Removal of bromide from natural waters: Bromide-selective vs. conventional ion exchange resins

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HIGHLIGHTS

- Br-selective resins were tested under typical and challenging conditions.
- Performance of Br-resins was better than conventional resins.
- Characteristics of natural organic matter did not affect Br-resin performance.
- Formations of Br-DBPs and total DBPs were reduced by 90% and 85% with Br-resin.

GRAPHICAL ABSTRACT
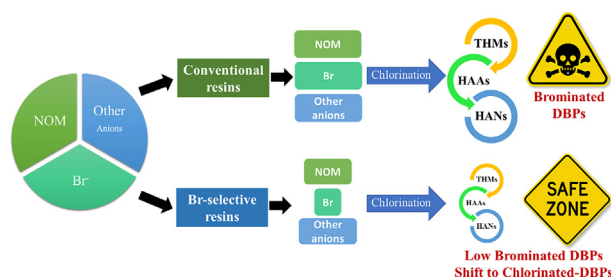
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ABSTRACT

The presence of bromide (Br⁻) in water results in the formation of brominated disinfection byproducts (DBPs) after chlorination, which are much more cytotoxic and genotoxic than their chlorinated analogs. Given that conventional water treatment processes (e.g., coagulation, flocculation, and sedimentation) fail to remove Br⁻ effectively, in this study, we systematically tested and compared the performance of different anion exchange resins, particularly two novel Br-selective resins, for the removal of Br⁻. The resins performance was evaluated under both typical and challenging background water conditions by varying the concentrations of anions and organic matter. The overall Br⁻ removal results followed the trend of Purolite-Br ≥ MIEX-Br > IRA910 ≥ IRA900 > MIEX-Gold > MIEX-DOC. Further evaluation of Purolite-Br resin showed Br⁻ removal efficiencies of $93.5 \pm 4.5\%$ for the initial Br⁻ concentration of 0.25 mg/L in the presence of competing anions (i.e., Cl^-, NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, and a mixture of all five), alkalinity and organic matter. In addition, experiments under challenging background water conditions confirmed the selectivity of the resins (i.e. Purolite-Br and MIEX-Br) in removing Br⁻, with SO_4^{2-} and Cl^- exhibiting the greatest influence upon the resin performance followed by NOM concentration, regardless of the NOM characteristic. After Br⁻ removal, both the subsequent formation of brominated DBPs (trihalomethanes, haloacetic acids, and haloacetonitriles), and the total organic halogens (TOX), decreased by ~90% under the uniform formation conditions. Overall, Br-selective resins represent a promising alternative for the efficient control of Br-DBPs in water treatment plants.

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1. Introduction

Bromide (Br⁻), which is ubiquitous in both fresh waters and seawaters with concentration ranges of 6–200 μg/L and 66,000–68,000 μg/L, respectively (Amy et al., 1993; Krasner et al.,

2002; Magazinovic et al., 2004). However, Br⁻ concentrations may present within a range of 800−1000 μg/L in surface waters as a result of seawater intrusion (Magazinovic et al., 2004). The concentration of Br⁻ in surface waters can be also elevated as a result of discharges from Br⁻containing anthropogenic sources (e.g., coal-fired power plants, industrial effluents, hydraulic fracturing, and wastewater treatment plants) (Amy et al., 1993; Krasner et al., 2002; Vanbriesen and Wilson, 2014). For example, Br⁻ concentration has been reported between 100 and 2000 μg/L in oil and gas produced waters (Vanbriesen and Wilson, 2014). Further, the recent and increasing trend of using impaired and alternative water sources that are characterized with high bromide levels makes their mitigation more imperative (Watson et al., 2012a, 2012b). Although Br⁻ itself possesses no direct public health impacts, it reacts with disinfectants during water treatment thus causing its manifestation as a precursor of brominated disinfection by-products (DBPs), which are more cyto- and genotoxic than chlorinated DBPs (Plewa et al., 2004; Richardson et al., 2007). Therefore, the removal of Br⁻ from water is critical for mitigating the formation of these toxic brominated DBPs (e.g., bromate, brominated trihalomethanes and haloaceticacids).

Membrane filtration (e.g., reverse osmosis, nanofiltration), electrochemical processes (e.g., electrolysis, capacitive deionization), and sorption processes (e.g., activated carbon and ion exchange resins) are the most used three techniques in Br⁻ removal (Watson et al., 2012a, 2012b; Gong et al., 2013; Wiśniewski et al., 2014; Krasner et al., 2016; Dorji et al., 2018). The use of membranes in Br⁻ was most effective, with a removal rate of approximately 93−99.3%, depending upon the membrane characteristics and operational conditions (Bartels et al., 2009; Watson et al., 2012a, 2012b; Dorji et al., 2018). However, membrane technologies are expensive to implement. Electrochemical removal, which involves oxidizing bromide to bromine in drinking water, is pH dependent, and it requires a higher energy level relative to conventional treatment processes and the formation of different toxic brominated DBPs after oxidation is also a concern (Kimbrough and Suffet, 2002; Watson et al., 2012a, 2012b). Activated carbon adsorption is also characterized by a low level of Br⁻ removal efficiencies (22−30%) (Watson et al., 2016). Therefore, various concepts have been developed to improve Br⁻removal efficiencies, most notably the development and use of silver impregnated activated carbons. Although results in the range of 40−90% were reported in the presence of background anions, chloride, and natural organic matter (NOM) negatively affected Br⁻ removal rates (Ateia et al., 2019; Chen et al., 2017; Krasner et al., 2016; Watson et al., 2012a, 2012b; Watson et al., 2016). It is also noteworthy that although conventional treatment and activated carbon adsorption processes remove NOM while failing to remove Br⁻ from water, the result was an elevated Br⁻:DOC ratio and an increased formation of brominated-DBPs in the treated water (e.g., Metcalfe et al., 2015; Phetrak et al., 2014).

Ion exchange (IX) is a sorption-based technology that is relatively easy-to-operate water treatment process in which IX resins are regenerated and reused to reduce the treatment cost (Walker and Boyer, 2011). See Table S1 for a detailed compilation of the previous studies regarding the use of IX resins for Br⁻ removal. Of the commercially available polyacrylic and polystyrene IX resins tested to determine their efficacy in removing Br⁻ from water (Boyer and Singer, 2006; Walker and Boyer, 2011; Phetrak et al., 2014), the removal efficiency of them all decreased dramatically in the presence of background anions (e.g., sulfate, chloride, nitrate), alkalinity, and NOM in water (Johnson and Singer, 2004; Humbert et al., 2005). Although a new series of bromide selective resins are now available, there is no study that investigate and compare their performance with other conventional anion exchange resins.

Herein, we detail our results of the first systematic study using two Br-selective IX resins (i.e., Purolite Bromide Plus/9218 and MIEX-Bromide) and traditional anion exchange resins (i.e. IRA900, IRA910, MIEX-Gold, and MIEX-DOC) for the removal of Br⁻ under varying water chemistry conditions. The specific objectives of this study were to investigate the effect of (i) background anion type and concentration, (ii) operational parameters (contact time, bed volume, pH, and regeneration), (iii) competing anions and alkalinity, and (iv) NOM characteristic and concentration on the removal of Br⁻ and subsequent formation and speciation of brominated DBPs after chlorination. Results clearly indicate the efficacy of IX resins for the selective removal of Br⁻ in water treatment plants.

2. Materials and method

2.1. Materials

Two commercially available Br-selective IX resins (i.e., Purolite Bromide Plus/9218 and MIEX-Bromide), two traditional styrene-based anion exchange resins (i.e. IRA900 and IRA910) and two traditional methacrylate-based (i.e. MIEX-DOC and MIEX-Gold) were examined in this study. Purolite Bromide Plus/9218 was obtained from the Purolite chemical manufacturing company (PA, USA), and the MIEX resin samples were obtained from IXOM Watercare, a water treatment solutions firm (Centennial, CO, USA). The IRA900 and IRA910 resins, the sodium chloride, sodium bicarbonate, sodium nitrate, sodium sulfate salts, and the Br⁻, chloride (Cl⁻), nitrate (NO₃⁻), nitrite (NO₂), phosphate (PO₄³⁻), and sulfate (SO₄²⁻) solutions were purchased from Sigma Aldrich, USA. A list of all resins and their respective characteristics are provided in Table 1 in SI.

2.2. Bromide removal experiments

The resins were pre-washed before the experiments to remove any impurities (Text S1 in SI), as described in our previous studies (Gan et al., 2013; Beita-Sandí and Karanfil, 2017). The preliminary experiments were then undertaken using varying Br⁻ concentrations (100−1000 μg/L), contact times (5−20 min), bed volumes (BV = 200−1400), and pH (5.5−10). Based on the results of the preliminary tests, the initial Br⁻ concentration, contact time, bed

Table 1
Characteristics of the tested resins.

Resin	Capacity (meq/ml)	Ionic Form	Particle size (μm)	Polymer structure	Functional Group
Purolite® Bromide Plus/9218	0.9	Cl⁻	520−620	Gel polystyrene crosslinked with divinylbenzene	Proprietary
MIEX-Bromide	0.9	Cl⁻	80−650	Macroporous crosslinked polyacrylate/divinylbenzene	Proprietary
IRA 900	≥1.00	Cl⁻	650−820	Styrene divinylbenzene copolymer	Trimethyl ammonium
IRA 910	≥1.00	Cl⁻	530−800	Macroreticular crosslinked polystyrene	Dimethyl ethanol ammonium
MIEX-DOC	0.4−0.5	Cl⁻	100−400	Macroporous poly methacrylate/divinyl benzene	Trimethyl Ammonium
MIEX-Gold	0.4−0.55	Cl⁻	100−400	Macroporous poly methacrylate	Trimethyl Ammonium

volume and pH were set at 250 μg/L, 15 min, 600, and 6.5, respectively (See Fig. S1 in SI). The resin was regenerated by mixing with a 10% NaCl solution (ACS grade) at three BV (mL %10 NaCl solution/mL resin volume) and the resin then rinsed three times with DDI (distilled and deionized) water prior to storage until further use. The resin was observed to recover its Br^- removal character after all regeneration cycles. All experiments were run in duplicates with the results reported as an average ± percentage difference.

Comparison of resins: The Br^- removal efficiencies of all selected resins were tested concurrently in DDI under varying background anion concentrations (i.e. SO_4^{2-} [25−400 mg/L], Cl^- [25−400 mg/L], Alkalinity [50−400 mg/L as $CaCO_3$], NO_3^- [10−50 mg/L] and PO_4^{3-} [5−25 mg/L]). The experimental design is detailed in Table S2 in SI.

Comprehensive resin testing: Here, the competition between Br^- and the other anions (i.e., NO_3^-, SO_4^{2-}, NO_2^-, PO_4^{3-}, Cl^-), as well as alkalinity, was examined under two experimental conditions: 1) testing the effect of each individual anion under a typical and challenging concentration level, and 2) testing the effect of the mixture of all anions under typical and challenging concentration levels (with the anion concentrations determined based upon the surface water level). The experimental conditions are detailed in Table S4. For selected anion concentrations, the Br^- removal rates were also examined in NOM solutions. NOM powders were extracted from surface water by reverse osmosis isolation. XAD-4 and XAD-8 resins were used to fractionate NOM to operationally hydrophobic (HPO) and transphilic (TPH) fractions. The detailed fractionation process was reported in our previous study (Karanfil et al., 2007; Liu et al., 2019; Song et al., 2009). The characteristics of the NOM fractions are detailed in Table S5 in SI. Experiments were conducted in two different NOM fractions with a specific ultraviolet absorbance ($SUVA_{254}$) of 1.7 and 3.0 L/m.mg and at two different dissolved organic carbon (DOC) concentrations of 2.0 and 7.5 mg/L (Table S6). The analytical methods used in this study and the detection limits (DL) are provided in the SI (Table S7).

2.3. Chlorination procedures

A modified uniform formation conditions (UFC) test was used to simulate the formation of DBPs from NOM solutions in distribution systems (See in Text S2 in SI). Prior to the addition of the oxidant, a phosphate buffer was used to adjust the pH of the samples to 7.8. Samples were chlorinated from a stock chlorine solution (1000 mg/L as Cl_2) to achieve a free chlorine residual of 1 mg/L as Cl_2 after 24 h. After 24 h of reaction time, the samples were analyzed for residual chlorine according to the DPD colorimetric method (SM 4500-Cl G) (APHA, 2005). The residual chlorine was quenched with a stoichiometric amount of ascorbic acid, and the samples analyzed for THMs, HAAs, HANs, and TOX (i.e. TOCl and TOBr). A detailed description of DBPs and TOX analyses is provided in the Text S2.

2.4. BSF and toxicity calculations

The bromine substitution factor (BSF) ranges, which fell between 0 and 1, were calculated by the ratio-of-molar concentration of bromine in a given DBP class (i.e. THMs, HAAs, HANs etc.) to the total molar concentration of chlorine and bromine in that class (Hua et al., 2006; Ersan et al., 2019) (Eq. (1)).

$$BSF = \frac{\sum Br_{DBP}}{\sum Br_{DBP} + \sum Cl_{DBP}} \quad (1)$$

The cytotoxicity of the samples were calculated by dividing molar concentration of DBPs (i.e. THMs, HAAs and HANs) by the LC_{50} (toxicity index) values (as shown in Eq. (2)) of the individual DBP species, which were obtained established methods (Muellner et al., 2007; Plewa et al., 2010; Wagner and Plewa, 2017; Liu et al., 2018). The toxicity index for DBPs is also detailed in Table S9 in SI. During this study, the aim was to evaluate the effect of individual DBPs on total calculated toxicity, and its change with removing Br^- by selective resin.

$$Cytotoxicity = \frac{DBP\ concentration}{LC_{50}} \times 10^{-3} \quad (2)$$

3. Results and discussion

3.1. The Br^- removal selectivity of different resins under changing anion levels

Different Cl^- form resins composed of varying polymeric structures and functional groups were analyzed, the characteristics of which are provided in Table 1. Purolite-Br resin is gel polystyrene crosslinked with divinylbenzene with proprietary functional groups and MIEX-Br resin is a macroporous crosslinked polyacrylate/divinylbenzene with proprietary functional groups. Both of the IRA900 and IRA910 are styrene-divinylbenzene copolymers and macroreticular crosslinked polystyrene with trimethyl and dimethyl ethanol ammonium functional groups, respectively (See in Table 1). Furthermore, MIEX-Gold and MIEX-DOC resins are macroporous polymethacrylate (known as polyacrylic) within the trimethylamine functional group. As summarized in Table S1, although the IRA900 and IRA910 are efficient mechanism for Br^- removal, there is no available data in the literature comparing the performances of these resins with both of the newly developed Br-selective resins under comparable conditions. Therefore, the Br^- removal efficiencies of the resins were evaluated under the same operating conditions and challenging water matrices of the selected anions (Table S2). Results from previous studies regarding the removal of Br^- indicated that Cl^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, and alkalinity were the most influential parameters in terms of decreasing the performance of IX resins (Table S1) (Boyer and Singer, 2005; Hsu and Singer, 2010). Therefore, the investigation of selective removal of bromide in the presence of competing anions is necessary to resolve these limitations during water treatment. Overall, under all conditions Purolite-Br resin exhibited the highest removal efficiencies (up to 90%) for Br^- followed by MIEX-Br, IRA910, IRA900, MIEX-Gold, and MIEX-DOC, respectively (Fig. 1 and Fig. S2). The increasing concentrations of SO_4^{2-} (25→400 mg/L) and Cl^- (25→400 mg/L) were the coexisting anions exhibiting the greatest influence in terms of decreasing the Br^- removal efficiency for all resins ([Br^-]$_0$ = 250 μg/L) at 600 BV and 15 min.

Although the ion-exchange mechanism is based on simple electrostatic interaction, particle size, the nature of the counter ions, the hydration energy of the anions, the types of functional groups on resin surfaces and the affinity for different ions significantly are all known as influencers upon the reaction. The selectivity of the resins for the removal of Br^- was evaluated by calculating the meq ratio of the total capacity of the resin and the meq concentration of each anion in the solution at each condition analyzed (Tables S2−3). As shown in Figs. S3a and S3b, the concentration of SO_4^{2-} and Cl^- were in the range of 0.5−7.5 times the capacity of the tested resins. No removal was observed in terms of both traditional polystyrene and polymethacrylate (IRA and MIEX) resins when the meq ratios were 2.5 and 3.5 for SO_4^{2-} and Cl^-, respectively. However, Br^- removal efficiencies using Purolite-Br were 60% and 40% at the same meq concentrations in 15 min contact time and 600 BV. Further, both the Purolite-Br and MIEX-Br
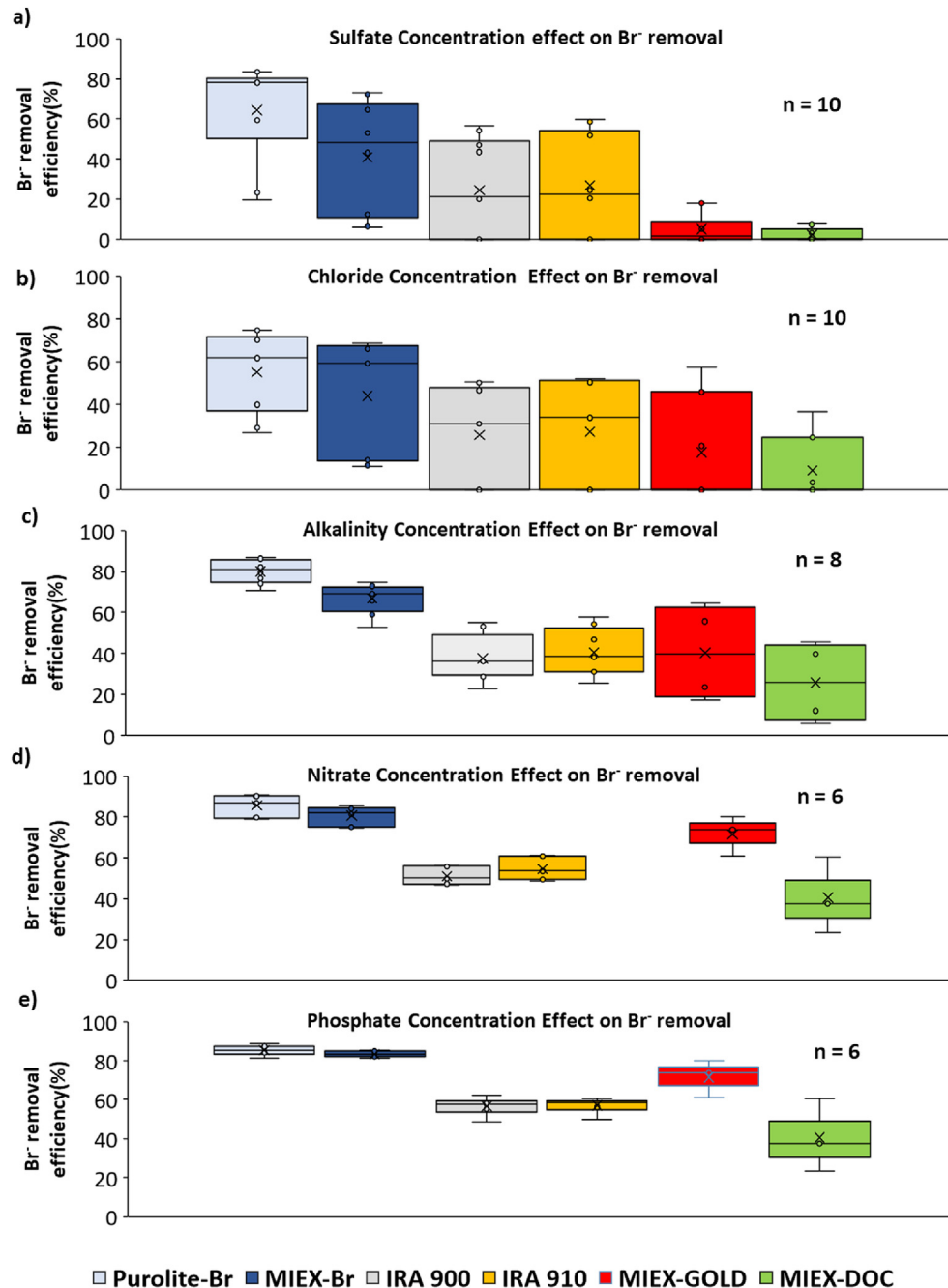
Fig. 1. The overall Br⁻ removal comparison with different resins under changing **a)** Sulfate (25, 50, 100, 200 and 400 mg/L), **b)** Chloride (25, 50, 100, 200 and 400 mg/L), **c)** Alkalinity (50, 100, 200 and 400 mg CaCO₃/L), **d)** Nitrate (10, 25, and 50 mg/L) and **e)** Phosphate (5, 10 and 25 mg/L) concentration in DDI. Experimental conditions: $[Br^-]_0 = 250 \, \mu g/L$, pH = Ambient, T = 21 ± 1 °C, Contact time = 15 min, Settling Time = 2 min, Mixing (rpm) = 150, BV = 600; **n** shows the number of measurements for individual anions.

maintained their Br⁻ removal efficacies even when the meq concentrations of SO_4^{2-} and Cl^- were 5.5 and 7.5-fold that of the reported resin capacities. Similar Br⁻ removal trends were observed for the calculated meq ratios in terms of the alkalinity, nitrate, and phosphate (Figs. S3c–e). Although the background competing anions were characterized by a concentration of $10^2 - 10^4$ times higher meq than Br,⁻ Purolite-Br, and MIEX-Br, the resins continued to remove Br⁻ under all tested conditions. Thus, it was important to determine the resin's selectivity towards Br⁻ in the presence of high concentrations of competing anions as well as understanding the impact of the resin's polymer structure and functional groups (Tables 1–S4). For instance, the hydrophobic character of the

polystyrene resin and contaminant has a significant effect on the selectivity of the resin. Therefore, while polystyrene resins are more efficacious in removing Br⁻ from water *(ΔG°, -348 kJ/mol for Br⁻)*, conventional polyacrylic resins tend to remove hydrophilic anions such as SO_4^{2-} with their higher hydration energy *(ΔG°, -1103 kJ/mol)* (Gu et al., 2004). It is a crucial point for the selective removal of Br⁻, given that also resin hydrophobicity is also influenced by the type of polymer structure of the resin and the chain length of functional groups. As the functional groups of the novel Br-resins are proprietary (i.e. no detailed information provided by the manufacturers) no comparison and discussion about functional groups and their effect on selectivity was undertaken in this study.

Although conventional styrene-based resins are characterized by different skeleton structures (i.e. IRA900 has a styrene-divinylbenzene copolymer and IRA910 a macroreticular cross-linked polystyrene), the adsorption abilities of both are nearly identical under all tested conditions. Furthermore, while the MIEX-Gold and MIEX-DOC resins have the same poly methacrylate structure with trimethylamine functional groups, the higher surface area of the MIEX-Gold gave it a greater efficiency over the MIEX-DOC resin. The polymer structure of the MIEX resins makes them particularly suite for SO_4^{2-} removal. Further an analysis of the NO_3^- concentration effect indicated that the acrylic resin was more efficient than styrene-based conventional resins in removing Br^- from water, as these traditional styrene-based resins remove monomers based on its hydration energy ($\Delta G°$, -314 kJ/mol for NO_3^-). Further the lower hydration energy and higher concentration of NO_3^- over Br^- means that traditional styrene-based resins are efficient in NO_3^- rather than Br^- removal. Overall, these results indicate the presence of Br-selective sites in both Purolite-Br and MIEX-Br as compared to conventional styrene and acrylic-based resins. Between the novel selective resins, gel type polystyrene Purolite-Br resin showed slightly higher sorption of Br^- relative to the macroporous crosslinked polyacrylate/divinylbenzene MIEX-Br resin. Although the Br-resins analyzed had identical capacities and counterions (Cl^-), both the polymer (Purolite-Br: polystyrene, MIEX-Br: polyacrylate) and pore structures (Purolite-Br: gel type, MIEX-Br: macroporous type) of those Br-resins affected the degree of the Br^- removal. Similarly, although the macroporous resins exhibit a greater physically stability, the gel resins are characterized by a much faster exchange kinetics during the given contact time (Flowers et al., 2012). As such, the Purolite-Br resin, which exhibited a superior performance under tested background conditions, was selected and used for the experiments detailed below.

3.2. Removal of Br^- in the presence of NOM and competing anions

In this section, the performance of Purolite-Br resin was tested under a varying set of challenging conditions of mixed anions and mixed anions with NOM, with concentrations selected using the surface water characterization as the criteria (see the detailed experimental conditions in Tables S4 and S6). For purposes of comparison, the individual effects of those various anions were tested under relevant concentrations in terms of their presence in natural water systems. The results showed that Purolite-Br removed 89–96% of Br^- ([Br]$_0$: 0.25 mg/L), 10 mg-NO_3/L, 0.5 mg-NO_2/L, 10 mg-SO_4^{2-}/L, 0.5 mg-PO_4^{3-}/L, and in the mixture of all four (Fig. S4). The anion with the greatest influence was Cl^-, as it reduced the Br^- removal to 81% at a Cl^- concentration of 7.5 mg/L (i.e., Cl^- : Br^- ratio = 30). Experiments were next conducted under challenging background water chemistry conditions in which the concentrations of anions were spiked (Table S4). The Br^- removal rate, which was within a range of 66–89% under these elevated conditions, was affected when all anions and alkalinity were mixed at very high concentrations (Fig. S4). It should be noted that the total meq concentration of all anions in the solution was 25.5, while the total meq of the reported resin available sites was a mere 4.5 for the 5 ml Purolite-Br resin.

To investigate the effect of NOM on Br^- removal, two NOM solutions with different aromaticity, as indicated by $SUVA_{254}$ values (Tables S5 and S6), were tested. At 2.0 mg-C/L DOC concentration, the Br^- removal efficiencies in both NOM were in the range of 83–85%, indicating that the difference in the NOM aromatic character had no effect upon the Br^- rate of removal [Fig. 2-a]. However, an increase in the DOC concentration to 7.5 mg-C/L did reduce the Br^- removal to 73%, indicating a competition of higher concentrations of negatively charged NOM with Br^- for available
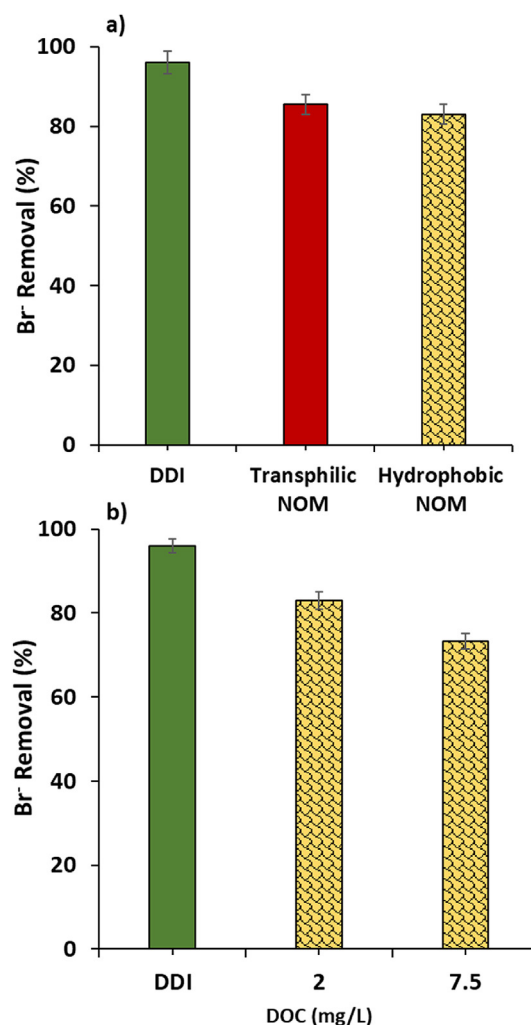

Fig. 2. Effect of **a) NOM type** and **b) DOC concentration (at hydrophobic NOM)** on Br^- removal. Experimental Conditions: $[Br^-]_0 = 250\,\mu g/L$, **a)** $[DOC]_0 = 2\,mg/L$, Transphilic NOM $SUVA_{254} = 1.7\,L/mg.m$, Hydrophobic NOM $SUVA_{254} = 3.0\,L/mg.m$, **b)** $[DOC]_0 = 2$ and $7.5\,mg/L$, Hydrophobic NOM $SUVA_{254} = 3.0\,L/mg.m$, pH = 6.5, T = 21±1 °C, BV: 600.

exchange sites on the resin surface, which also blocked Br^- access to some of the pores [Fig. 2-b]. Regardless, over 70% Br^- removal in waters was possible with the DOC with a mass ratio of 30 indicating the selectivity of Br^- in natural waters. In previous studies, it was also reported that 3–4 mg/L DOC increase has decreased Br^- removal by 10–30% (Hsu and Singer, 2010; Walker and Boyer, 2011). In those studies, removal efficiencies were within the range of 32–58% for 0.1 mg/L initial Br^- concentration at 250→1000 BV. (Table S1).

The adverse effect of the coexisting NOM and other anions on Br^- removal is established (Table S1). Boyer and Singer (2006) observed a low Br^- removal (6–28%) by polyacrylic resins in the presence of SO_4^{2-} (10–50 mg/L) and NOM (5.1–6.5 mg-C/L). Similarly, the use of polystyrene and polyacrylic resins in Br^- was within a range of 8–65% after the addition of NO_3^- (8.7 mg/L) and SO_4^{2-} (13.5 mg/L) in a NOM background (5.6–6.7 mg-C/L) (Humbert et al., 2005). In our study, the resin performance was analyzed under a challenging mixture of NOM (2–7.5 mg-C/L) and five competing anions (i.e., NO_3^-, SO_4^{2-}, NO_2^-, PO_4^{3-}, and Cl^-), only a 20% decrease in the rate of Br^- removal was observed (Fig. S5). This continued high selectivity of the resin for Br^- removal represents a good alternative

for use in water treatment systems.

3.3. DBP formation and speciation

3.3.1. THMs, HAAs and HANs

In Fig. 3 and S8, the formation and speciation of THMs, HAAs, and HANs is provided before (control) and after resin treatment in both transphilic and hydrophobic NOM solutions (SUVA$_{254}$: 1.7 and 3.0 L/mg.m, respectively) at two different DOC concentrations (i.e. 2.0 and 7.5 mg/L). At 2.0 mg/L, the DOC concentration in the presence of 250 μg/L Br$^-$ and the formation of THMs in transphilic and hydrophobic NOM solutions were 98 ± 4 and 102 ± 0.2 μg/L, with an ordered speciation of DBCM > TBM > DCBM > TCM and DBCM > DCBM > TBM > TCM, respectively [Fig. 3-(a)]. Although similar concentrations of total THMs were observed in both waters, the measured concentration of THM species was slightly different, which may be ascribed to the higher reactivity of chlorine with a higher SUVA$_{254}$ NOM (that is more hydrophobic with a larger aromatic structure) (Hua et al., 2015; Osawa et al., 2017). After treatment with the Br$^-$ selective resin, the overall formation of THM decreased by 90% and 60% in both transphilic and hydrophobic NOM backgrounds, respectively. Within the treated fraction
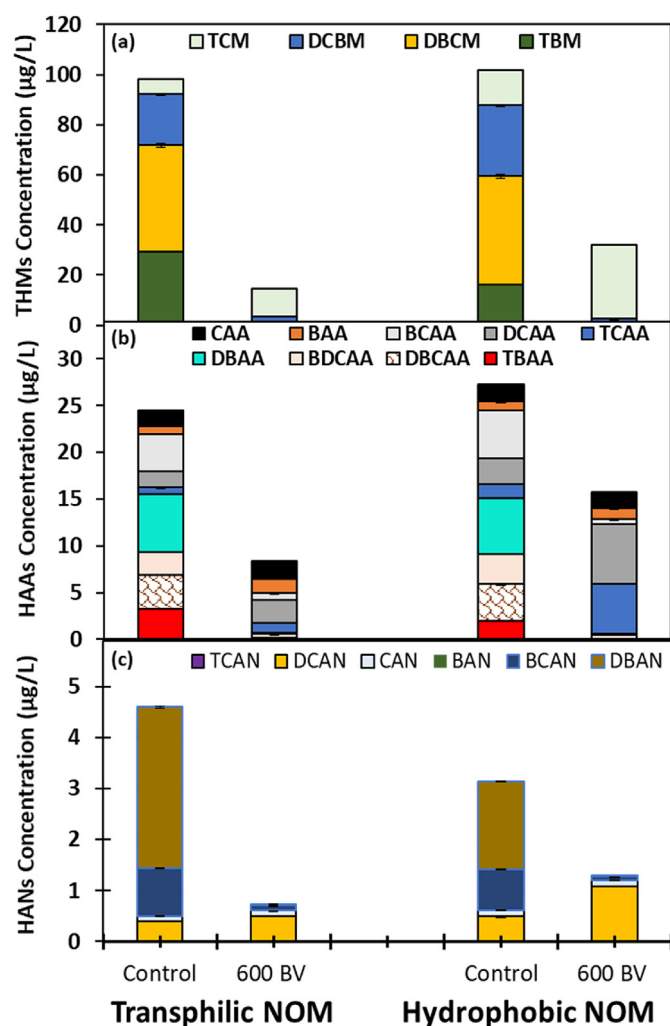

Fig. 3. DBPs speciation by Purolite-Br resin at DOC 2 mg/L **(a)** THM, **(b)** HAA and **(c)** HAN. Experimental Conditions: [Br$^-$]$_0$ = 250 μg/L, [DOC$^-$]$_0$ = 2 mg/L, Transphilic NOM SUVA$_{254}$ = 1.7 L/mg.m, Hydrophobic NOM SUVA$_{254}$ = 3.0 L/mg.m, pH = 6–9, T = 21±1 °C, Reaction time = 24 h.

of water, the higher removal rate of Br$^-$ (up to 85%) resulted in a subsequent decrease in Br/Cl-THMs (>90% DCBM, >98% DBCM and >99% TBM). After the resin treatment, the speciation shifted from Br-THMs to Cl-THMs with the TCM the dominant species due to the lower removal rate of DOC by Purolite-Br resin (<25% DOC removal). This change in Br/DOC ratio significantly affect the DBPs speciation, which is in line with previous studies (Watson et al., 2015). Since the NOM molecules have number-average molecule between 1000 and 10000 Da, this gel type Purolite-Br resin has a smaller pore size than the macroporous resins. Therefore, the larger pore size increases the access of the larger NOM molecules over the gel type resin (Hu et al., 2016). When the experiments were conducted at 7.5 mg/L DOC concentration, the higher formation of THMs was observed due to the high correlation of DOC with the THM formations (Liang and Singer, 2003; Bond et al., 2014) (Figs. S9–(a)). Nevertheless, the observed degree of the Br$^-$ removal, in transphilic and hydrophobic NOM solution, was 73% and 71%, respectively, which reduced the formation of Br-THMs by 93% and 96%.

As shown in Fig. 3-(b), at 2 mg/L DOC concentration, the formation of HAAs in the control samples were 25 ± 0.5 and 27 ± 1.7 μg/L for the transphilic and hydrophobic NOM backgrounds, respectively. After treatment with the Br$^-$ resin, the removal of Br$^-$ and the decrease in the formation of Br/Cl-HAAs (i.e. DBAA, TBAA, DBCAA, BCAA, and BDCAA) was in excess of 90%. On the other hand, the formation of Cl-HAAs (i.e. DCAA and TCAA) increased after the treatment of the resin for both NOM types, which can be ascribed by the out competition of HOCl over HOBr to form Cl-HAAs. A DOC concentration of 7.5 mg/L increased the HAA formation in the control sample to 89.5 ± 0.1 and 114.7 ± 1.8 μg/L in both of the transphilic and hydrophobic NOM backgrounds, respectively [Figs. S6–(b)]. An increase in the DOC concentrations (7.5 mg/L) also resulted in reducing the Br$^-$ removal, thus increasing the formation of Br-HAAs in treated water.

A representation of the formation and speciation of HANs in both transphilic and hydrophobic NOM solutions at 2 mg/L DOC is detailed in Fig. 3-(c). The total formation of HANs in these waters were 4.7 ± 0.1 μg/L and 3.1 ± 0.1 μg/L, respectively. These results indicate the relationship of the HAN precursor with the nitrogen-enriched low molecular weight organic matter (OM) in surface waters, as detailed in Table S5, indicating a higher percentage of nitrogen in 1.7 L/mg.m of SUVA$_{254}$ than in 3.0 L/mg.m of SUVA$_{254}$. Therefore, organic matter composed of 1.7 L/mg.m SUVA$_{254}$ has a higher formation of HANs than 3.0 L/mg.m. It is also known that the characteristic of OM with the nitrogen fraction is effective in the formation of HAN (Osawa et al., 2017). In both background waters, the speciation order of the HANs was DBAN > BCAN > DCAN > CAN > BAN~TCAN in the control samples. Further, although the overall HAN concentration decreased by 85% and 60% in both of the transphilic and hydrophobic NOM waters, after the resin treatment, a decrease of more than 90% was observed in both the Br$^-$ and Br/Cl-HANs (i.e. DBAN and BCAN) levels. In contrast, there was a near %55 increase in the formation of DCAN in both the BDAN and BCAN.

At 7.5 mg/L DOC concentration, an increase in the total formation of HANs was observed in both transphilic and hydrophobic NOM solutions to the level of 10.9 μg/L and 8.2 μg/L, respectively [Figs. S6–(c)]. After Br resin treatment, a >94% decrease in the formation of Br-HANs was observed in both waters. Regardless of their lower detected concentrations (~10–20 times) than THMs and HAAs, HANs were the main DBP class that were determined as the control behind the calculated cytotoxicity of the waters, due to the formation of the two toxic Br-HANs (i.e. BCAN and DBAN) (Krasner et al., 2016; Wagner and Plewa, 2017; Liu et al., 2018; Muellner et al., 2007).

The calculated cytotoxicity values before and after the Br resin treatment under different DOC concentrations and NOM backgrounds is provided in Figs. 4 and S7. Note that in the control samples the order of the calculated toxicity index values for DBPs were HANs > HAAs > THMs. However, the regulated THMs had the lowest contribution because of their lower toxicity index values. Of the detected species, the major contributor to the calculated cytotoxicity value was DBAN, the concentration of which greatly decreased to >99% upon treatment with the Br resin. Also, cytotoxicity caused by other Br-DBPs (i.e. TBM, DBCM, DBAA, DBCAA, TBAA, etc.) decreased by more than 98% (Fig. S8). Therefore, the observed decrease in Br-HANs concentrations significantly reduced the toxicity of studied waters, as to be discussed later. More detailed information regarding the calculated toxicity (i.e. NOM effect and DOC concentration effect) is provided in Text S3 in SI.

The formation and speciation of DBPs (THMs, HANs, and HAAs) in the presence of competing anions were also examined (Fig. S9). As discussed in section 3.2., the removal efficiency of Br^- was slightly reduced in the presence of competing anions, which resulted in a higher formation of Br-DBPs in the presence of competing anions in the NOM background.

3.3.2. TOX

The formation of TOCl, TOBr, and TOX following the chlorination of both transphilic and hydrophobic NOM is provided in Fig. 5, which details the DOC concentrations of 2 and 7.5 mg/L respectively. The reported TOX values are the sum of TOCl and TOBr concentrations. Both the known, or measured fractions of the THM, HAA, and HAN DPBs and the unknown fraction of TOCl, TOBr, and TOX are also provided in Fig. 5, as determined by subtraction of the identified and measured halogenated DBPs from the TOX.

At a 2 mg/L DOC concentration, TOX concentrations were 279 ± 0.5 and 371 ± 0.5 μg/L in transphilic and hydrophobic NOM solutions, respectively. In the control samples, a high Br^- concentration (250 μg/L), resulted in a higher known TOBr than the known TOCl concentrations. This higher TOX concentration in hydrophobic NOM over the transphilic NOM solutions is caused by the increased formation of chlorinated species within high SUVA backgrounds (i.e. the hydrophobic structure of NOM and the high $SUVA_{254}$). Although the NOM did affect the TOCl formation, no such effect was observed on the TOBr formation. After treatment with the Br resin,
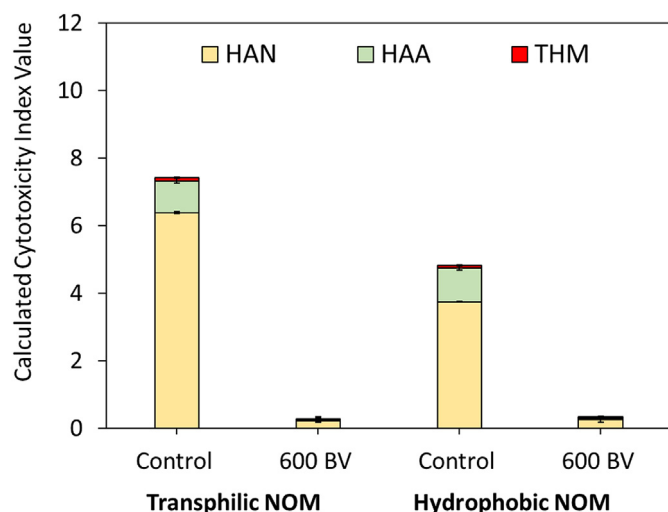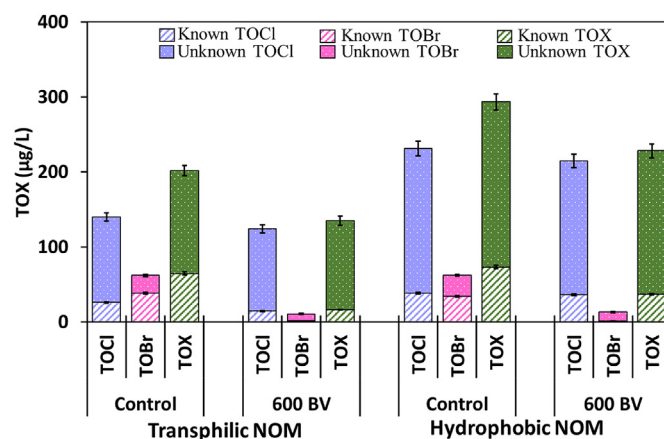
Fig. 5. Formation of known and unknown TOBr, TOCl and TOX concentrations at $[DOC]_0 = 2.0$ mg/L during the chlorination of NOM from two SUVA values. Experimental conditions: $[Br^-]_0 = 250$ μg/L, Transphilic NOM $SUVA_{254} = 1.7$ L/mg.m, Hydrophobic NOM $SUVA_{254} = 3.0$ L/mg.m, pH = 7.5, T = 21 ± 1 °C, Reaction time = 24 h.

a decrease in the concentration of known and unknown TOBr of >93% and >60%, was observed respective to the rate of Br^- removal (73−85%). At a 7.5 mg/L DOC concentration, however, an increase in the TOX concentration in transphilic and hydrophobic NOM waters to 774 ± 1 and 1005 ± 1 μg/L, respectively was observed (Fig. S10). Among the TOCl and TOBr fractions, TOCl was the main catalyst behind the increase in TOX concentration by 568 ± 0.4 and 802 ± 0.5 μg/L in transphilic and hydrophobic NOM solutions, respectively. Similar to the 2 mg/L DOC condition, the observed increase in TOX is associated with the formation of Cl-DBPs.

3.3.3. Bromine substitution factor

Fig. 6 shows the BSF values for THM, HAA, HAN and TOX for the different DOC concentrations and NOM before and after Br^- removal by the resin. In all of the examined conditions, the calculated BSF values prior to treatment were always higher due to the presence of Br^-, which favored the formation Br-DBPs and thus resulted in a higher BSF value. After the Br resin treatment at a 2 mg/L DOC concentration, in both the transphilic and hydrophobic NOM backgrounds, a significant decrease in the BSF values of $95 \pm 0.4\%$, $87 \pm 0.1\%$, $95 \pm 0.4\%$, and $68 \pm 0.2\%$ was observed for THMs, HAAs, HANs, and TOX in both solutions, respectively. Further, although the order of the calculated BSF values prior to treatment were $BSF_{HAN} > BSF_{HAA} > BSF_{THM} > BSF_{TOX}$, after treatment, these ordered values were $BSF_{HAA} > BSF_{TOX} > BSF_{HAN} > BSF_{THM}$ respectively. The change in DBP speciation with decreasing Br:DOC ratio also observed in BSF values after resin treatment. The assessment of the NOM solution noted lower BSF values in a hydrophobic NOM background, caused by the formation of Cl-DBPs (Tan et al., 2016; Liu et al., 2018; Ersan et al., 2019). At a 7.5 mg/L DOC concentration, a decrease in the BSF values occurred due to the increased formation of Cl-DBPs in high DOC water in both NOM backgrounds [Fig. 6 (b)]. Analogous to the DOC 2 mg/L, after a Br^- selective resin treatment, a decrease in the BSF values of $95 \pm 0.7\%$, $87 \pm 0.2\%$, $95 \pm 0.7\%$, and $72 \pm 0.6\%$ were observed for the THMs, HAAs, HANs, and TOX respectively.

4. Conclusions

In this study, three categories of anion exchange resins (Novel-Br resins, styrene-based resins, and acrylic-based resin) were tested to determine their efficacy for the removal of Br^- from four
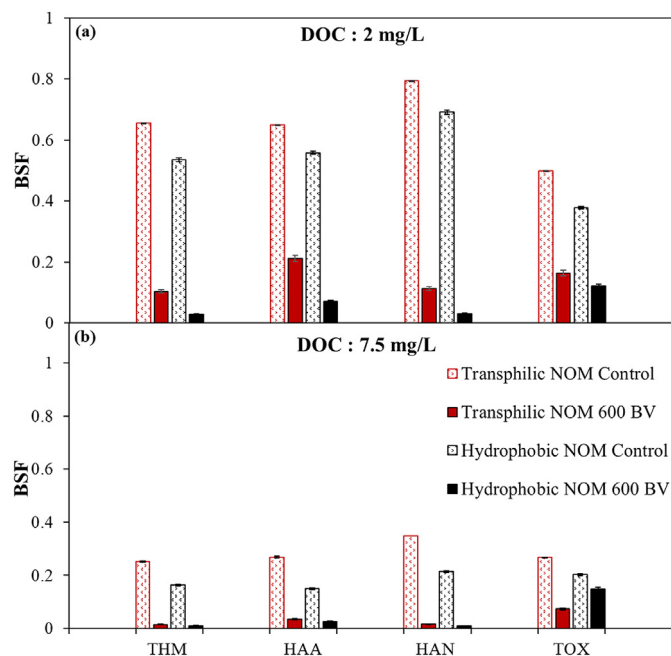
Fig. 4. Calculated cytotoxicity (CHO) values as a function of HAN, HAA and THM. Experimental conditions: $[Br^-]_0 = 250$ μg/L, $[DOC^-]_0 = 2$ mg/L, Transphilic NOM $SUVA_{254} = 1.7$ L/mg.m, Hydrophobic NOM $SUVA_{254} = 3.0$ L/mg.m.

Fig. 6. Effect of the NOM type and the DOC concentration on the BSF of THM, HAA, HAN and TOX during chlorination: (a) at $[DOC]_0 = 2.0$ mg/L and (b) at $[DOC]_0 = 7.5$ mg/L during chlorination of NOM from two NOM characteristics. Experimental conditions: $[Br-]0 = 250$ μg/L, $[DOC]0 = 2.0$ mg/L and $[DOC]0 = 7.5$ mg/L, Transphilic NOM $SUVA254 = 1.7$ L/mg.m, Hydrophobic NOM $SUVA254 = 3.0$ L/mg.m, pH = 7.5, T = 21 ± 1 °C, Reaction time = 24 h.

background anions (i.e. SO_4^{2-}, Cl^-, Alkalinity, NO_3^- and PO_4^{3-}). Results indicated that novel Purolite-Br and MIEX-Br resins exhibited the best performance in terms of the selective removal of Br^- from the water even when the concentration of solution anions was greater than the reported resin capacity. In contrast to the conventional anion exchange resins, Purolite-Br resin exhibited the highest adsorption performance for Br^- removal, a performance possibly associated with its gel pore structure and propriety functional groups. Purolite-Br was also effective in the selective removal of Br^- under both typical and challenging background water conditions (i.e., Cl^- & $SO_4^{2-} = 25-400$ mg/L, and NOM = 2.0–7.5 mg-DOC/L). Most importantly, the subsequent formation of Br-DBPs (THMs, HAAs, and HANs) and total organic halogens (TOX) decreased by ~90% under the uniform formation conditions. As a result, the bromine substitution factor and calculated toxicity values also decreased after the IX treatment, no effect of the difference in water aromaticity (i.e. transphilic and hydrophobic) upon the Br^- removal via Purolite-Br. Thus, the high capacity and superior performance of Purolite-Br in removing both low and high Br^- levels in various water backgrounds makes it the best system for use in water treatment operations. Finally, these newly developed Br-selective resins represent promising alternatives for the efficient control of Br-DBPs in such operations.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.124583.

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