

REMOVAL OF DISSOLVED ORGANIC CARBON AND BROMIDE BY A HYBRID ANION EXCHANGE-ULTRAFILTRATION SYSTEM

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ABSTRACT

Dissolved organic carbon (DOC) and bromide (Br⁻) are principal precursors in the formation of halogenated disinfection by-products resulting from chlorination of drinking water. Their effective removal from water represents, thus, one of the main challenges faced by drinking water treatment plants worldwide. The objective of this study was to evaluate the performance of a hybrid system based on the patented magnetic ion-exchange resin (MIEX®) combined with ultrafiltration (UF) in the removal of DOC and Br⁻ from water. The DOC removal was further investigated according to the molecular size distribution by high-performance size-exclusion chromatography (HPSEC) to identify which organic fractions were preferentially removed by the MIEX/UF process.

The pilot-scale hybrid MIEX/UF system was composed of a stirred tank where feed water was contacted in a fluidized bed mode with the MIEX resin followed by a UF module operating in an inside-out cross-flow filtration mode. Both concentrate and permeate streams from the UF unit were recirculated into the feed tank. Two different doses of MIEX (1 mL/L and 3 mL/L) were applied and compared. Samples of feed water, UF permeate and tank solution were regularly collected to assess the system performance in terms of removal of DOC and Br⁻.

Results demonstrated that the hybrid MIEX/UF system was able to remove TOC from water. The removal depended upon the MIEX dose applied. At a MIEX dose of 3 mL/L, the TOC removal was persistent over the 18-hr experiment at 48%. However, at a MIEX dose of 1 mL/L the removal ceased after 14 hr indicating likely saturation of MIEX towards TOC. With regard to Br⁻, the observed initial removals were lower (25% and 40% at MIEX dose of 1 mL/L and 3 mL/L, respectively), and they decreased to zero over the experiment indicating saturation of MIEX toward Br⁻ at both doses. Fractionation of DOC by HPSEC indicated that the highest molecular weight fraction was mainly removed by size-exclusion by the UF membrane, while lower molecular weight fractions seemed to be better removed by ion-exchange on the MIEX resin.

Keywords: anion-exchange resin, ultrafiltration, hybrid system, dissolved organic carbon, bromide, MIEX

1. Introduction

Dissolved organic carbon (DOC) and Br⁻ are found in many surface, ground and soil waters. Because they are principal precursors in the formation of disinfection by-products resulting from chlorination of drinking water, their removal from water is nowadays one of the main challenges faced by drinking water treatment plants (DWTP) worldwide. This need has favoured the development of novel technical approaches to achieve better removals of DOC and Br⁻ than conventional ones such as coagulation, activated carbon adsorption or membrane processes. One of such approaches is the combination of ion exchange (IEX) and ultrafiltration (UF) processes. The benefits of combining IEX-UF include enhanced removal of DOC by IEX that would not be retained by UF alone and prevention of UF membrane fouling during water treatment (Jarvis *et al.*, 2008).

In this work, the patented magnetic IEX resin (MIEX®) was evaluated. MIEX is a strong-base anion exchange that differs from conventional IEX resins by two unique properties: it is produced in the form of micro-sized beads (~180 µm, i.e. 2–5 times smaller than conventional resins) and it incorporates magnetic iron oxide within its core. The small size of the beads provides a high surface area that facilitates rapid exchange between DOC and the exchangeable ion (Cl⁻ in this case). The magnetic iron oxide allows the beads to agglomerate into larger, fast-settling particles facilitating separation and recycling of the resin in a continuous process (Drikas *et al.*, 2011). Moreover, MIEX has been reported to also exchange other anions from water such as Br⁻ (Hsu and Singer, 2010).

The objective of this study was to evaluate the performance of a hybrid MIEX/UF system in the removal of both DOC and Br⁻ from sand-filtered water collected at a DWTP. The DOC removal was further investigated according to the molecular size distribution by high-performance size-exclusion chromatography (HPSEC) to identify which organic fractions were preferentially removed by the MIEX/UF process.

2. Materials and methods

2.1. Experimental set-up

The pilot-scale hybrid MIEX/UF system was composed of a stirred tank where feed water was contacted in a fluidized bed mode with the MIEX resin followed by a UF module (Fig 1). The water/resin slurry was pumped then to a UFC M5-type (X-Flow) ultrafiltration (UF) module containing 100 1-m long and 0.8-mm-diameter hollow fibres corresponding to a filtration surface equal to 0.25 m². The UF polyethersulfone membranes (nominal MWCO of 100 kDa) operated in an inside-out cross-flow filtration mode. Both concentrate and permeate streams were recirculated into the feed tank. Periodic hydraulic backwashes with permeate (occasionally enhanced with NaOH+NaClO and HCl) were applied to restore the membrane's permeability. Two different doses of MIEX (1 mL/L and 3 mL/L) were applied and compared. Samples of feed water, UF permeate and tank solution were regularly collected to assess the system performance in terms of removal of DOC and Br⁻.

2.2. Analytical techniques

TOC was measured using a TOC analyser (TOC Shimadzu Model V CPH). Br⁻ was determined by ion chromatography (Dionex ICS-1000). Fractionation of DOC was performed by HPSEC using a Toyopearl TSK HW-50S column coupled to on-line UV254, organic carbon and organic nitrogen detectors. Such system separates DOC fractions according to their hydrodynamic molecular size. Table 1 gives details on the time elution, molecular weight (MW) and constituents of each fraction (Huber *et al.*, 2011).

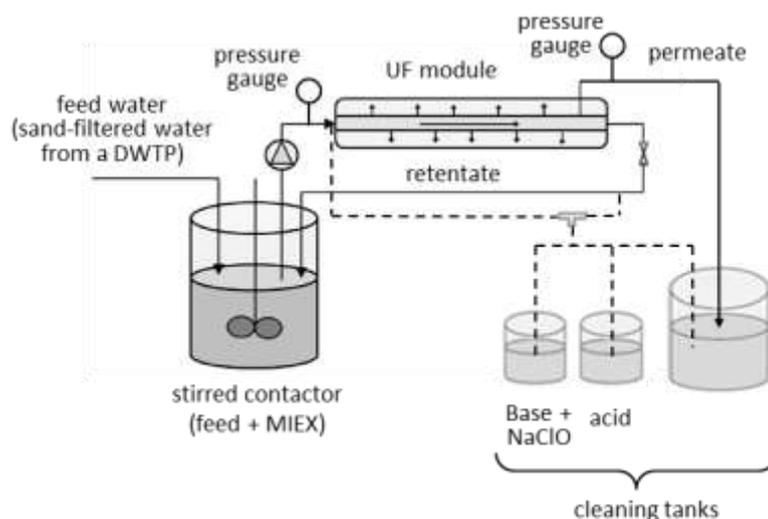


Figure 1: Schematic diagram of the pilot-scale hybrid MIEX/UF system.

Table 1: Chromatographic fractions of DOC as determined by the HPSEC technique.

DOC fraction	Abbreviation	Time (min)	MW (g/mol)	Constituents within fraction
Biopolymers	BP	31.0	>20000	Polysaccharides, proteins
Humic substances	HS	45.3	≈1000	Fulvic and humic acids
Building blocks	BB	49.2	300-500	Breakdown products of humics
Low Molecular Weight Neutrals	LMWN	52.4	<350	Alcohols, aldehydes, ketones, sugars and amino acids
Low Molecular Weight Acids	LMWA	57.3	<350	

3. Results

3.1. TOC and Br⁻ removal

Feed water showed TOC and Br⁻ concentrations of approx. 3.2 mg/L and 1.5 mg/L, respectively, over the course of the study (Fig 2a and b). It is of note that TOC concentration steeply decreased to 0.8 mg/L after 14 hr at a MIEX dose of 1 mL/L. Results showed that the MIEX/UF system was able to remove TOC and Br⁻ (Fig 2). However, the evolution and extent of these removals depended on the MIEX dose.

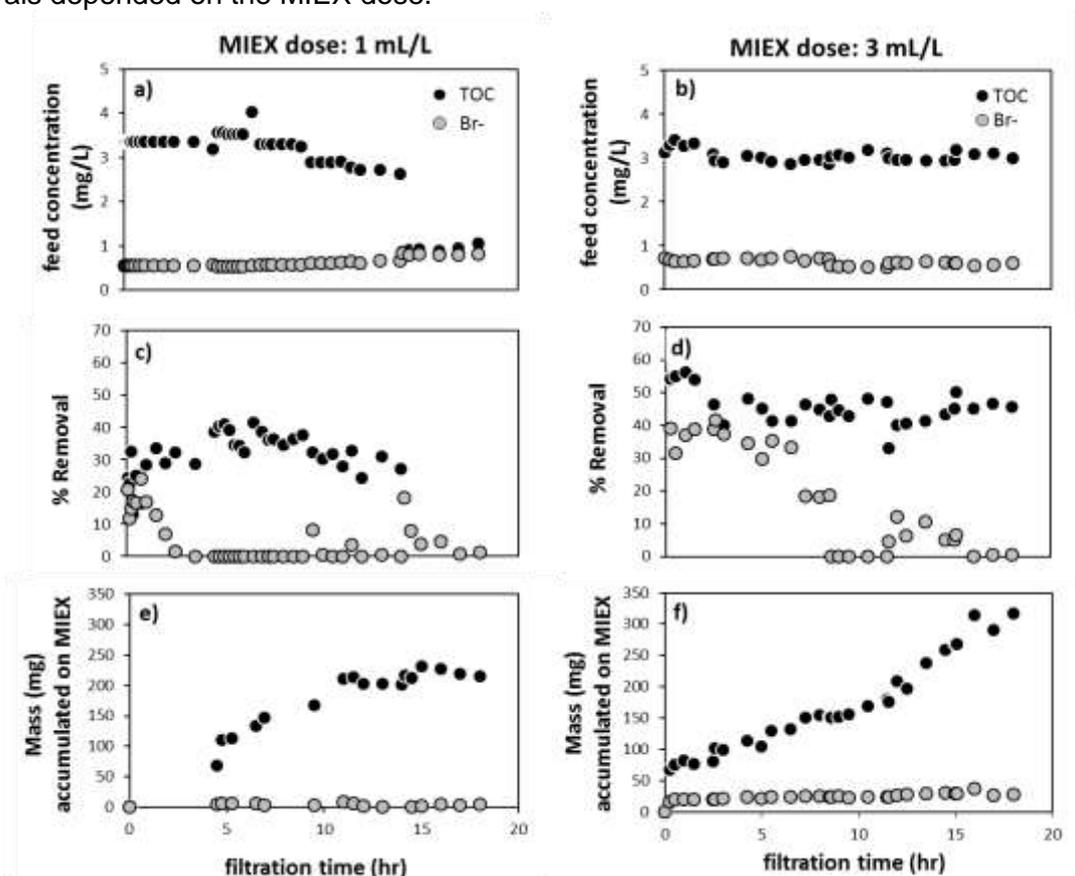


Figure 2: Evolution of a) inlet TOC and Br⁻ concentration, b) TOC and Br⁻ removal by the hybrid MIEX/UF system and c) TOC and Br⁻ mass accumulated on the MIEX resin

At a MIEX dose of 1 mL/L, initial removals of 32% and 16% were observed for TOC and Br⁻, respectively (Fig 2c). Br⁻ removal ceased 1 hr after the start of the experiment, suggesting saturation of MIEX toward Br⁻. As reported in previous studies, the MIEX effectiveness at removing Br⁻ can be inhibited by the presence of other anions (e.g. sulphate) (Hsu *et al.*, 2010). Removal of TOC persisted over approx. 14 hr, but then it sharply fell to undetectable levels. Although this may be indicative of saturation of MIEX also toward TOC, the coincidence of this abrupt decline with the steep decrease of inlet TOC concentration to near the detection limit

(~0.8 mg/L) (Fig 2a) suggests that TOC removal calculations may not be accurate and should be taken with precaution. Fig 2e shows the total amount (mg) of TOC and Br⁻ exchanged on the MIEX resin calculated through a mass-balance. The figure shows that the amount of TOC and Br⁻ on MIEX reached a plateau at 220 mg TOC and 4 mg Br⁻. The appearance of this plateau suggesting MIEX saturation was concomitant with the fall of its removal capacity.

At a MIEX dose of 3 mL/L, the system achieved higher and more persistent TOC and Br⁻ removals (Fig 2d). The initial TOC removal was 55%, and it maintained stabilized at 48% over the experiment, indicating that MIEX was able to decrease TOC concentration without reaching saturation yet. Br⁻ was initially removed at a percentage of 37%, but after approx. 7 hr the removal decreased to zero indicating that MIEX was saturated toward Br⁻ and that fresh Br⁻ entered into the system remained in water. In accordance with the continuous removal of TOC, Fig 2f shows an increasing amount of TOC accumulated on the MIEX resin (>300 mg TOC by the end of the experiment).

3.2. Removal of DOC fractions

Results showed that, under both MIEX doses, TOC was removed since the very beginning of the experiment, but also that there was a fraction of TOC that was not exchanged onto MIEX and permeated the UF membranes. Comparison of HPSEC chromatograms between feed water and UF permeate (Fig 3a and b) showed that the system basically removed mid- to low-MW fractions (reduced peaks for BB and LMWA) and high MW fractions (BP). Comparison against the chromatogram for the solution in the tank with MIEX revealed that the removal mechanisms for these fractions were different.

The removal mechanism for BP seemed to be not via ion-exchange onto MIEX (BP remained in solution when in contact with MIEX as highlighted by the large peak in Fig 3c) but via size exclusion by the UF membrane. This is in accordance with previous works reporting poor removals of high MW compounds by MIEX (Humbert *et al.*, 2012) but moderate or high removals of high MW compounds by UF (Gibert *et al.* 2015).

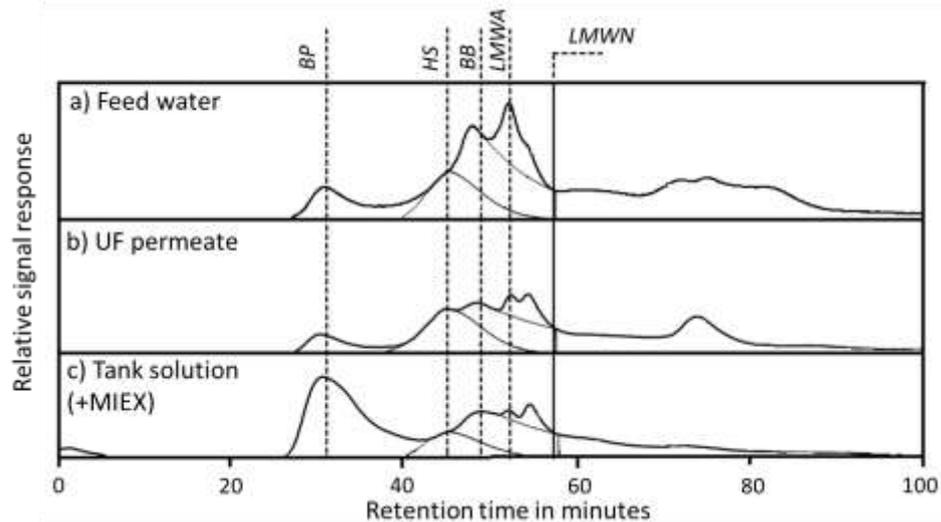


Figure 3: HPSEC chromatograms for feed water, UF permeate and tank solution

Contrarily to BP, the lower MW fractions BB, LMWA and LMWN seemed to be better removed by ion-exchange on MIEX, as highlighted by decreased peaks in the tank solution (Fig 3c), but not by the UF membrane, as little differences in their peaks were observed between the tank solution and the UF permeate. This agreed with the preferential removal of low MW fractions by MIEX (Humbert *et al.*, 2012) but its low retention by UF membranes (Gibert *et al.*, 2015) reported in previous studies.

4. Conclusions

Results demonstrated that the hybrid MIEX/UF system was able to remove TOC from sand-filtered water. At a MIEX dose of 3 mL/L, the removal was persistent over the 18-hr experiment at 48%. However, at a MIEX dose of 1 mL/L the removal ceased after 14 hr indicating likely saturation of MIEX towards TOC. With regard to Br⁻, the observed initial removals were lower (25% and 40% at MIEX dose of 1 mL/L and 3 mL/L, respectively), and they decreased to zero over the experiment indicating saturation of MIEX toward Br⁻ at both doses. Fractionation of DOC by HPSEC indicated that the highest MW fraction was mainly removed by size-exclusion by the UF membrane, while lower MW fractions seemed to be better removed by ion-exchange on the MIEX resin.

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