Impact of natural organic matter characteristics and inorganic anions on the performance of ion exchange resins in natural waters

Fuhar Dixit, Benoit Barbeau and Madjid Mohseni

ABSTRACT

Ion exchange (IX) process is increasingly used as a cost-effective treatment for the removal of natural organic matter (NOM) from drinking water. However, fundamental studies under the influence of variable NOM characteristics and inorganic anions have often been overlooked. This is important given NOM characteristics (such as charge density and molecular weight) and inorganic anions concentrations are geographically and seasonally variable. We examined the performance of a strongly basic IX resin for the simultaneous removal of NOM, inorganic ions and micropollutants (Per- and polyfluoroalkyl substances (PFAS) and algal toxins), from different surface and recycled waters. The results indicated >70% removal of NOM for ~20,000 Bed Volumes (BV) with an uptake of NOM fractions following the order of their respective charge densities. IX pore blockage and consequent site reduction was observed in the presence of higher molecular weight NOM fractions (breakthrough ~7,000 BV). Moreover, NOM and inorganic ions breakthrough corresponded to ~85–90% site occupancy (in meq) in the absence of pore blocking compounds. IX also provided simultaneous removal of inorganic ions (>90%) and charged micropollutants. Complete removals of Microcystin-LR and multiple long- and short-chained PFAS were achieved at environmentally relevant concentrations with dosages of 1,000 mg/L (or 4.5 mL/L) or higher.

Key words | competitive interactions, diffusion, GenX, microcystin, multiple-loading, PFAS

HIGHLIGHTS

- Ion exchange can provide simultaneous removal of NOM, inorganic ions and micropollutants.
- Microcystin-LR and PFAS are removed effectively via ion exchange process.
- NOM fractions with higher charge are preferentially removed over lesser charged fractions.
- Uptake of NOM is limited by pore diffusion.

INTRODUCTION

Natural organic matter (NOM) is a complex mixture of organic substances originating from natural sources (such as plants and animals) (Levchuk et al. 2018). NOM is chemically heterogeneous, comprised of hydrophobic, hydrophilic and neutral fractions with a wide range of molecular weights and chemical characteristics, and it majorly originates from dead and decaying plant and animal bodies (Mergen et al. 2008; Kaewsuk & Seo 2011). Although predominantly hydrophobic, characteristics of aquatic NOM are geographically and seasonally variable and may change significantly from one water body to another (Huber et al. 2011; Finkbeiner et al. 2018).

Scientific studies have indicated that the majority of surface water sources are comprised of organic matter with the...
dissolved organic carbon (DOC) content in the range of 2–20 mg/L (Matilainen et al. 2002; Al-amoudi 2010; Levchuk et al. 2018). Further, most of the published studies in scientific literature have reported a molecular weight distribution in the range of 500–3,000 Da for NOM in surface waters (Huber et al. 2011; Teixeira & Sousa 2013). However, NOM compounds with higher molecular weights have also been reported in a few studies (Teixeira & Sousa 2013).

The presence of NOM brings many potential issues with respect to water quality and treatment processes. It significantly impacts the aesthetic properties of water such as taste, odor and color of potable water (Sharma et al. 2013). Moreover, it is also a potential substrate for bacteria and deteriorates the biological stability of water by increasing bacterial regrowth and biofilm formation within distribution systems (Mellor et al. 2015). One of the most critical concerns associated with NOM in drinking water is the risk of formation of disinfection by-products (DBPs) during the treatment process (Wang et al. 2015; Levchuk et al. 2018).

The presence of NOM impacts the efficacy of many water treatment processes. In activated carbon, it reduces the adsorption capacity for micropollutants (Bjelopavlic et al. 1999; Quinlivan et al. 2005). Additionally, NOM can reduce the efficiency of ultraviolet (UV) irradiation for disinfection by reducing the radiation dose delivered for microorganism inactivation (Carré et al. 2018; Jin et al. 2018). Evidence of membrane fouling and scavenging of hydroxyl radicals (-OH) by NOM compounds during UV-based oxidation processes have also been documented in the scientific literature (Bolto et al. 2004; Swietlik et al. 2004).

Anion exchange resins (IX) offer a cost-effective solution for NOM removal from drinking water systems because of their effectiveness, ease of operation, scale up or down capabilities and small footprint (Boyer & Singer 2005; Levchuk et al. 2018). In addition to removing NOM, IX also exhibits superior (simultaneous) removal of other negatively charged micropollutants (with NOM) in a single treatment step (Verdickt et al. 2011; Dixit et al. 2019). For instance, the growing interest in adopting IX for perfluorinated alkyl acids (PFAS) removal is evidenced in the past recent years (McCleaf et al. 2017; Maimaiti et al. 2018). More importantly, anionic IX resins that are commonly used for water treatment (NOM removal), can be regenerated and reused by using concentrated brine solutions (NaCl) to restore the exhausted resin back to its ionic form of service and used for multiple cycles, a significant advantage over other commercial adsorbent materials, which require frequent replacement after saturation (Levchuk et al. 2018). The operational cost of a typical ion exchange system ranges between ($0.1–$0.2 per 1,000 liters of water treated), which is lower than membrane filtration and UV-based oxidation processes ($0.4–$3 per 1,000 liters) and comparable to coagulation/activated carbon-based adsorption processes ($0.03–$1.8 per 1,000 liters, depending upon the water characteristics (Federal Remediation Technologies Roundtable 2007; Maul et al. 2014)). Note, IX regeneration (salt usage and elution efficiency) represents a major portion of its operational cost. Based on the scientific literature, NaCl-based regeneration processes are more economical when compared to KCl and KHCO3 (IX operational cost and environmental burden (based on life cycle assessment of mining and processing): NaCl < KCl < KHCO3 (Maul et al. 2014)).

In addition to NOM and charged micropollutants, the IX resins have the potential to remove inorganic ions such as sulphate and nitrate (Ates & Incetan 2013; Hu et al. 2016). Consequently, a comprehensive understanding of the competitive uptake process is essential for optimizing the treatment process. This is critical considering the fact that inorganic ions (5–100 mg/L) in the natural environments co-occur with high concentrations of natural organic constituents (2–20 mg C/L) (Ates & Incetan 2013; Hu et al. 2016). Additionally, NOM characteristics, specifically the charge density and molecular weight distribution, play a key role in the uptake process, either via size exclusion or via direct competition for active charged sites (Dixit et al. 2018). For commercial application, this necessitates an understanding of the long-term performance of the resin with optimized regeneration and operational procedures (resin dose and contact time) under different NOM sources. Although NOM removal via IX process is well established in scientific literature (Levchuk et al. 2018), studies involving the impact of NOM characteristics on IX fouling and subsequent competitive interactions with other inorganic species in long operational cycles are rare.
In the present study, the performance of IX resins for the removal of NOM, inorganic species and micropollutants (PFAS and microcystins) was conducted via multiple loading tests using 10–2,000 mg/L resins (or 0.03–3.5 mL/L) for 25,000 Bed Volumes (~300 hours). The impact of NOM characteristics was evaluated by testing the resins with four standard International Humic Substance Society (IHSS) NOM standards, as depicted in Table 1 (initial concentration of ~5 mg C/L). These NOM standards exhibited a wide range of charge density and molecular weight distribution encountered in natural water matrices (Arias-Paic et al. 2016; Dixit et al. 2018). The NOM removal was examined under the presence of four ubiquitous inorganic ions species, namely sulphate, phosphate, nitrate and bicarbonate. Further comparative studies were performed with three natural drinking water sources and one recycled wastewater from various communities in British Columbia, Canada. The studies with recycled wastewater were performed to evaluate the impact of effluent organic matter (EfOM) on IX performance by mimicking scenarios relevant to potable reuse considering its growing interest with changing climatic variability (Gerrity et al. 2013; Stanford 2017). Finally, the obtained results were utilized to examine the removal of micropollutants (perfluorinated compounds and microcystins) under optimized conditions and examine the competitive interactions in natural waters. The engineering significance of this research is to provide the essential knowledge required to optimize the IX operational parameters and regeneration procedures depending upon the source water quality, a key knowledge essential for water utilities and operators globally.

### METHODS

#### Reagents and chemicals

Four standard NOM fractions were purchased from the International Humic Substance Society (St. Paul, MN, USA). These NOM fractions were Suwannee River Natural Organic Matter (SRNOM) Suwannee River Fulvic Acid (SRFA), Pony Lake Fulvic Acid (PLFA) and Suwannee River Humic Acid (SRHA). These selected fractions offer a wide range of charge density and molecular weight distribution encountered in natural waters and are commonly adopted by scientists across the globe (Hu et al. 2016; Parker et al. 2016). Sodium nitrate, Sodium sulphate, sodium phosphate and sodium bicarbonate were obtained from Fisher Scientific (Fair Lawn, NJ). Microcystin-LR (MCLR, dry powder: 1 mg) was obtained from Enzo Life-sciences in Farmingdale, NY, USA. Perfluorinated alkyl acids (PFAS) were obtained from Millipore Sigma (Oakville, ON). 2,2,3,3-Tetrafluoro-3-(trifluoromethoxy) propionic acid (CAS# 377-73-1, PN# 2121-3-66), also referred to as GenX (or HFPO-DA), was purchased from Synquest laboratories (FL, USA). All the reagents were used as received and deionized water (DI water, resistivity 18.2 MΩ.cm) was used to prepare all the reagent stock solutions (see properties in Table 1).

#### Resin selection

Purolite® A860 (Purolite, Bala Cynwyd, PA, USA), a strongly basic anionic macroporous acrylate-based resin,
was used for all the experiments. The resin had a total capacity of 0.8 meq/mL (221 mg dry weight = 1 mL), a median pore diameter of 7.2 nm and average resin diameter of 750 μm (see details in the Supplementary Information (SI)) (Dixit et al. 2018).

**Natural waters**

Surface water was collected from the water treatment plant in the city of West Vancouver (referred to hereafter as Eagle Lake), Priest Lake (Texada Island), and Middle River (a First Nations Reserve), all in BC, Canada. The collected surface waters were pre-filtered with 0.45 μm membrane filters (Millex-HV Syringe Filters, Catalog number: SLGP033RS, Duluth, GA, USA), and then stored in dark at 4°C for a maximum period of four weeks. Recycled wastewater was collected from the Vancouver Convention Centre, BC (a membrane bioreactor effluent). Prior to all experiments, the wastewater (not surface water) was passed through microfiltration (0.3 μm, GE Osmonics Flat Sheet, JX, PVDF, MF (Sterlitech Corporation, Kent, WA, USA)) and ultrafiltration membranes (200 kDa, Synder Flat Sheet, V5, PVDF, UF (Sterlitech Corporation, Kent, WA, USA)), operated on a CF042 pressurized cell at 15 mL/min (or 200 LMH) and operating pressures of 5–25 psig, to mimic scenarios relevant to potable reuse.

**Multiple loading tests**

A resin dosage of 1,000 mg (dry weight) or 4.5 mL was mixed with 1 L of water (synthetic/natural) in a circular 1 L beaker in a Phipps & Bird 9,900 Jar tester (Richmond, VA, USA), which was operated at 150 rpm. After the mixing period, the resin was separated from the treated water by filtering through a 0.45 μm filter (Millipore, Cat. No. HAWG047S6, Sigma Aldrich, ON, Canada). The separated resins were then transferred to a new 1 L beaker (Amini et al. 2018). These conditions were selected based on previous scientific studies where resin doses of 5–20 mL/L have been reported for use at commercial scale (Boyer & Singer 2006; Greffe et al. 2013). Resin regeneration was performed using 10% NaCl solution as specified by the manufacturer (Purolite 2017).

**Analyses**

A Total Organic Carbon (TOC) analyzer (GE Sievers M5310 C, Boulder, CO, USA) was employed to measure the TOC, DOC (Dissolved Organic Carbon), and DIC (Dissolved Inorganic Carbon). A UV-Vis spectrophotometer (path length of 1 cm, Cary 100 U-Vis Spectrophotometer, Agilent Technologies, USA) was used to perform the UV254 analyses. Microcystin-LR was detected using HPLC (high performance liquid chromatography, Dionex Ultimate 3000, USA) as previously described (Dixit et al. 2018). PFAS were detected using an Agilent 1,200 series HPLC system (Agilent Technologies, CA, USA) combined with mass spectrometric analysis (Agilent Technologies, CA, USA) in negative electro-spray ionization and multiple reaction monitoring (MRM) modes (details in SI). Chloride, nitrate, phosphate and sulphate ions were measured using an ion chromatograph (Dionex ICS- 1100, USA), according to the USEPA 300.0 reference method. Liquid chromatography with organic carbon detection (LC-OCD) was performed using an HPLC (Perkin Elmer, Canada) connected to a 900 Turbo Potable DOC Analyzer (GE Sievers, Canada) (Huber et al. 2011).

**RESULTS AND DISCUSSION**

**Selection of resin dose**

Aquatic NOM co-exists with a variety of other inorganic ions in the natural environment (such as nitrate, sulphate, etc.) (Croue & Humbert 2005; López-Ortiz et al. 2018). The collected surface waters exhibited a DOC in the range of 3–6 mg C/L in co-existence with 3–35 mg/L of sulphate, nitrate and bicarbonate ions (see details in Table 3). Scientific studies with other natural surface waters have also reported similar inorganic and DOC concentrations globally (Croue & Humbert 2005; Willison & Boyer 2012). Consequently, we examined the effect of resin dosage in a water matrix with 5 mg C/L and approximately 30 mg/L of sulphate, nitrate, phosphate and bicarbonate ions. Note, the selected resin dosage of 10–2,000 mg/L (or 0.05–9 mL/L) exhibited a wide range of resin charge (considering 1 mL = 221 mg and 0.8 meq/mL resin charge). Hence, we
tested conditions with a resin: contaminant ratio (in meq) of approximately 100:1–1:10, a broad range to examine the competitive interactions. Moreover, the selected range also include commercial resin dosages, which are typically 4–20 mL/L (Boyer & Singer 2006). Note that we performed the synthetic water studies here with Suwannee River NOM (SRNOM) as it is a surrogate widely used for performing synthetic water studies and exhibited a similar molecular weight distribution to our collected natural waters (see LC-OCD data in the Supplementary Information (SI)).

Figure 1 depicts the effect of initial resin loading on the removal of NOM ($C_0 = 5$ mg C/L) and inorganic ions ($C_0 = 30$ mg/L of individual sulphate, nitrate, phosphate and bicarbonate ions, all together as in natural waters). At a resin dosage of 10 mg/L or $\sim 0.05$ mL/L, we observe an approximate 50% removal of SRNOM along with $< 10\%$ removal of individual inorganic ions. Note that the charge density of SRNOM (10.2 meq/g of C) is lower than that of any inorganic ions (see Table 1) and the selected concentration of inorganic ions is $6$ fold higher than that of SRNOM (in mg/L). This dosage condition also corresponds to a resin:contaminant ratio of $\sim 1:10$, indicating more contaminants in comparison to available uptake sites and thereby a limited uptake of all ions. As the resin dosage increases to 250 mg/L (or $\sim 1.2$ mL/L) the uptake of DOC and inorganic ions increases to $\sim 60$–75%. Among the inorganic ions, sulphates are removed the most (76%) followed by phosphates (73%), nitrates (66%) and bicarbonates (58%) ($p < 0.05$). Further, increasing the dosage to 1,000 mg/L results in $> 90\%$ reduction for all organic and inorganic ions. Note, there is no significant difference in the removal of DOC and inorganic ions for the resin dosages of 1,000 mg/L, 1,500 mg/L and 2,000 mg/L ($p > 0.05$). Consequently, a dosage of 1,000 mg/L was selected as the most optimized dosage and was used for future competitive studies. Of note, at dosages of 1,000 mg/L (or 4.5 mL/L) or higher, we observe a consistent removal of $\sim 90\%$ DOC (while it is $> 99\%$ for all inorganic ions) even though the available uptake sites are abundant. This part of DOC would be referred to as the non-removable fraction of DOC, which can be estimated to be composed of neutral components or bio-polymers (Bolto et al. 2004; Bazri & Mohseni 2016).

**NOM and inorganic ions removal: kinetic studies**

Kinetic studies were performed at a resin dosage of 1,000 mg/L (or 4.5 mL/L) with varied contact times (up to 150 minutes) using a jar tester operated at 150 rpm to ensure complete mixing. The studies were performed to evaluate the impact of NOM loading, especially considering the variability in NOM concentrations encountered in natural environments. Considering the fact that NOM characteristics (charge density and molecular weight

![Graph](image)
distribution) are spatially variable and can change seasonally, we selected four standard NOM isolates to examine the impact of NOM characteristics on uptake kinetics. Moreover, we evaluated the impact of inorganic ions on NOM removal and examined the uptake kinetics of different inorganic ions under concentrations relevant to water treatment.

Figure 2(a) depicts the uptake kinetics of IX resin with changing initial SRNOM concentration (1–7.5 mg C/L). We present the data in equivalents (rather than conventional mg/L approach) as it is more relevant from fundamental perspectives of ion exchange. The experimental data were fitted with pseudo-first order ($R^2 < 0.9$), pseudo-second-order ($R^2 > 0.95$), and intraparticle diffusion models ($R^2 < 0.8$) (see model details in SI). The pseudo-second order model offered the best fit to the observed experimental data. Figure 2(b) illustrates the effect of NOM characteristics (5 mg C/L) on uptake via IX process. All data agreed well with the pseudo-second-order kinetic model (see Table 2) with an exception of SRHA. The pseudo-second-order rate constant values ($k_2$) followed the order of respective charge densities of NOM fractions. For instance, the $k_2$ values for SRFA (10.9 meq/g C) were approximately 1.2-fold higher than those of PLFA (6.8 meq/g C). SRHA molecules (Figure 2(c)), although being more charged than PLFA, exhibited a lower uptake, a phenomenon that can be attributed to pore blockage. The higher molecular weight fractions of SRHA block the resin pores and thereby reduce the uptake capacity, a fact well evident from published scientific literature (Pelekani & Snoeyink 1999; Zhang et al. 2014; Dixit et al. 2018). This was further confirmed with the LC-OCD analysis on SRHA water, where we analyzed the response before and after IX treatment (lesser removal of NOM in comparison to, say, SRNOM or PLFA, details and graphs in SI).

The rate controlling step was further investigated using the dimensionless Biot number. The Biot number is the ratio of internal mass transfer (pore diffusion) to external...
Table 2 | Kinetic parameters for NOM fractions and inorganic ions

<table>
<thead>
<tr>
<th>Matrix</th>
<th>( k_f ) (meq/meq/min)(^a)</th>
<th>( q_e ) (meq/meq × 10(^{-7}))(^b)</th>
<th>( R^2 )</th>
<th>Biot</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRNOM</td>
<td>572 ± 32</td>
<td>0.60 ± 0.03</td>
<td>0.98</td>
<td>12</td>
</tr>
<tr>
<td>SRFA</td>
<td>644 ± 38</td>
<td>0.62 ± 0.02</td>
<td>0.99</td>
<td>11</td>
</tr>
<tr>
<td>SRHA</td>
<td>413 ± 42</td>
<td>0.49 ± 0.07</td>
<td>0.86</td>
<td>24</td>
</tr>
<tr>
<td>PLFA</td>
<td>523 ± 32</td>
<td>0.54 ± 0.04</td>
<td>0.97</td>
<td>8</td>
</tr>
</tbody>
</table>

Inorganic ions

<table>
<thead>
<tr>
<th>Anion</th>
<th>Sulphate</th>
<th>Phosphate</th>
<th>Nitrate</th>
<th>Bicarbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Affinity coefficient ((\alpha))</td>
<td>9.4</td>
<td>9.2</td>
<td>4.6</td>
<td>1.1</td>
</tr>
</tbody>
</table>

\(^a\)Data reported with 95% confidence intervals of their respective parameters.

Table 3 | Removal of different ions and DOC from surface and recycled waters

<table>
<thead>
<tr>
<th>Anions</th>
<th>Before IX(^a)</th>
<th>After IX(^a)</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eagle Lake</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC</td>
<td>3 ± 0.1</td>
<td>0.8 ± 0.1</td>
<td>73</td>
</tr>
<tr>
<td>Sulphate</td>
<td>3.2 ± 0.1</td>
<td>0.6 ± 0.1</td>
<td>81</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>4.5 ± 0.1</td>
<td>0.5 ± 0.1</td>
<td>88</td>
</tr>
<tr>
<td>Priest Lake</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC</td>
<td>5.9 ± 0.2</td>
<td>2.8 ± 0.1</td>
<td>53</td>
</tr>
<tr>
<td>Sulphate</td>
<td>32.2 ± 2.2</td>
<td>2.4 ± 0.1</td>
<td>93</td>
</tr>
<tr>
<td>Nitrate</td>
<td>3.7 ± 0.1</td>
<td>1.2 ± 0.1</td>
<td>68</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>27 ± 2.5</td>
<td>8 ± 0.5</td>
<td>70</td>
</tr>
<tr>
<td>Middle River</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC</td>
<td>4.9 ± 0.2</td>
<td>2.2 ± 0.1</td>
<td>55</td>
</tr>
<tr>
<td>Sulphate</td>
<td>4.8 ± 0.3</td>
<td>0.9 ± 0.2</td>
<td>81</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>8.5 ± 0.5</td>
<td>2.5 ± 0.3</td>
<td>70</td>
</tr>
<tr>
<td>Vancouver Convention Centre Recycled Wastewater</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC</td>
<td>5.6 ± 0.3</td>
<td>2.5 ± 0.2</td>
<td>55</td>
</tr>
<tr>
<td>Sulphate</td>
<td>32.2 ± 3.2</td>
<td>3.6 ± 0.2</td>
<td>88</td>
</tr>
<tr>
<td>Nitrate</td>
<td>26.2 ± 2.2</td>
<td>4.5 ± 0.2</td>
<td>83</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>20 ± 0.9</td>
<td>6 ± 0.3</td>
<td>70</td>
</tr>
<tr>
<td>Phosphate</td>
<td>10.2 ± 1.2</td>
<td>1.8 ± 0.4</td>
<td>82</td>
</tr>
</tbody>
</table>

\(^a\)Data reported with 95% confidence intervals of their respective parameters.

mass transfer (film diffusion) as is estimated as (Ko et al. 2001):

\[
Bi = \frac{k_f R_p}{D_{pe}}
\]

where \( k_f \) (cm/s) is the external mass transfer coefficient \((k_f = D_f/\delta)\), \( D_{pe} \) is the pore diffusion coefficient (cm\(^2\)/s), \( D_f \) is the film diffusion coefficient (cm\(^2\)/s), \( \delta \) is the film thickness \((10^{-3} \text{ cm})\) (Bazri & Mohseni 2016). Biot number < 1 indicates the film resistance as the rate limiting step, whereas Biot number > 1 indicates the pore diffusion to be the rate-controlling step. Parameters were estimated by fitting the equations into the kinetic data using nonlinear optimization schemes as reported in previous studies (Bazri & Mohseni 2016). The obtained Biot numbers for all NOM fractions were > 1 (see Table 2), with the highest Biot number reported for SRHA (nearly 2-fold higher than other NOM fractions) indicating pore diffusion to be the rate limiting step.

Figure 2(d) depicts the kinetic data for inorganic ions (30 mg/L). In addition, we conducted experiments in SRFA, SRNOM, SRHA and PLFA as well (5 mg C/L, data not presented). As observed sulphate ions exhibited fastest removal followed by nitrate and bicarbonate ions an order following their respective charge densities. Phosphate ions, although with charge density higher than sulphate ions, exhibited slightly slower kinetics (but higher than nitrate and bicarbonate ions). We hypothesized this to be a consequence of resin affinity towards ions. To evaluate further, the resin affinity for different compounds was determined using the following equation proposed for determining the equilibrium constant \((\alpha)\) for i compound within a ternary equilibrium (Li & Sengupta 2000).

\[
Y_i = \frac{\alpha_i X_i}{1 + \alpha_i X_i}
\]

For DOC, \( Y_{DOC} \) is the fraction of DOC in the resin phase (meq/meq), and \( X_{DOC} \) is the fraction of DOC in the solution phase (meq/meq) and \( \alpha_i \) is the equilibrium constant for the inorganic anion species j. Compounds with higher \( \alpha_i \) values are preferably removed in a ternary equilibrium (e.g. NOM, equivalent released chloride ions, and the tested inorganic ions such as sulphate). The estimated values of \( \alpha_i \) for sulphate and phosphate are 9.4 and 9.2 \((p < 0.05)\), while the \( \alpha_i \) for nitrate and bicarbonate ions are 4.6 and 1.1 respectively. Therefore, based on the model, the sulphate ions are preferably removed over phosphate, nitrate...
and bicarbonate ions by the resin, which agrees well with the experimental data presented in Figure 2(d). Further, the values for SRNOM, PLFA, SRHA and SRFA were 4.5, 3.8, 2.6 and 4.7 respectively.

**Multiple loading tests**

The characteristics of NOM in the water matrix is expected to influence the service life and consequent regeneration protocol for the IX resin (Finkbeiner et al. 2018). Additionally, the concentration of inorganic ions is also expected to impact the resin saturation (Levchuk et al. 2018). Hence, multiple loading tests were performed to evaluate the extent of resin saturation with NOM and inorganic ions. This was done by performing consecutive batch treatments of water (with NOM, inorganic ions etc.) with 1,000 mg/L or resin (or 4.5 mL/L, corresponding to 1,000 mL/4.5 mL = 220 Bed Volumes (BV)) with 60 minutes of contact time. These conditions were selected based on previous scientific studies where resin doses of 5–20 mL/L have been reported for use at commercial scale (Boyer & Singer 2006).

Figure 3(a) depicts the performance of IX resin for 25,000 BV of operation under different NOM fractions. The influent NOM concentration remained nearly constant (5 ± 0.2 mg/L) for all the three NOM fractions. As observed, SRFA and SRNOM were reduced to ~1 mg C/L for the initial 15,000 BV of operation, whereas SRHA was reduced to ~2.5 mg C/L for the first 5,000 BV of operation. The resin breakthrough (C/C₀ > 2.5) for SRFA containing water was observed approximately at 19,000 BV, after which the effluent DOC rose to ~2.5 mg/L and increased with consequent loading. Note that this corresponds to an approximate 90% saturation of IX sites with SRFA compounds. Similarly, the breakthrough for SRNOM-containing water was approximately observed near 20,000 BV corresponding to ~86% IX site saturation. Of note, the breakthrough for SRHA was around 4,000 BV further supporting the claim on pore blockage and subsequent site reduction (12% site occupancy).

The impact of resin loading on inorganic ions removal is illustrated in Figure 3(b). The influent inorganic ions concentration was maintained at 30 ± 0.4 mg/L. These studies were performed in NOM-free waters to evaluate the impact of individual inorganic ions. As depicted, the reduction of phosphate ions remained constant at ~1.1 mg PO₄³⁻/L for up to 700 BV of operation after which the effluent concentration spiked to >3 mg/L. Similarly, sulphate ions concentration remained <1 mg/L until 1,000 BV of operations. The breakthrough (>3 mg/L) for both sulphate and phosphate ions corresponded to an approximate 92–95% saturation of IX sites. For nitrate ions, the concentration of ions in treated samples remained <4.5 mg/L for ~4,500 BV of operation (91% saturation) while it remained <7 mg/L for bicarbonate ions for 4,700 BV (~90% saturation). Consequently, the breakthrough and approximate removals correspond well with the observed affinity values and the respective charge densities.

After saturation, resins were regenerated by using 10 Bed Volumes of 10% NaCl solution (manufacturer specified (Purolite 2017)) for a contact time of 60 minutes (Figure 4). The recovery of SRNOM, SRFA, and SRHA were ~78, 85 and 68% respectively. Consequently, a high fraction of removed DOC could be recovered. Recovery rates for all inorganic ions were >85%. However, change in regeneration protocols (brine concentration or contact time)
might improve the recovery, which we plan to investigate in future studies.

Studies in natural water

The resin performance for natural waters was evaluated by performing multiple loading tests in natural waters. Three surface waters, namely, Eagle Lake, Middle River and Priest Lake and one recycled wastewater from Vancouver Convention Centre were tested. The observed initial ion concentrations of the natural waters are depicted in Table 3. Figure 5 illustrates the resin performance (multiple cycles) for Eagle Lake water, a drinking water source for the city of West Vancouver, BC. As previously observed, the experimental data corresponded to an approximately ∼85–90% saturation of IX sites before breakthrough. For instance, the Eagle Lake water comprised 3 mg C/L DOC, 5 mg/L sulphates and 4.5 mg/L bicarbonate ions. This corresponds to an approximate resin saturation at ∼16,000 BV of operation, considering a DOC reduction to 1 mg C/L, and final concentration of 0.5 mg/L for sulphates and bicarbonate ions (4.5 mL/L resin, 0.8 meq/mL). As depicted, we observed a resin breakthrough (DOC > 2.5 mg C/L) at approximately 14,500 BV of operation (∼90% of estimated capacity, 0.8 meq/mL of resin). Nonetheless, this is consistent with previous observation with NOM fractions and inorganic ions where ∼85–90% resin saturation is observed. Consequently, it can be deemed that ∼10% of the resin sites are inaccessible due to phenomena such as pore blockage or as a result of inaccessible sites deep inside resin microstructure. It is also possible that the stated capacity of the resin (0.8 eq/L) is slightly overestimated since Amini et al. (2018) measured a max capacity of 0.7 eq/L for the same resin. Nevertheless, IX was able to simultaneously remove >50% DOC along with >70% inorganic ions removal of inorganic ions from all natural waters.

IX for removal of micropollutants

Micropollutants of emerging concern such as microcystins (from algal bloom) and PFAS, co-exist in natural environments with NOM and other inorganic ions (Chatzieftimiou et al. 2016; Hopkins et al. 2018; Dauchy 2019). It has been well documented that the presence of NOM has a detrimental effect on the efficacy of technologies commonly adopted for micropollutant removal (such as oxidation, activated carbon, etc.). Hence, we tested the resin performance for the removal of Microcystin-LR (MCLR), the most commonly occurring and most toxic variant of microcystins (Kotak & Zurawell 2007). We also tested four common PFAS, two long-chained (perfluorooctanoic acid, perfluorooctane sulfonate) and two short-chained (perfluorobutanoic acid and perfluoro butane sulfonate) with two different functional groups (carboxylic and sulphonyl) (Taniyasu et al. 2005; Huang et al. 2018). Further we also tested GenX, an emerging perfluorinated compound of concern with an ether group (Hopkins et al. 2018; Ji et al. 2018). The spiked waters were tested with 20 μg/L of MCLR and 500 ng/L of respective perfluorinated compounds (pH ∼ 7). This was selected based on the recent scientific data on commonly occurring concentrations of these compounds in
natural environments (Svrcek & Smith 2004; Betts 2007; Brandsma et al. 2019). Note that the pKa of all selected micropollutants is >2, indicating that all existed in negative form during the tested conditions (Goss 2008; Pavagadhi et al. 2003). The studies were performed in DI water, spiked SRNOM water, Eagle lake surface water and micro/ultrafiltration (MF/UF) treated recycled wastewater at two resin dosages of 50 mg/L and 1,000 mg/L. As depicted in Figure 6(a), a resin dosage of only 50 mg/L was sufficient to remove ~100% of micropollutants from all DI waters but failed to achieve >40% removal of PFAS and MCLR from NOM-containing waters. This can be a consequence of competition with NOM and inorganic ions since the ratio of IX sites to contaminant meqs were approximately 1:1 in 50 mg/L resin dose, indicating a strong competitive uptake. In DI waters where we observed nearly 100% uptake, the resin sites (in meq) were sufficient for micropollutants (which are in µg/L or ng/L), but the sites offered at 50 mg/L resin dosage were limited in the presence of NOM and inorganic ions (which are in mg/L, ~1,000 fold higher and more charged). Nonetheless, as depicted in Figure 6(b), increasing the dosage to the commercial resin dosage of 1,000 mg/L (or 4.5 mL/L, at which we did all our previous testing) ensured a complete removal of all micropollutants with >50% DOC and >70% inorganic ions removal. Consequently, IX exhibits strong potential for simultaneous removal of NOM, inorganic ions, perfluorinated compound and other negatively charged micropollutants.

CONCLUSION

The following conclusions were derived from this research:

- IX can achieve ~90% removal of NOM for dosages of 1,000 mg/L or above. However, a certain fraction ~10% is non-removable even at high resin dosages (non-removable neutral fractions).
- Resin breakthrough correlates well with resin capacity (in meq) with ~85–90% site occupancy.
- NOM fractions with higher charge are preferentially removed over lesser charged fractions.
- IX pore blockage and consequent site reduction can be observed in the presence of higher molecular weight fractions such as SRHA.

- Sulphates and phosphates are the most favorable inorganic ions followed by nitrates and bicarbonates based upon affinity studies.
- Uptake of NOM is limited by pore diffusion.

In sum, it was identified that an optimized IX procedure with a resin dosage of 1,000 mg/L (or 4.5 mL/L) can achieve simultaneous removal of NOM, inorganic ions and micropollutants (such as Microcystin-LR and PFAS) from surface and recycled wastewater sources. Moreover, we observed that IX can be effectively regenerated and reused with 10% NaCl (and 1-hour contact time) to recover ~70% of NOM and >85% of all inorganic ions. Overall, this research provides the essential knowledge required to optimize the IX operational parameters and regeneration procedures. Hence, the results are of great value to the scientific community and water treatment utilities worldwide.
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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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