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Simultaneous removal of ammonium ions and sulfamethoxazole by ozone regenerated high silica zeolites

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ABSTRACT

Continuous development of industry and civilization has led to changes in composition, texture and toxicity of waste water due to the wide range of pollutants being present. Considering that the conventional wastewater treatment methods are insufficient for removing micropollutants and nutrients to a high level, other, alternative, treatment methods should be used to polish wastewater treatment plant effluents. In this study we developed an alternative, polishing concept for removal of ammonium and micropollutants that could potentially be incorporated in existing wastewater treatment plants. We demonstrated a method to use high silica MOR zeolite granules as an adsorbent for simultaneous removal of the micropollutant sulfamethoxazole (SMX) and ammonium (NH_4^+) ions from aqueous solutions. At an initial NH_4^+ concentration of 10 mg/L the high silica zeolite mordenite (MOR) granules removed 0.42 mg/g of NH_4^+, similar to the removal obtained by commonly used natural zeolite Zeolita (0.44 mg/g). However, at higher NH_4^+ concentrations the Zeolita performed better. In addition, the Langmuir isotherm model showed a higher maximum adsorption capacity of Zeolita (q_{max}, 4.08 mg/g), which was about two times higher than that of MOR (2.11). The adsorption capacity of MOR towards SMX, at both low (2 μg/L) and high (50 mg/L) initial concentrations, was high and even increased in the presence of NH_4^+ ions. The used adsorbent could be regenerated with ozone and reused in consecutive adsorption–regeneration cycles with marginal decrease in the total adsorption capacity.

1. Introduction

The presence of organic micropollutants in industrial and municipal wastewater has become a major concern (Rogowska et al., 2019; Kamaz et al., 2019). These emerging pollutants include pharmaceuticals, personal care products, industrial chemicals, pesticides, fire retardants, etc. The increasing concentration of these compounds in wastewater requires that wastewater treatment facilities introduce an additional removal technology, although discharge guidelines for many of these compounds do not exist. Various studies have shown the presence of these pollutants in effluents from sewage treatment (up to 10 μg/L) and in surface water with average values up to 1 μg/L, and maximum values up to 10 μg/L (Sathiskumar et al., 2020; Liwarska-Bizukojc et al., 2018; Zhou et al., 2019). Given that most existing wastewater treatment

plants (WWTPs) are not designed for removal of these compounds, they end up in WWTP effluent, while, in practice, water authorities aim at reducing or eliminating the adverse effects of trace organic compounds on the aquatic environment and on human health (Loos et al., 2013; Guillossou et al., 2019).

Additionally, ammonium is a key component in most domestic WWTPs. Anticipated new treatment targets to avoid water pollution require a large number of WWTPs to meet discharge consents between 1 and 3 mg NH_4^+/L (WHO, 1996; Milieurecht 2017).

The conventional process for ammonium removal consists of aerobic nitrification and anoxic denitrification, consuming high amounts of energy (van der Hoek et al., 2018). A possible solution to move towards energy consumption reduction and efficient ammonium removal could lie in ion exchange (Amini 2017). A variety of materials can be used in such an ion exchange process, including polymeric ion exchange resins, as well as natural and synthetic zeolites. Especially natural zeolites, including Clinoptilolite, MOR and Chabazite, with Clinoptilolite being the most commonly

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used, tend to be effective in ammonium removal (Langwaldt, 2008; Widiastuti et al., 2011; Wang et al., 2010). The purity, chemical composition, crystal size, porosity and pore diameter of these zeolites vary, which influences their efficacy for wastewater treatment in terms of their capacity and selectivity towards ammonium (Moshoeshoe et al., 2017).

On the other hand, in recent years, synthetic, high silica, zeolites have been evaluated as alternative adsorbents for activated carbon, for organic micropollutant removal from water. A synthetic zeolite is made by modification of clay and other aluminium bearing minerals, and shows promising operating efficiencies, comparable to the natural zeolites (Ham et al., 2018). The capacity and selectivity of the various zeolites are influenced by a combination of the internal pore sizes of the lattice structure, the ratio of Si/Al and the distribution of Al within the lattice frame (Jiang et al., 2018). MOR was selected as a high silica zeolite, amongst others, due to its commercial availability and proven removal of wide range of different organic micropollutants (Jiang, 2019). The removal of micropollutants (in this case pharmaceuticals) on MOR might benefit from the wide range of pores sizes, i.e. 2.6 Å-7.0 Å, from two types of channels with opening sizes 2.6 Å*5.7 Å and 6.5 Å*7.0 Å (Jiang, 2019). In addition, MOR has been, next to clinoptilolite, reported as a zeolite for ammonium removal (Chen et al., 2018). The possibility of regenerating MOR zeolite by ozone is reported (Wang, 2020). Therefore, MOR could have potential adsorption characteristics for micropollutants, rather than clinoptilolite, with a simultaneous decrease of ammonium concentrations in water."

The above mentioned processes are, in principle, reversible so that, after the zeolite has been exhausted, it could be regenerated by treating the zeolite with e.g. an advanced oxidation technology such as ozonation (Zhang et al., 2014), being economically and environmentally competitive when compared to the large amounts of salts required for the conventional regeneration of exhausted zeolites (Deng et al., 2014). Additionally regeneration is done on-site making it more attractive than granular activated carbon (GAC), for which reactivation plants are normally used (Clements et al., 2004).

Due to the co-existence of multiple contaminants in water sources, including ammonium and micropollutants as indicated above, technologies for their simultaneous removal are desirable. The rationale behind promoting simultaneous removal of micropollutants and ammonium, is to promote so-called "one-step" treatment methods, replacing complex and multi-step methods of already existing conventional processes mentioned in the paragraph above. In the current study, we developed an innovative and sustainable polishing concept that can remove multiple contaminants in a single process and could potentially be incorporated in existing wastewater treatment plants. We demonstrated the potential of this treatment strategy using laboratory-scale experiments. The innovation thus lies in 1) simultaneous removal of organic micropollutants and ammonium from water by zeolite granules and 2) regeneration of granules with ozone. Accordingly, the current paper provides the comparison of a synthetic (MOR) and natural zeolite (Zeolita) in a series of batch experiments in ultra-pure water to evaluate the performance and assess the impact of initial ammonium concentration on ammonium and sulfamethoxazole (SMX) removal efficacy. Sulphonamide antibiotic SMX was chosen as a model compound. Nowadays, the sulfonamide group is present in many drugs as antibiotics, antimalarics, diuretics, hypoglycemics, antiinflammatories, antihypertensives, antitumor compounds, antithyroid compounds, etc., making SMX good representative drug for broad range of antibiotics (Zhou et al., 2018; Thiebault, 2020). Additionally, SMX was chosen as a model compound due to its resistance to remediation and natural attenuation and due to its extensive use in both human and veterinary medicines (Jiang, 2019;

Bueno et al., 2012; Loos et al., 2013). This antibiotic has been classified as emerging contaminant, and has been found in water resources at concentration levels from ng/L to μg/L (Bueno et al., 2012; Al Aukidy et al., 2012; Loos et al., 2013). SMX has been detected in the concentration range from 1 to 150 ng/L in WWTP effluents and along Dutch rivers (Zhou et al., 2018; Sabri et al., 2020).

2. Materials and methods

2.1. Zeolite materials and zeolite characterisation

For the experiments two zeolites were used: a natural Clinoptilolite NZ (Zeolita, Spain) and a synthetic Mordenite (MOR, 690 HOA, Si/Al~240, Tosoh Corporation, Tokyo, Japan). MOR powder zeolite had a surface area (BET) around 450 m²/g with a crystal size of 0.1 × 0.5 μm (Jiang, 2019). The number in parentheses refers to the Si/Al ratio of the zeolite. Preliminary tests on SMX removal by four different types of synthetic zeolites (MOR, FAU, BEA and MFI) indicated that the best ammonium removal was achieved by MOR zeolite (Jiang et al., 2018), and, therefore, MOR was used during the experiments.

Both granular and powdered zeolites can be used in liquid-phase applications (Jiang et al., 2018). However, in this study the granular form was chosen since it can be used in continuous processes and can be regenerated, whereas the powdered form is generally used in batch processes, without regeneration. Additionally, the granulation process transforms the fine powders into dust-free granules that are easy to compress. The granules had a spherical shape, for content uniformity and an adequate moisture and hardness to prevent breaking (determined previously by Elshof, 2019), dust formation during process and loss of material. Zeolite granules were made using zeolite powders combined with bentonite (Honeywell Fluka™, USA), which functions as a binder, in the percentage ratio of 85:15 (zeolite/bentonite). Pre-treatment of the zeolites was done by washing it with Mili-Q water. Afterwards the samples were dried for a day in an oven at 105 °C to remove moisture. Finally, the granules were calcinated in the oven for 3 h at 600 °C for NZ and for MOR at 850 °C.

In order to compare the crystal structure and the mineralogy of the zeolite, X-Ray (XRD, Bruker-AXS D5005 diffractometer, using filtered Cu Kα radiation, with accelerating voltage 45 kV, current 30 mA and scanned at 2θ from 4 to 50°) diffraction analyses were performed. The chemical composition of the zeolite samples was determined by using X-Ray Fluorescence (XRF), using a Panalytical Axios Max WD-XRF spectrometer, and data evaluation was done with SuperQ5.0i/Omnian software (Boatemaa et al., 2018).

2.2. Batch study for SMX and ammonium removal using zeolita and MOR

Equilibrium adsorption was determined in batch experiments, using 1 L flasks for each of the zeolites. Experiments were conducted in demineralised water (RiOs Reverse Osmosis System). Various studies have shown the presence of SMX in effluents from sewage treatment (up to 10 μg/L) and in surface water with average values up to 1 μg/L, and maximum values up to 10 μg/L (Sathiskumar et al., 2020; Liwarska-Bizukojc et al., 2018; Zhou et al., 2019). In the SMX adsorption experiments, the initial concentrations of SMX were 2 μg/L and 50 mg/L. The latter was chosen to study the changes in competitive adsorption (Jiang et al., 2018).The MOR concentration was varied between 0.01 g/L and 1 g/L, obtained from previous research (Jiang et al., 2018). A blank measurement (0 mg/L adsorbent dose) was included in each of the isotherm series. The solutions with granules were mixed using a magnetic stirrer. After 10 d for the 50 mg/L initial concentration and after 4 weeks for 2 μg/L, samples were filtered through

a 0.20 μm membrane filter and analysed. Moreover, to study the effect of initial ammonium concentration and adsorption isotherm, batch experiments were conducted by varying the initial ammonium of 10 – 100 mg/L with Zeolita/liquid ratio 2 g/100 ml at 72 h contact time and at a temperature of 20 °C. Ammonium-containing water was prepared from ammonium chloride (Sigma Aldrich).

To determine the above contact times, to reach equilibrium, kinetic studies of ammonium and SMX removal by Zeolita and MOR from aqueous solution were carried out by agitating 1 L of ammonium or SMX solution of known initial concentration with 1 g of MOR and Zeolita for SMX and 20 g of Zeolita or MOR for ammonium at room temperature (20 °C). A quantity of 1 mL of uniform dispersion was pipetted out, using a 5 mL-syringe at different time intervals. The collected samples were then filtered (0.2 μm syringe filter, Whatman SPARTAN™), and the concentration in the solution was analysed.

The pH of all solutions was measured by using a pH metre (Inolab® Multi 9420 IDS, WTW, Germany) and was adjusted by using 0.1 M NaOH or 0.1 M NaCl solutions to get pH 7.The ammonium concentration was determined by cell tests (Hach® LCK Cuvette Tests, LCK302, LCK303 and LCK304), using a spectrophotometer (Hach® LANGE model DR3900, the Netherlands) and confirmed by Ion chromatography (IC, 883 Basic IC plus, Metrohm, Switzerland). For this method a cation exchange C6 column (Metrohm, Switzerland) was used, with 3 mM HNO$_3$ (Sigma-Aldrich, Germany) as the eluent. The samples were placed in an autosampler (919 IC Autosampler plus, Metrohm, Switzerland) and measured with a flowrate of 0.9 mL/min.

For SMX analyses 1 ml of sample was acquired from the sample bottle. SMX in water samples of the experiments with initial concentration of 50 mg/L were determined with a HPLC system (Shimadzu Corporation, Japan), equipped with reversed phase C18 column; 2.6 μm, 100 × 4.6 mm (Kinetex Core-Shell C18 column, Phenomenex®, USA). 10 μL of sample was injected into the system and the elution was conducted with a mixture of acetonitrile and ultrapure water (60:40, v/v) at a flow rate of 0.6 ml/min. The column oven was set at 30 °C. The eluted compound was monitored with UV detector at a wavelength of 215 nm.

For the samples of the experiments with low initial SMX concentration (2 μg/L), the Waters Acquity UPLC Plus system was used, with an ACQUITY UPLC® BEH C18 (1.7 μm particle size, 2.1 × 50 mm, Waters Ireland) analytical column. The column temperature was 40 °C. The injection volume and flow rate, pumped by an ACQUITY UPLC IClass Plus (Waters/USA), were 10 μl and 0.35 ml/min, respectively. A gradient mobile phase was used: water containing 0.1% (v/v) formic acid (mobile phase A) and acetonitrile containing 0.1% (v/v) formic acid (mobile phase B). The system was coupled with tandem mass spectrometry (MS). MS was conducted on a Xevo TQ-S micro tandem quadrupole mass spectrophometer (Waters/USA), equipped with electrospray ionization in positive mode (ESI+), detecting two fragments (quantifier & qualifier, verified against the Metlin or Massbank MS/MS databases) of each analyte and deuterated internal standards (Torronto Research Chemicals/Canada), with quantification by 10-point calibration at levels from 0.0025 μg/L to 10 μg/L. The MassLynx V4.2 software was used for data acquisition and quantitative analysis.

2.3. Adsorption isotherm and data analysis

The amount of contaminant adsorbed from the aqueous solution was expressed as equilibrium loading per mass of the zeolite (q$_e$)

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

Where, C_o is the initial pollutant concentration (mg/L), C_e is the equilibrium concentration (mg/L), V is the batch volume (L) and m is the zeolite mass. Equilibrium data for each of the zeolites was then compared to Freundlich and Langmuir isotherm models (Ayawei et al., 2017).

In the Langmuir model it is assumed that adsorption is monolayer and that adsorption energy is constant. The Langmuir adsorption isotherm can be expressed as:

$$q_e = \frac{q_{max}K_LC_e}{1 + K_LC_e} \tag{2}$$

where q_e (mg/g) is the amount of compound adsorbed per unit mass of adsorbent, C_e (mg/L) is the equilibrium concentration of the compound, q_{max} (mg/g) and K_L (L/mg) are Langmuir constants related to adsorption capacity and rate of adsorption (Ayawei et al., 2017).

On the other hand, the Freundlich model assumes that the surface energy of the adsorbent is heterogeneous and that first sites with stronger binding will be occupied.

The Freundlich adsorption isotherm is shown as:

$$q_e = K_FC_e^n \tag{3}$$

where K_F (mg/g (L/mg)$^{1/n}$) is the adsorption capacity. The n value (0–1) is factor that indicates adsorption intensity (Ayawei et al., 2017).

A typical isotherm of the obtained experimental data consists of 5–10 points, performed in triplicates (Al-Ghouti et al., 2020; Maksin et al., 2012).

2.4. Zeolite regeneration

Oxidation by ozone was found to be robust, scalable and cost effective (Ateia et al., 2018) for the regeneration of zeolites. Ma et al. (2019) already studied the effective adsorption and regeneration of SMX loaded high-silica zeolites. Therefore, the specific objectives of regeneration in this study were: (a) optimal pH by regeneration of granules loaded with ammonium by ozone; (b) evaluation of regenerated zeolites over several adsorption/regeneration cycles.

a) Oxidation of ammonium by ozone

To perceive under which conditions zeolite granules, saturated with ammonium, can be regenerated, experiments were conducted by dissolving ammonium in buffers with different pH values (7, 8 and 9) and subsequently oxidizing the dissolved ammonium by ozone. Boric acid-sodium borate mixtures were employed to maintain a constant pH. Before the ozonation test, the initial pH was measured using a pH metre (Inolab® Multi 9420 IDS, WTW, Germany). The reaction solution was sampled every 5 min to analyse the changes in pH values and concentrations of ammonium. Concentrations of ammonium were measured by spectrophotometry methods and ion chromatography (IC, 883 Basic IC plus, Metrohm, Switzerland).

a) Adsorption-Regeneration Cycles

Adsorption-regeneration cycles were conducted to examine the regeneration efficiency of the zeolite granules after use. The adsorption cycle consisted of loading the zeolite granules with ammonium. Adsorption in a batch reactor was followed by a regeneration cycle. After regeneration, another loading cycle was executed.

Therefore, granules, loaded with ammonium, were added into the 200 mL glass- reactor after the adjustment of pH for the regeneration process. Then ozone was introduced in the solution through the glass diffuser. The zeolite granules were stirred by a magnetic stirrer. Ozonation was performed for 2 h, whereas ozone concentration in the gas phase was 90 g/m^3 with flow rate of

Table 1
Chemical composition of natural and synthetic zeolite.

Compound name	Type zeolite	
	Zeolita (wt%)	MOR (wt%)
SiO_2	75.911	94.656
Al_2O_3	13.687	3.933
Fe_2O_3	1.368	0.668
MgO	1.48	0.392
CaO	4.181	0.19
K_2O	2.253	0.057
TiO_2	0.156	0.047
SO_3	0.333	0.02
P_2O_5	0.033	0.013
ZrO_2	0.005	0.009
NiO	/	0.008
SrO	0.029	0.005
Y_2O_3	/	0.001
Nb_2O_5	/	0.001
Na_2O	0.454	/
MnO	0.043	/
BaO	0.029	/
Cl	0.017	/
Rb_2O	0.01	/
ZnO	0.005	/
CuO	0.005	/
PbO	0.003	/

0.7 L/min (O_3 concentration in water 25 mg/l). Ozone was produced from pure oxygen with an ozone generator and measured with analysers (Ozone analyzer BMT 964C model, RMG MESSTECH-NIK GmbH, Berlin, Germany), installed before and after the reactor. Moreover, removal of the compound during ozonation can be attributed to either oxidation by ozone and/or formed hydroxyl radicals (·OH). However here ·OH radical contribution to the regeneration of the granules at pH 9 is assumed to be very small since it was found that ·OH formation accelerates at pH 10 (Zhang et al., 2015; Elovitz et al., 2008).

The regeneration process was followed by rinsing the granules with demineralised water and drying them in an oven at 60 °C. Then the regenerated zeolites were, again, exposed to batch adsorption in a fresh ammonium solution. The procedure was repeated three times (3 cycles) for different initial ammonium concentrations. After each regeneration cycle, the adsorption capacity of the regenerated granules was measured. All adsorption and regeneration experiments were conducted in duplicates. An air stripping experiment was set as a blank experiment to exclude the stripping removal of ammonia by ozone. The removal efficiency (R) was calculated by Eq. (2) as follows:

$$R = \frac{(C_0 - C)}{C_0} \cdot 100\% \tag{4}$$

where C_0 is the initial concentration of ammonia (mg/L) and C is the concentration (mg/L) at reaction time t (min).

3. Results and discussion

3.1. Characteristics of natural and synthetic zeolite

Chemical characteristics of the natural, Zeolita, and the synthetic zeolite, MOR, were analysed using XRD and XRF and are presented in Table 1, showing that both Zeolita and MOR mainly consist of silica and alumina. However, the hydrophilic/hydrophobic features, controlled by varying the Si/Al ratio, can influence the behaviour of zeolites towards polar/non-polar reactants and products in adsorption processes (Sarti et al., 2017). This is confirmed by the observation that MOR, with Si/Al~240, was an effective adsorbent for the removal of SMX (Figs. 4 and 5). Table 1 also reveals
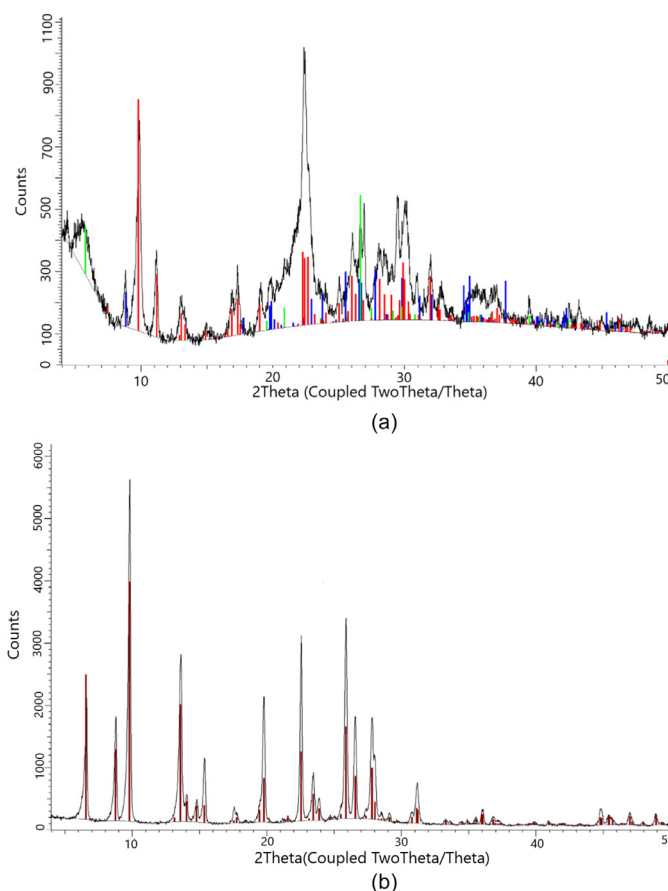

Fig.. 1. XRD pattern plots for a) natural (red – Clinoptilolite-Na, blue – Muscovite, green - Nontronite) and b) synthetic zeolite (red - Mordenite).

that both zeolites contain exchangeable cations such as Fe^{3+}, Ca^{2+}, Mg^{2+}, K^+ and Na^+, potentially being able to be exchanged with other cations in the solution, such as, in this case, ammonium.

The zeolites were additionally characterised by XRD to determine the mineral structure, and the results are given in Fig. 1. It was revealed that Zeolita comprised, besides clinoptilolite, muscovite and nontronite (Fig. 1a), and the MOR of mordenite (Fig. 1b), which was to be expected. In case of natural zeolites used in other research, the XRD analyses have shown that the dominant mineral component is clinoptilolite (Langwaldt, 2008). However, the content of clinoptilolite in zeolitic material can differ from 25% to 70–75% (Franus et al., 2011). Besides clinoptilolite in natural zeolites small amount of opal, quartz, montmorillonite or heulandite can be found (Langwaldt, 2008). When comparing MOR zolites, in general, the overall x-ray investigation of natural or modified MOR zeolite samples in the literature mainly consist of mordenite which agrees with the findings in Fig. 1b) (Sakizci et al., 2015; Hussain et al., 2019).

3.2. Ammonium and SMX removal using zeolites

3.2.1. Ammonium removal by zeolita and MOR

Zeolita and MOR (Table 2 and Fig. 2) were tested on ion-exchange capacity, focusing on ammonium removal. The ammonium adsorption was found to increase with increasing initial ammonium concentration from 10 – 100 mg/L at a constant zeolite amount of 20 g/L. Based on Fig. 2, it can be observed that ammonium adsorption capacity on Zeolita was between 0.5 – 3 mg/g and on MOR between 0.4 – 2 mg/g.

Table 2
Langmuir and Freundlich ammonium and SMX adsorption isotherm parameters.

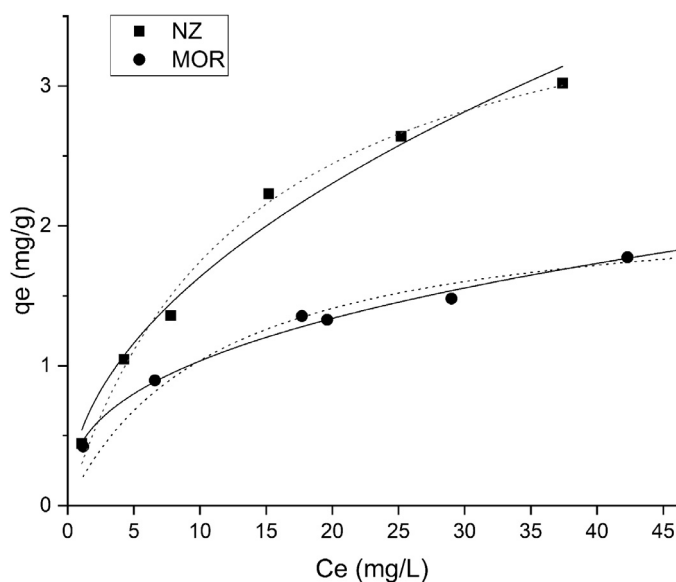| Model	Parameters	Type of zeolite	
		NZ	MOR
Langmuir	q_{max} (mg/g)	4.081	2.11
NH_4^+ (40 mg/L)	K_L (L/mg)	0.075	0.115
	R^2	0.990	0.958
Freundlich	K_F(mg/g (L/mg)^n)	0.524	0.439
NH_4^+ (40 mg/L)	$1/n$	0.494	0.371
	R^2	0.983	0.993
Langmuir	q_{max} (mg/g)	/	58.75
SMX (50 mg/L)	K_L (L/mg)	/	0.092
	R^2	/	0.987
Langmuir	q_{max} (mg/g)	/	80.44
SMX (50 mg/L)+NH_4^+	K_L (L/mg)	/	0.073
	R^2	/	0.981
Freundlich	K_F(µg/g (L/µg)^n)	/	9.63
SMX (2 µg/l)+NH_4^+	$1/n$	/	0.996
	R^2	/	0.991

Fig. 2. Adsorption isotherm plots for ammonium onto Zeolita and MOR zeolites. The solid points belong to experimental data while the lines are calculated according to Equations (2) (dashed line) and (3) (solid line).

The adsorption process was evaluated by fitting the data to two adsorption isotherms; the Langmuir and Freundlich. The isotherm Eqs. (2) and (3) and the experimental adsorption equilibrium data were used to determine the Langmuir and Freundlich parameters, for ammonium both for Zeolita and MOR, and for SMX only for MOR. Both the Langmuir and Freundlich isotherm models equally best fitted the experimental adsorption data with high coefficient of determination R^2. The Langmuir parameters (K_L and q_{max}) and Freundlich parameters (K_F and $1/n$) for the adsorption isotherms are given in Table 2. However, in view of the higher R^2 value, listed in Table 2, the Freundlich model showed to be the best fitting model for MOR. The conformity to the Freundlich model is a result of the heterogeneous nature of the zeolite surface and supports the earlier multi-linear nature of ammonium adsorption (Wasielewski et al., 2018; Kotoulas et al., 2019).

On the other hand, it was found that the Langmuir model yielded a better fit to the data compared to the Freundlich when using Zeolita. In this case it is assumed that adsorption happened at specific homogeneous sites within the zeolite, and that there was no interaction between adsorbate molecules. Langmuir parameters with other natural zeolites from various ori-
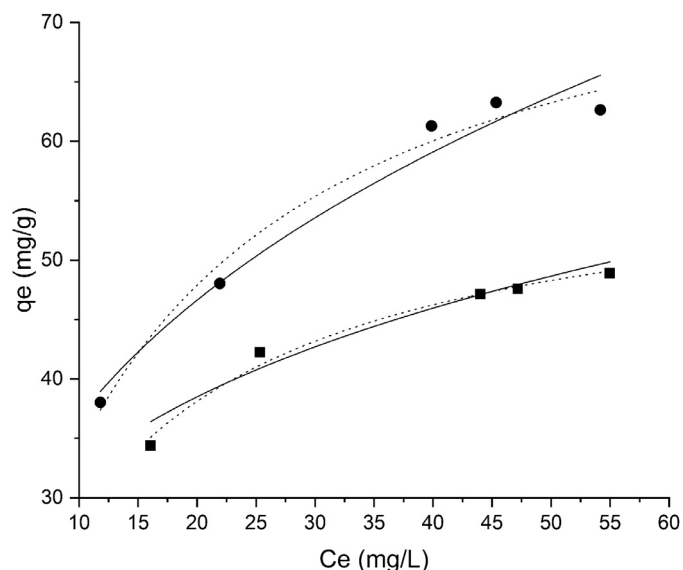

Fig. 3. Adsorption of SMX (50 mg/L) on MOR granule zeolites at 20 °C with the absence (■) and presence (●) of NH_4^+ ions (40 mg/L). The solid points belong to experimental data while the lines are calculated according to Equations (2) (dashed line) and (3) (solid line).

gins, Widiastuti et al. (2011) has reported that a q_{max} value of 6.032 mg/g at initial ammonium concentration of 5 −120 mg/L using an Australian zeolite. However, q_{max} values of 0.608- 6 mg/g at initial ammonium concentration of 10–80 mg/L (Demir et al., 2002) and 6.65 mg/g (Rahmani et al., 2004) have also been reported. In our case the maximum achieved adsorption capacity of 4.081 mg/g, was less compared to Australian zeolite. Lower adsorption capacity can be attributed to the variation in their mineralogical compositions and morphology (Selvam et al., 2018; Widiastuti et al., 2011). Although the results show a large variation with regard to the maximum ammonium adsorption capacity at the varied concentrations, it can nevertheless be found in the literature that in the range from 10 to 80 mg/l maximum removal efficiency of zeolite can be achieved, while increasing the initial ammonium concentration decreased its removal percentage (Wasielewski et al., 2018; Kotoulas et al., 2019).

For the Freundlich model similar values of K_F and $1/n$ ranged from 0.522 to 0,607 have been reported for ammonium removal using natural zeolites (Demir et al., 2002; Widiastuti et al., 2011). For all initial ammonium concentrations, the $1/n$ parameter ranges from 0 to 1. On this basis, it can be assumed that adsorption conditions of ammonium on zeolites were favourable.

The adsorption capacities of ammonium by MOR were similar to those of Zeolita at low initial ammonium concentration (10–40 mg/L). The measured data showed a larger difference in adsorption efficiencies when higher initial ammonium concentrations were present (60–100 mg/L). Similar outcome was found when comparing Romanian zeolite tuff and synthetic zeolites 5A and 13X (Wang et al., 2010).

3.2.2. SMX removal

Adsorption of SMX onto the selected zeolite granules has been carried out at room temperature (20 °C) under different initial SMX concentrations (about 50 mg/L and 2 µg/L, respectively), and with and without the presence of NH_4^+ ions (40 mg/L). However, no measurable reduction in SMX concentration in the presence of the natural zeolite clinoptilolite has been reported in literature (Farías et al., 2003) or observed experimentally (data not shown). Figs. 3 and 4 illustrate the adsorption isotherms of SMX on the MOR granules. The adsorption capacity increased with increasing
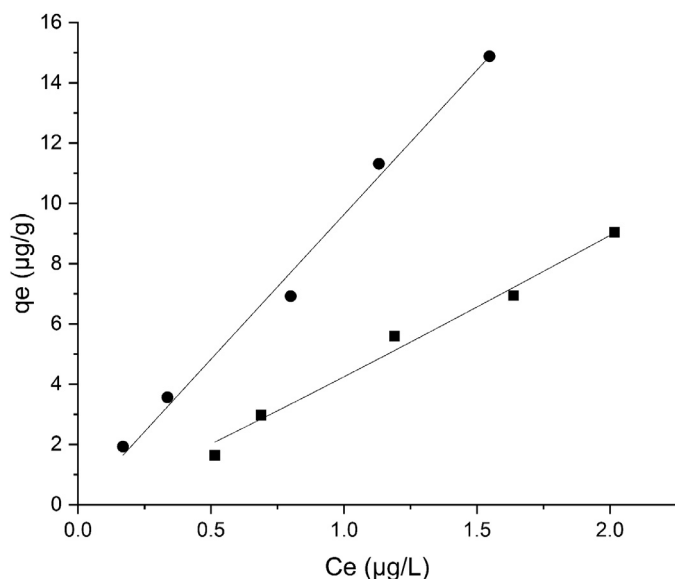
Fig. 4. Adsorption of SMX at low initial concentration (2 µg/L) on MOR granule zeolites at 20 °C with the absence (■) and presence (●) of NH_4^+ ions (40 mg/L).

the equilibrium concentration, as expected (Jiang et al., 2020). Removal of SMX by initial SMX concentration of 50 mg/L by MOR zeolite (1 g/L) in the absence of NH_4^+ ions was 71.6% (from initial 56.59 mg/L of SMX, 40.52 mg/L was removed from the solution by adsorbent) in agreement with prior work (Braschi et al., 2010). From the results in Table 2 it can be concluded that the experimental data are found to be best fitted by Freundlich equation. Therefore adsorption isotherms were fitted by the Freundlich isotherms in Fig. 3 and 4. Similar behaviour was obtained by de Sousa (2018) showing that stronger binding sites on the surface are occupied first and that the binding strength decreases with the increasing degree of site occupancy. Additionally, he presented a SMX adsorption isotherm as a characteristic profile of type S-curves, indicative of vertical orientation of adsorbed molecules at the surface (de Sousa et al., 2018).

In addition, isotherms' comparison of single SMX adsorption on MOR and adsorption of SMX in the presence of ammonium on MOR are shown in Fig. 3 and Fig. 4. Increased SMX adsorption on MOR occurred in presence of NH_4^+ ions at concentration of 40 mg/L, where, in this case, the adsorbed amount was 78.3% of the initial amount present in the solution. This rise in adsorption efficiency of SMX probably reflects that the process was assisted by surface complexation amongst SMX, NH_4^+ and MOR, as suggested by Bajusz et al. (1998), who studied the adsorption of N_2-O_2 mixtures at different P_{N_2}/P_{O_2} ratios on a series of NaCaX zeolites with different degrees of Na^+ replacement. It was shown that, for single adsorbates, the adsorption increased when Na^+ cations were replaced by Ca^{2+} cations. An exchange causes an increase in adsorption, suggesting that Na^+ is replaced at the sites which are accessible to the molecules. Sato et al. (2003) gave an additional explanation on this behaviour through the observation of structural changes of zeolites during ion exchange. In this research experiments on structural changes of zeolite were conducted (XRD and XRF analysis) with "clean" and loaded zeolite. However, no changes could be detected (data not shown in the manuscript). Therefore, we hypothesize that structural changes of the zeolite occur during the ion exchange and we support it with literature findings and measurements done by Sato et al., 2003, Price et al., 2017, Munthali et al., 2014; Azambre et al., 2020. They found that the zeolitic framework structure deteriorated as evidenced by decreases in the crystallinity and micropore surface area. amongst three zeo-

lites, one of them showed the most prominent dealumination and mesopore formation. Price et al. (2017) confirmed the same structural changes occurrence on another type of zeolite after partially exchanging the extra framework Na^+ ions with monovalent, Li^+, K^+, Rb^+ and NH_4^+ and divalent, Ca^{2+} cations. The results that she obtained from the NMR and FT-IR spectra indicated that the local framework environment was affected and that a loss of some aluminium from the framework had occurred. Dealuminated zeolites contain less Al which corresponds to a higher Si/Al molar ratio. The increased SMX adsorption in the presence of NH_4^+ ions, could thus be explained by structural changes of MOR, during ion exchange with NH_4^+, leading to a zeolite with a more favourable Si/Al ratio and mesoporosity, enhancing the accessibility of active sites, for SMX adsorption, as observed in similar studies (Munthali et al., 2014; Azambre et al., 2020).

However, the presence of NH_4^+ at the surface might also have resulted in a higher positive surface charge, which could have increased the adsorption capacity of SMX, which, at higher pH values, is negatively charged (Liu et al., 2018).

The isotherm model, shown in Fig. 4 and fitted for the data for the removal of SMX (2 µg/L) in the presence of NH_4^+ ions, describes an appropriate fit to the adsorption of adsorbate at relatively low concentrations.

Apart from the effect that the presence of ammonium ions had on the adsorption of SMX by the zeolite granules, the adsorption of ammonium (initial concentration of 40 mg/L) in the same mixture was tested. From Table 3 it can be seen that there was hardly any effect of SMX on ammonium adsorption even at high concentrations (about 50 mg/L) of SMX. Accordingly, it is assumed that the effect of SMX at a concentration of 2 µg/L on ammonium removal is absent and therefore was not further tested.

3.3. Regeneration

To study the effect of initial pH on ammonia removal by ozone oxidation, a series of experiments were conducted with different initial pH values (7, 8 and 9) at an ozone flow rate of 0.7 L/min and an ozone concentration in the gas phase of 90 g/m³. The results are shown in Figs. 5a) and 5 b).

The decrease in the concentration of ammonium in Fig. 5a) indicates that ammonium was oxidized by ozone at pH 9 according to the reaction (Singer et al., 1975; Khuntia et al., 2012):

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \tag{4}$$
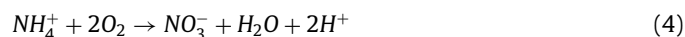
This is in accordance with the alkaline pH range reported to be the most effective for the ozone oxidation of ammonia (Singer et al., 1975; Khuntia et al., 2012). Almost no removal of ammonium at initial pH 8 (8% removal) was observed, while the removal efficiency reached 96% at pH 9 after 120 min. It is observed from Fig. 5b) that the pH value of the solution reduced with reaction time. The decrease in pH was mainly due to continuous production of H^+ ions during the oxidation reaction (eq. (4)). Luo et al. (2015) observed the same trend in pH decrease, while they studied the effect of initial pH on ammonia removal by ozone oxidation. They also found that the higher the pH value is, the larger the ammonium removal efficiency.

In order to avoid interference of air stripping of NH_3 (Mohammed-Nour et al., 2019) with the removal of ammonium by oxidation with ozone, the stripping process was tested. The pKa value for ammonia 9.25 indicates that it can be predicted that some electrically neutral ammonia would exist at pH $\leqq$9 (Danutė Vaičiukynienė et al., 2020). At pH 9 it was found that no NH_3 was transferred to the atmosphere. This was in accordance with findings from literature where at the higher pH range (pH 10-pH 12) greater proportions of nitrogen in form of gaseous NH_3 are present,

Table 3
Exchange of NH_4^+ ions on MOR granule zeolites at 20 °C with the absence and presence of SMX (about 50 mg/L).

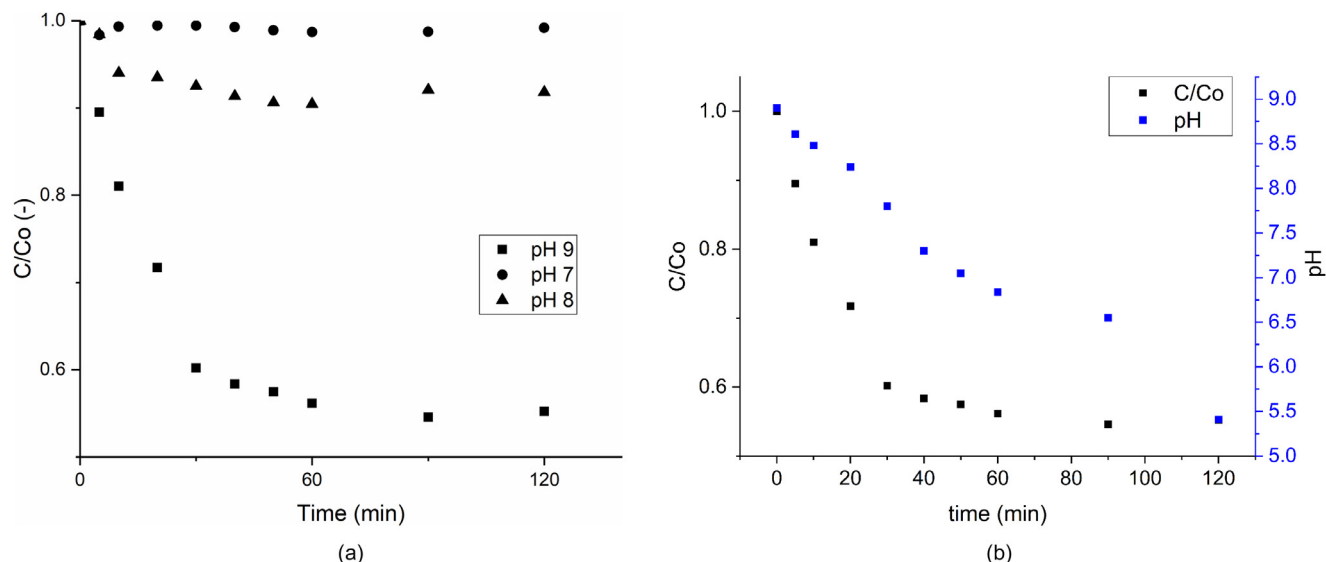|	Adsorption capacity q_e mg/g	Initial NH_4^+ concentration mg/L	Initial SMX concentration mg/L
No competition	1.355	40	50
Competition	1.24	40	50

Fig. 5. Ammonium removal by ozonation of NH_4Cl solutions containing 40 mg/L ammonium at initial pH 7, 8 and 9. a) effect of pH on removal efficiency; b) effect of ozone on ammonium removal and buffer (pH 9).
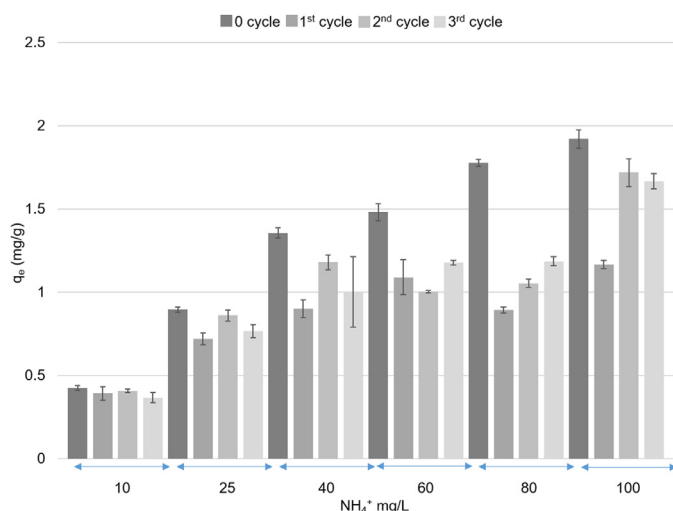

Fig. 6. Adsorption capacity of MOR with different initial ammonium concentrations (10, 25, 40, 60, 80 and 100 mg/L) at 20 °C, up to three regeneration cycles with ozone.

and a larger percentage of NH_3 could be stripped (Guštin et al., 2011; Campos et al., 2013).

When adsorption equilibrium by MOR granules with NH_4^+ was obtained at various initial concentrations, as shown in Fig. 6, its regeneration was conducted by oxidation using an ozonated water. Fig. 6 shows the results of adsorption/oxidation cycles performed over the ammonium loaded MOR granules.

As can be noticed, after the first regeneration cycle the adsorption capacity dropped for each initial ammonium concentration. The initial adsorption capacity for low initial ammonium concen-

tration (10 mg/L) of 0.4235 mg/g was decreased, after three regeneration cycles, by 0.057 mg/g. At the high initial ammonium concentrations (e.g. 100 mg/L) the decrease after first regeneration cycle was higher (from 1.92 mg/g to 1.22 mg/g). However the adsorption capacity after the second and third regeneration cycle recuperated and reached 70% of the initial adsorption capacity. This drop in the adsorption capacity could be related to slow diffusion of ozonated water to inner adsorption sites of the granules, resulting in incomplete regeneration. This is in a good agreement with the study of Zhang et al. (2014), who concluded that ozone dosages must be sufficiently high to lead to surface modification of zeolites, making the adsorption sites more approachable and available for regeneration and consequently adsorption.

4. Conclusions

In recent years efforts have been made towards advanced removal of organic micro-pollutants and nutrients from wastewater. . In this study it was demonstrated that NH_4^+ adsorption by Zeolita and MOR zeolites, as well as simultaneous adsorption of NH_4^+ and SMX by MOR offers an alternative, opening ways to simultaneous removal of NH_4^+ ions and SMX (and potentially other micropollutants) from wastewater using synthetic zeolites. Based on the results the following conclusions can be drawn:

- Ammonium adsorption capacity on Zeolita granules was found to be between 2.3 – 3 mg/g, whereas MOR manifested similar adsorption performance at low initial ammonium concentrations (10–40 mg/L) and lower at high ammonium concentrations (60–100 mg/L).
- Presence of ammonium ions enhances SMX adsorption by MOR possibly due to the local structure changes in the zeolite framework upon ion exchange with ammonium.

- Hardly any effect of SMX on ammonium adsorption by MOR was observed, even at high concentrations (50 mg/L) of SMX.
- The adsorption capacity of ammonium drastically decreased after the first regeneration cycle by ozonation, probably due to incomplete regeneration. However, after the second and third regeneration cycle adsorption capacity was restored to 86% of the initial capacity at low (10 mg/L) ammonium concentration and to 70% at high (100 mg/L) ammonium concentration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Al Aukidy, M., Verlicchi, P., Jelic, A., Petrovic, M., Barcelò, D., 2012. Monitoring release of pharmaceutical compounds: occurrence and environmental risk assessment of two WWTP effluents and their receiving bodies in the Po Valley. Italy. Sci. Total Environ. 438, 15–25. doi:10.1016/j.scitotenv.2012.08.061.

Al-Ghouti, M.A., Da'ana, D.A., 2020. Guidelines for the use and interpretation of adsorption isotherm models: a review. J. Hazard. Mater. 393, 122383. doi:10.1016/j.jhazmat.2020.122383.

Amini, A., 2017. The sustainability of ion exchange water treatment technology. Dissertations, Doctor of Philosophy (Ph.D). University of South Florida.

Ateia, M., Ceccato, M., Budi, A., Ataman, E., Yoshimura, C., Johnson, M.S., 2018. Ozone-assisted regeneration of magnetic carbon nanotubes for removing organic water pollutants. Chem. Eng. J. 335, 384–391. doi:10.1016/j.cej.2017.10.166.

Ayawei, N., Ebelegi, A.N., Wankasi, D., 2017. Modelling and interpretation of adsorption isotherms. J. Chem. 2017. doi:10.1155/2017/3039817, Article ID 3039817.

Azambre, B., Chebbi, M., Hijazi, A., 2020. Effects of the cation and Si/Al ratio on CH3I adsorption by faujasite zeolites. Chem. Eng. J. 379, 122308. doi:10.1016/j.cej.2019.122308.

Bajusz, I.-G., Goodwin, J.G., Greenlay, D.G., 1998. Effect of Ca2+ exchange on adsorption of N2−O2 Mixtures by NaCaX zeolite. Langmuir 14 (10), 2876–2883. doi:10.1021/la971408l.

Boatemaa, L., Brouwer, H., van der Zwaag, S., Sloof, W.G., 2018. The effect of the TiC particle size on the preferred oxidation temperature for self-healing of oxide ceramic matrix materials. J. Mater. Sci. 53 (8), 5973–5986. doi:10.1007/s10853-017-1973-x.

Braschi, I., Blasioli, S., Gigli, L., Gessa, C.E., Martucci, A.A., 2010. Removal of sulfonamide antibiotics from water: evidence of adsorption into an organophilic zeolite Y by its structural modifications. J. Hazard. Mater. 178 (1–3), 218–225. doi:10.1016/j.jhazmat.2010.01.066.

Bueno, M.J.M., Gomez, M.J., Herrera, S., Hernando, M.D., Agüera, A., Fernández-Alba, A.R., 2012. Occurrence and persistence of organic emerging contaminants and priority pollutants in five sewage treatment plants of Spain: two years pilot survey monitoring. Environ. Pollut. 164, 267–273. doi:10.1016/j.envpol.2012.01.038.

Campos, J.C., Moura, D., Costa, A.P., Yokoyama, L., da Fonseca Araujo, F.V., Cammarota, M.C., Cardillo, L., 2013. Evaluation of pH, alkalinity and temperature during air stripping process for ammonia removal from landfill leachate. J. Environ. Sci. Heal. A 48 (9), 1105–1113. doi:10.1080/10934529.2013.774658.

Clements, M., Haarhoff, J., 2004. Practical experience with granular activated carbon (GAC) at the water treatment plant. Water SA 30 (1), 89–95. doi:10.4314/wsa.v30i1.5031.

de Sousa, D.N.R., Insa, S., Mozeto, A.A., Petrovic, M., Chaves, T.F., Fadini, P.S., 2018. Equilibrium and kinetic studies of the adsorption of antibiotics from aqueous solutions onto powder zeolites. Chemosphere 205, 137–146. doi:10.1016/j.chemosphere.2018.04.085.

Demir, A., Gunay, A., Debik, E., 2002. Ammonium removal from aqueous solution by ion-exchange using packed bed natural zeolite. Water SA 28 (3), 329–335. doi:10.4314/wsa.v28i3.4903.

Deng, Q., Dhar, B.R., Elbeshbishy, E., Lee, H.S., 2014. Ammonium nitrogen removal from the permeates of anaerobic membrane bioreactors: economic regeneration of exhausted zeolite. Environ. Technol. 35 (16), 2008–2017. doi:10.1080/09593330.2014.889759.

Elovitz, M.S., von Gunten, U., Kaiser, H.P., 2008. Hydroxyl radical/ozone ratios during ozonation processes. ii. the effect of temperature, pH, alkalinity, and DOM properties. Ozone: Sci. Eng. 22 (2), 123–150. doi:10.1080/01919510008547216.

Elshof, A.A., 2019. Engineering of zeolite pellets for the adsorption of organic micropollutants. Master Thesis. Delft University of Technology http://resolver.tudelft.nl/uuid:12cd16a6-eb4a-4083-bb68-bef2e2755591.

Farías, T., Ruiz-Salvador, A.R., Rivera, A., 2003. Interaction studies between drugs and a purified natural clinoptilolite. Micropor. Mesopor. Mater. 61, 117–125. doi:10.1016/S1387-1811(03)00391-3.

Franus, W., Wdowin, M., 2011. Removal of ammonium ions by selected natural and synthetic zeolites. Gospodarka Surowcami Mineralnymi 26 (4), 133–148.

Guillossou, R., Le Roux, J., Mailler, R., Vulliet, E., Morlay, C., Nauleau, F., Gasperi, J., Rocher, V., 2019. Organic micropollutants in a large wastewater treatment plant: what are the benefits of an advanced treatment by activated carbon adsorption in comparison to conventional treatment? Chemosphere 218, 1050–1060. doi:10.1016/j.chemosphere.2018.11.182.

Guštin, S., Marinšek-Logar, R., 2011. Effect of pH, temperature and air flow rate on the continuous ammonia stripping of the anaerobic digestion effluent. Process Saf. Environ. 89 (1), 61–66. doi:10.1016/j.psep.2010.11.001.

Ham, K., Kim, B.S., Choi, K.Y., 2018. Enhanced ammonium removal efficiency by ion exchange process of synthetic zeolite after Na+ and heat pretreatment. Water Sci. Technol. 78 (6), 1417–1425. doi:10.2166/wst.2018.420.

Hussain, H.M., Mohammed, A.A.K., 2019. Preparation and characterization of mordenite zeolite from Iraqi Sand. IOP Conf. Series: Mater. Sci. Eng. 518, 062002. doi:10.1088/1757-899X/518/6/062002.

Jiang, N., Shang, R., Heijman, S.G.J., Rietveld, L.C., 2018. High-silica zeolites for adsorption of organic micro-pollutants in water treatment: a review. Water Res 144, 145–161. doi:10.1016/j.watres.2018.07.017.

Jiang, N., 2019. High-silica Zeolites as Novel Adsorbents for the Removal of Organic Micro-pollutants in Water Treatment. Dissertation. Delft University of Technology 10.4233/uuid:d4e7d2a8-aed1-48c8-98c3-eb61f18dde0b.

Jiang, N., Erdős, M., Moultos, O.A., Shang, R., Vlugt, T.J.H., Heijman, S.G.J., Rietveld, L.C., 2020. The adsorption mechanisms of organic micropollutants on high-silica zeolites causing S-shaped adsorption isotherms: an experimental and Monte Carlo simulation study. Chem. Eng. J. 389, 123968. doi:10.1016/j.cej.2019.123968.

Kamaz, M., Wickramasinghe, S.R., Eswaranandam, S., Zhang, W., Jones, S.M., Watts, M.J., Qian, X., 2019. Investigation into micropollutant removal from wastewaters by a membrane bioreactor. Int. J. Environ. Res. Public Health 16 (8), 1363. doi:10.3390/ijerph16081363.

Khuntia, S., Ghosh, S.K., 2012. Removal of ammonia from water by ozone microbubbles. Ind. Eng. Chem. Res. 52 (1), 318–326. doi:10.1021/ie302212p.

Kotoulas, A., Agathou, D., Triantaphyllidou, I.E., Tatoulis, T.I., Akratos, C.S., Tekerlekopoulou, A.G., Vayenas, D.V., 2019. Zeolite as a potential medium for ammonium recovery and second cheese whey treatment. Water (Basel) 11, 136. doi:10.3390/w11010136.

Langwaldt, J., 2008. Ammonium removal from water by eight natural zeolites: a comparative study. Sep. Sci. Technol. 43 (8), 2166–2182. doi:10.1080/01496390802063937.

Liu, X., Mäki-Arvela, P., Aho, A., Vajglova, Z., Gun'ko, V.M., Heinmaa, I., Kumar, N., Eränen, K., Salmi, T., Murzi, D.Y., 2018. Zeta potential of beta zeolites: influence of structure, acidity, pH, temperature and concentration. Molecules 23 (946). doi:10.3390/molecules23040946.

Liwarska-Bizukojc, E., Galamon, M., Bernat, P., 2018. Kinetics of biological removal of the selected micropollutants and their effect on activated sludge biomass. Water, Air, & Soil Pollution 229, 356. doi:10.1007/s11270-018-4015-7.

Loos, R., Carvalho, R., António, D.C., Comero, S., Locoro, G., Tavazzi, S., Paracchini, B., Ghiani, M., Lettieri, T., Blaha, L., Jarosova, B., Voorspoels, S., Servaes, K., Haglund, P., Fick, J., Lindberg, R.H., Schwesig, D., Gawlik, B.M., 2013. EU – wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents. Water Res 47, 6475–6487. doi:10.1016/j.watres.2013.08.024.

Luo, X., Yan, Q., Wang, C., Luo, C., Zhou, N., Jian, C., 2015. Treatment of ammonia nitrogen wastewater in low concentration by two-stage ozonization. Int. J. Environ. Res. Public Health 12, 11975–11987. doi:10.3390/ijerph120911975.

Ma, S., Zuo, X., Xiong, J., Ma, C., Chen, Z., 2019. Feasibility of high silica ZSM-5 recovery by ozone with sulfamethoxazole removal from water. J. Water Process Eng. 32, 100956. doi:10.1016/j.jwpe.2019.100956.

Maksin, D.D., Nastasović, A.B., Milutinović-Nikolić, A.D., Suručić, Lj.T., Sandić, Z.P., Hercigonja, R.V., Onjia, A.E., 2012. Equilibrium and kinetics study on hexavalent chromium adsorption onto diethylene triamine grafted glycidyl methacrylate based copolymers. J. Hazard. Mater. 209-210, 99–110. doi:10.1016/j.jhazmat.2011.12.079.

Mohammed-Nour, A., Al-Sewailem, M., El-Naggar, A.H., 2019. The Influence of alkalization and temperature on ammonia recovery from cow manure and the chemical properties of the Effluents. Sustainability 11, 2441. doi:10.3390/su11082441.

Moshoeshoe, M., Nadiye-Tabbiruka, M.S., Obuseng, V., 2017. A review of the chemistry, structure, properties and applications of zeolites. Am. J. Mater. Sci. 7 (5), 196–221. doi:10.5923/j.materials.20170705.12.

Munthali, M.W., Elsheikh, M.A., Johan, E., Matsue, N., 2014. Proton adsorption selectivity of zeolites in aqueous media: effect of Si/Al ratio of zeolites. Molecules 19, 20468–22048. doi:10.3390/molecules191220468.

Price, L., Leung, K.M., Sartbaeva, A., 2017. Local and average structural changes in zeolite A upon ion exchange. Magnetochemistry 3 (4), 42. doi:10.3390/magnetochemistry3040042.

Rahmani, A.R., Mahvi, A.H., Mesdaghinia, A.R., Nasseri, S., 2004. Investigation of ammonia removal from polluted waters by Clinoptilolite zeolite. Int. J. Environ. Sci. Technol. 1 (2), 125–133. doi:10.1007/BF03325825.

Sabri, N.A., Schmitt, H., Van der Zaan, B., Gerritsen, H.W., Zuidema, T., Rijnaarts, H.H.M., Langenhoff, A.A.M., 2020. Prevalence of antibiotics and antibiotic resistance genes in a wastewater effluent-receiving river in the Netherlands. J. Environ. Chem. Eng. 8, 102245. doi:10.1016/j.jece.2018.03.004.

Sarti, E., Chenet, T., Pasti, L., Cavazzini, A., Rodeghero, E., Martucci, A., 2017. Effect of silica alumina ratio and thermal treatment of beta zeolites on the adsorption of toluene from aqueous solutions. Minerals 7 (22). doi:10.3390/min7020022.

Sathiskumar, P., Meena, R.A.A., Palanisami, T., Ashokkumar, V., Palvannan, T., Gu, F.L., 2020. Occurrence, interactive effects and ecological risk of diclofenac in environmental compartments and biota - a review. Sci. Total Environ. 698, 134057. doi:10.1016/j.scitotenv.2019.134057.

Sato, K., Nishimura, Y., Matsubayashi, N., Imamura, M., Shimada, H., 2003. Structural changes of Y zeolites during ion exchange treatment: effects of Si/Al ratio of the starting NaY. Microporous Mesoporous Mater. 59 (3), 133–146. doi:10.1016/S1387-1811(03)00305-6.

Sakizci, M., Özgül Tanriverdi, L., 2015. Influence of acid and heavy metal cation exchange treatments on methane adsorption properties of mordenite. Turk. J. Chem. 39, 970–983. doi:10.3906/kim-1501-71.

Selvam, T., Schwieger, W., Dathe, W., 2018. Histamine-binding capacities of different natural zeolites: a comparative study. Environ. Geochem. Health 40, 2657–2665. doi:10.1007/s10653-018-0129-5.

Singer, P.C., Zilli, W.B., 1975. Ozonation of ammonia in wastewater. Water Res. 9 (2), 127–134. doi:10.1016/0043-1354(75)90001-9.

Thiebault, T., 2020. Sulfamethoxazole/Trimethoprim ratio as a new marker in raw wastewaters: a critical review. Sci. Total. Environ. 715, 136916. doi:10.1016/j.scitotenv.2020.136916.

Vaičiukynienė, D., Mikelionienė, A., Baltušnikas, A., Kantautas, A., Radzevičius, A., 2020. Removal of ammonium ion from aqueous solutions by using unmodified and H2O2-modified zeolitic waste. Sci. Rep. 10, 352. doi:10.1038/s41598-019-55906-0.

van der Hoek, J.P., Duijff, R., Reinstra, O., 2018. Nitrogen recovery from wastewater: possibilities, competition with other resources, and adaptation pathway. Sustainability 10, 4605. doi:10.3390/su10124605.

Wang, S., Peng, Y., 2010. Natural zeolites as effective adsorbents in water and wastewater treatment. Chem. Eng. J. 156 (1), 11–24. doi:10.1016/j.cej.2009.10.029.

Wang, J., 2020. Ozone-Based Regeneration of Granular Zeolites Loaded with Organic Micropollutants. Master Thesis. Delft University of Technology http://resolver.tudelft.nl/uuid:593f2bd9-175e-453a-8882-5184b859e161.

Wasielewski, S., Rott, E., Minke, R., Steinmetz, H., 2018. Evaluation of different clinoptilolite zeolites as adsorbent for ammonium removal from highly concentrated synthetic wastewater. Water (Basel) 10, 584. doi:10.3390/w10050584.

WHO, 1996. Guidelines For Drinking-Water Quality. World Health Organization, Geneva.

Widiastuti, N., Wu, H., Ang, H.M., Zhang, D., 2011. Removal of ammonium from greywater using natural zeolite. Desalination 277 (3), 15–23. doi:10.1016/j.desal.2011.03.030.

Zhang, S., Zhao, Y., Yu, G., Wang, B., Huang, J., Deng, S., 2015. Dual roles of hydroxyl radicals and effects of competition on ozonation kinetics of two phenazone-type pollutants. Emerg. Contam. 1 (1), 2–7. doi:10.1016/j.emcon.2015.05.004.

Zhang, Y., Mancke, R.G., Sabelfeld, M., Geißen, S.U., 2014. Adsorption of trichlorophenol on zeolite and adsorbent regeneration with ozone. J. Hazard. Mater. 271, 178–184. doi:10.1016/j.jhazmat.2014.02.020.

Zhou, C., Chen, J., Xie, H., Zhang, Y., Li, Y., Wang, Y., Xie, Q., Zhang, S., 2018. Modeling photodegradation kinetics of organic micropollutants in water bodies: a case of the Yellow River estuary. J. Hazar. Mater. 349, 60–67. doi:10.1016/j.jhazmat.2018.01.051.

Zhou, Y., Meng, J., Zhang, M., Chen, S., He, B., Zhao, H., Li, Q., Zhang, S., Wang, T., 2019. Which type of pollutants need to be controlled with priority in wastewater treatment plants: traditional or emerging pollutants? Environ. Int. 131, 104982. doi:10.1016/j.envint.2019.104982.