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Impact of removal of natural organic matter from surface water by ion exchange: A case study of pilots in Belgium, United Kingdom and the Netherlands

I. Caltran^{a,*}, S.G.J. Heijman^a, H.L. Shorney-Darby^b, L.C. Rietveld^a

^a Delft University of Technology, Department of Water Management, Stevinweg 1, 2628CN Delft, The Netherlands

^b PWN Technologies, Dijkweg 1, 1619HA Andijk, The Netherlands

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ABSTRACT

Natural organic matter (NOM) fractions cause problems in drinking water treatment and supply. In the North Sea region, anionic ion exchange (IEX) in non-fixed bed configurations has been considered for NOM removal in drinking water treatment plants. This paper discusses several experiences of the impact of anion IEX on NOM removal and on NOM-related problems in water treatment locations of the North Sea region, considering the specific situation of the sites. The investigated parameters include the effect of anionic IEX on the removal of total NOM and specific NOM fractions, the amount of chemicals used for coagulation, the development of trans membrane pressure in microfiltration, the formation of assimilable organic carbon and the energy consumption during advanced oxidation, the removal of organics by activated carbon, and the formation of disinfection by-products. The pilot experiences at three treatment locations in Belgium, United Kingdom and the Netherlands show that anionic IEX (1) removed typically 40 to 60 percent of total NOM; (2) targeted mostly humic NOM fractions, and was not effective to remove biopolymers (3) contributed to lower coagulant doses and energy consumption in UV/advanced oxidation; (4) had limited influence on limiting the fouling of microfiltration membranes; (5) lowered the formation of disinfection by-products; and (6) it can improve biological stability.

1. Introduction

Natural organic matter (NOM) is a complex mixture of organic molecules. NOM is always present in surface water, and is responsible for several problems in drinking water treatment and supply. Some of these problems are related to drinking water consumption and distribution, e.g., colour, odour, formation of disinfection byproducts (DBPs) and biological instability of the water [1]. In addition, NOM reduces the efficiency of water treatment. For instance, activated carbon might be used to decrease NOM concentrations [1–4], but this reduces the sorption sites available for the removal of other pollutants [5]. Also, NOM removal by granular activated carbon (GAC) is limited to the first few months of the running of the filter. After these months, the remaining removal is supposed to be attributed to biological breakdown in the filter [6]. Moreover, NOM increases the demand for coagulants and disinfectants, and it fouls membranes [1]. Therefore, drinking water utilities remove NOM to address different problems, depending on the specific situation on the site.

In the North Sea Region, a survey including 10 drinking water

utilities in the Netherlands, Belgium, United Kingdom and Sweden showed that coagulation, the conventional NOM removal technique, was applied in all surveyed drinking water treatment plants for NOM removal (owned data). However, several companies were in the process of investigation and implementation of complementary technologies for improving NOM removal. In particular, anion ion exchange (IEX) pre-treatment was considered in this region as a part of a multi-barrier approach to NOM in drinking water treatment.

The conventional configuration of anion IEX is a fixed resin bed. Therefore, IEX is typically used in the late stage of the treatment process [7], after the suspended solids have been removed by pre-treatment. The use of fixed bed at the beginning of the treatment train, e.g., during direct treatment of surface water, would lead to fouling or clogging of the IEX reactor within a short time [8], due to the solids being retained in the resin bed. More recent configurations use non-fixed bed ion exchange configurations [7].

Based on the information that a water utility wants to know, several analytical methods can be used to quantify and/or characterize the NOM on the treatment site and along the treatment. Water companies

* Corresponding author.

E-mail address: i.caltran@tudelft.nl (I. Caltran).

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often use carbon analytical measurements to quantify NOM. Carbon detectors can measure total organic carbon (TOC), particulate organic carbon (POC) and dissolved organic carbon (DOC). In addition, specific ultraviolet absorbance (SUVA, $L/(mg \cdot m)$) gives an indication about the hydrophobicity of the NOM, where SUVA is the UV absorbance of water at 254 nm (UV_{254} , $1/m$) normalized by the DOC concentration (mg/L). NOM in water with a high SUVA (greater than $4 L/(mg \cdot m)$) is mostly more hydrophobic and aromatic than in water with low SUVA (less than $3 L/(mg \cdot m)$) [9,10]. Hydrophilic NOM is known as a major component of easily biodegradable NOM [11], while humic substances (HS), that are generally considered hydrophobic, are more biologically persistent [12]. NOM is composed of fractions with various sizes. Therefore, size exclusion chromatography (SEC), combined with organic compounds detection techniques, is used as another method to characterise organics. In the fractionation method of Huber et al. [13], after SEC (using liquid chromatography – LC), samples are analysed with a UV_{254} detector (UVD); then, carbon concentrations are measured with organic carbon detection (OCD); after UVD, a side stream is analysed by organic-bound nitrogen detection (OND). The hydrophobic and cation-exchange characteristics of the SEC column give indications about the charge and hydrophobicity of the NOM fractions [13]. The LC-OCD-OND fractions are subdivided into hydrophobic organic carbon (HOC), biopolymers (BP), HS, building blocks (BB), low molecular weight acids (LMWa), and low molecular weight neutrals (LMWn). These fractions together are the chromatographic fractionation of organic carbon (CDOC). BP are mostly polysaccharides and nitrogen-containing components (e.g., protein and amino sugars); they are hydrophilic and uncharged [13]. HS are fulvic and humic acids, and their breakdown products are referred as BB [13]. LMWa includes small humics and acids, and are negatively charged [13]. Finally, LMWn consists of alcohols, aldehydes, ketones, amino acids, sugars and biogenic NOM; they are hydrophilic or amphiphilic and have low charge [13]. The fractions have different sizes: BP are larger than 10,000 Daltons [13], HS are mostly 1000–800 Daltons, BB are 500–300 Daltons, and both LMWa and LMWn are smaller than 350 Daltons [14]. They also have a different response to UV_{254} : HS respond to the detector, and BB have variable response and BP and LMWn have typically no or very little response [13].

Fractionation techniques cannot give information about the possible biological transformation of NOM. Moreover, the NOM concentrations involved in the biological processes are typically very low, which makes the detection difficult. As a result, specific methods are used to measure biodegradable NOM and evaluate the biostability of drinking water. One of them is the determination of assimilable organic carbon (AOC), based on bacteria biomass growth [15].

In a specific site, variations of NOM concentrations and characteristics in the source of a specific site may change over time. Evans et al. [16], e.g., analysed NOM data from 22 lakes or streams of the Acid Waters Monitoring Network (AWMN) in the United Kingdom, and observed that the DOC concentration at the majority of the sites was increasing with 0.06 to 0.51 mg/L per year, during the five years of monitoring. NOM concentrations and/or composition can also vary with the seasons. The variation of NOM concentration and character is due to either autochthonous (e.g., linked to the presence of algae) or allochthonous variations (e.g., changing origins of water sources, and NOM in runoff from the surrounding area) [17]. In addition, NOM charge can change, as shown, for instance, by Sharp et al. [18], who reported that the charge density of fulvic acids fluctuated during a period of almost three years in an observed water source. Seasonal changes in SUVA and NOM fractionation and the effect on, e.g., coagulation have also been studied by Jarvis et al. [19], for a moorland catchment in Yorkshire. The greatest seasonal fraction change was an increase in fulvic acids by 20 percent in the winter, which was compensated by a decrease of humic acids; in winter, the SUVA was lower (NOM became less hydrophobic), and thus the required coagulant dose was higher [19].

This paper presents an overview of the performance of anion IEX for NOM removal as a pre-treatment step of surface water used in drinking water production in the North Sea region. While the mechanisms for NOM removal by anion IEX are described in detail by, e.g., Cornelissen et al. [20], the focus of this paper is on local experiences for NOM removal with IEX. As NOM characteristics and removal are linked to the specific situation of the water treatment site, the case study fully describes each treatment plant. We studied the impact of anion IEX on NOM removal for different water companies that recently implemented anion IEX in their treatment plants, or are considering to implement anion IEX at full scale (i.e., Blankaaert in Belgium, Plymouth in the United Kingdom, and Andijk in the Netherlands). Firstly, we described the main characteristics of the raw water sources and existing treatment plants and the way IEX was or will be incorporated into the treatment process. Then, we discussed reviewed publications, conference papers, reports, and unpublished data from various studies the water companies conducted at bench and pilot scale. We used these experiences to gain information on the NOM fractions that were removed by anion IEX pre-treatment and the effect on several NOM-related problems, i.e., coagulant consumption, membrane fouling, AOC formation during advanced oxidation, limitation of efficiency of UV-based oxidation and activated carbon, and formation of DBPs.

2. Materials and methods

2.1. Detection of NOM and NOM-related parameters in IEX pilot studies

2.1.1. Blankaaert

At the pilot site Blankaaert, Belgium, UV_{254} absorption was measured on site using a spectrometer (Thermo Scientific, Evolution 160); the samples were filtered using a $0.45 \mu m$ filter prior to measurement. TOC samples were measured at the laboratory of De Watergroep, Belgium, with an Analytik Jena Multi N/C 3100 analyser; here there was no filtration prior to measurement. The samples were acidified with 6 M HCl; afterwards, the inorganic carbon was stripped with pure oxygen; then, 0.5 mL of the sample was burned at $720^\circ C$ using a Pt catalyst to oxidize all organic carbon to CO_2 . The amount of formed CO_2 was measured with a non-dispersive infrared detector. The SUVA was calculated using TOC instead of DOC, thus the SUVA values reported for this case study are lower than the real SUVA values, considering that TOC is always higher than DOC. However, according to Edzwald and Van Benschoten [10], undissolved organic carbon concentrations are typically much lower than TOC concentrations. In the work of Wetzel [21], for instance, the average DOC: undissolved organic carbon ratio from many surface water bodies was 6:1 for rivers and 10:1 for lakes. In this case, the SUVA calculated with DOC would be in the range of only 10 to 16 percent higher than the SUVA calculated with TOC.

2.1.2. Plymouth and Andijk

At the pilot sites of Plymouth, United Kingdom, and Andijk, the Netherlands, NOM related parameters, including DOC, UV_{254} , and the concentrations of HOC, BP, HS, BB, LMWa and LMWn, were measured by Het Water Laboratorium (the Netherlands), using LC-OCD analyses (as described in Huber et al. [13]. At Andijk, AOC analyses were performed according to the procedure of Van der Kooij [22]. At Plymouth, DBP formation potentials were measured at the laboratory of South West Water, United Kingdom, according to the procedure described by Metcalfe et al. [23].

2.2. Non-fixed bed IEX for NOM removal in the North Sea region

Non-fixed bed IEX techniques include the use of small size magnetic resin systems (MIEX®), IEX in fluidized bed (FIX), and suspended IEX (SIX®) [8].

MIEX® (now commercialized by Ixom Water care, and previously by Orica Watercare) uses a mixed bed of magnetic resin. The magnetic

resin is smaller than conventional resins, i.e., 0.1 to 0.2 mm instead of, e.g., 0.4 to 2 mm; therefore, due to the larger specific surface area the kinetics is rapid [24], and less contact time is required in the contactor [25]. The resin is strong base, and it has a magnetic core of iron oxides [25]. After removing NOM, the magnetic resin agglomerates, and the formed larger particles settle rapidly [26]. High resin concentrations enhance the agglomeration of resin and can reduce the resin loss [27]. MIEX® is available in different configurations, including mixing contactors and a settling vessel resin separator in series, and FIX.

FIX can use small bead MIEX® resin because of its rapid settling, but also larger, conventional resins can be used in this configuration. Raw water flows upward in a reactor containing a resin bed. The controlled velocity of the raw water fluidizes the resin bed, and at the same time it should avoid that the resin is washed out of the reactor. The sedimentation rate of the resin depends on the resin characteristics and on the water temperature [28]. The upflow velocity should be high enough to fluidize the resin bed and to prevent solids present in the raw water from getting trapped in the resin bed [28]. At the same time, the upflow velocity should be low enough to guarantee sufficient contact time between water and resin and to limit the required height of the reactor.

In SIX®, the resin is dosed into the raw water and flows through five mixed contactors. A conventional strong base resin is used in the system, and it is selected according to the characteristics of the water source to be treated [8]. The resin concentration is in the range of 4 to 20 mL/L, and the typical contact time is between 10 and 30 min [8]. The resin in the contactors has the same contact and retention time as the water. Afterwards, the resin is separated from the water by a lamella settler and then regenerated and reused.

MIEX® and FIX, on the one hand, use long resin retention times for the resin, until it has a high NOM loading, with the aim to make efficient use of the exchange capacity of the resin and reduce the use of regeneration salt [8]. On the other hand, SIX® is a single-pass process with a shorter resin retention time and regeneration at low NOM loadings; the aim is to reduce bacteria growth on the resin, which can occur when the raw water contains high concentrations of growth promoting nutrients, such as phosphate [8].

2.3. Introduction of non-fixed bed IEX in drinking water treatment plants in the North Sea region

2.3.1. Blankaart

De Watergroep has planned to introduce IEX pre-treatment, amongst others, in the full scale water works at Blankaart. IEX is being considered as a pre-treatment to the existing enhanced coagulation (Fig. 1a). The new post-treatment will include advanced oxidation with hydrogen peroxide and ozone, dual stage GAC, and UV/NaOCl disinfection. Membrane filtration has also been considered for further modifications to the treatment process. The current pre-treatment consists of pre-filtration, biological ammonia oxidation, enhanced coagulation, settling and filtration; the current post-treatment consists of GAC filtration and disinfection with NaOCl (Fig. 1b).

2.3.2. Plymouth

South West Water has been introducing anion IEX in the new full-

scale water works of Plymouth. IEX will be used as pre-treatment before in-line coagulation and ceramic microfiltration. The post-treatment will consist of GAC, UV and chlorination and stabilisation (Fig. 2a). The current pre-treatment includes coagulation and flocculation before rapid sand filtration; the post-treatment is chlorine disinfection and final conditioning for plumbosolvency (Fig. 2b).

2.3.3. Andijk

PWNT has built a new treatment plant at Andijk, the Netherlands. This new plant, that uses anion IEX as pre-treatment before ceramic microfiltration, is operated in parallel to an older conventional plant. The post-treatment of the new plant is advanced oxidation with UV/H₂O₂, GAC filtration, and final disinfection with chlorine dioxide (Fig. 3a). The current conventional pre-treatment uses iron-based coagulation in the water reservoirs of the IJssel Lake, and includes also softening in the reservoirs, sedimentation and double layer filtration; the post-treatment is primary UV/H₂O₂ advanced oxidation and disinfection, GAC filtration, and final ClO₂ disinfection (Fig. 3b).

2.4. Pilots for IEX with non-fixed bed

Three different IEX systems were studied at Blankaart, Plymouth and Andijk, and these were MIEX®, FIX and SIX® (Table 1). Table 1 gives an overview of the different design characteristics of the pilot plants. Table 2 shows the characteristics of the resins used in the pilot studies.

A cost-analysis of the introduction of anion IEX pre-treatment in a water treatment plant is not the scope of this paper, because the optimisation of the system depends on many limiting factors, e.g., contact time between water and resin, contact surface of the resin, pH, the character of NOM fractions, and the concentration of uncharged, refractory NOM. Nevertheless, in Andijk and in Plymouth cost considerations were made in preliminary studies, that compared the existing or conventional treatment to a treatment that includes anion IEX and microfiltration. For Andijk, less energy consumption and waste volumes were predicted in the new treatment, with similar construction costs [33]. For Plymouth, it was considered that the new treatment requires a smaller footprint, and the expected operational costs were similar, as the result of a combination of reduced coagulant dose, increased energy consumption due to microfiltration, and higher chemical and disposal costs for IEX [23].

When comparing the non-fixed anionic IEX systems, Table 1 shows that suspended reactors work with lower resin concentrations and a higher contact time than fluidized reactors. Therefore, SIX® requires reactors with a larger volume, in the range of 10 to 20 times higher, and thus a larger footprint.

2.4.1. FIX with MIEX® and conventional resins at Blankaart

A MIEX® pilot in FIX configuration was operated at Blankaart from June 2008 to July 2009. At Blankaart, the pH in the water source was mostly in the range between 8 and 9. The pilot consisted of an upflow mixed reactor followed by a lamella separator [7]. A small flow of resin was continuously removed from the contactor and replaced by freshly regenerated resin. Regeneration was performed batch wise [7]. The

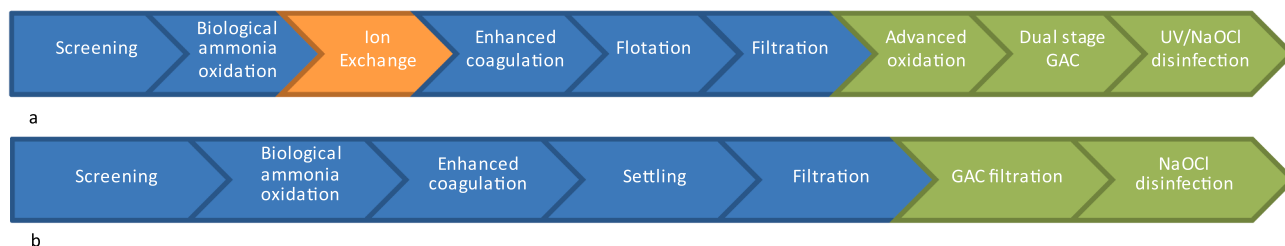


Fig. 1. Planned upgrading of treatment plant with ion exchange in Blankaart (a), and current treatment plant in Blankaart (b).

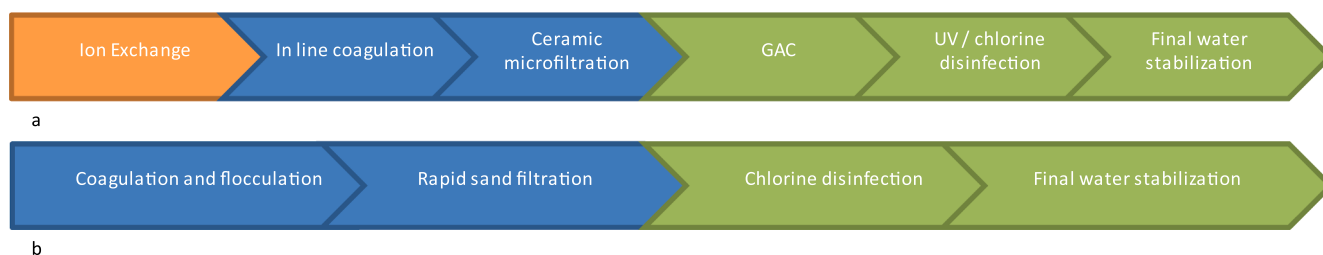


Fig. 2. Upscaled treatment plant with ion exchange in Plymouth (a), and current conventional treatment plant in Plymouth (b).

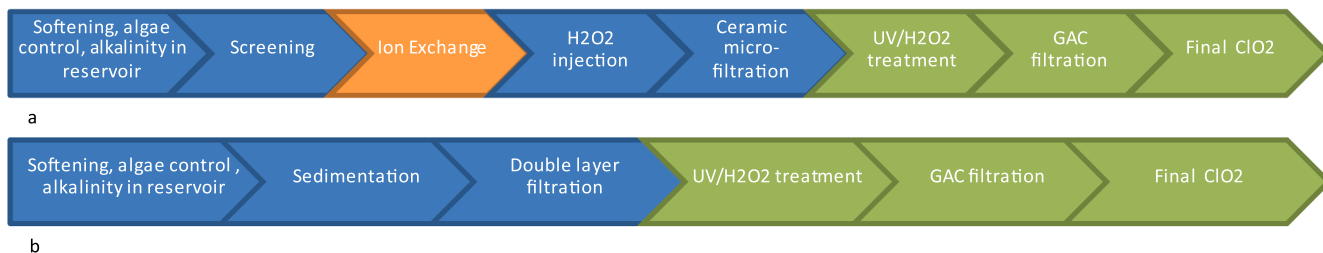


Fig. 3. New treatment plant with ion exchange in Andijk (a), and current conventional treatment plant in Andijk (b).

pilot had a capacity of 1.25 m³/h, with an upflow velocity of 20 m/h. The dose of MIEX® resin is given as an effective resin dose, which is the amount of regenerated resin per liter of treated water, and it was 1.0 mL/L [7].

Jar experiments were also performed to test the effect of MIEX® resin IEX on subsequent coagulant doses. Raw water was contacted with MIEX® resin, subtracted from the contactor, for 20 min at a concentration of 25 mL resin/L. The pH of the raw water before the MIEX® treatment was adjusted to a value between 7.6 and 7.8, while the pH after the MIEX® treatment is unknown. Subsequently, coagulation tests were performed on the supernatant with coagulant doses of 0 to 20 mg Fe/L. The results with respect to NOM and turbidity removal were compared with the results obtained by coagulating the raw water directly with ferric after pH conditioning with 80 mg/L H₂SO₄ [7]. The pH conditioning was applied if needed to reach the optimal pH of 6, depending on the water quality of the moment. The dosage of coagulant, varied from 0 to 20 mg/L as Fe [7].

At Blankaart, FIX was tested again between 2008 and 2010, this time in a column with various strong base resins, i.e., MIEX® resin, Purolite A860S, and Lewatit VPOC 1071 [7]. The last two resins have bead sizes between 0.4 and 1.2 mm, respectively. The column had a diameter of 0.1 m and the resin volume in the column was 2 L. The pilot had a capacity of 50 to 200 L/h (0.05 to 0.2 m³/h), resulting in upflow velocities of 7.5 to 25 m/h and contact times of 37 to 120 s [7]. The resin was regenerated in situ with a 10 percent NaCl solution every 1,500 bed volumes of treated water resulting in a resin residence time of 925 to 3000 min between regenerations [7]. The approximate resin concentration in the fluidized bed was in the range of 150 to 700 mL/L (according to our calculation in Table 1).

Based on the results of the small scale pilot tests, a larger FIX pilot, with a capacity of 50 to 58 m³/h, was built and operated from 2016 to 2018. The effluent of the pilot was treated further by means of enhanced coagulation (using FeCl₃ and H₂SO₄) and flotation [34]. In this case, Purolite PPA860S was used, with contact times in the range of 108 to 125 s. The fluidized bed had a height of about 0.6 m, and periodically, a resin volume of 25–50 L was removed to be regenerated batch wise [34]. The approximate resin concentration in the fluidized bed, according to our calculation in Table 1, ranged from 250 and 500 mL/L, and the effective resin concentration was 2 mL/L.

2.4.2. SIX® at Andijk and Plymouth

At Andijk, the pH of the water source was mostly 7.8–8. There, a

SIX® pilot was installed with a capacity of about 100 m³/h and Lewatit VPOC 1017 resin (strong base, effective bead size of 0.5 to 0.6 mm) was selected after bench-scale kinetics tests for further application. The selection took various characteristics into account, such as mechanical strength, sedimentation properties, and regeneration salt consumption [8]. The resin concentration in Andijk was 13 to 15 mL/L, with 25 to 30 min contact time [8]. At Plymouth, with the water sources used had a pH mostly in the range of 6.6 and 8. There, SIX® was tested with a pilot with a capacity of 6.25 m³/h, with pre-rinsed Lewatit S5128 resin, using a concentration of 18 mL/L and an average contact time of 30 min [23]. Both at Plymouth and Andijk, SIX® has been tested in combination with conventional and in-line coagulation to study their impact on fouling of microfiltration membranes (ceramic microfilter, Metawater, Japan). At Plymouth, the effect of SIX® on DBPs' formation has also been studied. At Andijk, the effect of pre-treatment with SIX® in combination with microfiltration membranes (Metawater, Japan) on UV/H₂O₂, activated carbon filters (Norit 0,8S or Chemiviron TL 830) and AOC formation has been compared to that of conventional, full-scale treatment. The H₂O₂ dosage was 6 mg/L in full-scale and pilot-scale and the UV dose was 600 mJ/cm² in full-scale and above 600 mJ/cm² in pilot-scale; for the activated carbon filters, the empty bed contact time was 25 min and the hydraulic loading rate was 9 to 13 m/h in full-scale and 10 m/h in pilot-scale. The regeneration frequency was 2 years in full-scale, and the pilot has been tested less than 2 years. Therefore, the average reactivation time of the carbon in both full- and pilot-scale during the test was 1 year.

3. Experiences of NOM removal and impact of anion IEX pre-treatment

3.1. NOM in water sources and NOM removal by conventional treatment in the North Sea region

In the surface water source at Blankaart, the average TOC was about 12 mg/L with a seasonal TOC fluctuation between 9 and 16 mg/L. The high TOC peaks were in summer and early autumn and can be attributed to algae blooms. Also the SUVA, calculated using TOC instead of DOC, fluctuated seasonally with low values in summer and early autumn, typically between 1.5 and 2.6 L/(mg*m) (Fig. 4), or between 1.6 and 3 L/(mg*m), if correcting the value for DOC using a typical DOC: undissolved organic carbon ratio between 6:1 and 10:1, as explained in section 2.1.1. However, at Blankaart has been observed that, when

Table 1
IEX technologies and resins in the studied cases.

Pilot	Resin	Magnetic resin	Contact time [s]	Retention time resin [min]	Resin concentration in non-fixed filter bed [mL/L]	Effective resin concentration [mL/L]	Flow rate pilot [m ³ /h]	Upward velocity pilot [m/h]
MIEX® (Blankaart)		Magnetic resin	Unknown	Unknown	unknown	1	1.25	20
FIX (Blankaart)	Purolite A860S, Lewatit VPOC 1017, Magnetic resin		37–120	925–3000	150–700*	not applicable	0.05–0.2	6–25
	Purolite PPA860S		108–125	840–960	250–500**	2	50–58	17–20
SIX*	Lewatit S5128 (Plymouth)		1800	30	18	18	6.25	–
	Lewatit VPOC 1017 (Andijk)		1500–1800	25–30	13–15	13–15	60	–

* Amount of regenerated resin per liter of treated water.

* Estimated value calculated from the height of the fluidized bed (in the range of 0.25 to 0.38 m), and range of expansion of the fluidized bed (40 to 500 percent) of resins with upward velocity between 12.5 and 25 m/h at water temperatures between 4 and 20°C (shown by Verdickt et al. [7]).

** Estimated value calculated from the height of the fluidized bed (0.6 m), and range of expansion of the fluidized bed (200 to 300 percent) of resins with upward velocity between 15 and 20 m/h at 4 °C in previous experiments (shown by Verdickt et al. [7]), and the expansion of the fluidized bed at 12 m/h at 20°C (100 percent), from the product information sheet of the resin [29].

algae blooms occurred in summer and early autumn, the DOC: undissolved organic carbon ratio could be in the range of 1:1, as micro-sieves of 30 µm could remove up to 50 percent of the TOC. In this case, the SUVA corrected for DOC would be considerably higher.

The current pre-treatment removed, on average, 60 percent of the TOC. The current post treatment, consisting of GAC filtration and disinfection NaOCl, removed an additional 25 percent of the remaining TOC, with an overall removal of 70 percent. Next to high NOM concentrations and seasonal NOM variations, the main challenges of the current treatment process are the negative influence of algae blooms in the settling and filtration steps, and the presence of micropollutants. Also, the water source has a high alkalinity, resulting in a high chemical demand for the enhanced coagulation.

The water works in the Plymouth area use three surface water sources: Burrator reservoir, river Tavy and river Tamar. Burrator had a low DOC concentration (i.e., as low as 1 mg/L); however, the concentration could increase to 5 mg/L in autumn. The Tavy and Tamar rivers had low DOC concentrations in periods without rainfall (i.e., 1.5 and 2 mg/L, respectively), but when it rained the DOC concentration could increase rapidly to 10 mg/L. The typical SUVA was 4 to 5 L/(mg*m), which indicates that NOM was mostly hydrophobic of character. The existing water plants removed most of the NOM by coagulation, with a typical DOC removal of 60 to 80 percent; in days without rainfall, DOC removal was about 50 percent. Further optimization of the coagulation process is difficult because of large variations in NOM concentration, which are due to the seasons and rainfalls. In addition, NOM concentrations have gradually increased over time in some water sources (Fig. 5).

The water source at Andijk is the IJssel Lake, an 110,000 ha freshwater basin fed by the river IJssel (90 percent) and by polders and other lakes (10 percent). Between 2012 and 2019, the DOC varied seasonally between about 4 and 8 mg/L (Fig. 6). The average SUVA was 2.5 L/(mg*m).

The IJssel Lake is shallow, it has a long residence time, and it is rich in nutrients. Therefore, the biological composition of the water had a high seasonal variation and a high concentration of algal NOM in summer. The lowest BP concentration has been observed in spring, before algae typically bloom [35]. Due to algae blooming, higher doses of iron-based coagulant for enhanced coagulation are used during summer. The TOC removal of the conventional treatment plant was more than 70 percent, on average. GAC filtration can also contribute to NOM removal, but NOM removal was not the reason for GAC contacting at Andijk.

3.2. NOM removal by anion IEX

Table 4 shows the NOM removal by anion IEX at the three pilots at Blankaart, i.e., MIEX® pilot (1.25 m³/h), FIX column (0.15 m³/h), and the large FIX pilot (50 m³/h). The MIEX® pilot at Blankaart (effective resin dose 1 mL/L) removed between 40 and 50 percent of TOC. The decrease in UV₂₅₄, by 60 to 70 percent, was larger than the decrease of TOC. Thus, as aromatic structures absorb UV₂₅₄ [10], MIEX® removed preferentially aromatic NOM fractions. When the UV₂₅₄ was the lowest (typically in summer and early autumn), less TOC removal was observed in the MIEX pilot [7].

For the FIX column, the removal of TOC ranged from 40 to 60 percent, and the removal of UV₂₅₄ ranged from 70 to 80 percent. The conventional resins (Purolite A860S and Lewatit VPOC 1017) required a longer contact time to achieve their maximum NOM removal, compared to the magnetic resin [7]. The magnetic resin has a smaller bead size, thus it has also a larger contact area and faster kinetics than the conventional resins [7]. After a contact time of 37 s, the maximum NOM removal by magnetic resin was already achieved; on average, 40 to 45 percent for TOC and 75 to 80 percent for UV₂₅₄ [7]. On the other hand, when the contact time increased from 37 to 120 s, the removal of TOC by Purolite A860S increased from 40 to 55 percent, and the

Table 2
Resin used in the pilot studies.

Resin	Characteristics
Miex® resin	Type I, Macroporous, bead size 0.15–0.18 mm, exchange capacity 0.52 meq/ml, acryl*
Purolite A860S	Type I, Macroporous, mean bead size 0.43–1.20 mm, exchange capacity 0.8 meq/ml, acryl**
Purolite PPA860S	Type I, Macroporous, mean bead size 0.63–0.85 mm, exchange capacity 0.8 meq/ml, acryl**
Lewatit S5128	Type I, Gel structure, effective bead size 0.50–0.75 mm, exchange capacity 1.25 meq/ml, acryl***
Lewatit VPOC 1017	Type I, Gel structure, effective bead size 0.50–0.60 mm, exchange capacity 1.25 meq/ml, acryl***

* From Verdickt et al. [7];

** from product information Purolite [29,30];

*** from product information Lewatit [31,32].

removal of UV₂₅₄ increased from 60 to 75 percent [7].

The FIX pilot of 50 m³/h (effective resin dose 2 mL/L) removed, on average, about 40 percent of TOC and 60 percent of UV₂₅₄ (Fig. 7), decreasing the SUVA. The lower average removal compared to the FIX column was attributed to seasonal algae growth [34]. Another possible cause is the difference in the regeneration procedure between the two pilots. In the smaller FIX column pilot, the spent brine was completely removed from the system; therefore, there was no spill of NOM going directly to the drinking water. In the larger FIX pilot of 50 m³/h, to reduce the volume of the spent regenerant, the resin was rinsed with less water, and a part of the NOM removed from the resin could spill in the drinking water.

The SUVA also decreased at the SIX® pilots at Andijk and Plymouth (effective resin dose of 13 to 15 mL/L and 18 mL/L, respectively). Table 4 shows that, at these sites, the DOC removal by anionic IEX was 52 percent at Andijk [35] and 54 to 60 percent at Plymouth (Table 3 and Zheng et al. [36]). There was a high removal of the humic fractions, i.e., HS and BB. The HS and BB decreased by 80 to 85 percent at Andijk [35], while the HS decreased by 70 to 80 percent and the BB by 60 to 80 percent at Plymouth (Table 3 and Zheng et al. [36]). Although in the raw water the LMW_a and LMW_n concentrations were much lower than the concentrations of HS, 60 percent of the LMW_n were removed by SIX® at Plymouth. For both sites there was no removal of BP [35–36].

The preferential removal of hydrophobic and charged humic fractions, and the inefficacy on the uncharged hydrophilic biopolymers is in accordance with previous research [37]. This has also been confirmed in the work of Hu et al. [38]: with canal water, anion IEX removed mostly HS (88 percent), BB (74 percent) and LMW_a (55 percent), while the removal of BP was ineffective. Electrostatic interactions are dominant in NOM removal by IEX, although NOM can also be partially removed by hydrophobic interactions [20]. This could explain why also

LMW_n were partially removed by SIX®. Not only can the character of NOM influence the efficiency of removal by IEX, but also competing ions might hinder the NOM removal capacity of the resin, as observed at Blankaart. There, the sulphate concentration in raw water was typically 100 mg/L. In the resin of the MIEX® pilot, only 11 percent of the resin capacity was used for NOM removal, while 68 percent of capacity was used to remove sulphate (the rest of the capacity was used for bicarbonate, 21 percent, and nitrate, about 4 percent) [7].

3.3. Effect on coagulant dose

Coagulation removes preferentially high molecular weight hydrophobic NOM (including part of HS) and BP [37]. At Plymouth, the combination of SIX® and in-line coagulation with ceramic membrane filtration, compared to conventional treatment, resulted not only in a higher NOM removal (up to 0.9 mg/L of DOC more), but also in 50 percent lower dose of coagulants [23]. At Blankaart, during the batch tests on raw water and on water treated with MIEX® resin, there was a reduction of the required coagulant dose as well, from 20 to 8 mg/L of Fe, and the same overall NOM removal efficiency was obtained [7], even if the coagulation pH of the water after the MIEX® resin treatment was not checked or adjusted to be optimal. In addition, the 50 m³/h FIX pilot at Blankaart showed that IEX could reduce the coagulant dose from a range of 23 to 30 mg/L of Fe (full scale plant without IEX) to a range of 10 to 15 mg/L of Fe [34].

Verdickt and Schoutteten [34] observed differences between the 50 m³/h FIX pilot at Blankaart and a FIX pilot at another drinking water treatment location at Kluizen. Firstly, due to higher sulphate concentration in the raw water, the treatment in Blankaart required higher resin doses than in Kluizen for the same NOM removal efficiency. Secondly, the NOM removal by ferric coagulation in Blankaart, at pH 6,

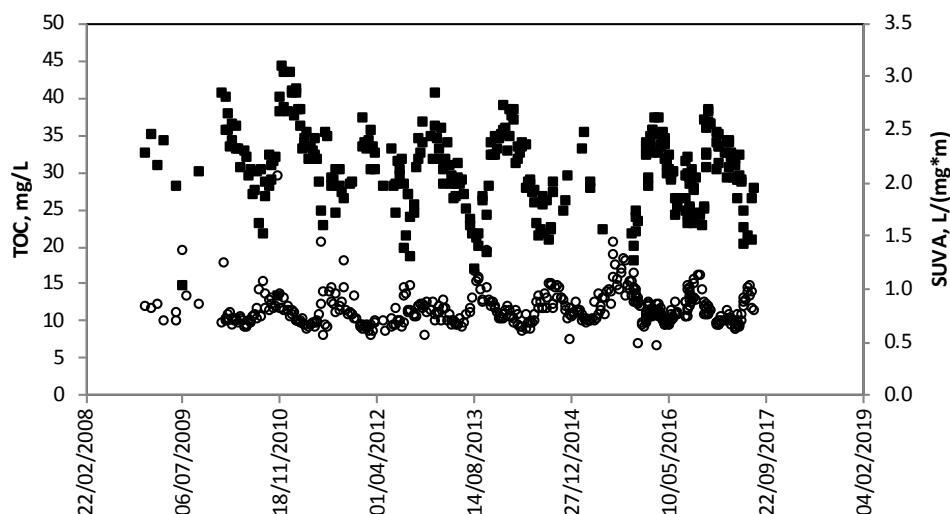


Fig. 4. Seasonal variations of NOM at Blankaart source water. SUVA is calculated using TOC instead of DOC. Squares represent the calculated SUVA, dots represent the measured TOC.

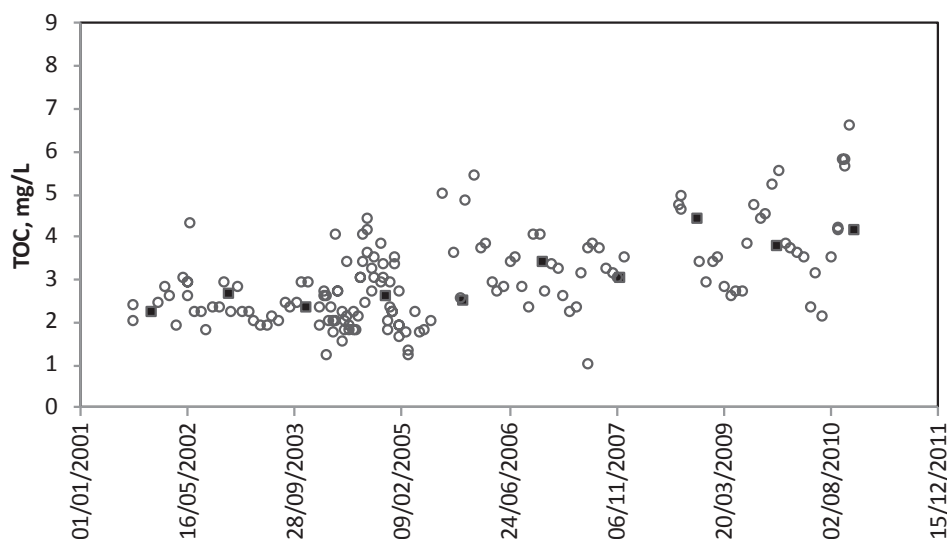


Fig. 5. TOC of a South West Water upland reservoir over 10 years (2001–2010). Squares represent the calculated yearly average TOC, dots represent the measured TOC.

was higher than in Kluizen. In Kluizen, the pH of the polyaluminum chloride conventional coagulation was 7.6, thus not at an optimal pH; therefore, the FIX pilot in Kluizen (with only 0.45 mL/L effective resin concentration) had more impact on reduction of the coagulant dosed. In addition, IEX had a larger contribution to the improvement of overall NOM removal at Kluizen, compared to the conventional treatment plant [34]. This experience shows that the overall NOM removal and the reduction of coagulant dose by IEX depend on the quality of the untreated water.

Verdickt and Schoutteten [34] also observed a potential disadvantage of using FIX before coagulation. During the algae blooms' season, the FIX bed of the 50 m³/h pilot experienced algae accumulation in the top layer of the resin bed; this caused stratification of the bed and consequently, uneven regeneration of the resin. In this case, the problem was mitigated by increasing the upflow velocity and the resin dose.

3.4. Limitation of membrane fouling

At Andijk and Plymouth, SIX®, coagulation (coagulation/clarification and in-line coagulation), or a combination of these two techniques

were tested to study their effect on fouling on ceramic microfiltration membranes [35,36]. When both SIX® and coagulation were used, the membrane performance was stable: 0 to 1.2 kPa/day of trans membrane pressure (TMP) increase were observed, depending on the location and the cleaning regime (i.e., backwash frequency and chemical cleaning). SIX® and in-line coagulation lowered the TMP and its rate of increase. With SIX® pre-treatment only, fouling varied at the different locations. At Andijk, there was a very low TMP increase (0.01 KPa/day with 68 LMH and 30 min filtration time) [39], whereas the TMP increase was still high for Plymouth (about 6.5 KPa/day, 112 LMH and filtration time 54 min) [36].

This can be attributed to the different characteristics of the BP at the two locations, which showed differences in the absorption of UV 254 nm. At Andijk, BP did not absorb UV, where the BP at Plymouth responded to UV [39]. A possible cause of the UV absorption of the BP at Plymouth could be the presence of aromatic structures. The fouling behaviour was also different: at Andijk, the BP could be removed easily by backwashing, and this was not the case for the BP at Plymouth [39]. When aromatic structures are present, calcium can bind to the acid functional groups of NOM and enhance membrane fouling by calcium bridging with a membrane surface or by charge screening [40,41]. For

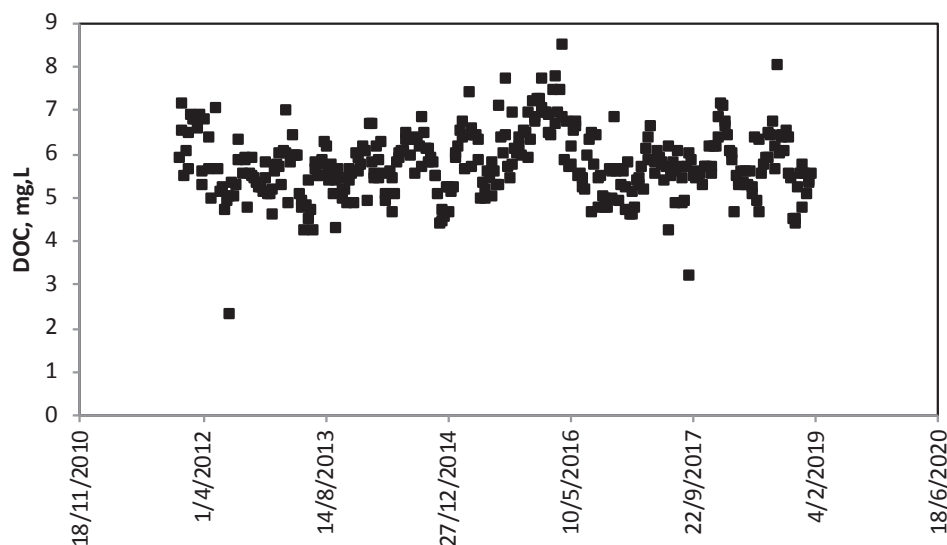


Fig. 6. Measured DOC concentration in the IJssel Lake between 2012 and 2019.

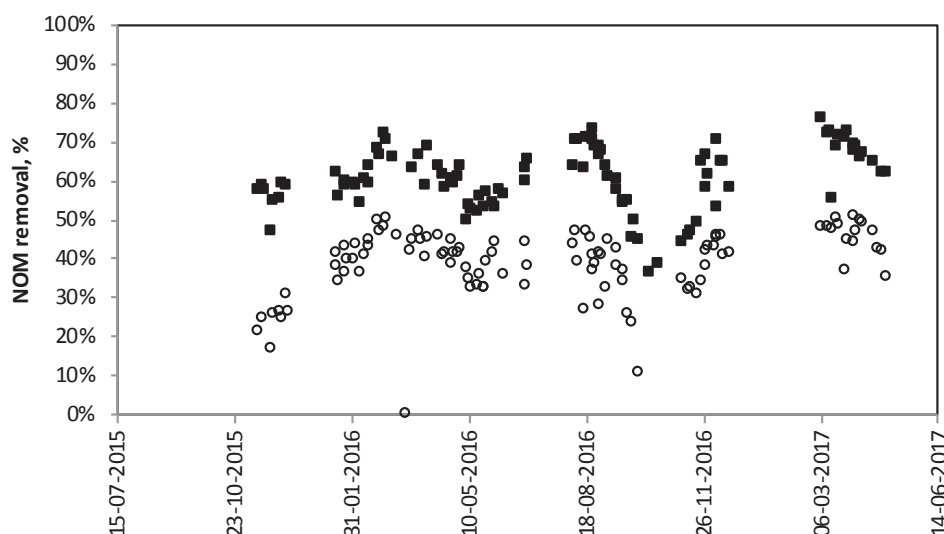


Fig. 7. TOC removal and UV₂₅₄ removal of the larger FIX pilot (50 m³/h) in Blankaart. Squares represent the UV₂₅₄ removal, dots represent the TOC removal.

ultrafiltration membranes it was found that backwashing with permeate water is then not effective [40].

The results at Andijk and Plymouth suggest that, depending on the characteristics of the water to be treated, coagulation may have a larger beneficial influence on ceramic microfiltration fouling than anion IEX. In particular, at Plymouth, coagulation was the key to control membrane fouling at IEX had no effect. Two possible causes were identified, namely the high level of BP removal by coagulation, and the protection of the membrane surface by coagulation micro flocs, i.e., forming a cake layer [39]. The BP, targeted by coagulation, has also been identified as main foulant of polymeric micro- and ultrafiltration membranes by others [17,42,43]. In some instances, humics, targeted by IEX, also might contribute to membrane fouling, depending on the type of membrane, e.g., in tighter polymeric membranes [44], or in case of sorption on the membrane [45]. However, Cornelissen et al. [46] observed that NOM removal by IEX is not always effective in reducing organic fouling on polymeric membranes, and showed that IEX can even be the cause of a flux decline due to biofouling. In the study of Cornelissen et al. [46], the fouling was attributed to the release of bacteria growing on the resin of a FIX system into the membrane system.

3.5. Effect on advanced oxidation based on UV/H₂O₂: AOC formation during oxidation and UV energy consumption

Advanced oxidation processes that are based on UV/H₂O₂ are used in drinking water treatment for disinfection and mainly for removal of organic micropollutants. At Andijk, the pilot scale pre-treatment with SIX® and ceramic microfiltration was more efficient in removing DOC than the conventional full-scale treatment. In both full-scale and pilot scale pre-treatment, the UV/H₂O₂ treatment did not change the concentration of DOC: on average, before and after this step, the average DOC remained 2.4–2.3 mg/L for the full-scale treatment and 1.8–1.7 mg/L for the pilot. However, the average AOC concentration during advanced oxidation increased considerably, from 6.2 µg C/L to 40.7 µg C/L in the conventional full-scale treatment, and from 12.9 µg

C/L to 35.1 µg C/L at the IEX/microfiltration pilot (Table 5).

This is confirmed by literature; when NOM is not fully mineralized after (advanced) oxidation, there is a preferential shift from NOM aromatic fractions into more biodegradable and hydrophilic fractions [47]. Thus, small assimilable compounds are formed, and the AOC concentration may increase, deteriorating the biostability of the water [15].

At Andijk, due to the two different pre-treatments, i.e., conventional pre-treatment and IEX/microfiltration, the water quality of the UV/H₂O₂ feed was different for the conventional full scale treatment and for the pilot. In particular, the average BP concentration in the UV/H₂O₂ feed after IEX/microfiltration pre-treatment, 0.2 mg/L, was larger than after the conventional pre-treatment, 0.1 mg/L. As BP are typically not aromatic [13] and thus not targeted by advanced oxidation, this could explain why the average AOC increased less during the UV/H₂O₂ after IEX/microfiltration treatment.

The test at Andijk showed that both coagulation and ion exchange had a role in reducing AOC formation during advanced oxidation with UV/H₂O₂, because these treatment steps lowered the incoming NOM concentration, which is a key precursor for AOC formation. Grefte et al. [37] studied the effect of FIX in pre-treatment before oxidation with ozone, and observed that prevention of AOC formation was more important than AOC removal in subsequent treatment steps, to achieve biostable drinking water. When FIX was added to the pre-treatment, the DOC concentration before ozonation was 49 percent lower and, as a consequence, the AOC formation during ozonation was then 53 percent lower.

Martijn et al. [48] showed another benefit of using IEX before UV/H₂O₂, as IEX removes both NOM and nitrate. Dissolved NOM and nitrate interfered in advanced oxidation, by absorbing UV light and consuming hydroxyl radicals that are produced and intended for oxidation of micropollutants. As a result, compared to conventional coagulation and sand filtration, the combination of IEX and ceramic microfiltration was able to lower by 30 percent the electrical energy per order, which is the specific electrical energy consumption per m³ of water required to reduce the micropollutant concentration by 90

Table 3
NOM concentration and SUVA before and after SIX® treatment in Plymouth, 07/03/2014.

	DOC, mg/L	BP, mg/L	HS, mg/L	BB, mg/L	LMWa, mg/L	LMWn, mg/L	SUVA, L/(mg*m)
Raw water	1.92	0.19	1.19	0.3	0	0.29	4.59
SIX® treated water	0.88	0.16	0.32	0.12	0	0.17	2.93

Table 4
NOM and NOM fractions removal by IEX at various locations.

Installation	Technology (resin)	Water type	NOM type	Initial NOM	NOM removal	Type measurement	Reference
MIEX® pilot (Belgium)	FIX (Miex® resin)	Reservoir water from river IJzel and lowlands	TOC (mg C/L) UV ₂₅₄ (m ⁻¹)	11 25	42% 68%	- -	[7]
FIX column Blankaaart (Belgium)	FIX (Miex® resin, Purolite A860S and VPOC1071)		TOC (mg C/L) UV ₂₅₄ (m ⁻¹)	- -	40–60% 70–80%	- -	
FIX pilot 50 m ³ /h Blankaaart (Belgium)	FIX (Purolite PPA860S)	Reservoir water from river IJzel and lowlands	TOC (mg C/L) UV ₂₅₄ (m ⁻¹)	11 23	39% 61%	Average value between 12 and 11-2015 and 2–5-2017	[34] and Fig. 7
Pilot treatment plant Plymouth (United Kingdom)	SIX® (Lewatit S5128)	River	CDOC (mg C/L) Bio-polymers (mg C/L) Humics (mg C/L) Building Blocks (mg C/L) LMW neutrals (mg C/L)	6.7 - - - -	60% Almost no removal in the range of 80% in the range of 80% in the range of 60%	Single measurement 16–08-2014, LC-OCD	[36]
	SIX® (Lewatit S5128)	Burrator reservoir	DOC (mg C/L) SUVA (L/(mg·m)) Bio-polymers (mg C/L) Humics (mg C/L) Building Blocks (mg C/L) LMW acids (mg C/L) LMW neutrals (mg C/L)	1.91 4.59 0.19 1.19 0.30 0 0.29	54% 36% 14% 73% 62% - 41%	Single measurement 07–03-2014, LC-OCD	Table 3
Pilot plant Andijk (The Netherlands)	SIX®	IJssel Lake water stored in a reservoir for several days, is chemically softened and the pH is adjusted with CO ₂	DOC (mg C/L) Humics and Building blocks LMW acids Biopolymers	5.6 - - -	52% In the range of 80–85% In the range of 60–70% ~0%	Average value from 01-2012 to 15-04-2015 Single measurement 31–07-2013, LC-OCD	[35]

Table 5

DOC and AOC before and after UV/H₂O₂ treatment, for SIX[®]/microfiltration pilot and for full scale treatment at Andijk. The standard deviation is indicated by “±” and number of measurement is indicated by “()”.

	DOC, mg/L Feed of UV/H ₂ O ₂	Effluent of UV/H ₂ O ₂	AOC, µg/L Feed of UV/H ₂ O ₂	Effluent of UV/H ₂ O ₂
SIX [®] /microfiltration pilot	1.8 ± 0.2 (30)	1.7 ± 0.2 (31)	12.9 ± 6.7 (43)	35.1 ± 21.1 (26)
Full scale treatment	2.4 ± 0.2 (13)	2.3 ± 0.1 (13)	6.2 ± 2.9 (27)	40.7 ± 22 (47)

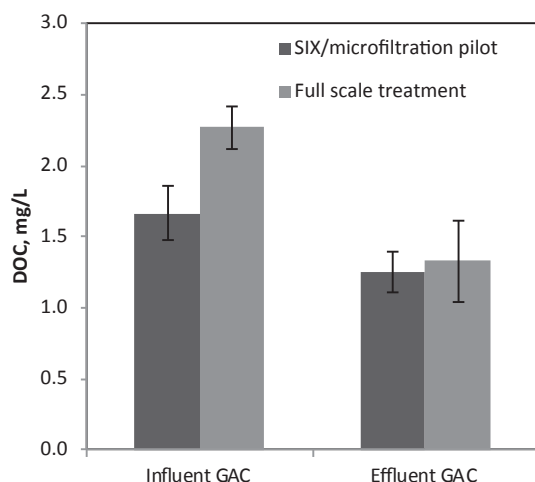


Fig. 8. DOC before and after GAC. The error bars give the standard deviations. The number of measurements is 13 for the influent GAC in full scale, 12 for the effluent GAC in full scale, 31 for the inlet GAC in the SIX[®]/microfiltration pilot and 31 for the effluent GAC at the SIX[®]/microfiltration pilot.

percent [48].

3.6. Effect on efficiency of activated carbon

At Andijk, the NOM and AOC removal by GAC was studied after conventional full-scale and SIX[®]/microfiltration pilot pre-treatment, and after UV/H₂O₂. At the pilot with SIX[®]/microfiltration pre-treatment, DOC removal in the GAC was less efficient than at the conventional full-scale plant, while the AOC removal in the GAC was almost the same (Fig. 8 and Fig. 9). After GAC, the average DOC was 1.3 mg/L DOC for both the pilot and the full-scale treatment, and the average

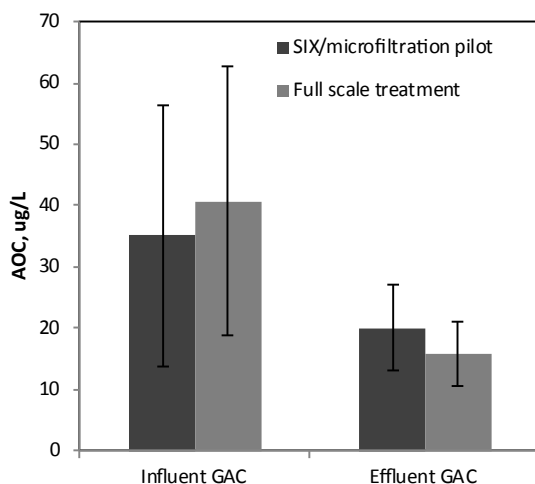


Fig. 9. AOC before and after GAC. The error bars give the standard deviations. The number of measurements is 47 for the influent GAC in full scale, 55 for the effluent GAC in full scale, 26 for the inlet GAC in the SIX[®]/microfiltration pilot and 26 for the effluent GAC in the SIX[®]/microfiltration pilot.

AOC was 20.1 µg/L for the pilot and 15.8 µg/L for the full-scale treatment.

The GAC at both pilot and conventional full-scale removed mostly HS and neutrals; however the contribution of the various fractions was different (Table 6). In particular, almost 50 percent of the average removed DOC was HS for the conventional full-scale plant, and at the SIX[®]/microfiltration pilot the average removal was lower, about 30 percent. One explanation is linked to the older carbon used in the pilot filter, which had a lifetime of 1.5 to 2 years. However, it could also be due to a lower concentration of HS in the GAC influent after the SIX[®]/microfiltration pre-treatment (0.7 ± 0.1 mg/L) compared to the GAC influent after the conventional pre-treatment (1.0 ± 0.1 mg/L).

Activated carbon has been used in water treatment with the aim to remove NOM, e.g., to meet local legislation standards for DBP concentration in drinking water [2], or to improve taste and odor of the drinking water [1]. However, most drinking water companies nowadays use GAC mainly to remove micropollutants. NOM can considerably reduce the efficiency of activated carbon for the removal of micropollutants, occupying available carbon surface through adsorption competition or pore blocking, as shown by, e.g., De Ridder et al. [5]. Hu et al. [38] showed that the removal of NOM by IEX, that targeted HS and BB and partially LMW_a, was beneficial to limit pore blocking of GAC filters. However, IEX did not limit the adsorption competition between NOM and micropollutants in powdered activated carbon (PAC), suggesting that HS and BB were not responsible for adsorption competition into the smaller pores of PAC [38]. Hu et al. [38] also argued that low molecular weight hydrophobic NOM, which is not removed by IEX, could be responsible for adsorption competition.

3.7. Effect on DBP formation

When NOM reacts with chlorine or other disinfection chemicals, it forms DBPs. The toxicity of an organic DBP is correlated to the production of organic halogens, and depends from, e.g., applied disinfection chemical, and presence of inorganic DBPs, such as bromate, chlorite and chlorate [49]. DBP concentrations in drinking water are regulated by, e.g., European Union legislation [50]. Because DBPs are potentially harmful for human health, the DBPs regulations from European Union from are in the process of becoming more stringent [51]. Two major groups of DBPs in drinking water after chlorination are trihalomethanes (THMs) and haloacetic acids (HAAs) [52]. THMs and HAAs are formed by various NOM fractions, and each with different potentials [53]. Hydrophobic, high molecular weight NOM is highly reactive with chlorine and is the main DBP precursor [54]. However, hydrophilic NOM can also contribute to DBP formation [54]. For example, hydrophilic NOM can form the more toxic bromated DBPs during chlorination when bromide is present [55]. The option of reducing the dose of disinfectant to lower DBP formation is limited [56]. Therefore, DBP formation should be lowered by adding an extra treatment step for NOM removal before disinfection, especially when enhanced coagulation is already in use [1].

At Plymouth, the pilot tested the role of SIX[®] and microfiltration on DBP/THM precursor removal and DBP/THM formation potential (DBPFP and THMFP) before disinfection. SIX[®] was tested both alone and in combination with in-line coagulation [23]. The performance was compared to the existing conventional water treatment plant which

Table 6

BP, HS, BB and LMWn before and after GAC treatment, with SIX®/microfiltration pilot pre-treatment and with conventional full scale pre-treatment. The standard deviation is indicated by “±” and number of measurement is indicated by “()”. The LMWn are not included because of their low concentration.

	BP µg/L		HS µg/L		BB µg/L		LMWn µg/L	
	Influent GAC	Effluent GAC	Influent GAC	Effluent GAC	Influent GAC	Effluent GAC	Influent GAC	Effluent GAC
SIX®/microfiltration pilot	177 ± 37 (31)	143 ± 24 (31)	669 ± 132 (31)	538 ± 94 (31)	358 ± 30 (31)	302 ± 41 (31)	370 ± 25 (31)	240 ± 31 (31)
Full scale treatment	124 ± 14 (13)	88 ± 18 (12)	989 ± 134 (13)	551 ± 126 (12)	559 ± 138 (13)	443 ± 103 (12)	468 ± 34 (13)	223 ± 51 (12)

used coagulation as the NOM removal technology. The SIX® and in-line coagulation pre-treatment with ceramic membrane filtration led to 58 to 67 percent lower THMFP and HAAFP than conventional coagulation. When SIX® was used without in-line coagulation as membrane pre-treatment, only in one case the DBPFP was lower than in conventional treatment, i.e., when the raw concentration of DOC was high, about 6 mg/L [23]. This was to be expected, because these high DOC concentrations were typically due to HS flushed into water supplies during rainfall events, and HS were readily removed by IEX. Also, the formation of brominated DBPs was 30 to 67 percent lower for the SIX® and in-line coagulation pre-treatment with ceramic microfiltration compared to conventional coagulation [23]. In the case of high DOC concentrations, the brominated DBPFP of the SIX®-treated water was, again, lower when compared to that of conventional treatment.

4. Conclusions

Three drinking water companies in the North Sea region use or are considering to use anionic IEX on surface water in the early stage of their full scale treatment plants. In this situation, the (considered) anionic IEX systems use non-fixed bed technologies: MIEX®, FIX, and SIX®. The studies on bench and pilot scale showed that anionic IEX removed typically 40 to 60 percent of the total NOM. The NOM removed by IEX was mostly in the hydrophobic range, and, according to LC-OCD, IEX predominantly targeted HS and BB, which are negatively charged, while almost no BP were removed.

Although the benefit of IEX pre-treatment depended on the type of NOM in the feed water quality, the studies revealed the following NOM-related effects in drinking water treatment:

- IEX removed NOM fractions that partially overlap the NOM targeted by coagulation. As a consequence, IEX before coagulation resulted in lower doses of coagulants to achieve NOM removal of 50 percent or more.
- Used as pre-treatment, IEX had a limited direct influence on improving fouling of ceramic microfiltration membranes.
- IEX removes precursors of AOC, which is formed during advanced oxidation with UV/H₂O₂, diminishing the impact on biological stability of treated drinking water.
- IEX removed NOM and nitrate, which interfere in UV treatment. This resulted in lower energy consumption during UV/H₂O₂ treatment.
- IEX in pre-treatment contributed to lower subsequent DBP formation. A combination of IEX, coagulation and ceramic microfiltration was shown to outperform conventional coagulation with sand filtration. The improvement in DBP formation by NOM removal by IEX was dependent on NOM character and concentrations.

CRedit authorship contribution statement

I. Caltran: Conceptualization, Methodology, Data curation, Writing - original draft. **S.G.J. Heijman:** Conceptualization, Methodology, Writing - review & editing. **H.L. Shorney-Darby:** Conceptualization, Funding acquisition, Resources, Writing - review & editing. **L.C. Rietveld:** Conceptualization, Methodology, Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

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