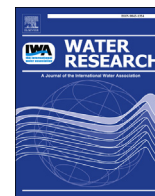


Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Fate and removal of trace pollutants from an anion exchange spent brine during the recovery process of natural organic matter and salts

Elisabeth Vaudevire ^{a, b, c, *}, Farzaneh Radmanesh ^d, Annemieke Kolkman ^e,
Dennis Vughs ^e, Emile Cornelissen ^{e, f, g}, Jan Post ^b, Walter van der Meer ^{d, h}

^a PWN Technologies, Dijkweg 1, 1916HA, Andijk, the Netherlands

^b Wetsus, European Centre of Excellence for Sustainable Water Technology, Oostergoweg 9, 8911 MA, Leeuwarden, the Netherlands

^c Department of Biotechnologies, TU Delft, Van der Maasweg 9, 2629 HZ, Delft, the Netherlands

^d University of Twente, Faculty of Science and Technology, De Horst 2, 7522LW, Enschede, the Netherlands

^e KWR Water Cycle Research Institute, Groningehaven 7, 3433 PE, Nieuwegein, the Netherlands

^f Particle and Interfacial Technology Group, Ghent University, Coupure Links 653, B-9000, Ghent, Belgium

^g Singapore Membrane Technology Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, Singapore, 637141, Singapore

^h Oasen NV, Nieuwe Gouwe O.Z. 3, 2801 SB, Gouda, the Netherlands

ARTICLE INFO

Article history:

Received 13 August 2018

Received in revised form

21 December 2018

Accepted 28 January 2019

Available online 4 February 2019

Keywords:

Metal traces

Organic micro-pollutants

Anion exchange

Electrodialysis

Humic substances

ABSTRACT

The results of this sampling campaign on pilot scale processes aim to evaluate the occurrence and behavior of trace organic micro-pollutants and metal elements during anion exchange treatment of surface water and the subsequent treatment of generated spent brine with two types of electro dialysis membrane pairs. This knowledge is relevant to assess the quality and reusability of secondary products created during brine treatment; specifically the excess of sodium chloride to be recycled onsite and the natural organic matter, mostly consisting of humic substances, which find multiple applications in the agricultural industry. This study highlights that (1) the attachment mechanism of organic micro-pollutants to anion exchange resin occurs through electrostatic interaction and the subsequent transfer through ion exchange membranes is restricted by size exclusion; and (2) the complexation of trace metals compounds with the natural organic matter partly explains their removal by anion exchange. Complexes remain stable during treatment of the brine with electro dialysis.

© 2019 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

In the drinking water industry, the removal of natural organic matter (NOM) through anion exchange (AIX) is establishing itself as a relevant alternative to conventional processes. The benefit is the removal of the specific fractions with low molecular weight and negative charges, which are typically difficult to coagulate (Humbert et al., 2005; Mergen et al., 2008). Global climate change makes this technology particularly applicable in places where acidification of water sources (due to acid rains etc.) lead to a modification of organic matter towards smaller species (Eikebrokk et al., 2004; Eimers et al., 2008; Evans et al., n.d. Lepistö et al., 2008; Monteith et al., 2007; Ritson et al., 2014). By removing this specific

fraction of organics, the technology permits not only a reduction of taste and odor, it also minimizes the formation of disinfection-by-products and increases the treatability of the water for downstream processes (Kingsbury and Singer, 2013; Metcalfe et al., 2015).

The generation of a spent brine, inherent to the process, probably constitutes its main drawback. These brines streams are characterized by a high conductivity and color due the excess of sodium chloride from the regenerant solution and the desorbed NOM and inorganic anions from the raw water. Their disposal can be considered difficult and expensive which favored the development of technologies for brine treatment (Ariono et al., 2016). More often, the problem is turned around by creating useful secondary products from brine components. Sodium chloride is the first possible secondary product that can be reused directly onsite, reducing in consequence the production, transportation, and spill of chemicals (Amini et al., 2015; Choe et al., 2015). The NOM

* Corresponding author. PWN technologies, Dijkweg 1, 1916HA, Andijk, the Netherlands.

E-mail address: evaudevire@pwnt.com (E. Vaudevire).

fraction in the spent brine that essentially consists of smaller and charged fractions due to resin selectivity, is often classified as humic or fulvic acids. When that is the case, they constitute a potentially valuable secondary product in circular economies. In fact humic substances (HS), the general term to describe both species, have raised interest in many industries lately; e.g., in livestock breeding HS can reduce the amount of necessary antibiotic animals ingest (Islam et al., 2005; Kucukersan et al., 2005), in open field agriculture, HS can diminish the use of mineral addition for crops (Lyons and Genc, 2016). These prospects in a time of ever-tighter regulation are worth the research and development effort for separation technologies capable of recovering these fractions. The authors realize that the actual purity of recovered HS will dictate the benefits of the recovered fractions.

In this work, the separation of spent brine components and recovery of secondary products is proposed with the use of a two stages process of electro dialysis (ED), a first stage for recycling a sodium chloride solution and a second stage for recovering the humic substances. ED has previously been referred to as a suitable technology to separate inorganics from organic compounds (Kabsch-Korbutowicz et al., 2011; Zhang, Y. Pinoy, L. Meesschaert, B. Van der Bruggen, 2011; Zhang et al., 2009). For the recovery of NaCl, the anion exchange membranes can be made monovalent selective either by employing a thin perm-selective surface layer with the same charge as the transferred ion or by increasing the degree of crosslinking within the polymer matrix (Vaselbehagh et al., 2015).

The proposed approach was tested at PWN, a water utility in North Holland. In this setting, illustrated in Fig. 1, AIX treats surface water from the IJssel lake (1) for NOM removal prior to further treatment with ceramic microfiltration and advanced oxidation processes (2). After a certain contact time, the resin is separated and regenerated with a sodium chloride solution (3) to be reused in the next cycle. The spent sodium chloride solution (4), or spent brine, contains the desorbed NOM, but also untargeted anions from the IJssel lake that had an affinity for the resin: typically nitrate, sulphate and bicarbonate and possibly trace pollutants. To separate and recycle the different chemical components, the brine (4) undergoes a first ED step with monovalent selective anion exchange and standard cation exchange membranes referred to as the monovalent selective step until full transfer of chloride ions occurs to the concentrate (5). In the next step, the diluate (6) enters a second ED stack equipped with standard anion and cation exchange membranes to separate the remaining multivalent salts in concentrate (8) from the organic matter in solution (7).

Three different streams are created from this treatment of the brine:

- The monovalent salt solution in concentrate 1 (5) consists of sodium, chloride and bicarbonate to be reused as a fresh salt solution (3).
- The multivalent salts solution (8), usually dominated by sodium sulphate.
- The NOM in solution (7) among which the humic and fulvic acids.

This article covers the effort to assess the fate and removal of naturally occurring trace pollutants within the drinking water pre-treatment using AIX, and subsequent brine treatment using ED leading to the recovery of sodium chloride and NOM. Previous work on trace pollutant removal with AIX or ED include single assessments of either processes, mostly in a laboratory controlled setting and targeting only specific compounds of interest. The removal of organic micro-pollutants with AIX resin was in fact previously investigated with regards to kinetics (Bä Uerlein et al., 2012; Landry et al., 2015a; Liu et al., 2011), selectivity of the resin (Landry et al., 2015b), the competitive effect of the water matrix (Bä Uerlein et al., 2012; Neale et al., 2010), and the chemistry involved in the removal mechanism (Landry et al., 2015a; Liu et al., 2011; Neale et al., 2010). Most studies highlight the co-existence of several sorption mechanisms: the electrostatic interaction and physical interactions driven by hydrophobicity or hydrogen bonding. One study however has carried the investigation over several adsorption/regeneration cycles to find the diminishing impact of the non-electrostatic interactions cycle after cycle (Wang et al., 2016). Trace metal removal with anion exchange resin in drinking water production has been subject to fewer studies. In municipal and industrial wastewater treatment, the combination of strong base anion exchange and complexing agents such as EDTA, NTA or newly developed biodegradable aspartic acid derivatives is used for the removal of heavy metals with restricted discharge regulation (Kołodziejka, 2011; Kołodziejka et al., 2009). ED has been studied for removal of metals in waste stream decontamination, results established a relation between the charges and hydrated radius of ions and their removals (Banasiak and Schäfer, 2009). One study used real brackish water to investigate the influence of the water matrix on trace metal transportation, which highlights membrane deposition and neutral complex formation phenomena previously disregarded in artificial waters (Onorato et al., 2017). Finally the

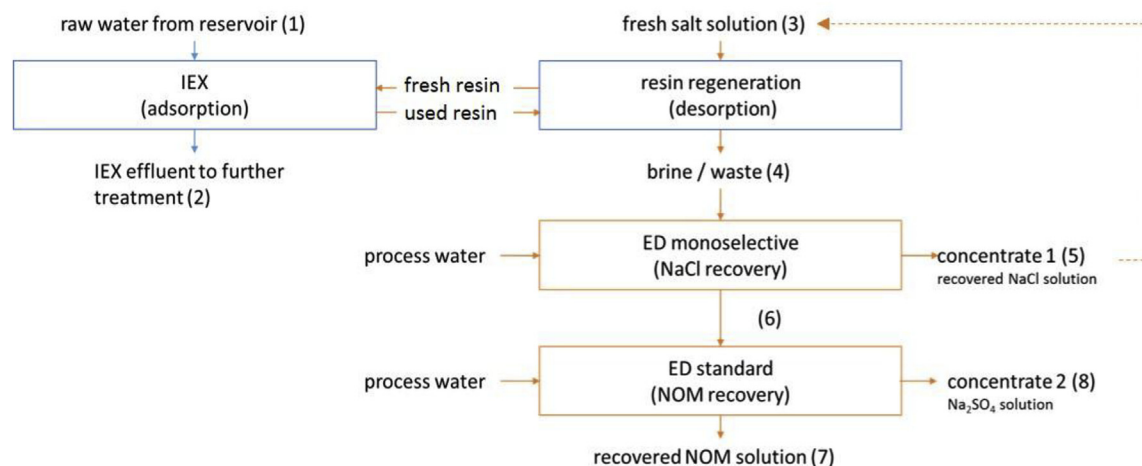


Fig. 1. Process scheme ion exchange water production and brine treatment.

passage of organic micro-pollutants through ion exchange membranes was isolated in (Vanoppen et al., 2015), in which diffusion is designated as the main transportation mechanism. To the best of the authors' knowledge, this is the first attempt to apply and compare the theories and observations from laboratory scale on the fate of trace pollutants in AIX and ED to industrial or pilot scale using natural and un-spiked water. Furthermore, this study differentiates from other studies by offering a complete assessment of trace pollutants in the combination of relevant technologies recreated on pilot scale. Anion exchange resin and ion exchange membranes may, in fact, experience synergetic (or complementary) effects in compounds interactions. The sampling results also relates to the operational process conditions and to the molecular properties to highlight trends in the transport of trace pollutants, including an attempt to evaluate the consequences on contamination of secondary products.

2. Material and methods

2.1. Sampling

2.1.1. Sample points

Samples points of the AIX include: inlet and outlet of the contactor, referred to in Fig. 1 as streams (1) and (2), as well as in the brine solution (4) obtained from the periodic regeneration cycle of AIX resin occurring immediately after a sufficient contact time. More details on the use of NaCl solution leading to brine production is available in (Galjaard and Koreman, 2015). In the ED pilots operated in batch mode, sample points include influent brine (4), effluent brines numbered (6) and (7) for ED1 and ED 2 respectively, and effluent concentrates (5) and (8).

2.1.2. Trace pollutants

For consistency, trace pollutants were sampled within a day. The study uses three AIX units available at Andijk with slight differences in kinetics due to their different scales (two generations of pilots and one full scale). The operational parameters for each AIX units are given below in detail. The brine from pilot 2 (Table 2) was manually collected to be further treated with ED in two consecutive batches.

2.1.3. Process performance

Routine samples were taken weekly in pilot 2 and the obtained analytical results from these samples were used to express the continuous AIX performances over a period of six months. For ED running in either in batch mode or feed and bleed mode, the sampling time affected the results. Therefore, a representative batch was chosen to determine the performance. ED routinely runs using brine from full scale.

2.2. Ion exchange pilots

All three pilot and full-scale ion exchange units in this study are SIX[®] processes developed by PWNT (Koreman and Galjaard, 2016) operating continuously on the parameters in Table 1. During SIX[®] operation, the resin is dosed in the raw water, kept in suspension during a fixed residence time, separated from effluent water through lamellas and fully regenerated before being used in the next cycle.

2.3. Electrodialysis pilot

The ED pilot includes two stacks operated in subsequent batch mode at a constant voltage of 45 V for 5 h. In both batches, the concentrate initially consists of 60 L of water produced by reverse osmosis in which the transferred salts will accumulate overtime. The diluate of ED 1 consists of 150 L of brine produced on AIX pilot 2, which will transfer to ED 2 to be further treated. Table 2 summarizes the operational parameters applied.

2.4. Membrane characterization

Membranes were characterized to determine differences in structural properties at the time of the study. Parameters evaluated include membrane thickness, perm-selectivity, electrical resistance, water content and contact angle determined with the captive bubble method. Results are presented in Table 3 and more information on the method is available from supporting information 1.

The difference between the two types of anion exchange membranes is an additional layer on the surface of the monovalent selective membranes. This can be observed from a difference in the determined membranes thicknesses between the two types of ED membranes (Table 3). (Ge et al., 2014; Saracco and Zanetti, 1994) suggest that this additional layer is a tighter cross linked polymer which is deposited onto the PVC internal structure to physically block the passage of larger molecules. Characterization data show that the monovalent selective and standard membranes have a similar water content despite differences in membrane thickness; in addition, a higher contact angle for the monovalent selective membrane indicates a lower hydrophilicity. Both characteristics could in fact result from a lower density of active groups caused by an additional layer of polymers (Kumar et al., 2009). In any case, an improved mono-selectivity of the Neosepta membrane was confirmed by the difference in electrical resistance in a NaCl solution ($10 \Omega \text{ cm}^2$) or in a MgSO_4 solution ($87 \Omega \text{ cm}^2$). The standard PC Cell membranes display a constant electrical resistance around $2 \Omega \text{ cm}^2$ in both solutions.

Table 1
Operational parameters on three scales SIX[®] ion exchangers used in this study.

	Pilot 1	Pilot 2	Full scale
influent water flow	30 m ³ /h	60 m ³ /h	2000 m ³ /h
Resin type	Lewatit S 5128, acrylic gel structure with Quaternary ammonium type 1 (strong bases) exchange sites		
Resin concentration	12 mg/L		
Residences time	30 min		
Operation	Suspended resin, single pass, the resin is regenerated after each residence time		
Suspension of the resin	mechanical rotor	air injection	air injection
Regeneration	NaCl in solution, at purity of 99%, the rest of the composition includes calcium (0.2%), sulfate (0.7%), and magnesium (0.1%)		
NaCl concentration for regeneration	55 g/L	45 g/L	35 g/L
	110 mS/cm	90 mS/cm	70 mS/cm

Table 2
Electrodialysis operational parameters.

	Stack 1	Stack 2
Commercial name	EUR6B-50 (Eurodia)	1000H-25 (PC Cell)
Membranes used	Neosepta CMXsb and ACS (monovalent selective)	PC Cell SA and SK
Active membrane area	560 cm ² /membrane	1000 cm ² /membrane
Number of cell pairs	50	25
Role	Monovalent salts separation	Multivalent salts separation
Initial diluate volume	150 L (brine IEX pilot 2)	135 L (diluate ED1)
Initial concentrate volume	60 L of reverse osmosis permeate	

Table 3
Membranes structural characterization parameters.

	Neosepta (ED1)		PC Cell (ED2)	
	ACS (mono selective)	CMXsb (standard)	SA (standard)	SK (standard)
Thickness (μm)	126	189	93	110
Perm-selectivity (%)	86 ± 1	100 ± 0	97 ± 1	90 ± 0
Contact angle (°)	31 ± 2	29 ± 0	22 ± 2	44 ± 8
Electrical resistance Na–Cl (Ω.cm ²)	10.0 ± 0.4	2.4 ± 0.0	1.9 ± 0.3	3.7 ± 0.0
Electrical resistance Mg–SO ⁴ (Ω.cm ²)	87.0 ± 7.0	8.2 ± 0.1	1.7 ± 0.3	3.6 ± 0.1
Water content (wt%)	26 ± 1	34 ± 1	33 ± 1	26 ± 3

2.5. Analytical method trace elements

2.5.1. Pre-treatment of samples

All samples were filtered using 0.20 μm filtration to remove larger particles. As dilution factor of 10, determined by validation tests, was applied to brine samples to reduce matrix effects during chemical analysis.

2.5.2. Organic micro pollutants

Ten organic micro-pollutants were selected on their probable presence in the IJssel lake (dr. ir. Th. H. M. Noij and E. Emke, 1999; Mons et al., 2000), a target liquid chromatography – tandem mass spectrometry (LC-MS/MS) method was used. The LC system consisted of an Accela Ultrahigh Pressure Liquid Chromatography – UHPLC (Thermo Fisher Scientific, Bremen, Germany). The chromatographic separation was performed on a Hypersil Gold column (2.1 × 100 mm, 1.9 μm, Thermo Fisher Scientific), preceded by a SecurityGuard Ultra C18 column (2.0 mm × 2.1 mm, Phenomenex, Torrance, USA). Mass spectrometric detection was performed using a tandem quadrupole mass spectrometer TSQ Vantage (Thermo Fisher Scientific) equipped with an electrospray ionization source operated in positive and negative mode.

For the general detection of micro pollutants in surface water, a suspect screening was performed using liquid chromatography – quadrupole time of flight mass spectrometry (LC-QToF). The LC system consisted of a Nexera X2 LC-30AD binary gradient pump, and a CTO-20AC column oven (Shimadzu Corporation, Kyoto, Japan). The chromatographic analysis was performed on an Xbridge C18 XP column (2.1 × 150 mm, 2.5 μm, Waters, Etten-Leur, the Netherlands) preceded by a SecurityGuard Ultra C18 column (2.0 mm × 2.1 mm, Phenomenex, Torrance, USA). Detection was performed on a QToF mass spectrometer (TripleTOF 5600+, AB SCIEX, Concord, Canada) operated in both positive and negative electrospray ionization mode.

Additional information on the analytical protocol for LC-MS/MS and LC-QToF methods is available in [supporting information II](#). The validation of the LC-QToF was performed with a recovery test spiked with 0.5 μg/L of 56 frequently occurring micro pollutants and showed a good recovery for surface water (ranging from 74.8% to 124.1%) and satisfying recoveries for diluted brine (ranging from 44.5% to 129%). Validation of LC-MS/MS resulted in better

recoveries and quantification in both surface water (ranging from 89.1% to 108.8%) and diluted brine (ranging from 76.3% to 140.8%). In the results section a star* marks the values obtained with LC-MS/MS.

2.5.3. Inorganic micro pollutants

For trace metal compounds analysis an ICP-MS screening method using a Xseries 2 ICP-MS (Thermo Fisher Scientific) was employed for the detection of 65 trace metal compounds in a single run. The trace metal compounds were quantified using an external calibration line consisting of four points. Because of its high salinity, dilution of the brine with a factor of ten and hundred were compared during a recovery test with 1 μg/L spiked compound and were found to be similar (range 43.6%–148.1%).

2.6. Mass balance formulas

Two parameters derived from simple mass balance equations were used to express the trace pollutants transport in the ion exchanger. First, the removal (in %) through adsorption of a compound, calculated by equation (1) as the difference in concentrations entering and exiting the AIX contactor, relatively to the concentration entering. Secondly, the percentage of compounds in the brine presumably transported from raw water through adsorption desorption is calculated as a ratio between the two in equation (2) under the assumption that the fresh NaCl solution for regeneration is not contaminated with trace pollutants.

$$\text{removal (\%)} \text{ from the raw water} = \frac{C_1 F_1 - C_2 F_2}{C_1 F_1} \cdot 100\% \quad (1)$$

$$\text{transport (\%)} \text{ to the brine} = \frac{C_4 F_4}{C_1 F_1} \cdot 100\% \quad (2)$$

In both equations, C refers to the concentration and F to flows of either ion exchange influent, referred to as stream 1 in [Fig. 1](#), the effluent (stream 2), or the brine (stream 4). Theoretically, the difference between equations (1) and (2) represents the percentage of compounds permanently adsorbed on the resin beads.

Similar mass balance equations were adapted for the trace pollutants transport in the ED processes. For each of the two ED steps, equations (3) and (4) express the removal (in %) by ion

exchange transfer as a difference between the concentrations in the brine at the beginning and the end of treatment relatively to the initial concentrations in the brine. The percentage recovered in the concentrate stream at the end of either the first-stage or the second-stage ED are expressed with equations (5) and (6) respectively. The initial concentration of trace pollutant in the concentrate prior to ED is estimated as null.

$$\text{removal (\%)} \text{ in the first - stage ED} = \frac{C_4V_4 - C_6V_6}{C_4V_4} \cdot 100\% \quad (3)$$

$$\text{removal(\%)} \text{ across the two - stage ED} = \frac{C_4V_4 - C_7V_7}{C_4V_4} \cdot 100\% \quad (4)$$

$$\text{first - stage recovery (\%)} = \frac{C_5V_5}{C_4V_4} \cdot 100\% \quad (5)$$

$$\text{second - stage recovery (\%)} = \frac{C_8V_8}{C_4V_4} \cdot 100\% \quad (6)$$

With C and V being respectively the concentrations and the volumes of, in reference to Fig. 1, stream 4 represents the initial brine, stream 5, the concentrate after monovalent selective stack, stream 8, the concentrate after standard stack, stream 6, the monovalent selective diluate and stream 7, the final diluate containing the NOM in solution.

3. Results

3.1. Ion exchange performance in drinking water treatment

The selected resin, Lewatit S5128, is designed for the adsorption and desorption of negatively charged dissolved organic matter (Lewatit-Lenntech, 2015). However, the charged quaternary ammonium functional groups results in the adsorption onto the resin material of both NOM and anions present in the raw water. Removal (eq (1)) and transport (eq (2)) percentages calculated over pilot 2 are displayed in Table 4. The data show a preferential order of removal of anions from the IJssel lake as: $\text{SO}_4^{2-} > \text{DOC} > \text{NO}_3^- > \text{HPO}_4^{2-} > \text{HCO}_3^-$. DOC, dissolved organic carbon, represents the NOM.

Half of the DOC is removed during the treatment which can be explained by the selectivity of the resin towards charged compounds with a low molecular weight referred to as the humic fraction of NOM. This selectivity is indicated by LC-OCD used for NOM fractionation (Metcalf et al., 2015). For this study, the focus is the fate of trace contaminants, NOM fractionation was not used. The percentages of compounds removed from the raw water (eq (1)) almost match the percentage transported in the brine (eq (2)), as an indication of a near complete regeneration. The production of brine constitutes in volume about 0.5% of the water treated.

Table 4
Operational performance of the SIX[®] pilot 2.

	Cl	Na	HCO ₃	SO ₄	NO ₃	HPO ₄ ²⁻	DOC
AIX influent (mg/L)	130	100	150	54 ± 3	6 ± 1	0.09	6 ± 0.3
	± 1	± 3	± 3			± 0.01	
AIX effluent (mg/L)	200	100	105	8	4	0.06 ± 0	3 ± 0.4
	± 4	± 3	± 6	± 0.5	± 4		
AIX brine (mg/L)	12.630	14.650	7070	7500	260	3.2	540
	± 1400	± 890	± 930	± 1100	± 60	± 2	± 100
% removal (eq. (1))	–	–	30%	85%	35%	33%	50%
% transport (eq. (2))	–	–	31%	91%	28%	23%	59%

3.2. Organic micro pollutants transport in anion exchange pilot

Twenty-three organic micro pollutants were detected with LC MS/MS and the 81 screened with QToF in the IJssel lake. Only 27 species were quantified in the AIX influent, effluent and/or brine and the removal (eq (1)) and transport (eq (2)) were calculated; the species detected under quantifiable limits are listed in supporting information III. Transport determined in pilot 2 are presented in Fig. 2 with similar trends for pilot 1 and full scale in supporting information IV. All species carrying negative charges, except for gabapentine, were transported substantially (5.5–30%) to the brine stream. Whereas only a limited amount (0–7.5%) of the neutral species and none of the positively charged metoprolol and tetra-propylammonium were transported. Other parameters related to the organic micro-pollutants in the IJssel lake, in the ranges summed up below, could not be correlated with their removal:

- Molecular weight with values between 119 and 390 g/mol
- Initial concentration in IJssel lake, between 0.1 µg/L and 0.61 µg/L
- The octanol/water coefficient (Log P), between –1.7 (most hydrophilic) and 4.26 (most hydrophobic).
- Van der Waals radius, between 99 and 368 Å
- pKa, between 1.16 and 15.96 as a measure of the acidity

This observation tends to indicate that, in practice, the transport of organic micro-pollutants in AIX is dominantly driven by electrostatic interactions with the quaternary ammonium group of the regenerated AIX resin material. To a lesser degree, physical interactions occur as well, as was indicated by the transport of neutral compound metazachlor ESA.

3.3. Trace metals compounds removal in anion exchange pilot

Metal cations in solution are not expected to adsorb on the resin because of charge repulsion effects, unless a ligand is present or negatively charged metal oxides are formed. In IJssel lake water, the HS, which contain a high density of carboxylic and other binding groups in their structure, can be considered as ligands. They are even often referred to as chelating agents; which involves the ability to form multiple bonds with a single metallic element, increasing the strength of the complex. Many studies (Davis, 1984; Mantoura et al., 1978a, 1978b; Olivier Pourret, Mélanie Davranche, Gérard Gruau, 2007; Ram and Raman, 1984) have theorized the complexation of trace metals compounds with humic substances, and the effect of surrounding conditions (pH, temperature, concentrations) and competition mechanisms.

To verify the attachment of trace metal compounds on Lewatit S5128 in the presence of HS, removal (eq (1)) and transport (eq (2)) were calculated; transport across pilot 2 are presented in Fig. 3. Results with pilot 1 and full scale showed similar trends and are displayed in supporting information V. The results are organized by

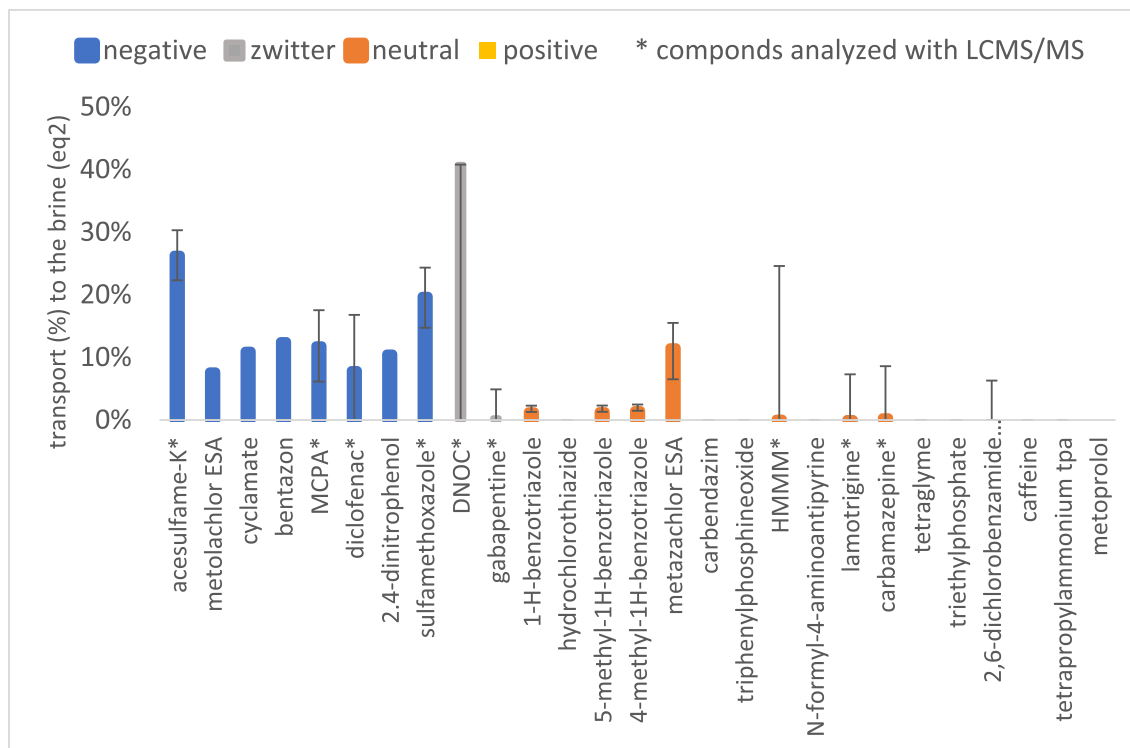


Fig. 2. Transport (%) of organic micro-pollutants from IJssel lake to AIX brine on pilot 2 (equation (2)).

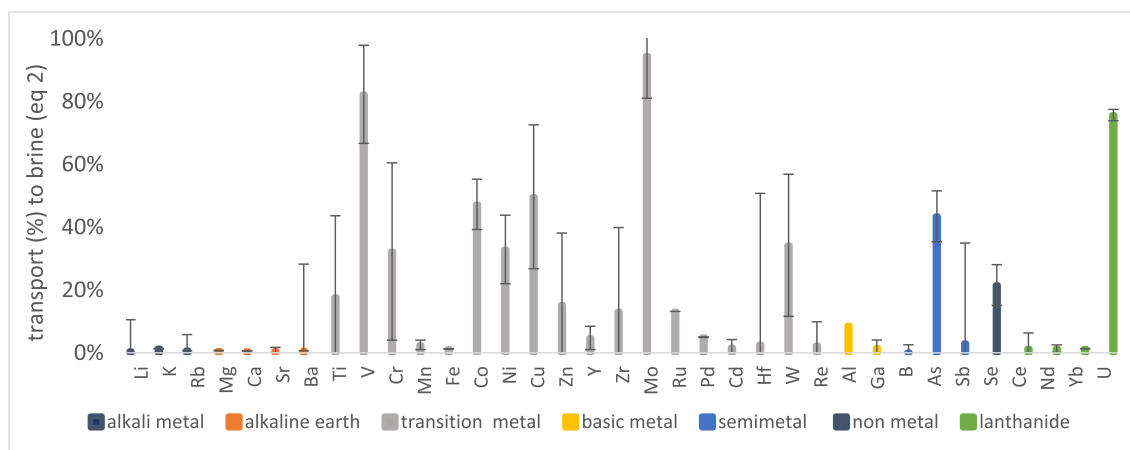


Fig. 3. Transport (%) of metals through direct or indirect attachment on AIX resin in pilot 2 (equation (2)).

groups of elements according to the periodic table to highlight possible group behaviors. The analysis revealed over 36 elements; among them sodium, magnesium, potassium and calcium entering the process ranging from 5 to 94 mg/L, while others range from 0.1 to 340 $\mu\text{g/L}$. Sodium is here deliberately excluded from the calculations since it is added in large amounts during regeneration.

The transition metals, as a group, and arsenic, selenium and uranium display the highest transport to the brine. To confirm they originate from IJssel lake rather than from the salt solution, their removal (eq (1)) and transport (eq (2)) are compared in [supporting information V](#). Only Tungsten and Zirconium could not be traced back because there were not quantifiable in raw water. Despite higher initial concentrations, the transport of alkali metals or alkaline earth metals is low.

All transported ions have in common a favorable electronic configuration towards complex or oxyanions formation. Aqueous forms of the transition metals are too numerous to be considered all; vanadium, molybdenum, tungsten, copper and cobalt, displaying the highest transport, are discussed below as examples. The first three elements share similar properties: (1) as a result of redox reaction, they are mostly found in surface waters as in oxyanions H_2VO_4^- , MoO_4^{2-} , WO_4^{2-} , which adsorption on the resin is possible. (2) There is also evidence of humic material partially reducing Mo, V and W to form weak organometallic complexes (Crans and Tracey, 1998; Lazaridis et al., 2003; Smedley and Kinniburgh, 2017; World Health Organisation, 2000). But for copper and cobalt which occur in surface water in their free Cu^{2+} and Co^{2+} forms, transport to the brine can only take place through complexation with organic molecules.

3.4. Performances of the two-stage electro dialysis

The performance of ED during routine operation on full scale brine is displayed in Table 5. Desalination data is provided in supporting information VI.

A high removal of chloride and nitrate, a moderate removal of bicarbonate and a low removal sulphate and DOC was observed during the first stage ED separation. The second stage of ED reduced the total inorganic content of the brine even further with a relatively limited loss of organics.

3.5. Micro pollutants removal in electro dialysis

All micro-pollutants detected in the brine in pilot 2 were retrieved in the ED mass balance, Fig. 4 displays their distribution between the different effluents. The recovery (equations (5) and (6)) illustrate the fractions transported to the concentrates after the monovalent (a) and standard (b) stacks respectively. Equation (4) is used to assess the compounds remaining in the brine at the end of the two-stage treatment (c). On the x axis, the micro pollutants are ordered by increasing Van der Waals volume. A clear cut off in removal is observed after the passage of 2,4,dinitrophenol at 141.85 Å over the monovalent ED stack. Compounds with a bigger radius were not found to be significantly transported. Such a cut off was not observed with the standard ED stack, and previously strictly retained micro-pollutants on the monovalent ED stack such as cyclamate (154 Å), MCPA (172 Å), benzonat (202 Å) or sulfamethoxazole (211 Å) could be transferred to the concentrate of the standard ED stack. The difference in removal over the two stacks could be attributed to the additional polymer layer on the surface of monovalent selective anion exchange membranes (Table 3) of which separation was based on size exclusion. At the end of the two stage ED treatment, only the largest compounds remain in the brine. The zwitterion gabapentine is also noticeably retained throughout the two stages ED whilst being relatively small; this could be explained by the double positive and negative charges which may lead to ineffective transport under the electrical current.

As illustrated in supporting documents VII, other molecular properties of the organic micro-pollutants, e.g. molecular weight, concentration in brine, octanol/water coefficient (log P), pKa and charge, did not affect the removal considerably.

3.6. Trace metals removal in electro dialysis

The hypothesis of metal cations transport through AIX process involved organometallic complexes and oxyanions that would have formed in surface water. Once in the brine, changes in salinity and pH can affect the stability of the complexes (Lores' and Pennock', 1998; Rehemanjiang Wufuera et al., 2014) and possible modification of the bonding mechanisms could be observed during ED treatment. The 36 elements screened in the brine were retrieved in the ED pilot. The results in Fig. 5 display the distribution of metal elements between the three effluents; i.e.: the removal over the monovalent selective ED stack (a), the standard ED stack (b) and the retention in the brine after the two stacks (c). Equations (4)–(6) are

Table 5
Operational performance of the two stages-ED process.

Compounds	NO ₃	Cl	Ca	Na	HCO ₃	SO ₄	DOC
AIX brine (mg/L)	113	9050	25	8530	2660	3 350	700
ED1 diluate (6) (mg/L)	4	1570	5	3460	2170	3 500	695
removal % (eq (3))	97%	85%	82%	65%	29%	9%	14%
ED2 diluate (7) (mg/L)	<0.5	20	1	810	26	650	470
removal % (eq (4))	100%	100%	98%	91%	99%	82%	32%

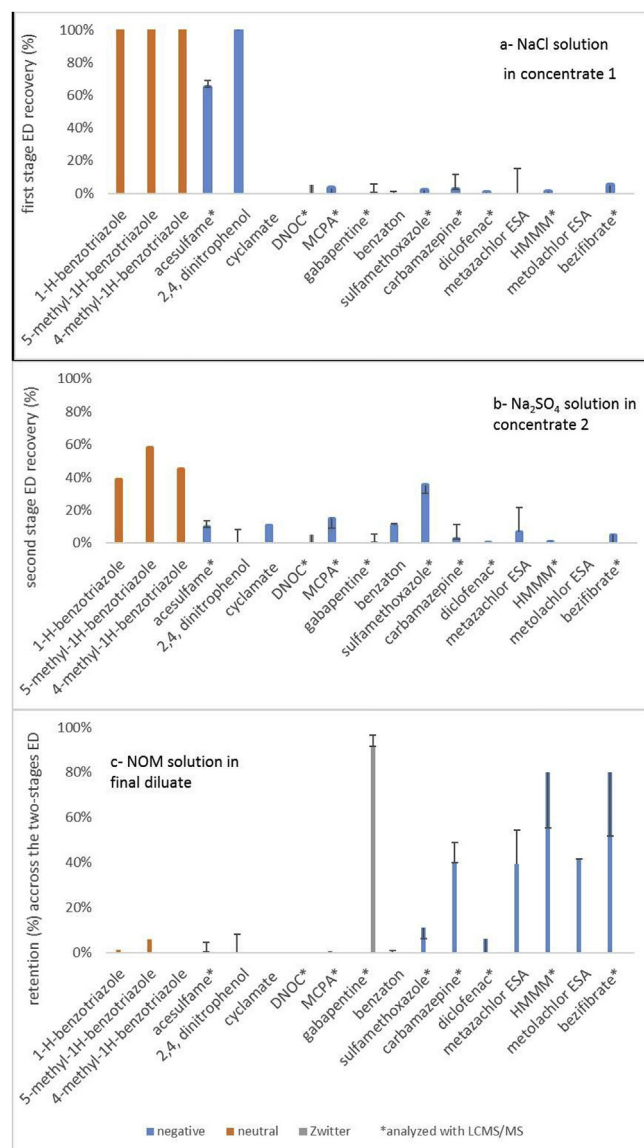


Fig. 4. Recovery (%) of micro-pollutants over the first-stage ED (a), and second-stage ED (b) and retention (%) across the two stages ED (c). Stream numbers are in reference to Fig. 1.

respectively used for the calculations. Fig. 5 shows that alkali metals and alkaline earth metals transfer relatively easily under the electrical current in the first stage ED (a) and the second stage (b) with the noticeable exception of calcium. Whereas the transition metals and other elements at the right side of the periodic element table are mostly retained by both ED stacks, with the noticeable exceptions of (1) rhenium, palladium and ruthenium in ED stage 1, and (2) basic and semi metals groups, and transition metals tungsten, molybdenum and vanadium in ED stage 2. The ease of transport of alkali metals and alkaline earth metals confirms their presence in an ionic form in the brine. The combined removal of calcium over the two stages did not exceed 31%, but its retention at the end of the treatment (c) is lower than 2%, which could suggest some scaling effects at high pH values (Onorato et al., 2017). Both types of cation exchange membranes (Table 3) used in the pilot are permeable to multivalent ions, and should not restrict the transport of free cations. Metal oxides formed in surface water would separate in ED stage 1 or 2 according to their valence as observed in the case of previously discussed for vanadium, tungsten and

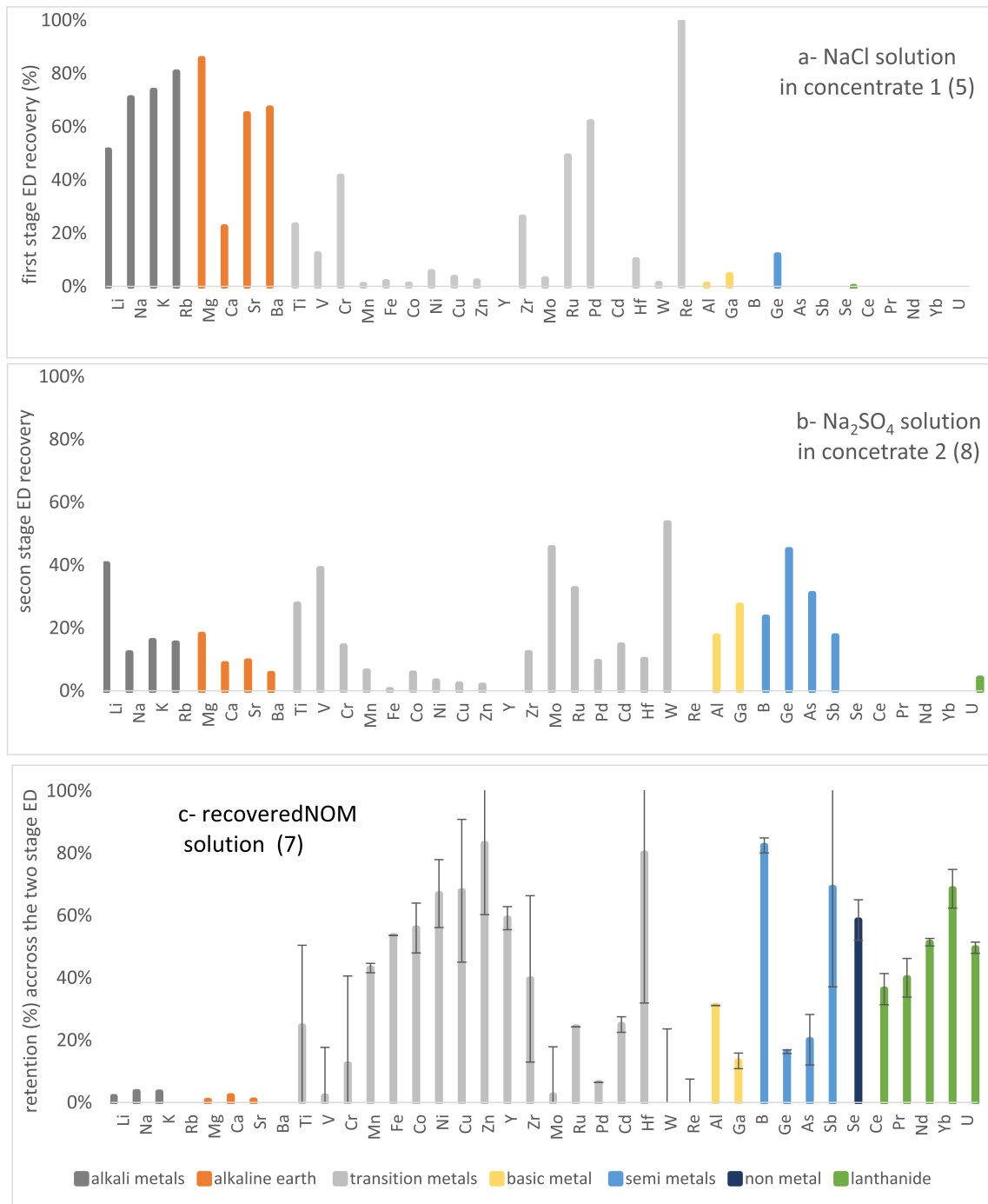


Fig. 5. : Recovery (%) of metals over the first-stage ED (a), and second-stage ED (b) and retention (%) across the two stages ED (c). Stream numbers are in reference to Fig. 1.

molybdenum. Therefore, the low removal of most transition metals, semi metals, non metals and lanthanide suggests they formed organometallic complexes which remained stable in brine. In addition, the Irving–Williams series implies the stability of organometallic complexes increases as they involve trace metals across the first row of the periodic table from titanium to zinc with the exception of vanadium (Mantoura et al., 1978b). Results show the removal rates of compounds decrease accordingly. Lanthanide which was not found transferring to the concentrate side however was reduced in the brine. The case of uranium and selenium deposition on the membrane due to the presence of calcium and carbonate is discussed in (Onorato et al., 2017).

4. Discussion

In addition to the assessment of the transport of trace pollutants through AIX and ED processes, sampling introduced the risk of contamination of the created secondary products.

The NaCl solution collected in concentrate 1 (5) can be reintroduced in the AIX through the next regeneration cycle. The excess of chloride in the brine after AIX is estimated to be around 30% of the total demand. If fully recovered through ED, it would be mixed with 70% of new solution. The main risk associated with this practice involves accumulation of anions other than chloride in time. The data provided in this article indicate that the initial salt

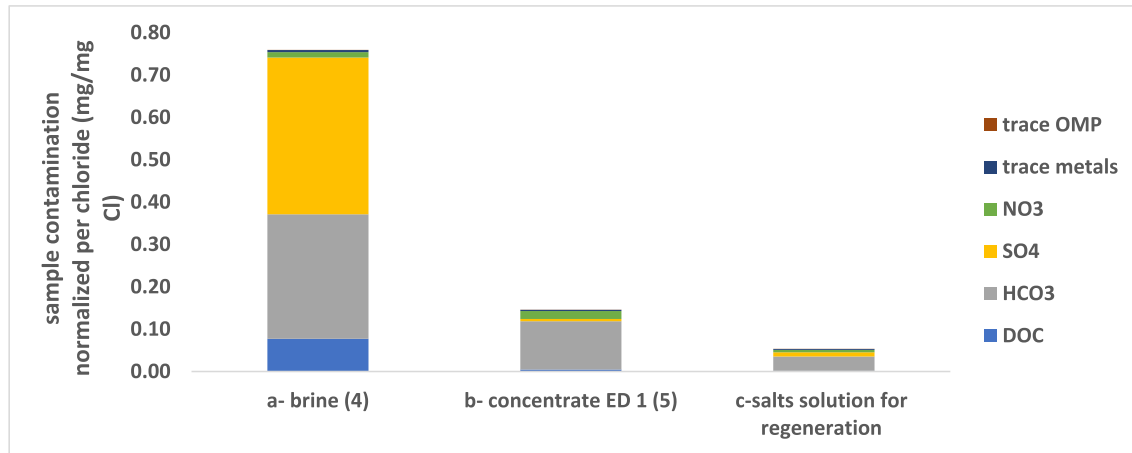


Fig. 6. Projected contamination of chloride in brine (4) in concentrate 1 (5) and in the hypothetical mix of regenerated and new salts (calculated). The stream numbers are in reference to Fig. 1.

purity of 99% (from provider) mixed with a recovered salt purity of 82% (from sampling) would decrease to 94% over one cycle. Contamination would mainly be caused by bicarbonate (2.5%) and different cations (calcium, magnesium, potassium). Only the presence of anions potentially reduces the regeneration efficiency of the resin; and a buffering effect of bicarbonate is expected to stabilize the contamination effect in time, which should be determined experimentally. A projected overview of anions contaminating chloride in the brine, after ED, and in the calculated composition of the regeneration solution as a mix of recovered and fresh NaCl is presented in Fig. 6. In this scenario, the combined contamination, normalized per mg of chloride, would reduce from 0.79 mg of anions and trace pollutants per mg of chloride to 0.22 mg/mg Cl after ED, and to 0.07 mg/mg Cl once blended with fresh salt.

The purification of NOM after the two ED steps before use as humic and fulvic supplement in agricultural applications is assessed in Fig. 7. The contamination with inorganic and trace pollutants is normalized per mg DOC and displayed in the brine (4), after ED 1 (6) and in the recovered NOM solution (7) after ED 2. It shows demineralization takes place with a concentration of combined inorganic ions falling from 36.2 mg/mg DOC to 5.3 mg/mg DOC during treatment. However, residual Na, HCO₃ and SO₄ will hamper the range of applications of NOM where there is no limitation on salts; animal feed supplement could be such example.

For direct application either on soil or for animal consumption, residual levels of trace pollutants in the NOM are relevant. Regulations are specific to application and location, so only general toxicity risks related to trace pollutants are considered. Among the micro-pollutants of concern:

- Dinitro-ortho-cresol (DNOC), a pesticide now banned from use, is fully eliminated during treatment (information subjected to the high inaccuracy of the analytical methods for this particular compound).
- Sulfamethoxazole, a potentially hazardous antibiotic, in the NOM solution amounts 0.04 µg/L. With no existing standard for this compound, this level is considered acceptable.
- Diclofenac, an anti-inflammatory recently put on a watch list for priority substance by the European Union, remains in the NOM solution at a concentration of 0.01 µg/L. This is below the standards currently set on 0.1 µg/L in the European water Framework for surface waters (“STOWA, 2013-23 Human pharmaceuticals in the water cycle,” n.d.) therefore not considered threatening to the environment.

Among the heavy transition metals, copper, nickel, arsenic, cobalt and chromium are regulated in large numbers of application i.e.: in the use as fertilizer (Kane et al., 2003), or in the standards for

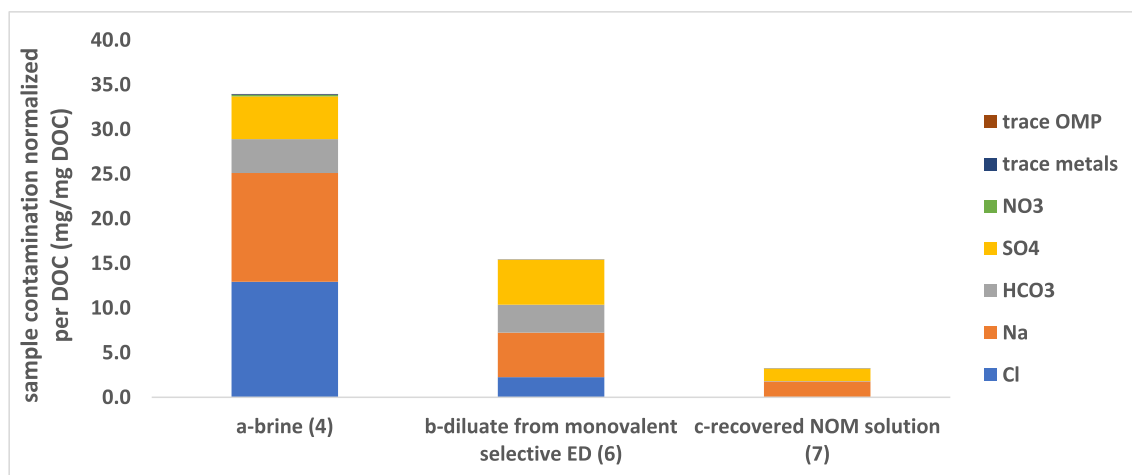


Fig. 7. Contamination of NOM in brine (4) diluate after ED 1 (6) and in the recovered NOM solution (7) after two steps ED. The stream numbers are in reference to Fig. 1.

surface water (WFD, 2000). Residual concentrations in the recovered NOM exceed the standards mentioned in both documents. In fact, this assessment implies that the removal of heavy metals was incomplete because of complex formation, which forms a serious risk for different applications. One possible easy solution could be for example acid treatment to de-complex the HS and the heavy metals. If unsuccessful, alternative treatment methods should be investigated for the purification of humic substances as a replacement to the second step of electro dialysis.

5. Conclusions

The sampling campaign confirmed the retention of organic and inorganic trace pollutants from raw water during AIX treatment, and indicated a probable dominance of electrostatic interaction during organic micro pollutants transport, and formation of oxy-anions and complexes with the organics during metals transport. During the treatment of the AIX brine in a two-stage ED (monovalent selective followed by standard stacks), trace pollutants were seemingly separated according to the following:

- Size separation of organic micro-pollutants with a clear cut off value related to Van der Waals volume was observed for the monovalent selective anion exchange membranes, this behavior did not appear with standard ion exchange membranes, due to its looser polymeric structure
- Passage of metals was related to the periodic table group properties. Alkali and alkali earth metals largely passed the membranes on both ED stacks, likely in their cationic form. Other metals, especially transition metals, were mostly retained presumably due to complex formation with NOM.

As a result, NaCl was found to be of sufficient quality for reuse in the process with however a specific attention to long term accumulation of bicarbonate. NOM contained heavy metals which forms a risk for potential reuse applications. Further research should focus on improving the NOM quality using for example nonionic resin extraction, as an alternative to the second ED stack, to remove greater quantities of heavy metals and improve desalination of NOM which would open the possibilities for industrial applications (Peuravuori, 2000).

Acknowledgments

Authors would like to acknowledge technical support obtained from KWR and the financial support from Interreg DOC2C's project and PWN water supply North Holland. This work was realized in the cooperation framework of Wetsus, European Centre of Excellence for Sustainable Water Technology (www.wetsus.nl). Wetsus is co-funded by the Dutch Ministry of Economic Affairs and Ministry of Infrastructure and Environment, the European Union Regional Development Fund, the Province of Fryslan, and the Northern Netherlands Provinces. We are grateful to the participants of the research theme "Concentrates" for fruitful discussions.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2019.01.042>.

References

- Amini, A., Kim, Y., Zhang, J., Boyer, T., Zhang, Q., 2015. Environmental and economic sustainability of ion exchange drinking water treatment for organics removal. *J. Clean. Prod.* 104, 413–421. <https://doi.org/10.1016/j.jclepro.2015.05.056>.
- Ariono, D., Purwasmita, M., Wenten, I.G., 2016. Brine Effluents: Characteristics, Environmental Impacts, and Their Handling. *J. Eng. Technol. Sci.* 48, 367–387. <https://doi.org/10.5614/j.eng.technol.sci.2016.48.4.1>.
- Bä Uerlein, P.S., Ter Laak, T.L., Hofman-Caris, R.C.H.M., De Voogt, P., Droge, S.T.J., 2012. Removal of charged micropollutants from water by ion-exchange polymers: Effects of competing electrolytes. <https://doi.org/10.1016/j.watres.2012.06.048>.
- Banasiak, L.J., Schäfer, A.I., 2009. Removal of boron, fluoride and nitrate by electro dialysis in the presence of organic matter. *J. Membr. Sci.* 334, 101–109. <https://doi.org/10.1016/j.memsci.2009.02.020>.
- Choe, J.K., Bergquist, A.M., Jeong, S., Guest, J.S., Werth, C.J., Strathmann, T.J., 2015. Performance and life cycle environmental benefits of recycling spent ion exchange brines by catalytic treatment of nitrate. *Water Res.* 80, 267–280. <https://doi.org/10.1016/j.watres.2015.05.007>.
- Crans, D.C., Tracey, A.S., 1998. The chemistry of vanadium in aqueous and nonaqueous solution. *ACS Symp. Ser.* 711, 2–29. <https://doi.org/10.1021/bk-1998-0711.ch001>.
- Davis, J.A., 1984. Complexation of trace metals by adsorbed natural organic matter. *Geochim. Cosmochim. Acta* 48, 679–691. [https://doi.org/10.1016/0016-7037\(84\)90095-4](https://doi.org/10.1016/0016-7037(84)90095-4).
- Eikebrokk, B., Vogt, R.D., Liltved, H., 2004. NOM increase in Northern European source waters: Discussion of possible causes and impacts on coagulation/contact filtration processes. In: *Water Science and Technology: Water Supply*, pp. 47–54.
- Eimers, M.C., Watmough, S.A., Buttle, J.M., 2008. Long-term trends in dissolved organic carbon concentration: A cautionary note. *Biogeochemistry* 87, 71–81. <https://doi.org/10.1007/s10533-007-9168-1>.
- Evans, C.D., Monteith, D.T., Cooper, D.M., n.d. Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. <https://doi.org/10.1016/j.envpol.2004.12.031>.
- Galjaard, G., Koreman, E., 2015. SIX @ A New Resin Treatment Technology for NOM-removal. IWA, Malmö, Sweden. IWA NOM6.
- Ge, L., Wu, L., Wu, B., Wang, G., Xu, T., 2014. Preparation of monovalent cation selective membranes through annealing treatment. *J. Membr. Sci.* 459, 217–222. <https://doi.org/10.1016/j.memsci.2014.02.025>.
- Humbert, H., Gallard, H., Suty, H., Croué, J.P., 2005. Performance of selected anion exchange resins for the treatment of a high DOC content surface water. *Water Res.* 39, 1699–1708. <https://doi.org/10.1016/j.watres.2005.02.008>.
- dr ir, Th, Noji, H.M., Emke, E., 1999. Organic micropollutants in Rhine and Meuse.
- Islam, K.M.S., Islam, K.M.S., Schuhmacher, A., Gropp, J.M., 2005. Humic Acid Substances in Animal Agriculture. *Pakistan J. Nutr.* 4, 126–134. <https://doi.org/10.3923/pjn.2005.126.134>.
- Kabsch-Korbutowicz, M., Wisniewski, J., Lakomska, S., Urbanowska, A., 2011. Application of UF, NF and ED in natural organic matter removal from ion-exchange spent regenerant brine. *Desalination* 280, 428–431. <https://doi.org/10.1016/j.desal.2011.06.068>.
- Kane, P.F., Hall, W.L., Averitt, D.W., 2003. Regulation of Heavy Metals in Fertilizer: The Current State of Analytical Methodology, pp. 61–74. <https://doi.org/10.1021/bk-2004-0872.ch005>.
- Kingsbury, R.S., Singer, P.C., 2013. Effect of magnetic ion exchange and ozonation on disinfection by-product formation. *Water Res.* 47, 1060–1072. <https://doi.org/10.1016/j.watres.2012.11.015>.
- Koreman, E., Galjaard, G., 2016. NOM-removal at SWTP Andijk (Netherlands) with a New Anion Exchange. In: *Gewässerschutz. wasser. abwasser*, pp. 50.1–50.13.
- Kołodziejka, D., Hubicka, H., Hubicki, Z., 2009. Studies of application of mono-disperse anion exchangers in sorption of heavy metal complexes with IDS. *DES* 239, 216–228. <https://doi.org/10.1016/j.desal.2008.02.024>.
- Kucukersan, S., Kucukersan, K., Colpan, I., Goncuoglu, E., Reisli, Z., Yesilbag, D., 2005. The effects of humic acid on egg production and egg traits of laying hen. *Vet. Med.* 50, 406–410.
- Kumar, M., Tripathi, B.P., Shahi, V.K., 2009. Ionic transport phenomenon across sol-gel derived organic-inorganic composite mono-valent cation selective membranes. *J. Membr. Sci.* 340, 52–61. <https://doi.org/10.1016/j.memsci.2009.05.010>.
- Landry, K.A., Sun, P., Huang, C.H., Boyer, T.H., 2015a. Ion-exchange selectivity of diclofenac, ibuprofen, ketoprofen, and naproxen in ureolyzed human urine. *Water Res.* 68, 510–521. <https://doi.org/10.1016/j.watres.2014.09.056>.
- Landry, K.A., Sun, P., Huang, C.H., Boyer, T.H., 2015b. Ion-exchange selectivity of diclofenac, ibuprofen, ketoprofen, and naproxen in ureolyzed human urine. *Water Res.* 68, 510–521. <https://doi.org/10.1016/j.watres.2014.09.056>.
- Lazaridis, N.K., Jekel, M., Zouboulis, A.I., 2003. Removal of Cr(VI), Mo(VI), and V(V) Ions from Single Metal Aqueous Solutions by Sorption or Nanofiltration. *Separ. Sci. Technol.* 38, 2201–2219. <https://doi.org/10.1081/SS-120021620doi.org/10.1081/SS-120021620>.
- Lepistö, A., Kortelainen, P., Mattsson, T., 2008. Increased organic C and N leaching in a northern boreal river basin in Finland. *Glob. Biogeochem. Cycles* 22. <https://doi.org/10.1029/2007GB003175>.
- Lewatit-Lenntech, 2015. Lewatit-S-5128-gelular-strongly-basic-anion-exchange-resin-Lenntech.
- Liu, Z., Yan, X., Drikas, M., Zhou, D., Wang, D., Yang, M., Qu, J., 2011. Removal of benzotriazole from micro-polluted water using MIEC resin: Kinetics, equilibrium, and mechanism. *J. Environ. Sci.* 23, 381–387. [https://doi.org/10.1016/S1001-0742\(10\)60441-X](https://doi.org/10.1016/S1001-0742(10)60441-X).
- Lores, E.M., Pennock, J.R., 1998. The effect of salinity on binding of cd, cr, cu and zn to dissolved organic matter. *Chemosphere* 37, 861–874.

- Lyons, G., Genc, Y., 2016. Commercial Humates in Agriculture: Real Substance or Smoke and Mirrors? *Agronomy* 6, 50. <https://doi.org/10.3390/agronomy6040050>.
- Mantoura, R.F.C., Dixon, A., Riley, J.P., 1978a. The Complexation of Metals with Humic Materials in Natural Waters. *Estuar. Coast Mar. Sci.* 6, 387–408.
- Mantoura, R.F.C., Dixon, A., Riley, J.P., 1978b. The Complexation of Metals with Humic Materials in Natural Waters R. *Estuar. Coast Mar. Sci.* 6, 387–408.
- Mergen, M.R.D., Jefferson, B., Parsons, S.A., Jarvis, P., 2008. Magnetic ion-exchange resin treatment: Impact of water type and resin use. *Water Res.* 42, 1977–1988. <https://doi.org/10.1016/j.watres.2007.11.032>.
- Metcalfe, D., Rockey, C., Jefferson, B., Judd, S., Jarvis, P., 2015. Removal of disinfection by-product precursors by coagulation and an innovative suspended ion exchange process. *Water Res.* 87, 20–28. <https://doi.org/10.1016/j.watres.2015.09.003>.
- Mons, M., van Genderen, J., van Dijk-Looijaard, A., 2000. Inventory on the presence of pharmaceuticals in Dutch waters.
- Monteith, D.T., Stoddard, J.L., Evans, C.D., De Wit, H.A., Forsius, M., Högåsen, T., Wilander, A., Skjelkvåle, B.L., Jeffries, D.S., Vuorenmaa, J., Keller, B., Kopéček, J., Vesely, J., 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* 450, 537–540. <https://doi.org/10.1038/nature06316>.
- Neale, P.A., Mastrup, M., Borgmann, T., Schäfer, A.I., 2010. Sorption of micropollutant estrone to a water treatment ion exchange resin. *J. Environ. Monit.* 12, 311–317. <https://doi.org/10.1039/b913338k>.
- Onorato, C., Banasiak, L.J., Schäfer, A.I., 2017. Inorganic trace contaminant removal from real brackish groundwater using electrodialysis. *Separ. Purif. Technol.* 187, 426–435. <https://doi.org/10.1016/j.seppur.2017.06.016>.
- Peuravuori, J., 2000. Precision of isolation of aquatic humic matter by XAD-resin technology from NMR spectroscopy's point of view. *Int. J. Environ. Anal. Chem.* 76, 179–198. <https://doi.org/10.1080/03067310008034130>.
- Pourret, Olivier, Davranche, Mélanie, Gérard Gruau, A.D., 2007. Rare earth elements complexation with humic acid. <https://doi.org/10.1016/j.chemgeo.2007.05.018>.
- Ram, N., Raman, K.V., 1984. Stability constants of complexes of metals with humic and fulvic acids under non-acid-conditions. *Zeitschrift für Pflanzenernährung und Bodenkd* 147, 171–176. <https://doi.org/10.1002/jpln.19841470205>.
- Ritson, J.P., Bell, M., Graham, N.J.D., Templeton, M.R., Brazier, R.E., Verhoef, A., Freeman, C., Clark, J.M., 2014. Simulated climate change impact on summer dissolved organic carbon release from peat and surface vegetation: Implications for drinking water treatment. *Water Res.* 67, 66–76. <https://doi.org/10.1016/j.watres.2014.09.015>.
- Saracco, G., Zanetti, M.C., 1994. Ion Transport Through Monovalent-Anion-Permeable Membranes. *Ind. Eng. Chem. Res.* 33, 96–101. <https://doi.org/10.1021/ie00025a013>.
- Smedley, P.L., Kinniburgh, D.G., 2017. Molybdenum in natural waters: A review of occurrence, distributions and controls. *Appl. Geochem.* 84, 387–432. <https://doi.org/10.1016/j.apgeochem.2017.05.008>.
- STOWA 2013-23 Human pharmaceuticals in the water cycle, n.d.
- Vanoppen, M., Bakelants, A.F.A.M., Gaublomme, D., Schouteten, K.V.K.M., Van Den Bussche, J., Vanhaecke, L., Verliefde, A.R.D., 2015. Properties governing the transport of trace organic contaminants through ion-exchange membranes. *Environ. Sci. Technol.* 49, 489–497. <https://doi.org/10.1021/es504389q>.
- Vaselbehagh, M., Karkhanechi, H., Takagi, R., Matsuyama, H., 2015. Surface modification of an anion exchange membrane to improve the selectivity for monovalent anions in electrodialysis - experimental verification of theoretical predictions. *J. Membr. Sci.* 490, 301–310. <https://doi.org/10.1016/j.memsci.2015.04.014>.
- Wang, W., Li, X., Yuan, S., Sun, J., Zheng, S., 2016. Effect of resin charged functional group, porosity, and chemical matrix on the long-term pharmaceutical removal mechanism by conventional ion exchange resins. *Chemosphere* 160, 71–79. <https://doi.org/10.1016/j.chemosphere.2016.06.073>.
- WFD, 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. *Off. J. Eur. Parliam.* L327, 1–82. <https://doi.org/10.1039/ap9842100196>.
- World Health Organisation, 2000. Chapter 6.12 Vanadium. *Air Qual. Guidel.* 3, 1–9. https://doi.org/http://www.euro.who.int/_data/assets/pdf_file/0016/123082/AQG2ndEd_6_12vanadium.PDF.
- Wufuera, Rehemanjiang, Liu*b, Ying, Muc, Shuyong, Songd, Wenjuan, Xue, Yangc, Zhangf, Daoyong, Pan, Xiangliang, 2014. Interaction of Dissolved Organic Matter with Hg(II) along Salinity Gradient in Boston Lake. *Geochem. Int.* 52, 1072–1077. <https://doi.org/10.1134/S001670291412009X>.
- Zhang, Y., Van der Bruggen, B., Pinoy, L., Meesschaert, B., 2009. Separation of nutrient ions and organic compounds from salts in RO concentrates by standard and monovalent selective ion-exchange membranes used in electrodialysis. *J. Membr. Sci.* 332, 104–112. <https://doi.org/10.1016/j.memsci.2009.01.030>.
- Zhang, Y., Pinoy, L., Meesschaert, B., Van der Bruggen, B., 2011. Separation of small organic ions from salts by ion-exchange membrane in electrodialysis. *AIChE J.* 57, 2070–2078. <https://doi.org/10.1002/aic>.