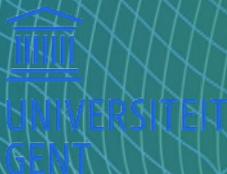# BTO rapport

Ion exchange in combination with coagulation for natural organic matter removal in surface water treatment

De Watergroep
WATER, VANDAAG EN MORGEN

UNIVERSITEIT
GENT

KWR

Bridging Science to Practice

Ion exchange in combination with coagulation for natural organic matter removal in surface water treatment

Reliable NOM removal using on-site fluidized IEX and coagulation/flotation

BTO 2020.012 | February 2020

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BTO Management summary

Reliable and robust natural organic material removal possible with fluidized ion exchange and coagulation / flotation

Author(s) Dr. Ir. Klaas Schoutteten (Universiteit Gent).

Natural organic matter (NOM) removal is essential in drinking water treatment, since the presence of NOM results in a yellow water color, has a detrimental impact on the biological stability of drinking water, is a precursor for disinfection by-product formation, and it has a negative impact on most downstream treatment processes. De Watergroep investigated the combination of fluidized ion exchange (IEX) followed by coagulation/flotation for NOM removal of surface water in a long term on-site pilot at WTW De Blankaart in Belgium. The investigated processes proved to be reliable and robust, however, the required capital cost for additional fluidized IEX was calculated to outweigh the benefits in the operational costs of the downstream processes. This study is part of the Flemish-Dutch water research program (VNWKO), part of the Joint Research Programm (Bedrijfstak Onderzoek, BTO).
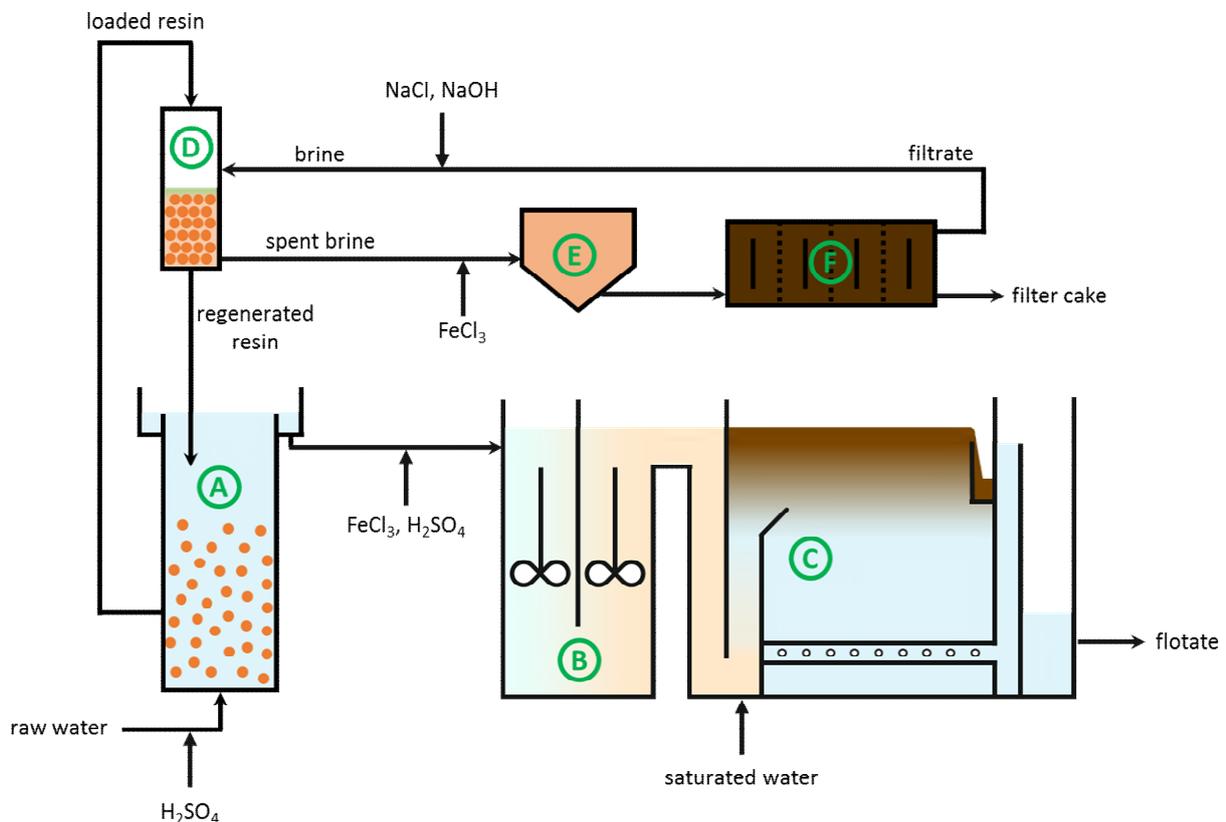
Schematic overview of the IEX – coagulation/flotation semi-industrial plant at WTW De Blankaart, with A: IEX contactor, B: coagulation, C: flotation, D: external regeneration vessel, E: spent brine coagulation, and F: filter press.

Method: On-site pilot IEX – coagulation/flotation for NOM removal

An on-site pilot study was performed in 2016 – 2019 on ion exchange and enhanced coagulation/flotation. A 50 – 58 m³/h semi-industrial pilot plant was operated consisting of a high rate fluidized bed IEX system with on-site spent brine treatment, followed by a coagulation/flotation unit. On-site IEX-coagulation/flotation treatment was compared to standalone coagulation of the full-scale installation at WTW De Blankaart.

No Translation 'InterestBTO': NOM removal essential for water quality improvement

The presence of NOM in sources for drinking water negatively impacts the quality of treated water and drinking water treatment processes. NOM can cause colour, taste and odour problems, biological stability problems, by-product formation after chemical disinfection and has a negative impact on most downstream treatment processes. The interest for the drinking water companies is to produce impeccable drinking water and no problems during the operation of water treatment processes.

Results: Innovative IEX – coagulation/flotation was reliable and robust

The high rate fluidized bed IEX system, the subsequent coagulation/flotation system and on-site treatment system for the spent IEX brine were all judged to be reliable. Only during algal bloom events a decrease in NOM removal by the IEX occurred which was compensated for by the coagulation/flotation system. At low temperatures below 3°C, precipitation of Na_2SO_4 occurred, blocking pipes of the spent brine treatment system which could be mitigated by heating.

At WTW De Blankaart, the NOM removal obtained by the IEX – coagulation/flotation treatment scenario was low compared to standalone coagulation. This is due to (i) the optimal coagulation conditions applied in the standalone coagulation process, resulting in very high NOM removal, and (ii) the high sulphate content of the raw reservoir water. Furthermore, 42% less coagulant was used in the IEX – coagulation/flotation treatment compared to standalone coagulation which resulted also in 35% less sludge production. In IEX – coagulation/flotation, coagulation is performed at a higher pH resulting in a lower SO_4^{2-} content of the treated water compared to the standalone coagulation process.

Implementation: CAPEX additional IEX outweighs benefits in OPEX

The operational costs of IEX – coagulation/flotation treatment are estimated to be 7.43 €cent/m³ for WTW De Blankaart. In comparison, standalone coagulation/flotation amounts to 8.00 €cent/m³. The capital expenditure of the IEX system is estimated to be 4.76 €cent/m³. As such, the decrease in operational expenditure does not cover the additional investment costs of the IEX system at WTW De Blankaart.

The Report

This research is reported in report *Ion exchange in combination with coagulation for natural organic matter removal in surface water treatment* (BTO 2020.012 | February 2020).

Summary

Natural organic matter (NOM) removal is essential in drinking water treatment, since the presence of NOM results in a yellow water color, has a detrimental impact on the biological stability of drinking water, is a precursor for disinfection by-product formation, and it has a negative impact on most downstream treatment processes. For the latter reason, NOM removal preferably takes place as early as possible in the water treatment train, and it is in this respect that De Watergroep investigated the combination of ion exchange (IEX) followed by coagulation for NOM removal of surface water at WTW De Blankaart in Belgium. This study falls within the Flemish-Dutch water research program (VNWKO), part of the Joint Research Program (Bedrijfstak Onderzoek,BTO).

This report summarizes a study performed in 2016 – 2019 on innovative technologies for removal of natural organic matter from surface water. The investigated technologies are ion exchange and enhanced coagulation/flotation, and pilot research was conducted on a 50 – 58 m³/h semi-industrial pilot plant consisting of a high rate fluidized bed IEX system with on-site spent brine treatment, followed by a coagulation/flotation unit. On-site IEX- coagulation/flocculation treatment was compared to standalone coagulation of the full-scale installation at WTW De Blankaart.

The high rate fluidized bed IEX system, the subsequent coagulation/flotation system and on-site treatment system for the spent IEX brine were all judged to be reliable. Only during algal bloom events a decrease in NOM removal by the IEX occurred which was compensated for by the coagulation/flotation system. At low temperatures below 3°C, precipitation of Na_2SO_4 occurred, blocking pipes of the spent brine treatment system which could be mitigated by heating.

At WTW De Blankaart, the NOM removal obtained by the IEX – coagulation/flotation treatment scenario was low compared to standalone coagulation. This is due to (i) the optimal coagulation conditions applied in the standalone coagulation process, resulting in very high NOM removal, and (ii) the high sulphate content of the raw reservoir water. Furthermore, 42% less coagulant was used in the IEX – coagulation/flotation treatment compared to standalone coagulation which resulted also in 35% less sludge production. In IEX – coagulation/flotation, coagulation is performed at a higher pH resulting in a lower SO_4^{2-} content of the treated water compared to the standalone coagulation process.

The operational costs of IEX – coagulation/flotation treatment are estimated to be 7.43 €cent/m³ for WTW De Blankaart. In comparison, standalone coagulation/flotation amounts to 8.00 €cent/m³. The capital expenditure of the IEX system is estimated to be 4.76 €cent/m³. As such, the decrease in operational expenditure does not cover the additional investment costs of the IEX system at WTW De Blankaart.

CONCEPT

Contents

BTO 2020.012 | February 2020
Ion exchange in combination with coagulation for
natural organic matter removal in surface water
treatment

1   Introduction

This report summarizes a study performed in 2016 – 2019 on innovative technologies for removal of natural organic matter from surface water. The investigated technologies are ion exchange and enhanced coagulation, and research was conducted both on small scale and pilot scale at the water treatment works of De Blankaart, owned by De Watergroep, Belgium.

In the report, background information and the rationale behind this study will be given in Section 2, followed by a description of the pilot plant (Section 3) and the results obtained with small scale and pilot scale experiments (Section 4). Assessments on the water quality, waste flows and economic impact will be described in Section 5, and finally Section 6 presents the conclusions of the research.

This study falls within the Flemish-Dutch water research program (VNWKO), part of the Joint Research Programm (Bedrijfstak Onderzoek,BTO),it also includes results from the DOC2C's project, a research project within the EFRO Interreg 2seas program on innovative DOC removal from surface water for drinking water treatment. More information on DOC2C's can be found on the project website www.doc2cs.com.

2   Background

2.1   Rationale behind this study

De Watergroep is the largest drinking water utility in Flanders, Belgium, serving over 3.2 million customers in 180 Flemish communities via a 32460 km network of pipes. In 2018, 25% of its produced drinking water originated from surface water, from which over 9.3 million m³ (7.2% of the total production) was produced at water treatment works (WTW) De Blankaart in Diksmuide and over 11.2 million m³ (8.6%) in WTW Kluizen, Belgium.

In 2011, De Watergroep started investigating ion exchange (IEX) followed by coagulation and flotation to improve natural organic matter (NOM) removal at WTW Kluizen. It was found that by introducing IEX the water quality could be improved both in terms of NOM concentration and ionic composition, while at the same time the coagulant demand could be reduced by 75% which effectively compensates the investment costs of the IEX unit. Based on these results, it was decided to evaluate the feasibility of combining IEX and coagulation at WTW De Blankaart as well.

Natural organic matter is a comprehensive parameter for different organic substances originating from decaying floral and faunal matter. NOM is found in every natural water, however its composition and concentration can show a wide variety depending on the origin of the water and seasonal influences. The total mixture of NOM is often determined as total organic carbon (TOC) or non-purgeable organic carbon (NPOC), while the dissolved fraction is generally determined after 0.45 μm filtration and measured as dissolved organic carbon (DOC), or UV absorbance at 254 nm. NOM removal is paramount to drinking water treatment, as its presence is not only easily recognized visually by a yellow water color, it also has a detrimental impact on the biological stability of drinking water, it is a precursor for disinfection byproduct formation, and it has a negative impact on most downstream treatment processes such as activated carbon adsorption. For the latter reason, NOM removal preferably takes place as early as possible in the water treatment train, and it is in this respect that De Watergroep investigates the combination of IEX followed by coagulation for NOM removal. The premise is that by applying IEX , a large fraction of NOM can be removed prior to the coagulation step, thereby reducing the chemicals demand of the coagulation process while improving the quality of the treated water. This premise was formulated based on previous research performed at WTW Kluizen.

2.2 Description of source water

WTW De Blankaart is located in the Western part of Flanders, Belgium, close to the city of Diksmuide (Figure 1).

Figure 1. Location of WTW De Blankaart in West Flanders and the surrounding drinking water protection area.

The raw water from De Blankaart originates for around 80% from the IJzer river and around 20% is overflow of the nearby lake at the Blankaart nature reserve (which is fed by small surrounding channels and streams). A 60 ha reservoir with a capacity of 3 million m³ is filled mainly during autumn, winter and spring. The raw water in the reservoir is characterized by a high NOM content (12.2 mg NPOC/L) and a high alkalinity (207 mg/L HCO_3^-), along with relatively high chloride (117 mg Cl^-/L) and sulphate (87 mg SO_4^{2-}/L) concentrations (Table 1). Due to the eutrophic nature of the raw water, algae blooms occur frequently in the reservoir typically during autumntime.

Table 1. *Average composition of the raw water at WTW De Blankaart during the test period.*

Parameter	Unit	Average	Median	5% percentile	95% percentile
NPOC	mg/L	12.2	11.3	9.4	16.4
UV_{254}	m^{-1}	24.0	23.9	19.7	28.7
Turbidity	NTU	4.1	3.5	1.0	8.6
Conductivity	µS/cm	823	813	693	1046
Cl^-	mg/L	117	112	84	179
SO_4^{2-}	mg/L	87	88	76	98
NO_3^-	mg/L	10	5	0	27
Na^+	mg/L	75	70	55	117
Ca^{2+}	mg/L	69	72	41	98
Mg^{2+}	mg/L	17	17	15	19
HCO_3^-	mg/L	207	212	135	283
	mmol/L	3.4	3.5	2.2	4.6
PO_4^{3-}	mg/L	0.37	0.31	0.08	1.04
Total chlorophyll	µg/L	20	8.1	1.8	63

2.3   Description of treatment processes

The conventional drinking water treatment train at WTW De Blankaart (capacity of 40 000 m³/d) is schematically depicted in Figure 2. Firstly, the raw water flows over a biological trickling filter where oxidation of ammonia occurs. Then, the suspended solids and DOC are removed by coagulation with ferric iron at a pH of 6, after which floc separation occurs through decantation in a sludge blanket clarifier. After decantation, the pH is adjusted back to 7 by NaOH dosing and remaining turbidity, iron and manganese are removed in rapid sand filters. Granular activated carbon filters remove traces of organic micropollutants, and finally the water is post-chlorinated before it is distributed in the region.

Figure 2. *Process flow diagram of the conventional drinking water treatment at WTW De Blankaart.*
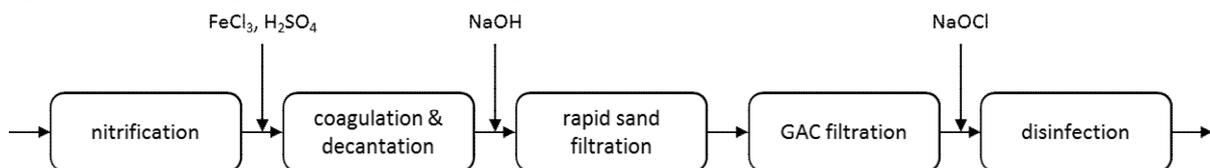
The combination of a high NOM content and high alkalinity in the water results in a high chemical demand for coagulation to achieve adequate NOM and turbidity removal, with ferric iron doses above 20 mg Fe/L combined with acidification with H_2SO_4 to pH 6. Because at WTW Kluizen research at a semi-industrial scale showed that a combination of IEX and coagulation/flotation could decrease the coagulant demand by 75% while at the same time the product water quality could be improved, this concept was also evaluated at WTW De Blankaart at a semi-industrial scale.

3 Description of the ion exchange and coagulation/flotation pilot plant

The semi-industrial pilot plant consists of a high rate ion exchange system with on-site spent brine treatment, followed by coagulation/flotation unit.
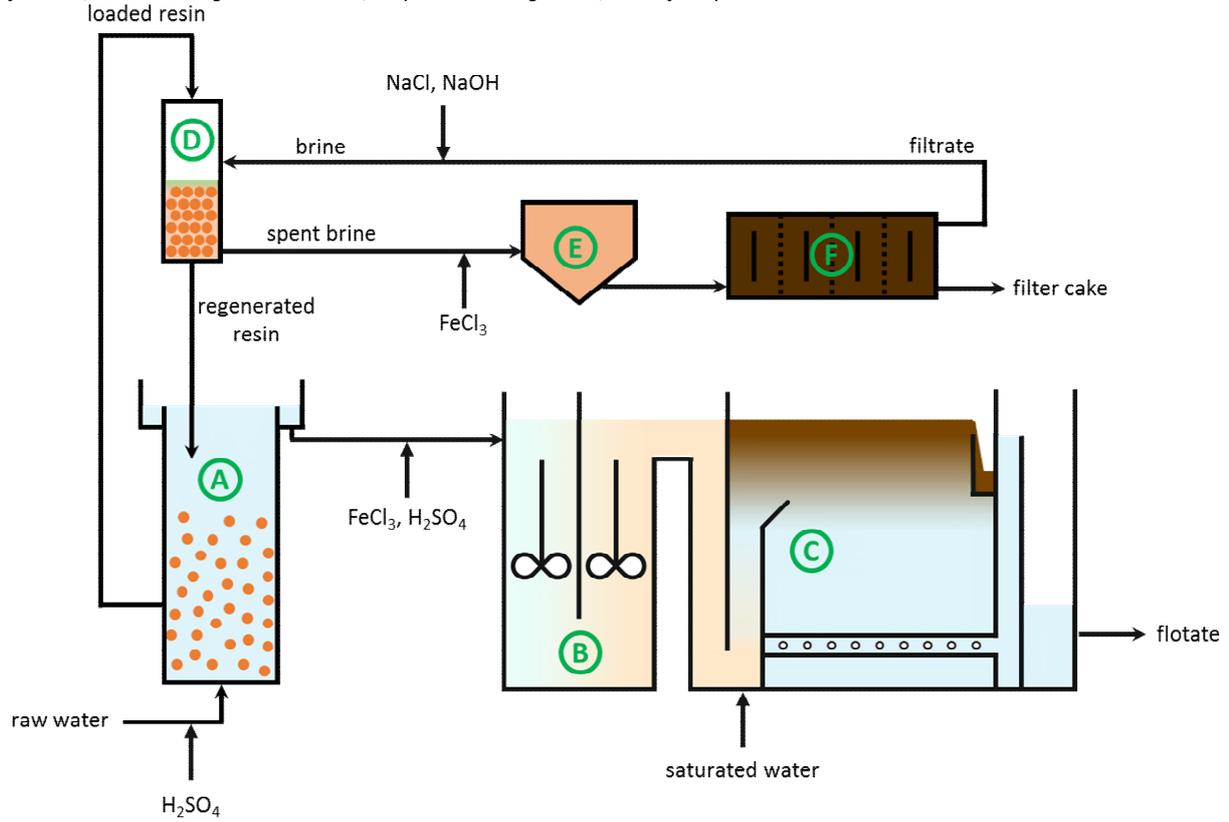
In Figure 3, the process of the semi-industrial pilot installation is shown, and in Figure 4, detail images are provided of different units of the plant. Raw reservoir water (see Table 1) is first screened with a 1 mm screen to remove coarse particles and is then acidified with 10 mg/L H_2SO_4 to prevent $CaCO_3$ scaling of the IEX resin. It is subsequently fed to the IEX contactor (Figure 3.A and Figure 4.A) at the bottom at a flow of $50 - 58$ m³/h. At the inlet a distribution system consisting of 48 downwards directed nozzles distributes the water over the surface area of the IEX contactor (Figure 4.B). The contactor contains 1670 L of a macroporous polyacrylic strong basic anion exchange resin (Purolite® PPA860S), which is fluidized by the upward motion of the water. The applied hydraulic loading rate of $17.3 - 20.1$ m/h ensures that the resin remains inside the contactor, while suspended solids in the feed water are washed out with the water leaving the contactor at the top (Figure 4.C).

Periodically, a small fraction of the resin is extracted from the IEX contactor using an air-lift pump, and transferred into an external regeneration vessel (Figure 3.D and Figure 4.D). In this regeneration vessel, the resin is regenerated by contact of 1 bed volume (BV) of brine for 10 minutes, and subsequently, the brine is displaced using tap water. Finally, the resin is resuspended and returned to the contactor. The effective resin dose, i.e. the volume of resin regenerated per volume of raw water treated, can be varied by changing the volume of the transferred resin in the regeneration vessel and/or the frequency of regeneration cycles. The maximum effective resin dose that can be applied in the pilot plant is equal to 2 mL$_{regenerated\ resin}$/L$_{water}$.

Because De Watergroep aims at operating the IEX process without discharge of liquid waste streams, the IEX spent brine is treated on-site by removing the NOM using coagulation (with $FeCl_3$ and Magnafloc® LT22S DWI, a cationic polyacrylamide flocculant) at a pH of 4 (Figure 3.E). The sludge is dewatered using a filter press (Figure 3.F), after which the filtrate is conditioned with NaOH to a pH of 6.2 and NaCl to a conductivity of 140 mS/cm before it is reused as brine in the regeneration process. The recirculation of spent brine as fresh brine implies that only a maximum of 1 BV of spent brine can be collected for 1 BV of brine dosed, and no rinsing of the IEX resin bed can be applied - the water that is added after dosing of the brine serves only as displacement water. Due to improper plug flow conditions, front broadening and mixing effects during regeneration, part of the eluting NaCl is not captured in the spent brine and ends up in the drinking water. In addition, coagulation and filter pressing removes a high fraction of the NOM present in the spent brine, but does not result in substantial sulphate removal. Hence, sulphate (originating from the surface water) accumulates in the brine solution.

The IEX effluent is coagulated (Figure 3.B and Figure 4.E) using ferric iron at pH $6.5 - 7.1$. Subsequently, flocculation takes place in two flocculation tanks in series with a total contact time of $11 - 15$ min, after which the flocs are separated by means of dissolved air flotation (Figure 3.C and Figure 4.E). The flotation unit is operated at a net hydraulic loading rate of $19 - 26$ m/h in the separation zone. The saturated water is produced at a pressure of 5.5 bar, and dosed to the water with pneumatically adjustable nozzles at recycle ratios of $0.06 - 0.10$ L$_{saturated\ water}$/L$_{influent}$. The treated water is removed from the bottom of the separation zone through perforated pipes. The sludge blanket formed at the top of the separation zone is periodically removed by increasing the water level in the flotation unit, allowing the sludge to overflow into a sludge gutter.

Figure 3. *Illustration of the IEX – coagulation/flotation semi-industrial plant at WTW De Blankaart, with A: IEX contactor, B: coagulation, C: flotation, D: external regeneration vessel, E: spent brine coagulation, and F: filter press.*

Figure 4. *Detail images of the semi-industrial plant, with A: IEX contactor, B: distribution system in IEX contactor, C: IEX effluent overflow weirs, D: external regeneration vessel, and E: coagulation/flotation.*
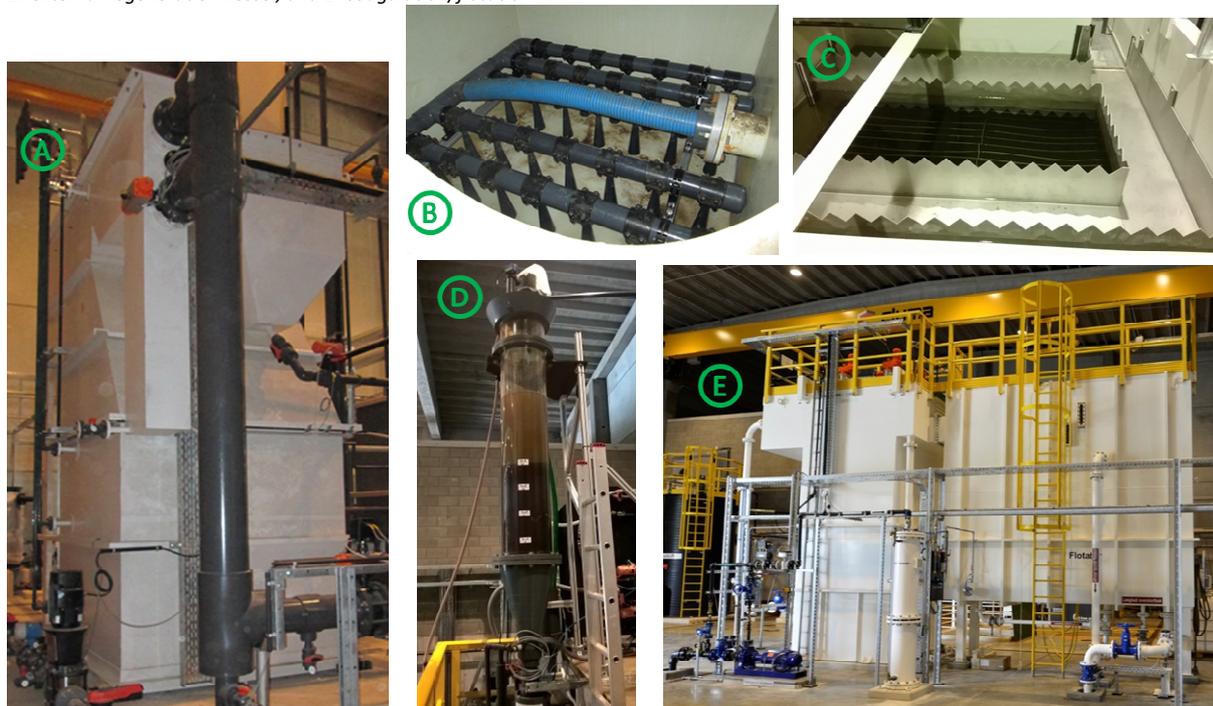
4   Process evaluations

4.1   NOM removal results from bench-scale experiments

4.1.1   IEX bench-scale experiments

Different IEX reactor configurations can be applied for NOM removal from water, amongst which suspended ion exchange, fluidized bed ion exchange, and a high rate ion exchange system.

- In suspended ion exchange, a certain volume of resin is suspended in a liter of raw water, and a contact time is allowed by passing the resin and water through plug flow contactors. Then the resin is separated from the water and regenerated. In this process the resin loading remains low, which ensures relatively fast exchange kinetics and by immediately regenerating the resin after contact with the water there is a low risk on biofouling. However, despite fast exchange kinetics the contact time remains high due to relatively low resin doses (e.g. 5 – 20 mg_{resin}/L_{water}). The footprint of the IEX contactors is high, and in order to remove an adequate amount of NOM also a large amount of competing ions (such as SO_4^{2-}) are removed.
- In fluidized bed ion exchange, the feed water is supplied from the bottom of the contactor, fluidizing the resin. The resin remains inside the contactor by controlling the hydraulic loading rate of the feed water. After breakthrough occurs, the entire resin bed is regenerated inside the contactor in fixed bed modus (top – bottom), which limits the risk on biofouling. A downside of fluidized bed ion exchange is that the obtained water quality varies with the run time of the contactor, therefore in order to reduce the varying water quality a carousel configuration of multiple contactors can be applied, with each contactor being regenerated in turn and thus each contactor having a different run time. This complicates the design of the system.
- A high rate ion exchange system is based on a single contactor containing a large inventory of resin, allowing for a short contact time and low effective resin doses (e.g. 0.5 – 2 mg_{resin}/L_{water}). Only a small part of the resin is regenerated in an external regeneration vessel, which results in a constant water quality of the IEX contactor effluent. The ratio of the flow of freshly regenerated resin to the raw water flow determines the effective resin dose. Note that also the remainder of the resin inventory (i.e. what is not freshly regenerated) contributes to ion exchange processes. This kind of ion exchange system allows for short contact times and therefore has a relatively low footprint, however the risk on biofouling increases because part of the resin inventory inside the contactor is allowed to get relatively old.

Even though the latter system is the only one applied at semi-industrial scale in the DOC2C's project, these three different systems were evaluated at small scale in this project. The results from these small scale experiments will be described in this Section.

4.1.1.1   Single contact jar tests for a suspended ion exchange system

The efficiency of the IEX process for NOM removal can be easily assessed by performing single contact jar tests, in which different resin concentrations are applied to feed water, and samples are taken at different contact times. Results of such an experiment are shown in Figure 5, depicting the residual $UV_{254\,nm}$ absorbance and NPOC concentration as a function of the CT-value (i.e., the product of the contact time and the applied resin dose). It is clear that a higher resin dose and/or a higher contact time result in better NOM removal. At first, there is a steep decline of the residual $UV_{254\,nm}$ absorbance and the NPOC concentration, followed by a slower decrease as the CT-value increases. The fact that the $UV_{254\,nm}$ absorbance decreases stronger than the NPOC concentration indicates that chromophoric NOM (i.e. with high specific UV absorbance) is preferentially removed with IEX.

Figure 5. Single contact jar tests – influence of CT-value (product of resin dose and contact time) on UV254 nm absorbance and NPOC.
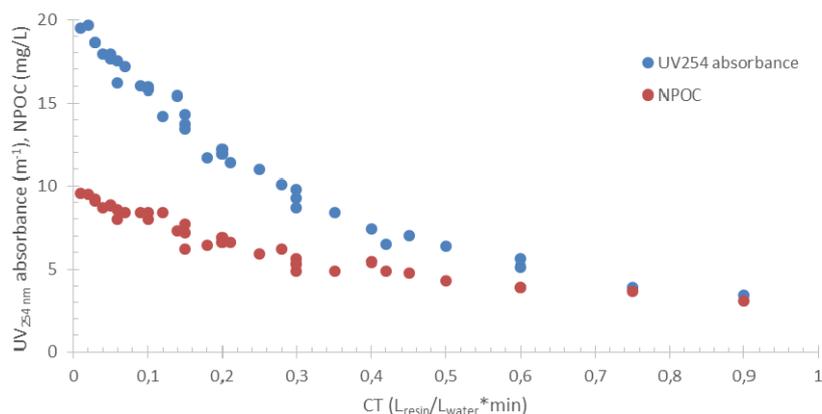

These single contact jar tests provide useful information on the residual NOM content that can be obtained with suspended IEX systems. For the raw water of WTW De Blankaart, $UV_{254\,nm}$ and NPOC residuals as low as 3.5 m^{-1} and 3.1 mg/L can be obtained at a CT-value of 0.9 L_{resin}/L_{water}*min (determined with a feed water of 21.4 m^{-1} and 9.7 mg/L). Jar experiments, however, are no good representation for fluidized bed systems such as a carousel fluidized bed IEX system or a high rate IEX system because the latter systems are based on different designs.

4.1.1.2   Carousel fluidized bed IEX system

The NOM removal which can be obtained with a fluidized bed system, where the resin remains inside the contactor and regeneration is performed inside the contactor itself, can be assessed by establishing breakthrough curves using small fluidized bed columns. To minimize the variation in effluent water quality, multiple fluidized bed IEX columns can be placed in parallel, forming a carousel configuration. The columns are regenerated each in turn, resulting in each column having a different run time, and the effluents of the other columns are mixed. Such a carousel system was simulated on a small scale using a transparent column with 10 cm diameter containing a resin bed of 25 cm (in rest). The fluidized bed IEX column was operated at an empty bed contact time (EBCT) of 1.18 minutes (i.e. a hydraulic loading rate of 12.7 m/h). The $UV_{254\,nm}$ absorbance and NPOC obtained as a function of the amount of bed volumes treated, was averaged over 13 breakthrough experiments, and is presented in Figure 6.A. In the beginning of the breakthrough curve, a short decrease in NOM concentration is observed. This is attributed to the inability of rinsing the resin in a zero liquid discharge plant (see Section 3), resulting in traces of NOM remaining inside the resin bed after regeneration. These will be flushed out with the first bed volumes of feed water upon starting the breakthrough run. After that, the $UV_{254\,nm}$ absorbance and NPOC concentration increase rapidly as a function of the amount of bed volumes treated until around 250 BV. After that, the increase is much slower. It is likely that the period of rapid increase (30 – 250 BV) coincides with primary exchange (NOM for Cl^- on the resin), while from 250 BV on secondary exchange (NOM for previously sorbed SO_4^{2-} on the resin) takes the upper hand. By integrating the data from Figure 6.A over different ranges (from 0 to *X* BV), and expressing the average water quality in function of the run time (*X* BV), the water quality of a carousel configuration can be modeled. This is presented in Figure 6.B. It is clear that shorter run times result in better NOM removal, especially in the shorter run time range (until approximately 500 BV, which is a lag time effect of the greater NOM removal during primary exchange (0 – 250 BV)). After 500 BV, the obtained water quality of the modeled carousel system remains relatively constant. Note that the obtained water quality is also dependent on the empty bed contact time (determined by the bed height and hydraulic loading rate), as a higher empty bed contact time will favor secondary exchange. From these fluidized bed IEX column experiments it is clear that shorter run times result in a better NOM removal. However, these small scale column breakthrough results are no perfect representation of the behavior of a high rate IEX system.

Figure 6. Fluidized bed breakthrough experiments – influence of run time on water quality, with A: average effluent UV$_{254\,nm}$ absorbance and NPOC of 13 breakthrough curves and B: UV$_{254\,nm}$ absorbance and NPOC modeled for a carousel system.
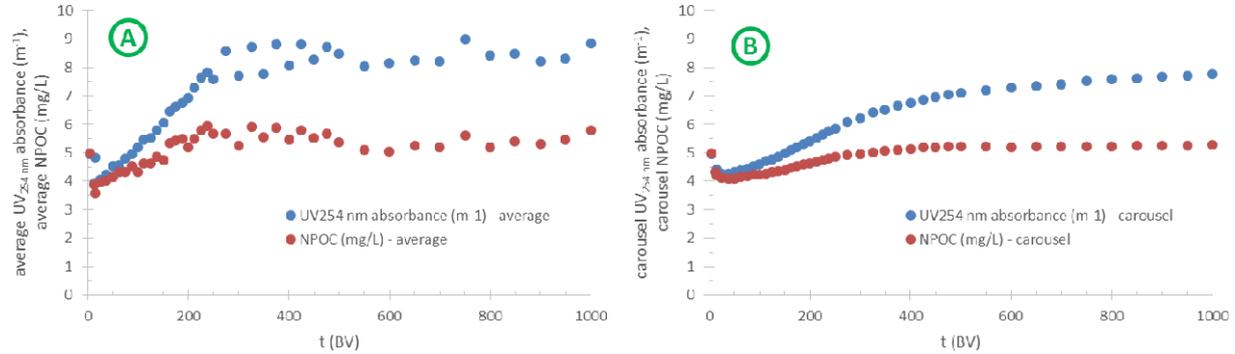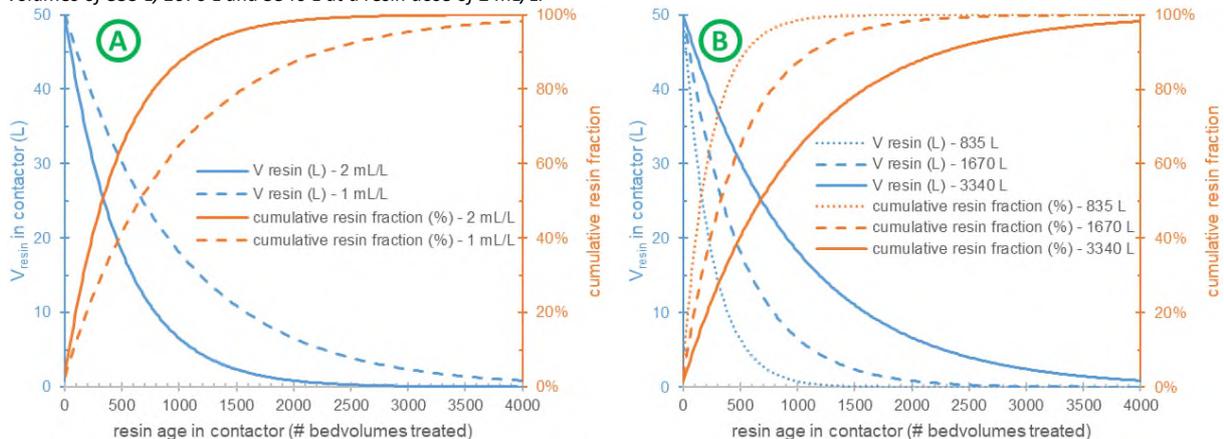
4.1.1.3   High rate fluidized bed IEX system with external regeneration

In this Section, the high rate fluidized bed IEX contactor from the semi-industrial pilot plant at WTW De Blankaart will be simulated as accurately as possible on a small scale.

As mentioned, the carousel fluidized bed system as described in Section 4.1.1.2 is not a perfect representation for a high rate fluidized bed IEX system with a single contactor, from which a small part of the resin is periodically extracted, regenerated in an external regeneration vessel, and then reintroduced into the contactor (the latter system is currently in place at WTW De Blankaart (Section 3)). The main difference between both IEX reactor configurations is that due to the regeneration system in the latter, the IEX resin inside the contactor is in fact a mixture of different resin fractions each having a different age. Since the IEX resin inside the contactor is completely mixed, during extraction and transfer of loaded resin a small part of recently regenerated resin is also extracted. Likewise, a part of the transferred resin mixture will be relatively old resin. This resin age distribution is illustrated in Figure 7.A for two resin doses at the semi-industrial pilot plant containing a total of 1670 L resin. The median resin age (based on 50% of the total resin volume) is 326 BV or 653 BV for resin doses of 2 mL/L and 1 mL/L, respectively. In a carousel type IEX system on the other hand, the resin age is half of the total run time of the columns. Note that these values can only serve to make a rough comparison between both IEX systems, as the exchange activity of the different resin age fractions is not normally distributed in neither of these IEX systems (i.e. a 'fresh' resin fraction (e.g. 0 – 50 BV) has a higher exchange activity than an 'older' resin fraction (e.g. 450 – 500 BV)). Also the resin age mixture is different between both systems.

The resin age distribution is also dependent on the total resin volume inside the contactor, as illustrated in Figure 7.B for three different resin volumes and a resin dose of 2 mL/L. Raising the total resin volume from 835 L to 1670 L to 3340 L will increase the median resin age from 153 BV to 326 BV to 673 BV.

Figure 7. Distribution of resin age in contactor, for A: resin doses of 1 mL/L and 2 mL/L at a total resin volume for 1670 L, and B: total resin volumes of 835 L, 1670 L and 3340 L at a resin dose of 2 mL/L.

A high rate fluidized bed IEX system cannot easily be simulated on a small scale. An attempt was made by recording a breakthrough curve in a small column operating at the same hydraulic load as the full scale contactor. The observed NOM removal in the breakthrough curve was discretized and expressed in NOM removal per unit of resin bed height. Integrating the product of the resin age distribution in the high rate IEX contactor (in units of resin bed height) with the measured NOM removal per unit of resin height was supposed to result in the potential NOM removal in a high rate IEX contactor. However, this approach is not valid for molecules that are measured as bulk parameters as is the case for NOM. The observed NOM removal in the small scale column breakthrough will be largely due to removal of easily removable NOM because the feed water is continuously refreshed, whereas in a high rate IEX contactor these NOM fractions will be depleted already in the first layers of the fluidized resin bed. Since each NOM molecule can only be removed once, the other resin layers will thus have to remove NOM fractions that are slightly less amenable to IEX, and that were not targeted in the small scale column breakthrough. As such, the potential NOM removal determined in this way is in fact an overestimation of the real NOM removal that will be observed in the high rate IEX contactor. Probably a better approach would be to conduct the column experiment at the same empty bed contact time as applied in full scale and discretizing the resin volume in the full scale contactor as fractions of the total volume based on resin age. By integrating the product of resin fraction with the measured NOM removal in the small scale experiment for each resin age, a more realistic estimation of the total removal efficiency will be obtained. By doing this for different resin volumes (and hence, different EBCTs), the impact of changing the resin volume in the full scale plant on NOM removal efficiency can be assessed. These experiments and calculations are the subject of ongoing research.

4.1.2   IEX – coagulation bench-scale experiments

In order to investigate NOM removal with a combination of IEX and coagulation at bench scale, samples were taken from small scale fluidized bed IEX breakthrough experiments, and coagulation jar tests were performed. It was chosen to evaluate the IEX step by means of a carousel fluidized bed type system rather than a high rate fluidized bed IEX system due to the former being a more simple setup than the latter. The fluidized bed IEX column was operated with a bed height of 25 cm and an EBCT of 1.18 minutes (i.e. a hydraulic loading rate of 12.7 m/h), and IEX run times of 500 BV and 250 BV were evaluated. Samples were taken at different times during the IEX breakthrough experiment and mixed to mimic the water quality which would be obtained by a carousel system. Subsequently coagulation was performed in a series of jars, using different coagulant conditions (in terms of coagulation pH and ferric iron dose). Compared to the industrial scale coagulation/decantation unit, these bench scale coagulation tests were carried out at relatively moderate coagulant doses, i.e. at higher pH and with a lower ferric iron dose, as the objective of this research is to achieve a similar or better NOM removal efficiency by introducing IEX as a pretreatment step, while at the same time decreasing the overall chemicals demand of the treatment. The results of the obtained water quality are presented in Figure 8.

Figure 8. Water qualities obtained after carousel fluidized bed IEX – coagulation tests at bench scale, and in standalone (industrial scale) coagulation/decantation serving as reference.
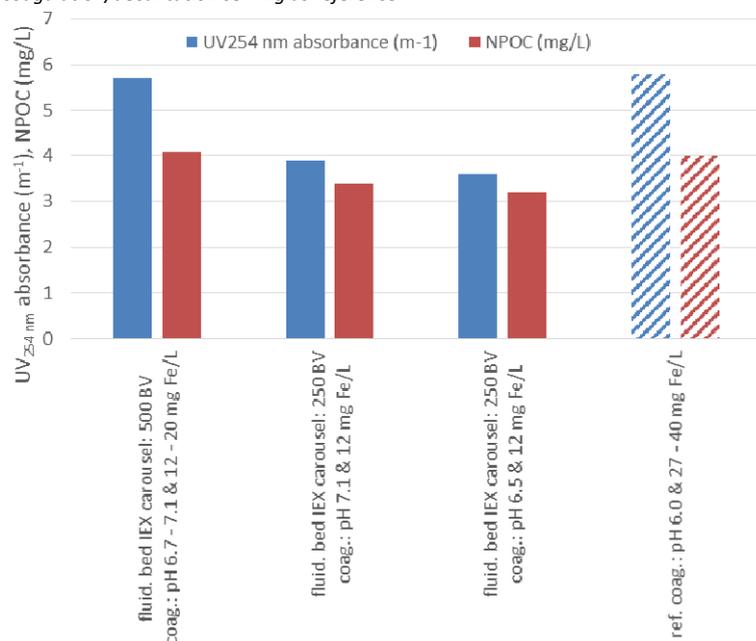
A combination of a carousel IEX system operating at a regeneration frequency of 500 BV and a subsequent coagulation at pH 6.7 – 7.1 with relatively moderate ferric iron doses of 12 – 20 mg/L results in a similar NOM removal as obtained with standalone coagulation at pH 6.0 using ferric iron doses of 27 – 40 mg/L, with residual $UV_{254\,nm}$ absorbances of 5.7 m^{-1} and 5.8 m^{-1} and residual NPOC concentrations of 4.1 mg/L and 4.0 mg/L, respectively (Figure 8). Increasing the NOM removal in the IEX step by reducing the runtime to 250 BV while coagulating with 12 mg/L ferric iron at pH 7.1 will further increase the overall NOM removal to a residual 3.9 m^{-1} $UV_{254\,nm}$ absorbance and 3.4 mg/L NPOC, and coagulating at pH 6.5 with 12 mg/L ferric iron after an IEX carousel of 250 BV will decrease the residual NOM content to 3.6 m^{-1} $UV_{254\,nm}$ absorbance and 3.2 mg/L NPOC. It is clear that a carousel IEX followed by coagulation can indeed improve the overall NOM removal while reducing the coagulant dose, compared to standalone coagulation at WTW De Blankaart, indicating that combining IEX and coagulation can indeed result in a lower NOM content of the treated water while saving on coagulant expenses.

4.2   Results from pilot-scale experiments

In this Section, the results obtained with the high rate fluidized bed IEX system and coagulation/flotation unit at a semi-industrial scale (capacity of 50 – 58 m³/h, see Section 3) are described.

4.2.1   Evaluation of NOM removal with IEX and coagulation/flotation at WTW De Blankaart

The semi-industrial scale plant was run for approximately two years, from January 2016 until mid-November 2017. The $UV_{254\,nm}$ absorbance and NPOC concentration of the raw water, after IEX, and after IEX with subsequent coagulation/flotation are presented in Figure 9. As a reference, the water quality obtained using standalone coagulation/decantation in the industrial scale plant (see Figure 2) is also presented. Note that the coagulant doses at the semi-industrial scale coagulation/flotation plant were lower (10 – 15 mg/L ferric iron and 10 – 40 mg/L sulfuric acid resulting in a coagulation pH of 6.5 – 7.1) compared to those at the industrial scale coagulation/decantation plant (23 – 45 mg/L Fe and 0 – 109 mg/L sulfuric acid resulting in a coagulation pH of 6.0), as the original goal of the research project is to reduce the coagulant dose by introducing an IEX step as a pretreatment to coagulation.

It is clear that the combination of a high rate fluidized bed IEX system at resin doses of 0.5 to 2 mL/L with coagulation/flotation using 10 to 15 mg/L Fe at pH of 6.5 – 7.1 could not improve the NOM removal compared to standalone coagulation/decantation, as both the $UV_{254\,nm}$ absorbance (Figure 9.A) and NPOC concentration (Figure 9.B) after IEX followed by coagulation/flotation is higher than after standalone coagulation/decantation.

In Table 2, a summary of the achieved water quality and NOM removal efficiencies is given for different resin doses. The reported values are based on results obtained in winter and spring. The IEX process resulted in a $UV_{254\,nm}$ absorbance reduction of 54% to 64% and an NPOC reduction of 37% to 45%, depending on the resin dose.

In summer and autumn, on the other hand, algae blooms were observed in the reservoir, the NPOC concentration of the raw water increased drastically (peaking at 30 mg NPOC/L in September 2017) and the NOM removal efficiency of the IEX process decreased (see Figure 9). The effect of algae blooms on the IEX system will be described in Section 4.2.6.1. As expected, higher resin doses result in a higher NOM removal (Table 2), although the observed gains are rather modest considering the resin doses were doubled. This is in agreement with the observation from Section 4.1.1.2, where a carousel system indicated that especially in the lower bed volume range a more substantial improvement in water quality can be expected, while from 500 BV on the gains were relatively low (likely due to secondary exchange, so NOM removal for previously sorbed SO_4^{2-}, taking the upper hand).

In winter and spring when the IEX plant was performing well (i.e. without stratification – see also Section 4.2.6.1), the subsequent coagulation step reduced the NOM content further, albeit only slightly (Table 2). These results represent the removal with low coagulant doses, however during two periods the coagulation pH was decreased to 6 to assess the importance of the coagulation pH after IEX pretreatment. No significant improvement on the NOM removal was found, indicating that to improve the NOM removal in the subsequent coagulation step, the ferric dose might be more essential than the coagulation pH. The results also indicate that a large portion of the NOM which is amenable to removal with coagulation was already removed with IEX.

Figure 9. *Water quality throughout the semi-industrial IEX – coagulation/flotation plant, and comparison with standalone coagulation/decantation, with A: UV$_{254\,nm}$ absorbance and B: NPOC concentration.*
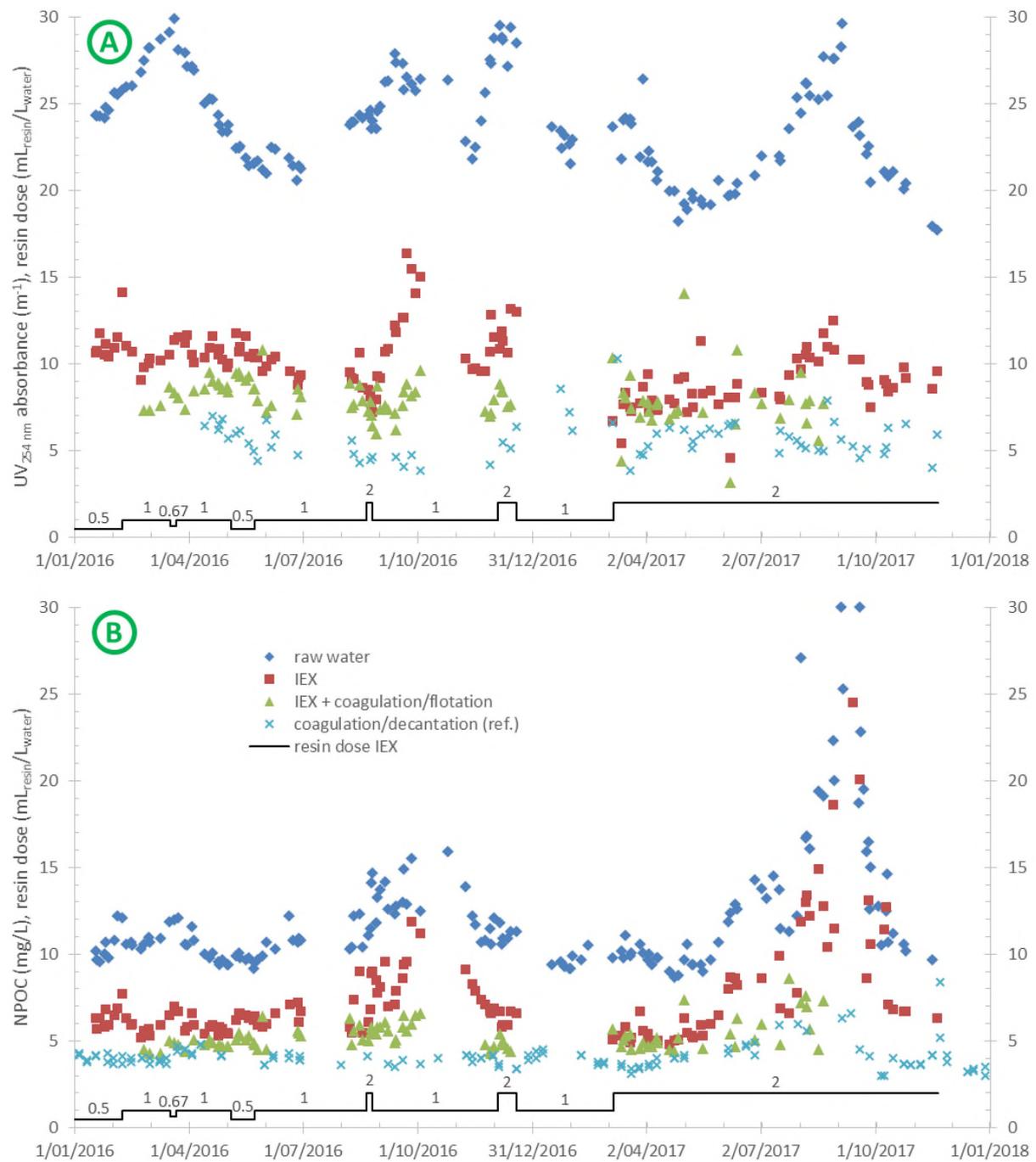
Table 2. Average water quality and NOM removal after IEX, IEX – coagulation/flotation, or standalone coagulation/decantation treatment at WTW De Blankaart, in winter and spring.

		IEX resin dose			
		0.5 mL/L	1 mL/L	2 mL/L	–
	Achieved water quality and removal				
IEX	UV_{254} absorbance (m^{-1})	9.9	9.0	7.3	
	$UV_{254 nm}$ removal (%)	*54*	*56*	*64*	
	NPOC (mg C/L)	6.4	5.9	5.2	
	NPOC removal (%)	*37*	*41*	*45*	
IEX – coagulation/flotation	UV_{254} absorbance (m^{-1})	8.2	7.4	7.1	
	$UV_{254 nm}$ removal (%)	*58*	*63*	*66*	
	NPOC (mg C/L)	5.1	4.8	4.8	
	NPOC removal (%)	*47*	*50*	*50*	
standalone coagulation/decantation (reference)	UV_{254} absorbance (m^{-1})				5.9
	$UV_{254 nm}$ removal (%)				*73*
	NPOC (mg C/L)				4.0
	NPOC removal (%)				*61*

4.2.2   Comparison of NOM removal between WTW De Blankaart and WTW Kluizen

The results from the semi-industrial IEX – coagulation/flotation plant at WTW De Blankaart are much less positive than the results previously obtained at WTW Kluizen (see Section 1). However, this can be explained by more competition of sulphate at WTW De Blankaart, as well as a higher NOM removal in standalone coagulation at De Blankaart as elaborated below.

At WTW Kluizen, industrial scale (standalone) coagulation is performed with polyaluminium chloride at pH 7.6, whereas at WTW De Blankaart it is performed with ferric iron at pH 6.0 creating much more favorable conditions for NOM removal compared to WTW Kluizen (73% $UV_{254 nm}$ absorbance removal and 61% NPOC removal at industrial scale coagulation in De Blankaart, versus 50% $UV_{254 nm}$ absorbance removal and 41% NPOC removal at industrial scale coagulation in Kluizen). Hence, it is more difficult to match or improve the NOM removal efficiency of the reference scenario at WTW De Blankaart than at WTW Kluizen.

To achieve the same NOM removal efficiency by means of IEX at the two treatment sites, a much higher resin dose is required at Blankaart compared to Kluizen. In the semi-industrial plant at Kluizen, the IEX step removed 59% of $UV_{254 nm}$ absorbance and 43% of NPOC at a resin dose of only 0.45 mL/L, while for De Blankaart it can be estimated that this removal would be obtained at a resin dose of around 1.5 mL/L (Table 2). In this respect it must be mentioned that the EBCT time in Kluizen was slightly lower than the EBCT at the Blankaart (1.53 versus 1.73 minutes). This difference in performance can likely be explained by the lower sulphate concentration in the raw water of WTW Kluizen (58 mg SO_4^{2-}/L) compared to WTW De Blankaart (87 mg SO_4^{2-}/L), resulting in less competition and a higher contribution of primary exchange at Kluizen.

4.2.3   Ionic balances of the high rate IEX process at WTW De Blankaart

Other anions present in the feed water of an IEX system will compete with the target NOM for the exchange sites on the resin, depending on their relative affinity. In Table 3, the ionic composition of the IEX influent and IEX effluent are given for the different resin doses tested in this research. It is clear that a substantial amount of exchange was attributed to sulphate and bicarbonate, which is a direct result of the high mineral content of the feed water (Table 1). Indeed, when the ratio of NPOC to inorganic anions is low, it can be expected that a large part of the exchange activity will be attributable to the competing anions. The increase in chloride corresponds to 8.3 mg Cl$^-$/L, 18.2 mg Cl$^-$/L and 33.0 mg Cl$^-$/L for resin doses of 0.5 mL/L, 1 mL/L and 2 mL/L.

Table 3. Ionic balances of the IEX process for different resin doses in the IEX process at WTW De Blankaart. The variation in IEX influent is due to the different time periods in which the resin doses were tested.

	IEX influent (mg/L)	IEX effluent (mg/L)	Δ_{IEX} (mg/L)	Δ_{IEX} (meq/L)
Resin dose 0.5 mL/L				
Cl^-	94.9	103.2	8.3	0.23
SO_4^{2-}	102.1*	95.0	-7.1	-0.15
NO_3^-	25.0	24.8	-0.2	0.00
HCO_3^-	252**	245	-7	-0.11
NPOC	10.2	6.4	-3.8	-0.04***
*Anion balance******				*-0.07*
Resin dose 1 mL/L				
Cl^-	89.9	108.1	18.2	0.51
SO_4^{2-}	99.4*	85.5	-14.0	-0.29
NO_3^-	24.3	23.7	-0.6	-0.01
HCO_3^-	240**	233	-7	-0.12
NPOC	10.4	5.9	-4.5	-0.05***
*Anion balance******				*0.05*
Resin dose 2 mL/L				
Cl^-	93.2	126.2	33.0	0.93
SO_4^{2-}	109.2*	73.1	-36.1	-0.75
NO_3^-	23.2	22.7	-0.5	-0.01
HCO_3^-	229**	213	-17	-0.27
NPOC	9.7	5.4	-4.4	-0.04***
*Anion balance******				*-0.15*

*   Including the 9.8 mg/L SO_4^{2-} increase due to acidification of the raw water with 10 mg/L H_2SO_4 to prevent resin scaling.

**   Assuming an 11 mg/L HCO_3^- decrease due to the acidification to prevent resin scaling, calculated with AquaCalc 3.1.1b.

*** Assuming a charge density of 10 meq/g NPOC[1].

****The anion balances represent the shortage (negative) or surplus (positive) amount of chloride equivalents measured after IEX, and were calculated by subtracting the sum of exchangeable anion equivalents (SO_4^{2-}, NO_3^-, HCO_3^- and NPOC) from the increase in Cl^- equivalents attributable to exchange.

The ionic balances are not completely conclusive, likely due to the presented data being averages of longer periods of time. The exchange share which could be attributed to NPOC removal was calculating as the ratio of NPOC removal over the sum of all exchanged ions (i.e. SO_4^{2-}, NO_3^-, HCO_3^- and NPOC) on equivalent basis. As such, the share which could be attributed to NPOC removal was found to be 12.8%, 9.8% and 4.1% for resin doses of 0.5 mL/L, 1 mL/L and 2 mL/L, respectively. It is clear that at higher resin doses a lower share of the exchange activity is attributed to the target NOM, which is directly linked to the resin age distribution in the high rate fluidized bed IEX contactor. At a higher resin age (or low resin dose), secondary exchange will be promoted, and a substantial part of the NOM removal will be due to exchange for e.g. sulphate resulting in a lower net sulphate removal from the feed water (see Table 3). On the other hand, a lower resin dose in the IEX system under investigation also removes a lower amount of NPOC from the feed water.

[1] Dempsey, B.A. & O'Melia, C.R. (1983). Proton and calcium complexation of four fulvic acids fractions. In *Aquatic and Terrestrial Humic Materials*, ed. R.F. Christman & E.T. Gjessing, pp. 239-273. Ann Arbor, MI: Ann Arbor Science.

These results imply that by stimulating the IEX system towards secondary exchange (thus by increasing the average resin age through e.g. increasing the total volume of resin inside the contactor, or by decreasing the hydraulic surface loading), the NOM removal can be increased without vastly increasing the release of chloride ions. On the other hand, there will be practical limitations to the maximum total resin volume and the minimum hydraulic surface loading to be applied, as the former determines the fluidization degree and the height of the contactor, while the latter should be high enough to ensure washing out of suspended solids and algal matter to prevent resin stratification (see Section 4.2.6.1). In addition, a higher bed height in the contactor will be accompanied by less mixing of the resin bed, therefore an increased risk on stratification. Active mixing of the resin bed (e.g. using a mixer or through continuous resin extraction and reintroduction) could reduce this risk, however this was not tested in this project.

4.2.4   Implications of zero liquid discharge to the ionic balances of the IEX process at WTW De Blankaart

De Watergroep operates the IEX process without disposal of liquid waste streams, meaning a maximum of 1 BV of spent brine can be collected for 1 BV of brine dosed. Since NOM removal is the main objective of the ion exchange process, the collected spent brine has always been as high in NOM as possible in the pilot plant. As a result, the other parts of the eluting stream are returned to the main drinking water line, resulting in a substantial loss of salt. This is illustrated in Figure 10: while the majority of NOM is collected in the spent brine, a total of 21.5 g Cl^-/L_{resin} will be added into the drinking water stream. This has serious implications for the chloride levels of the treated water, especially at higher resin doses, as this chloride loss corresponds to an increase of 43 mg Cl^-/L water at a resin dose of 2 mL/L. Additionally, an equivalent amount of sodium will be added to the drinking water.

The ionic balance of the high rate IEX system (taking into account loss of salt during regeneration) can then be calculated by adding these quantified losses (21.5 g Cl^-/L_{resin}, and an equivalent 13.9 g Na^+/L_{resin}) to the values from Table 3. In addition, after regeneration all desorbed ions are present in Na^+-form (e.g. Na_2SO_4 and $NaNO_3$). Only small amounts of these salts are removed during spent brine coagulation through the pore water of the filter cakes, while the majority will eventually end up back in the main drinking water treatment stream during next regeneration cycles. The removal of ions via the filter cake was accounted for based on an analysis of the filter cake (see Section 5.2.1). Bicarbonate is assumed to be removed completely from the spent brine, due to acidification to pH 4. These additions to the ionic balance of the IEX system (taking into account on-site spent brine treatment) are presented in Table 4, only for a resin dose of 2 mL/L.

Figure 10. Regeneration profile of IEX resin, with the vertical lines indicating the points where exactly 1 BV of spent brine based on NOM elution falls in between.
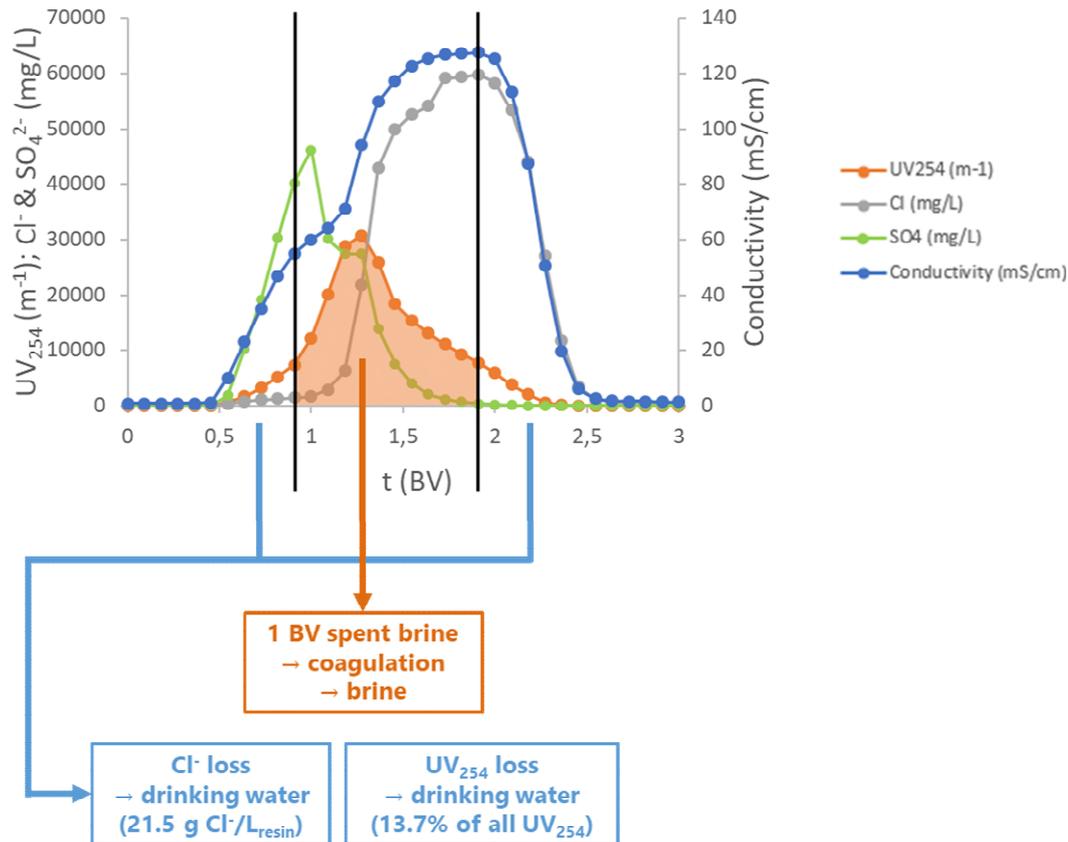
Table 4. Ionic balances of the IEX contactor and IEX system (taking into account the implications of on-site spent brine treatment) at WTW De Blankaart for a resin dose of 2 mL/L, with collection of 1 BV of spent brine based on NOM elution.

	Raw water (mg/L)	Influent IEX contactor (mg/L)	Effluent IEX contactor (mg/L)	Effluent IEX system (mg/L)
Na^+	57.7	57.7	57.7	101.6
Cl^-	93.2	93.2	126.2	169.1
SO_4^{2-}	99.4	109.2*	73.1	106.4
NO_3^-	23.2	23.2	22.7	23.0
HCO_3^-	240	229**	213	213
NPOC	9.7	9.7	5.4	6.0

*   Including the 9.8 mg/L SO_4^{2-} increase due to acidification of the raw water with 10 mg/L H_2SO_4 to prevent resin scaling.

** Assuming an 11 mg/L HCO_3^- decrease due to the acidification to prevent resin scaling, calculated with AquaCalc 3.1.1b.

4.2.5   Ionic composition for a combination of IEX and coagulation/flotation, and comparison to standalone coagulation/decantation

In Table 5, the ionic composition of the treated water after IEX (at a resin dose of 2 mL/L) and coagulation/flotation (at a coagulant dose of 16 mg Fe/L and by adjusting the pH to 6.5 with H_2SO_4) is presented. A comparison is made to standalone coagulation/decantation from the industrial treatment line, described in Section 2.2 (coagulation at

pH 6.0 with 34 mg Fe/L). For both treatment scenarios, also the subsequent conditioning step with NaOH to pH 7.0 (before rapid sand filtration) was taken into account, as coagulating at lower pH will be accompanied with a higher NaOH consumption.

Table 5. *Ionic balances of IEX – coagulation/flotation treatment (with collection of 1 BV of spent brine based on NOM elution) and standalone coagulation/decantation treatment at WTW De Blankaart.*

	Raw water (mg/L)	Effluent IEX system (mg/L)	Effluent IEX – coagulation/flotation/ conditioning (mg/L)	Effluent standalone coagulation/decantation/ conditioning (mg/L)
Na^+	57.7	101.6	121.1	89.0
Cl^-	93.2	169.1	199.6	158.0
SO_4^{2-}	99.4	106.4	127.0	149.4
NO_3^-	23.2	23.0	23.0	23.2
HCO_3^-	240	213	190	195
NPOC	9.7	6.0	4.8	4.0

As can be seen from Table 5, the ionic composition of the water is very different for both treatment scenarios. IEX combined with coagulation/flotation results in higher sodium and chloride concentrations in the treated water compared to standalone coagulation/decantation, which is due to the loss of salt occurring during regeneration and the addition of uncoagulated anions (such as sulphate and nitrate) in their Na^+ form as mentioned in Section 4.2.4. For the latter reason, the final Na^+ concentration after standalone coagulation/decantation is lower than for the IEX – coagulation/flotation scenario, despite the higher NaOH demand for adjusting the water pH from 6.0 to 7.0. On the other hand, the SO_4^{2-} concentration of the treated water is lower in the scenario comprising IEX, due to a higher coagulation pH of 6.5 compared to standalone coagulation (i.e. less H_2SO_4 is consumed due to milder coagulation conditions).

Taking into account the varying quality of the raw water (Table 1), the increase in chloride from IEX – coagulation/flotation is unacceptable, as the drinking water standard is 250 mg Cl^-/L. Therefore, research was conducted on minimization of the Cl^- loss (see Section 4.3).

4.2.6   Practical difficulties encountered during the pilot study

4.2.6.1   Effect of algae blooms in the raw water reservoir on IEX – coagulation/flotation

As mentioned in Section 4.2.1, in summer and autumn algae blooms in the reservoir occurred, resulting in elevated NPOC concentrations in the raw water (see Figure 9). This strong increase in NPOC could be attributed to particulate algal matter, since filtration over 30 µm reduced the NPOC concentration with approximately 51%, and the $UV_{254\,nm}$ absorbance analysis (measured after 0.45 µm filtration) did not show a proportionally increasing trend (merely a rise from 20 m^{-1} to 27 m^{-1}). The period of algae bloom in September 2016 resulted in biofouling (attachment of biomass) of the IEX resin in the fluidized bed contactor and stratification of the resin bed. This was confirmed by measuring the $UV_{254\,nm}$ and NPOC load on the resin at different heights inside the contactor (data not shown). When algae adhere to the resin beads, their bulk density decreases, which results in migration of bio-fouled resin beads towards the top of the resin bed, and ultimately stratification. Because the extraction point of loaded resin and re-introduction point of regenerated resin are both situated at the bottom of the IEX contactor part of the resin bed was not withdrawn anymore for regeneration, staying inside the contactor and ultimately losing its exchange activity. This is reflected in the rising residual $UV_{254\,nm}$ absorbance in September 2016. In 2017, despite a much more severe algae bloom, this behavior was not noticed anymore: while the NPOC concentration increased, the $UV_{254\,nm}$ removal remained relatively constant. Two factors that may have contributed to the absence of stratification are the application of a higher resin dose (2 mL/L for summer 2017 compared to 1 mL/L for summer 2016) and an increased hydraulic loading rate in 2017 (20.1 m/h) compared to 2016 (17.3 m/h)), increasing the probability that algal matter would wash out from the contactor before significant biofouling would

occur. These results indicate that during algae bloom periods, it is paramount to avoid the occurrence of stratification in order to maintain a high NOM removal efficiency. Stratification could be reduced by extracting the loaded resin from the contactor from the top of the fluidized resin bed, however this is challenging due to design reasons: the resin concentration in a fluidized bed contactor is most constant at the bottom, meaning extraction of a fixed amount of resin can easily be programmed based on elapsed time when extraction is performed from the bottom. As mentioned in Section 4.2.3, active mixing of the resin bed could also reduce the risk of stratification, however this was not tested in this project.

During the periods of algae blooms (summer and autumn in Figure 9), the reduced NOM removal during IEX is compensated by the subsequent coagulation/flotation step, indicating that coagulation/flotation at the applied coagulation conditions is a more robust process than IEX during algae blooms.

4.2.6.2   Accumulation of SO42- in the brine – spent brine loop

After NOM removal from the spent brine, the filter press filtrate is conditioned and reused as brine in the regeneration process. As a result, dissolved ions which are not removed by coagulation, such as Na_2SO_4, will accumulate in the brine – spent brine loop. While no significant deterioration of the NOM removal from the feed water was found due to sulphate accumulation in the brine, a practical difficulty was encountered with decreasing temperature of the water. In January 2017 the temperature of the raw water dropped to 3°C, which resulted in precipitation of Na_2SO_4 into large crystals and blockage of the spent brine piping. This problem was encountered again in December 2017. This event led to temporary shutdowns of the semi-industrial scale plant. To mitigate this problem, heating of the spent brine – brine loop should be implemented, however another solution could be to limit the accumulation of sulphate in the brine (see Section 4.3).

4.3   Optimized spent brine collection during IEX resin regeneration

The loss of Cl^- during regeneration can, evidently, be minimized through shifting the collection of 1 BV of spent brine based on the elution of NOM to the elution of Cl^-. This is shown in Figure 11. However, in this scenario only around 58% of all eluting NOM will be collected in the 1 BV of Cl^- rich spent brine. The precedingly eluting NOM therefore also needs to be collected in a second spent brine fraction, to avoid its direct addition to the drinking water. This extra fraction is rich in Na_2SO_4, as sulphate is the first major anion to elute during regeneration. The advantages of this scenario are that both the Cl^- loss and NOM loss are minimized, while also the accumulation of sulphate in the brine – spent brine loop will be reduced and precipitation of Na_2SO_4 at low temperatures is less likely to occur. The major downside is that dual coagulation and filter pressing equipment is required to enable separate treatment of these two spent brine fractions. The Cl^- rich spent brine fraction will, after coagulation with $FeCl_3$, be recirculated to be reused as brine, whereas the SO_4^{2-} rich spent brine fraction can be added back into the drinking water stream after NOM removal (e.g. through coagulation with $Fe_2(SO_4)_3$ to avoid an additional rise in chloride). In such a scenario, the ionic balances will change as shown in Table 6. Note that to date, this alternative spent brine collection method has not been tested yet on a pilot scale.

Figure 11. *Regeneration profile of IEX resin, with the vertical lines indicating the points where exactly 1 BV of spent brine based on Cl⁻ elution falls in between.*
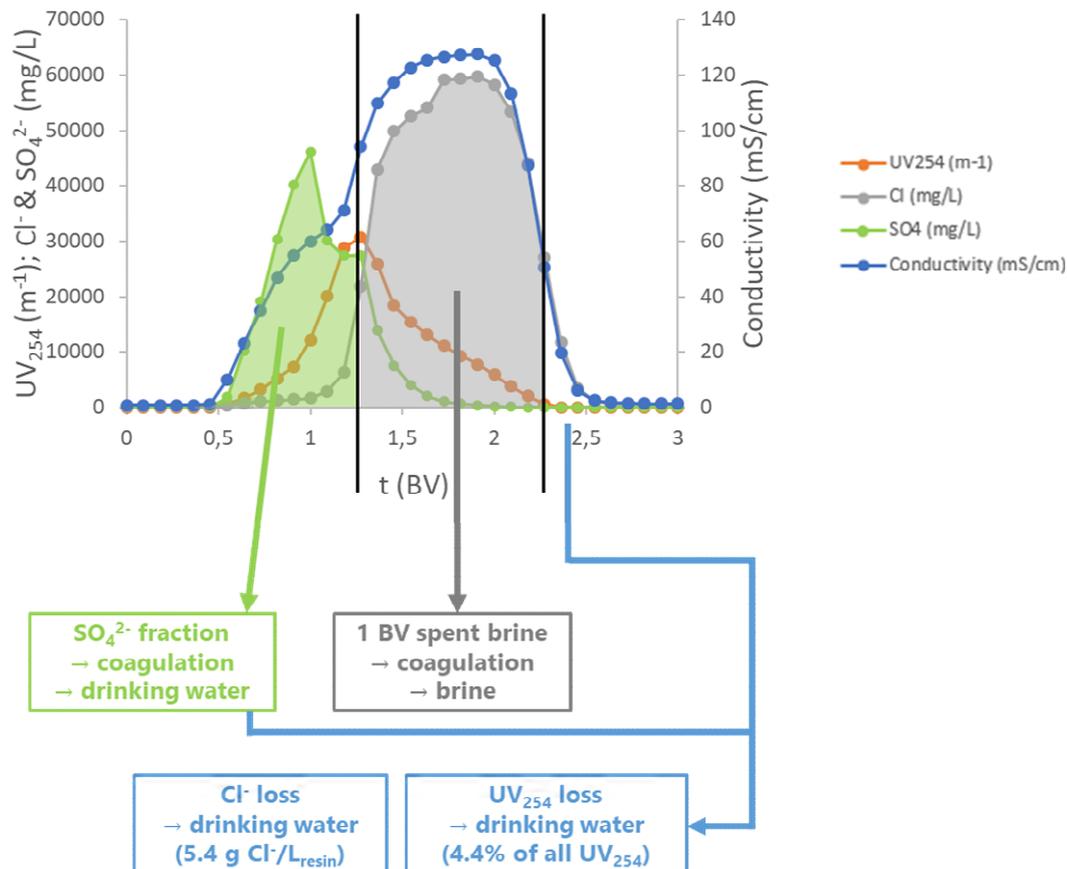
Table 6. *Ionic balances of IEX – coagulation/flotation treatment (with collection of 1 BV of spent brine based on Cl⁻ elution preceded by 0.82 BV of SO₄²⁻-rich spent brine) and standalone coagulation/decantation treatment at WTW De Blankaart.*

	Raw water	Effluent IEX system	Effluent IEX – coagulation/flotation/ conditioning	Effluent standalone coagulation/decantation/ conditioning
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Na^+	57.7	81.6	101.2	89.0
Cl^-	93.2	136.9	167.3	158.0
SO_4^{2-}	99.4	112.9	133.4	149.4
NO_3^-	23.2	23.0	23.0	23.2
HCO_3^-	240	213	190	195
NPOC	9.7	5.6	4.5	4.0

Through adjusting the spent brine collection method, the final chloride concentration can be decreased from 199.6 mg/L to 167.3 mg/L, however this is still higher compared to standalone coagulation/decantation. To decrease the final chloride concentration even further, the average resin age in the IEX contactor would need to be increased (e.g. through increasing the total resin volume in the IEX contactor), therefore stimulating NOM removal through secondary exchange (as was also mentioned in Section 4.2.3), which ultimately could result in lower resin doses being required. The effect of different total resin volumes could not be evaluated on a pilot scale within the DOC2C's project, because the height of the IEX contactor and the fluidization degree of the resin did not allow for larger resin volumes to be tested.

5 Feasibility assessment of IEX with coagulation for NOM removal

5.1 Water quality and reliability

As already mentioned, the treatment scenario IEX – coagulation/flotation was evaluated at WTW De Blankaart based on previous results from WTW Kluizen. Where this combination of technologies improved the overall water quality at WTW Kluizen in terms of NOM and mineral content compared to standalone coagulation/flotation, at WTW De Blankaart this was not the case. IEX resin doses of 0.5 to 2.0 mL/L combined with coagulation/flotation using 10 to 15 mg Fe/L at a pH of 6.5 to 7.1 did not allow to achieve a similar NOM removal efficiency as the one obtained by standalone coagulation/decantation at WTW De Blankaart (using 23 to 45 mg Fe/L at a coagulation pH of 6.0). In winter and spring, the IEX process could be operated in a stable manner, achieving removal efficiencies of 54% to 64% $UV_{254 nm}$ absorbance and 37% to 45% NPOC, depending on the resin dose. After subsequent coagulation/flotation, NPOC residuals of 4.8 to 5.1 mg/L were found in the semi-industrial scale plant (where the spent brine is collected based on NOM elution). When two spent brine fractions would be collected (i.e. a sulphate rich fraction and a chloride rich fraction), the residual NPOC concentration would be around 4.5 mg/L. Regardless, these residual concentrations are higher than those of the reference treatment (i.e. standalone coagulation/decantation – 4.0 mg NPOC/L).

The mineral composition of the treated water is unacceptable when 1 BV of spent brine is collected based on NOM elution, especially for Cl^- as its final concentration will exceed the water standard when the raw water chloride concentration is higher than 143 mg/L. This occurs yearly in autumn due to minimal rainfall in the catchment area. When two spent brine fractions would be collected, the residual Cl^- concentration is expected to be 167.3 mg/L. Although acceptable, this is still slightly higher compared to standalone coagulation/decantation.

Moreover, in summer and autumn algae blooms can result in stratification of the IEX resin bed, decreasing its overall performance. Strategies to mitigate this problem include increasing the hydraulic loading rate and increasing the resin dose, which was successfully evaluated in 2017.

Being a well-established technology, also in this study the coagulation/flotation process was judged to be overall very robust. Moreover, during periods of decreased IEX performance, the coagulation/flotation process could compensate for the lower NOM removal in IEX.

Based on these results, and contrary to WTW Kluizen, it is unlikely that IEX – coagulation/flotation will be implemented at WTW De Blankaart. This is mostly due to the fact that the reference water quality (i.e. the water quality obtained after standalone coagulation) is significantly different for both WTWs. With a much higher NOM removal in the reference treatment at WTW De Blankaart compared to WTW Kluizen (due to higher chemical doses), it is more difficult to achieve the same NOM residuals with the IEX – coagulation treatment concept. Still, improvements both in NOM removal and the minimization of Cl^- increase could be obtained, mainly by increasing the total resin volume inside the IEX contactor. This is the subject of further research.

5.2 Waste flows

5.2.1 IEX process waste flows

IEX results in a spent brine, rich in anions removed from the feed water (mostly NOM, SO_4^{2-}, and HCO_3^-), as well as the active component of the brine itself (Cl^-). Since the resin regeneration is carried out with NaCl, all these anions are present in Na^+ form. As mentioned, the spent brine was treated on-site by means of coagulation with $FeCl_3$, flocculation with Magnafloc® LT22S DWI, and dewatering using a filter press. The filtrate was conditioned with

NaOH to pH 6.2, and NaCl was added until a conductivity of 140 mS/cm, after which it was reused as brine for IEX resin regeneration. The filter cake cannot be used on-site and is considered a waste product.

The average composition of the spent brine and brine is given in Figure 12 for resin doses of 1 mL/L (left) and 2 mL/L (right). HCO_3^- is not included in this figure due to analytical constraints. Doubling the resin dose resulted in a decrease of the average NPOC concentration in the spent brine from 4.49 g NPOC/L to 2.67 g NPOC/L. This was accompanied by a decrease from 0.62 g NPOC/L to 0.35 g NPOC/L in the brine. The sulphate and chloride concentrations did not change much by increasing the resin dose. These results confirm that secondary exchange plays an important role, especially at relatively high resin ages (i.e. at lower resin doses).

Figure 12. Average composition of the spent brine and brine for resin doses of 1 mL/L (left) and 2 mL/L (right), error bars indicate the 10% and 90% percentiles.
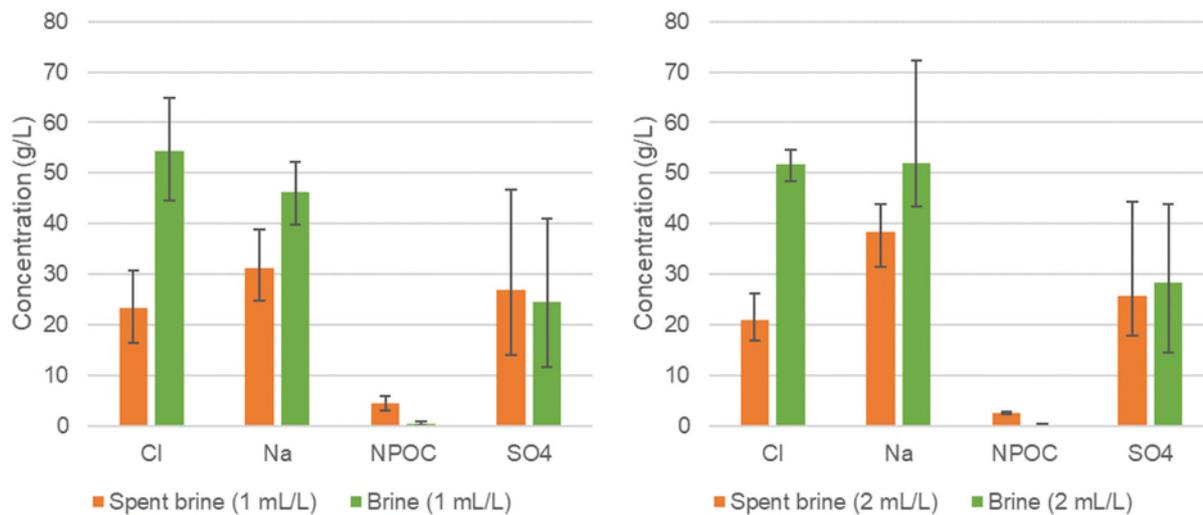
The coagulation of the spent brine was optimized using bench scale jar tests in terms of coagulation pH, Fe dose, flocculant dose and flocculant type, for the spent brine obtained at a resin dose of 2 mL/L (collection based on NOM elution). The optimum coagulation pH was found to be pH 4, while the optimal coagulant dose was found to be 2 g Fe/L. Out of seven flocculant types tested (FO4115, FO4140, FO4190, FO4290, FA920 (each part of the FLOPAM™ SEP product line of SNF), Superfloc® N-100 PWG (Kemira), and Magnafloc® LT22S DWI (BASF)), optimum turbidity removal and sludge filtration results were found for Magnafloc® LT22S DWI at a concentration of 75 mg/L. The spent brine treatment process was evaluated to be generally reliable and robust. Only when the temperature of the water dropped below 3°C, problems were encountered with precipitation of Na_2SO_4 in the spent brine pipes. This problem can be mitigated by heating the spent brine – brine circuit during such cold conditions, however it is also possible that this problem will not occur anymore when adjusting the collection method of the spent brine is adjusted as described in Section 4.3. The latter is yet to be evaluated.

The filter cake, of which the composition is given in Table 7, is a waste product that cannot be used on-site and needs to be disposed of. As can be seen in Table 7, the salt content of the filter cake is relatively high, with around 27% of the dry solids content being sodium, sulphate and chloride. Within the scope of this project, the filter cake was sent free of cost for use in anaerobic digesters as a sulfide binding agent, as is also the current practice for non-saline filter cakes rich in iron (e.g. originating from coagulation processes in drinking water). It is projected that this means of filter cake use can be continued if the IEX process would be implemented on a full scale.

Table 7. Composition of the filter cake, originating from spent brine treatment.

Parameter	Concentration in filter cake
Dry solids	29.9% (m/m)
Ash content	56.2% of DS
VSS	42.1% of DS
Iron	180 g/kg DS
Sodium	85 g/kg DS
Nitrate	< 9 mg/kg DS
Sulphate	130 g/kg DS
Chloride	52 g/kg DS

5.2.2   Coagulation/flotation waste flows

The coagulation/flotation process results in a similar filter cake (albeit non saline) as the one originating from the IEX spent brine treatment. As is common practice, this filter cake can be applied as a sulfide binding agent in anaerobic digesters at no cost.

5.3   Cost analysis

The consumption of chemicals, required working hours of staff, energy consumption and waste stream production and the associated costs are estimated for the IEX – coagulation/flotation scenario and the standalone coagulation/flotation scenario (see Table 8). The chemicals consumption of the standalone coagulation/flotation process is assumed to be identical to the chemicals consumption of the current full scale coagulation/decantation plant. This is likely an overestimation, as the coagulant dose is sometimes increased drastically to keep the sludge blanket from rising, and this will be no longer required when the flocs are removed by means of flotation. For the scenario comprising IEX, it was assumed that two spent brine fractions would be collected (as illustrated in Section 4.3), of which the sulphate rich fraction (0.82 BV) would be treated with $Fe_2(SO_4)_3$ and the chloride rich fraction (1 BV) would be treated with $FeCl_3$ before being recirculated for use as brine. A required coagulant dose of 1.5 g Fe/L was assumed for both the sulphate rich and the chloride rich spent brines.

The expenditure on chemicals of the IEX process (1.92 €cent/m³) is amply compensated by the reduced chemical consumption of the subsequent coagulation process (3.23 €cent/m³ in comparison to 7.05 €cent/m³ for standalone coagulation). However, this saving is cancelled out by the estimated staff expenses related to the IEX process. Even though the latter expenditure is difficult to estimate, treatment of the spent brine will require additional staff efforts. Moreover, IEX is still an emerging technology for drinking water production on an industrial scale, whereas coagulation/flotation is a well-established technology. For these reasons, the staff efforts are thought to be considerably higher in the IEX – coagulation/flotation scenario. Still, with 7.43 €cent/m³, the total operational expenditure was slightly lower for the scenario comprising IEX in comparison to standalone coagulation/flotation (8.00 €cent/m³).

Table 8. Estimated chemical consumption, staff efforts, energy consumption and waste stream production, and associated operational expenditure based on market prices of 2018 and projected time investments.

	IEX – coagulation/flotation resin dose 2 mL/L 16 mg Fe/L, pH 6.5		coagulation/flotation 23-45 mg Fe/L, pH 6	
	Consumption	OPEX (€cent/m³)	Consumption	OPEX (€cent/m³)
Chemicals IEX				
Resin Purolite® PPA860S	0.001 mL/L	0.81		
H_2SO_4	13 mg/L	0.16		
$FeCl_3$	3 mg Fe/L	0.21		
$Fe_2(SO_4)_3$	2.5 mg Fe/L	0.39		
NaOH	2.3 mg/L	0.11		
Magnafloc® LT22S DWI	0.15 mg/L	0.06		
NaCl	23.5 mg/L	0.19		
Chemicals coagulation/flotation				
$FeCl_3$	16 mg Fe/L	1.13	32 mg Fe/L	2.25
H_2SO_4	21 mg/L	0.26	59 mg/L	0.72
NaOH	34 mg/L	1.58	76 mg/L	3.52
$Ca(OH)_2$ sludge treatment	16 mg/L	0.26	32 mg/L	0.52
Polymer sludge treatment	0.043 mg/L	0.02	0.083 mg/L	0.03
Staff expenses				
Operator	1500 h/yr	0.84	600 h/yr	0.33
Graduate	1500 h/yr	1.06	600 h/yr	0.42
Master	300 h/yr	0.24	150 h/yr	0.12
Energy				
Total dynamic head	3.5 m H_2O	0.14	2 m H_2O	0.08
Waste streams				
Filter cakes IEX	0.072 kg/m³	0		
Filter cakes coagulation/flotation	0.24 kg/m³	0	0.48 kg/m³	0
Total OPEX		**7.43**		**8.00**

The capital expenditure of the IEX process was estimated by the department of project engineering within De Watergroep at 6.7 M€ for six parallel high rate IEX fluidized bed systems and a maximum production capacity of 48000 m³/d. This corresponds to a capital expenditure of 4.74 €cent/m³ assuming a depreciation period of 20 years at a yearly interest rate of 3% and an annual production of 9.5 Mm³ drinking water. The capital expenditure of the coagulation/flotation process is equal in both scenarios. As such, the total production cost of the IEX – coagulation/flotation scenario is estimated to be 4.17 €cent/m³ higher compared to standalone coagulation/flotation.

5.4   Chemicals consumption and environmental impact

In this Section, the consumption of chemicals and the environmental impact of both treatment scenarios in WTW De Blankaart and WTW Kluizen is discussed.

The coagulant demand in the drinking water treatment line is a quantitative measure for one of the main objectives of the study, i.e. reducing the consumption of coagulant by introducing IEX. This parameter comprises the active component of the coagulant (in mg Fe/L or mg Al/L) used in the coagulation/flotation step (either after IEX or as single treatment technology), as well as coagulant demand for treatment of IEX spent brine fractions that are added back into the drinking water line. It is assumed that at WTW De Blankaart two spent brine fractions will be collected, therefore the required coagulant for treatment of the sulphate-rich spent brine fraction is taken into account, whereas coagulant for chloride-rich spent brine fraction treatment is not included (as this stream will be recirculated for use as brine, and therefore falls outside of the drinking water line). For WTW Kluizen the coagulant consumption for spent brine treatment is not included as only one spent brine fraction is collected and reused as brine here.

At De Blankaart, the coagulant demand in the drinking water treatment line is 42% lower when applying IEX – coagulation/flotation treatment (18.5 mg Fe/L) compared to only coagulation/flotation (32 mg Fe/L). At Kluizen, the coagulant demand in the drinking water treatment line is reduced with 75% by introducing IEX (from 11 mg Al/L to 2.8 mg Al/L).

These differences are mainly due to the target NOM removal being higher at De Blankaart, as was already mentioned in Section 4.2.2. As a result, the coagulant dose cannot be decreased as much as was the case at Kluizen.

Similar observations can be made for the total sludge production, since the vast majority of sludge originates from the coagulant being dosed. In De Blankaart, the sludge production is around 35% lower in the IEX – coagulation/flotation scenario (0.31 kg/m³) compared to the sludge production with only coagulation (0.48 kg/m³), whereas in Kluizen the sludge production was reduced by 53% (from 0.25 kg/m³ in standalone coagulation to 0.12 kg/m³ by introducing IEX).

It is also worth mentioning that in the treatment systems under consideration, the water loss is negligible, as the only loss of water is via the pore water of the filter cakes.

5.5   System integration and footprint

The IEX system under consideration at WTW De Blankaart comprises the following units:
- 6 IEX contactors (300 m²)
- Regeneration (250 m²):
    - 6 regeneration systems
    - 2 salt storage silos and equipment for producing and storing saturated brine
    - 2 buffers for brine storage
    - 2 buffers for sulphate-rich spent brine storage and 2 buffers for chloride-rich spent brines
- Spent brine treatment (1200 m²):
    - 2 coagulation reactors
    - Polymer production/dissolution equipment
    - 2 membrane filter presses
    - 2 buffers for filtrate storage
    - 2 filter cake storage places.

The total footprint of the IEX system is estimated to be 1750 m².

The coagulation/flotation system being designed at this moment for WTW De Blankaart consists of:
- Coagulation and flotation (600 m²):
    - 3 coagulation – flotation units with a surface area of 16.5 x 6.0 m
    - 2 saturators with a diameter of 1.7 m

- Compressors and saturation pumps
- Sludge treatment (400 m²):
    - 2 sludge buffers with a capacity of 100 m³ each
    - A sludge thickener 11 m in diameter
    - 2 membrane filter presses for sludge dewatering
    - Sludge conditioning with polymer and $Ca(OH)_2$
- Storage and dosing units for H_2SO_4, $FeCl_3$ and NaOH (300 m²).

The total footprint of the coagulation/flotation system is estimated to be 1300 m².

6 Conclusions

In this Section, the major conclusions and specific results are summarized in bullet points.

- The high rate fluidized bed IEX system was judged to be generally reliable. Only during algae bloom events a risk of resin bed stratification occurs, which results in a decreased NOM removal in the IEX process. This was mitigated by increasing the resin dose (from 1 to 2 mL/L in this study) and the hydraulic loading rate (from 17.3 to 20.1 m/h in this study). Active mixing of the resin bed is expected to reduce stratification.
- The subsequent coagulation/flotation compensated for the lower NOM removal efficiency observed for the IEX process during algae blooms and was judged to be very reliable.
- On-site treatment of the IEX spent brine by means of coagulation was judged to be technologically and economically feasible, and was generally reliable. Only when the temperature of the water drops below 3°C, precipitation of Na_2SO_4 occurred, blocking pipes of the spent brine treatment system. It is expected that this problem will not occur anymore if two spent brine fractions are collected. Otherwise, this should be mitigated by heating up the spent brine – brine loop during such cold events.
- At WTW De Blankaart, the NOM removal obtained by the IEX – coagulation/flotation treatment scenario was low compared to standalone coagulation. This is due to (i) the optimal coagulation conditions applied in the standalone coagulation process, resulting in very high NOM removal, and (ii) the high sulphate content of the raw reservoir water. IEX – coagulation/flotation is a feasible treatment scenario where competition with sulphate is lower, and where the reference NOM removal is lower, as is the case for WTW Kluizen.
- The mineral content of the treated water is slightly different for both treatment scenarios. In IEX – coagulation/flotation, coagulation is performed at higher pH resulting in a lower SO_4^{2-} content of the treated water. The Na^+ and Cl^- concentrations however are slightly higher due to the zero liquid discharge constraint.
- In the drinking water line at WTW De Blankaart, 42% less coagulant is used in the IEX – coagulation/flotation treatment compared to standalone coagulation, whereas in WTW Kluizen 75% less coagulant was required with IEX. The difference between both WTWs is largely explained by the higher NOM removal in the reference line in De Blankaart, which does not allow to decrease the coagulant dose as much.
- Tied to the lower chemical consumption, around 35% less sludge is produced in the treatment scenario comprising IEX at WTW De Blankaart.
- The operational costs of IEX – coagulation/flotation treatment are estimated to be 7.43 €cent/m³ for WTW De Blankaart. In comparison, standalone coagulation/flotation amounts to 8.00 €cent/m³. The capital expenditure of the IEX system is estimated to be 4.76 €cent/m³. As such, the decrease in operational expenditure does not cover the additional investment costs of the IEX system at WTW De Blankaart, whereas this was the case at WTW Kluizen. This difference between both WTWs is explained by the higher required resin dose at De Blankaart, the limited decrease in chemical demand of the subsequent coagulation process, but also the use of different chemicals in coagulation: in WTW Kluizen, a reduction of the more expensive polyaluminiumchloride coagulant consumption resulted in a vast OPEX decrease, whereas in WTW De Blankaart coagulation is performed with cheaper ferric chloride.

Note that the above numbers are specific for the case at WTW De Blankaart with the high rate IEX contactor and the operating conditions evaluated within the pilot study. It is expected that the NOM removal during IEX can still be improved by changing the total resin volume in the high rate fluidized bed IEX contactor. Unfortunately, the dimensions of the pilot contactor did not allow to evaluate a higher resin volume in the IEX contactor. Applying a higher resin volume will also have an impact on the mineral composition of the treated water, the chemical consumption, the sludge production, and the cost analysis of the IEX system.