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Removal of dissolved organic carbon and bromide by a hybrid MIEX-ultrafiltration system: Insight into the behaviour of organic fractions

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HIGHLIGHTS

- A continuous-flow hybrid system MIEX/UF for the removal of DOC and Br^- is proposed.
- MIEX exhibited higher affinity toward DOC than toward Br^-.
- High molecular weight organic fractions were mainly removed by size exclusion by UF.
- Low molecular weight organic fractions were mostly removed by ion-exchange on MIEX.
- The hybrid system removed DOC (by 32–46%) more efficiently than UF alone (<5%).

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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 pilot-scale hybrid system based on the patented magnetic ion-exchange resin (MIEX) combined with ultrafiltration (UF) in the removal of DOC and Br^- from water. 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^-. DOC was characterised by high-performance size-exclusion chromatography (HPSEC) and 3D-fluorescence excitation-emission matrix (FEEM) to identify which organic fractions were preferentially removed by the MIEX/UF process. Results demonstrated that the hybrid MIEX/UF system was able to remove DOC and Br^- from water. The evolution and extent of these removals depended on the MIEX dose applied, with percentage removals clearly increasing when the MIEX dose was increased from 1 mL/L to 3 mL/L. MIEX exhibited higher affinity toward DOC than toward Br^-. Saturation of MIEX toward Br^- was achieved short after the start of the experiment, while removal of DOC persisted until the end of the experiment. 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. FEEM analysis revealed a poor affinity of MIEX toward microbial by-products, whereas fulvic and humic acid-like material were the most retained by MIEX.

1. Introduction

Dissolved organic carbon (DOC) and bromide (Br^-) are principal precursors of halogenated disinfection by-products resulting from chlorination of drinking water [1]. The need for efficiently removing DOC and Br^- has prompted drinking water treatment plants (DWTPs) to explore novel technical approaches that outperform conventional treatments (such as coagulation/flocculation, sand filtration or activated carbon adsorption) [2–4].

One of such approaches is the filtration by membranes. Microfiltration (MF) and ultrafiltration (UF) membranes can effectively remove particles, colloids and bacteria at low transmembrane pressures (not exceeding 2 bar), but are poorly effective at removing DOC and ions such as Br^- due to their relatively large mem-

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List of symbols and acronyms

AER	anion exchange resin
BB	building blocks
BP	biopolymers
$c^{t}_{DOC,feed}$	DOC concentration in feed at any time (mg/L)
$c^{t}_{DOC,permeate}$	DOC concentration in permeate at any time (mg/L)
$c^{t}_{DOC,tank}$	DOC concentration in the tank at any time (mg/L)
DOC	dissolved organic carbon
DWTP	drinking water treatment plant
FEEM	fluorescence excitation emission matrix
HPSEC	high-performance size-exclusion chromatography
HS	humic substances
LMWA	low molecular weight acids
LMWN	low molecular weight neutrals
MF	microfiltration
MIEX	magnetic ion exchange
MW	molecular weight
NF	nanofiltration
Q_{feed}	feed flow rate (L/s)
$Q_{permeate}$	permeate flow rate (L/s)
$q^{in,t}_{DOC}$	total DOC amount entered the hybrid system at any time (mg)
$q^{out,t}_{DOC}$	total DOC amount exited the hybrid system at any time (mg)
$q^{accum,t}_{DOC}$	DOC amount accumulated within the hybrid system at any time (mg)
$q^{diss,t}_{DOC}$	DOC amount dissolved in water (mg)
$q^{MIEX,t}_{DOC}$	DOC amount loaded onto the MIEX resin (mg)
$q^{MIEX,t}_{Br}$	Br^- amount loaded onto the MIEX resin (mg)
RO	reverse osmosis
UF	ultrafiltration
V_{tank}	volume of the tank (L)

brane pore sizes [5,6]. The removal of DOC and ions can be attained by using denser membranes such as nanofiltration (NF) and reverse osmosis (RO) membranes, but at expenses of applying high transmembrane pressures.

A significant drawback of the application of membrane technology, regardless the type of membrane used is membrane fouling with the subsequent reduction of the hydraulic permeability of the membrane [5]. DOC is acknowledged to be a main foulant even for MF and UF membranes, which can be fouled by organic substances through sieving effects and sorption on/in the membrane [6,7]. Thus, removal of DOC prior to a membrane step is usually necessary to alleviate membrane fouling.

Another approach to remove DOC is the application of an anion exchange resin (AER), taking advantage that most organic compounds in natural waters are in ionic form [4,8]. An AER that is receiving particular attention is the patented MIEX marketed by Orica Watercare. When in contact with it, negatively charged DOC is removed by exchanging with the mobile counterion on active sites on the MIEX surface (usually Cl^-), resulting in a reduction in the DOC concentration and a small increase in Cl^- concentration in the treated water [9,10]. MIEX differs from conventional AER 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 Cl^- [9–11], whereas the magnetic iron oxide within its core allows the beads to agglomerate into larger, fast-settling particles facilitating separation and recycling of the resin in a continuous process [2,5,12]. Due to these properties, MIEX resin is designed to be used either in a slurry contactor or in a fluidized bed, unlike larger, traditional AER commonly operated in packed beds [12]. In addition to DOC, MIEX has been reported to also exchange other anions from water such as Br^- [13].

The MIEX resin only removes part of DOC from water but does not remove turbidity, which needs to be removed (together with any resin beads that might be carried away from the system) by some form of treatment, e.g. by UF membranes. This combination gives rise to the hybrid MIEX/UF system, whereby water is first contacted with the MIEX resin and then the slurry MIEX/water is filtered through the UF membrane, which retains the loaded MIEX beads and turbidity. The premise of such an approach is that the hybrid system benefits from the enhanced removal of DOC by MIEX that would not be retained by UF alone [14], the removal of turbidity (and part of DOC) by UF not retained by MIEX alone and, according to some studies, the prevention of UF membrane fouling by DOC sorption onto the membrane [15]. Moreover, since fouling has recently been reported to be worsened by upstream oxidation processes (e.g. ozonation) commonly applied in DWTP [16], it is likely that MIEX would serve as a more desirable upstream treatment unit than oxidation.

Like with any treatment targeting DOC, characterisation of DOC by novel techniques such as high-performance size-exclusion chromatography (HPSEC) and fluorescence spectroscopy providing the 3-D fluorescence excitation-emission matrix (FEEM) has attracted the attention of researchers working with MIEX. Nevertheless, there are still some discrepancies on how physicochemical properties of DOC affects its removal by MIEX [9,10]. As outlined by Mergen and co-workers, "the current opinion with regard to the types or organic material preferentially removed by the [MIEX] resin is unclear" and, therefore, "there is a strong need for further research into the types of organic material that can be removed by the [MIEX] resin" [17].

There is relatively abundant research on MIEX for the removal of DOC from natural water. However, and although full-scale application of MIEX resin is intended for use in a continuous-flow process, most of the published studies have been carried out on a batch basis following either the single-loading procedure or, in an attempt to better mimic a continuous-flow mode, multiple-loading procedure [3,8,12,15]. To get insight into the behaviour of DOC fractions, some of these studies have applied HPSEC and/or FEEM [4,7,18,19]. Some others have included Br^- as target solute to be removed together with DOC, but often at relatively low concentrations of both Br^- and SO_4^{2-}, which is a competitor for the MIEX exchangeable sites [13,20,21]. While these batch studies provide useful information on the capabilities of MIEX resin to remove DOC (and to a lesser degree Br^-) their results cannot always be extrapolated to continuous-flow systems. Published studies based on continuous-flow systems can be found in the scientific literature [11,12,22–24] and, of these, some have characterised DOC by means of HPSEC [11,12,22] but to our knowledge none with FEEM. Finally, even less studies exist on hybrid systems based on MIEX/UF (or MF). Of these, some focus on the treatment of secondary- and tertiary- wastewater effluents that exhibit different organic composition and treatability from surface water [14,25], and fewer on surface water [2,5]. Again, some of these studies characterise DOC by HPSEC but not by FEEM.