface flow electrical conductivity is an average of baseflow conductivities over a twenty-four hour period prior to the storm event. The separation was mainly composed of the pre-event water (78 %) for the November storm event (E3).

Table 1. Electrical conductivity of the event and pre-event water used in the hydrograph separation of discharge in the Hollow sub-catchment

	Electrical conductivity (μS/cm)		
Event	November 2009 (E3)	January 2010 (E4)	March-April 2010 (E5)
Event water (overland flow)	11	43	11
Pre-event water (baseflow)	819	984	971

CONCLUSIONS

The application of the two-component hydrograph separation shows that for all events, the overland flow and subsurface flow are present. However, the overland flow is not the dominant flow process in the sub-catchment during storm events.

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Linkages Between Energy Management and Management Accounting: An Empirical Study with Special Focus on German Water Supplying Companies

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INTRODUCTION

The intrinsic connection between water and energy has already been documented in numerous publications (Morales et al., 2013). But also from an economic perspective, a more conscious use of energy at company level seems reasonable in the context of the climate change debate and the increased public pressure to optimize the use of energy and resources. The costs of energy purchase in Germany have increased steadily in recent decades and according to the latest forecasts they won't decline in the coming years either. Against this background, it is not surprising that companies with high electricity demand are increasingly striving to reduce their energy consumption and increase their own energy production.

The water industry is also increasingly concerned with energy-efficiency issues due to an increased public awareness. However, the technical concepts for implementing a more energy-efficient water supply and wastewater disposal are diverse and complex, and thus require targeted control in order to manage the mostly implicit trade-offs (e.g. between energy cost savings and maintenance cost increases). This leads to complicated decision situations in which management accounting and its tools could offer support.

ENERGY EFFICIENCY AND MANAGEMENT ACCOUNTING

State of science and research at a glance

Energy efficiency in companies is influenced by several factors, such as organizational structures (e. g. production program planning taking into account environmental condition, production control according to energy efficiency criteria), process design (e. g. process development, combination and substitution, choice of process parameters), resources (e. g. careful determination of requirements and capacities, market position, component selection, design, loss reduction, substitution of energy sources), human capital (e. g. qualification, awareness, responsibility), and products (e. g. production concept taking into account the energy demand characteristics, careful specification of tolerances, avoidance of unnecessary production costs) (Weinert, 2010). An energy management system in accordance with DIN EN ISO 50001 can give structure to a company's efforts to reduce its energy consumption by introducing an energy policy and respective strategic energy objectives, as well as processes to achieve these goals.

Unfortunately, currently there is only little knowledge on possible synergies between management accounting and energy management processes available, so that it can be assumed that not all potentials for improvement of company's in-house processes are exploited. For example, there is extensive and reliable theoretical foundation in the field of sustainainability control, but so far, there has been hardly any transfers in relation to water management (von der Crone and Hoch, 2002). Possible explanations for this could be, that in comparison to the deregulated electricity and gas markets, water management is so far only to a very limited extent represented in management accounting literature (Pedell, 2008) and that international research on business administration in net industries has been more focused on data provision for external accounting within the last decades (Chalmers et al., 2012).

Methodological approach of the empirical study

In order to identify and develop suitable methods and tools for monitoring and controlling of energy-related consumption and cost data in the field of water management, relevant concepts and instruments of corporate energy management controlling discussed in the scientific literature were examined in a first step. Afterwards, an empirical study was performed in order to document the status quo of interactions between management accounting and energy management staff (if applicable), to derive the essential drivers of this “management accounting change” and to develop approaches for the best possible combination of energy management and management accounting. For this purpose, an interview guide had been developed, with the help of which a qualitative-explorative study was conducted with more than ten participating companies of different sizes and corporate forms. The focus of the study was therefore less on the technical possibilities of increasing the efficiency of water supply companies than on the resulting challenges for the ‘functional’ planning and reporting.

Extract from the results of the empirical study

With regard to management accounting in water supply companies, the empirical study shows that management accounting systems have become increasingly important in recent years but differ a lot in dependence of the company’s size. The processes in management accounting of utilities active in several sectors are significantly influenced by the requirements of the regulated electricity and gas markets and have only little focus on the water division.

Nearly all companies that participated in the survey have established a management accounting system in accordance with DIN EN ISO 50001 that is integral part of the structures and process within the company and practiced on an ongoing basis. Overlapping contents between management accounting and energy management mainly appear in the areas of cost accounting, reporting, investment and maintenance planning. In addition, most companies make use of energy related figures also within their key performance indicators for the purposes of corporate management. Even though in daily routine trade-offs between technical and economic interests create potential for conflicts, the cooperation between the two departments is described as well functioning and harmonious - but still highly improvable! - by most of the interview partners.

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Comparison of Recovered Lithium from Waste Lithium-ion Battery Recycling Process in the Presence of Organic Pollutants

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INTRODUCTION

With the fourth industry revolution, the use of electronic devices, lithium-ion batteries that can be reused through charging, are in the spotlight. Under these circumstances, recycling of lithium-ion batteries is not only a way to stabilize the lithium-ion market and bring economic benefits, but also to raise the price competitiveness of lithium-ion batteries. Currently, most of the metals (Co, Ni, Cu, Al, etc.) in lithium-ion batteries are recycled, but lithium is largely discarded, even though it contains high concentrations (500 to 2,500 ppm). This is because lithium contained in waste liquid contains electrolyte during the recycling process, resulting in organic pollutants and odours during the recovery process, which is complex and cost-effective. This research aims to develop eco-friendly technologies that can recover lithium from waste lithium ion batteries and remove organic pollutants from waste water. Although organic pollutants are known to have an effect on lithium recovery, it was not clearly identified as to what effect they had on lithium recovery. Therefore, in the corresponding experiment, simple and economical method using $NaAlO_2$ was proposed to recover lithium, and the effect of organic pollutants on lithium recovery was verified by comparing the recovered lithium from wastewater and treated water.

MATERIALS AND METHODS

The lithium-ion battery used in the experiment is a small battery made in Japan, which is mostly used in mobile phones. The ingredients are composed of 25 % carbon, 23 % cobalt, 7 % copper and 3 % lithium, while the others (25 %) include electrolytes and additives. The waste solution was manufactured in the same way as the waste battery recycling process for accurate experimentation and for checking if organic pollutants and odours were removed. About 30 kg of lithium-ion battery with some current was pulverized in about 10 litres of water (discharge). At this time the electrolyte was released and mixed.

The total organic carbon hot oxidation method (TOC, Teledine tekar, LOTIX TOC model) was used as a method for verifying the removal of organic pollutants from the waste liquid used in the experiment, and the TOC of wastewater was found to be 5700 ppm. The lithium concentration of the above waste solution was measured using an inductive coupling plasma (ICP-OES, model ARCOS2 of SPECTRO Company), and the concentration of lithium was confirmed to be 2.621 ppm.

As for the method of removing organic pollutants and odour in waste liquid, the removal rate was checked with duration by leaving the waste liquid in the atmosphere, and also by agitating with 300 rpm. In addition, the removal rate was checked by heating the wastewater to about 200 °C on the hot plate, and removing organic pollutants by blowing up the air in the waste water.

RESULTS AND DISCUSSION

Removal of organic pollutants

As a result of the preliminary test conducted for about one hour to check the removal rate according to different methods (agitation, heating and aeration). It was found that the rate of elimination caused by aeration was 37.9 %, the highest reduction compared to raw material with no odour on an hour basis. We then checked the elimination rate of the aeration method with duration. The rate of elimination was the highest at 48 % on a three-hour basis, and the elimination rate was reduced afterwards, confirming that the removal rate was not significantly different between 5 and 7 hours (Table 1).

Table 1. Elimination rate with duration by aeration

Duration (hr)	Rate of elimination (%)
1	37.9
3	48.5
5	52.2
7	54.8

Recovery of lithium

An experiment was conducted to recover lithium by agitation and heating for a day, respectively, using $NaAl_2$ in waste liquid containing organic pollutants and treated water that was aerated for about 7 hours. Three or more times, the weight of the recovered lithium was measured. As a result, the weight of the lithium compounds recovered from the original water was confirmed to be 5.43 g, 5.49 g and 5.47 g. The weight of lithium recovered from the treated water was 5.55 g, 5.57 g and 5.52 g, similar to that of the original. Comparing recovered lithium from wastewater and treated water, respectively, using ICP, confirmed that the percentage of recovered lithium does not differ much from each other at 31.2 % and 31.8 %, respectively.

Figure 1. Recovered lithium

Through the above experiment, it was found that lithium recovery and elimination of organic pollutants that could be a problem for environmental pollution, were possible in a relatively simple way. As for the recovered lithium from waste liquid, it was shown that the removal of organic pollutants had little effect on the purity or rate of recovery of lithium.

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History
Founded in 1953 by Georg H Endress and Ludwig Hauser, Endress+Hauser has been solely owned by the Endress family since 1975. The Group has developed from a specialist in level measurement to a provider of complete solutions for industrial measuring technology and automation, with constant expansion into new territories and markets.

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