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Organic matter removal with bicarbonate-form ion exchange: water quality, kinetics and mass transfer mechanisms

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Abstract

Ion Exchange (IEX) has been widely explored for the removal of organic matter. Chloride is traditionally used as counter-ion, but its release into water can increase the risk of corrosion. Research has shown that bicarbonate IEX can be an efficient alternative, and whilst some studies have compared its efficiency to chloride IEX, none have compared their performance in relation to the potential for disinfection by-product (DBPs) formation. The differences in organic matter removal between the two regenerants were assessed by looking at the molecular weight fractions derived from liquid chromatography organic carbon detection (LC-OCD) and dissolved organic carbon (DOC). Uptake kinetics, resin age and mass transfer diffusion were also investigated. DOC removal was similar for both

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chloride and bicarbonate resins, achieving ca 50% DOC removal. LC-OCD analysis revealed that organic matter between 0.35-1 kDa was the most efficiently removed, with slightly better uptake with bicarbonate IEX. However, these differences did not impact DBP formation potential. Trihalomethane (THM) and haloacetic acid (HAA) formation potentials followed the trends of DOC removal with up to 70% reduction after IEX treatment with both resin forms. However, the bromine substitution factor (BSF) increased with resin age -from 5-10% for THMs and from 4-7% for HAAs. Resin age resulted in up to 20% decrease in the organic matter uptake rates (from 0.19 to 0.15 min^{-1}) and up to 34% decrease in pore diffusivities (from 9.4 x 10^{-12} to 7.1 x 10^{-12} m^2/s for chloride IEX and from 1.0 x 10^{-11} to 6.6 x 10^{-11} m^2/s).

Keywords:disinfection by-products; HAAs; mass transfer; organic matter; THMs

1. Introduction

Ion exchange (IEX) consists of a reversible exchange of ions between solid and liquid phases (SenGupta, 2017; Wachinski, 2016). Removal of organic matter by IEX occurs mostly via the stoichiometrical exchange of charged ions, although some limited physical adsorption also takes place (Bazri and Mohseni, 2016). Most IEX resins used for organic matter removal are strong basic anionic (SBA) resins with polystyrenic or acrylic structures regenerated in the chloride form (Boyer and Singer, 2008; Metcalfe et al., 2015). In most cases, the regenerant used is NaCl due to its good performance, wide availability and relatively low cost.

IEX changes the treated water chemistry as ions (organic and inorganic) are exchanged. In turn this can change the corrosivity and plumbosolvency of the water in distribution. For example, the use of IEX in the chloride form has been shown to increase the aggressiveness of the source towards cast iron and lead pipes from the release of chloride into treated water (Willison and Boyer, 2012). A solution to this is to consider alternative regenerants that are less aggressive. For example, bicarbonate could be beneficial due to its potential to reduce the corrosivity of the treated water via the formation of a protective layer that inhibits corrosion (Takasaki and Yamada, 2007; Nguyen *et al.*, 2011). Moreover, disposal of bicarbonate-based brine waste into sewers may have positive effects, such as increasing the pH buffering capacity and aiding nitrification in wastewater (Maul et al., 2014).

Previous research has outlined the similarities between the removal capabilities of chloride and bicarbonate IEX for organic matter at both laboratory (Rokicki and Boyer, 2011; Walker and Boyer, 2011) and pilot scale (Hu and Boyer, 2017; Ness and Boyer, 2017; Liu et al., 2021), using magnetic ion exchange (MIEX) and conventional polymer resin (Table S1). In these studies, organic matter removal difference between chloride-form and bicarbonate-form IEX ranged between 4-20%.

Despite these studies comparing DOC removal by chloride or bicarbonate IEX, to the authors knowledge, no research has been carried out investigating the impact of bicarbonate IEX on the resulting potential for disinfection by-product (DBP) formation in treated water. In particular, trihalomethanes (THMs) and

haloacetic acids (HAAs) are DBPs of interest in drinking water sources as either THMs or both THMs and HAAs are usually regulated. Moreover, this is the first study comparing the organic matter molecular weight fractions removed by chloride and bicarbonate IEX using liquid chromatography with organic carbon detection (LC-OCD). Previous studies have reported on the organic matter molecular weight fractions removed by bicarbonate IEX derived from high performance size-exclusion chromatography (HPSEC) (Rokicki, 2013). However, HPSEC is limited to organic compounds absorbing at specific UV wavelengths (Brezinski and Gorczyca, 2019). LC-OCD analysis classifies all organic matter molecules by their molecular weight fractions. These fractions have been linked to different organic matter groups and functionalities (e.g., biopolymers, humic-like substances or low molecular weight acids) and has been successfully used to characterise water treatability by chloride IEX (Carra et al., 2021; Metcalfe et al., 2015). Changing regenerant can impact the swelling pressure in the resin and, therefore, so can selectivity. Thus, the organic matter fractions removed by bicarbonate IEX might be different from chloride IEX, affecting the resultant formation potential of DBPs. This highlighting the need for further research to characterise and compare the organic matter fractions removed by chloride and bicarbonate IEX.

The aim of this work, therefore, is to: i) investigate and compare the molecular weight fractions removed by chloride and bicarbonate IEX; ii) assess potential for THM and HAA formation; iii) study the kinetics and mass transfer mechanisms; and iv) assess the impact of inorganic ion removal on water corrosivity.

2. Materials and methods

2.1 Water and resin samples

Samples were collected from a lowland river source in the east of England (Table S2). All samples were stored in at 4ºC until they were used for testing or analysis.

The resin used in all tests was Lewatit S-5128, a strong gel type 1 resin with an acrylic structure. Three resin samples were used: new (virgin resin); used resin from a pilot plant that had treated the same water source for 6 months; and resin from a full scale Suspended Ion Exchange (SIX) plant in the Netherlands that had been used for more than 3 years. The virgin resin was stored in the dry until use (as suggested by the manufacturer). The used resins, were stored in water and kept in the dark at room temperature until use.

2.2 SIX resin conditioning and batch tests

This study has been based on the use of Suspended Ion Exchange (SIX) as an IEX process, where the IEX resin is suspended through jar testing described below. The resin conditioning was performed using a similar methodology to that of Finkbeiner *et al.*, 2019 and described as follows:

To change the mobile counterion, the resin was regenerated overnight with 1 M solution of $NaHCO_3$ (90 g/l) or NaCl (63 g/l). Prior to regeneration, the resin was stirred with 10 bed volumes (BV) of deionized (DI) water for 10 minutes. After regeneration, an initial wash with 20 BV of DI was performed followed by 30

minutes stir with 20 BV of DI water, to ensure that all non-adsorbed ions were washed away.

To measure the exchange capacity, a 10 ml resin sample was placed on a beaker with 30 BV of nitrate solution (1% w/v) on an orbital shaker stirring overnight, to ensure complete exhaustion of the resin counterion. To compensate for evaporation of the sample, the weight was measured before and after the experiments. The capacity of the resin was calculated by measuring the concentration of exchanged counter-ions after 24 h contact time and normalised by the resin dose used (SenGupta, 2017). The exchange capacity was experimentally measured to be 1 eq/l.

In the SIX process, the reactor kinetics follow a plug-flow configuration. Therefore, batch mixing tests using a jar tester can be used to obtain representative results of the process performance (Galjaard and Kamp, 2014). All tests used a resin dose of 20 ml/l in 1 l samples of raw water, considered a typical dose for SIX treatment (Carra et al., 2021). Mixing was carried out on a Phipps and Bird jar tester using a stirring speed of 200 RPM.

Continuous batch regeneration tests were conducted by performing 15 sequential cycles regenerating the resin after each cycle with either 1.0 or 0.5 M solutions of chloride or bicarbonate regenerant (Table S3). A blank test was carried out in parallel without regeneration (15 consecutive tests without regenerating the resin). Samples were taken after 30 minutes, a residence time equivalent to that used in operational SIX systems and a point close to the pseudo-equilibrium

(Caltran *et al.*, 2020). The volume of brine and rinse water was two times the resin volume (40 ml each), with the regeneration and rinse time being 30 minutes.

Kinetic tests were conducted in duplicate using different aged resins at sequential cycles 1 and 15 (Table S3). Experiments were performed with the resin samples in chloride and bicarbonate form, taking samples after 3, 6, 10, 20 and 30 minutes of operation. All samples were filtered using a 0.45 μm syringe filter before analysis.

2.3 Organic matter adsorption kinetics and mass transfer during IEX treatment

The DOC uptake by the resin (q_t) was normalised to the resin dose for each experiment, expressed as:

$$q_t = \frac{C_0 - C_t}{V_r * \rho_r} * V \quad (1)$$

Where C_0 was the initial concentration of DOC (mg/l), C_t was the concentration of DOC at time t, the resin dose was represented by V_r (0.02 l resin/l sample), ρ_r was the wet resin density (1.09 g/ml, according to the manufacturer) and V was the sample volume (1 l).

The kinetics of suspended ion exchange can be investigated using pseudo-first order (PFO) and pseudo-second order (PSO) kinetic models (Caetano *et al.*, 2009; Bazri and Mohseni, 2016; Tien and Ramarao, 2017). The kinetic constants for the PFO and PSO models were calculated considering the DOC uptake at the end of the experiment (30 min) as a pseudo-equilibrium. While the physical significance of the PFO and PSO models is limited (Tien and Ramarao, 2017;

Inglezakis *et al.,* 2019), they provide a useful means of comparing the rates of pollutant removal for different experimental set-ups and have been used widely in similar studies.

2.3.1 Pseudo first order (PFO) model

The most used form of the PFO equation was proposed by Ho and McKay (1999):

$$\log(q_e - q_t) = \log * q_e + k_1 * \frac{t}{2.303} \quad (2)$$

Which can also be expressed as:

$$q_t = q_e * (1 - \exp(k_1 * t) \quad (3)$$

With t as the experimental time in minutes, q_t defined as the amount of adsorbed solute, q_e being the amount of adsorbed solute at the pseudo equilibrium time, and k_1 the PFO kinetic constant.

If the uptake at the pseudo-equilibrium time is known, the expression above can be expressed in terms of fractional uptake U(t):

$$U(t) = \frac{q_t}{q_e} = \frac{C_0 - C_t}{C_0 - C_e} \quad (4)$$

Therefore, the PFO equation expressed in terms of fractional uptake is as follows:

$$U(t) = 1 - \exp(k_1 * t) \quad (5)$$

2.3.2 Pseudo-second order (PSO) model

The most utilised formula of the PSO expression is the one proposed by Simonin, (2016):

$$\frac{t}{q_t} = \frac{1}{k_2 * q_e^2} + \frac{t}{q_e} \quad (6)$$

Eq. (6) could also be rewritten as:

$$q_t = \frac{q_e^2 * k_2 * t}{1 + q_e * k_2 * t} \quad (7)$$

Which expressed as a function of the fractional uptake is:

$$U(t) = \frac{k_2 * q_e * t}{1 + k_2 * q_e * t} \quad (8)$$

Where k_2 is the pseudo second order kinetic constant.

2.3.3 Mass transfer rate limiting step

In the suspended ion exchange process, the ion exchange step is considered to be fast and not rate-limiting, where film or pore diffusion are slower steps. To elucidate the rate transfer limiting step, the DOC kinetic data was fitted using the homogeneous particle diffusion model (HDPM). This model discerns whether the diffusion is limited by pore diffusion (PDM) or film diffusion (FDM). The model assumes diffusion occurring only on the phase of interest (film or particle) being the resistance to mass flow defined by the diffusion coefficient of the model (Helfferich, 1995; Najid et al., 2021). The purpose of these calculations was to determine the changes in the film and pore diffusivities derived from the resin age and the regenerant change. The application of the models to an individual species despite the exchange of other species also occurring is an approach that has been taken by other researchers (Boyer *et al.*, 2008a; Singh *et al.*, 2012; Dixit *et al.,*2019).

The DOC was determined experimentally to be approximately 0.5% of the available exchange sites on the resin (0.12 meq/l DOC over 20 meq/l for 20 ml/l resin), which was consistent with previous experiments using IEX resins for DOC removal (Mergen *et al.*, 2008; Bazri and Mohseni, 2016; Finkbeiner *et al.*, 2018). Therefore, the reduced DOC concentrations relative to the resin exchange capacity (the ion displaced from the exchanger) allowed for the assumption of infinite solution conditions for the mass transfer calculations (i.e., $C_0 * V \ll q_r * V_r$) (Singh *et al.*, 2012).

The diffusion models are expressed as a function of the fractional uptake at equilibrium U(t). For example removed DOC at time t versus removed DOC at 30 minutes contact time (Bazri and Mohseni, 2016).

For homogeneous spherical particles, under infinite solution conditions, the analytical solution of the diffusion differential equation becomes (Helfferich, 1995):

$$U(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} * \exp\left(-\frac{D_a * \pi^2 * n^2 * t}{r_p^2}\right) \quad (9)$$

t was the time, n was the term of the infinite series, Da was the apparent pore diffusion coefficient and r_p was defined as the particle radius.

The Vermeulen's approximation (Vermeulen, 1953) can be applied across the entirety of the U(t) range ($0 \leq U(T) \leq 1$):

$$U(t) \cong \left[1 - \exp\left(-\frac{D_a * \pi^2 * t}{r_p^2}\right)\right]^{\frac{1}{2}} \quad (10)$$

If linearised, equation 10 can be used to fit the experimental data:

$$\ln(1 - U(t)^2) = \frac{2 * D_a * \pi^2 * t}{r_p^2} \quad (11)$$

If film diffusion controls mass transfer, the film diffusion model equation derived represents the changes in the fractional uptake:

$$\mathrm{U(t)} = 1 - \exp\left(-\frac{3 * \mathrm{D_f} * \mathrm{C_e} * \mathrm{t}}{\mathrm{r_p} * \delta * \mathrm{C_s}}\right)$$

D_f was the film diffusion coefficient, C_e was the concentration of solute at equilibrium in the bulk solution, C_s was defined as the concentration of solute at equilibrium in the sorbent and δ was the film thick thickness (10^{-5} m) (Harland, 1995; Bazri and Mohseni, 2016).

This term can be linearised to fit the experimental data:

$$\ln\big(1 - \mathrm{U(t)}\big) = -\frac{3 * \mathrm{D_f} * \mathrm{C_e} * \mathrm{t}}{\mathrm{r_p} * \delta * \mathrm{C_s}} \quad (12)$$

All variables used in this section are defined in Table S4.

2.4 Analysis

DOC was measured by a Shimadzu TOC-V analyser as non-purgeable organic carbon (NPOC). Prior to analysis, samples were filtered with a 0.45 μm syringe-filter. All samples were acidified using 2 M HCl and purged with carbon-free air to remove CO_2 derived carbonates and bicarbonates. The method used was tuned to measure DOC in the 1-10 mg/l range with a limit of quantification (LOQ)

of 1 mg/l, with quality control samples measured every 10 samples. The TOC calibration curve was prepared from a stock solution of 1000 mg/l potassium hydrogen phthalate stock standard. Dilutions of 0, 1, 2, 5, 8, 10 mg/l were used for the calibration curve.

Chloride, sulphate and nitrate were analysed using a Dionex ion chromatography system (ICS-1600) with an electrical conductivity detector. An ASH9C column and an AG14A pre-column were used with an eluent flow of 1 ml/min and Na_2CO_3 concentration of 9 mM. LOQs were 0.12 mg/l for nitrate, 3.4 mg/l for sulphate and 12 mg/l for chloride with quality control checks run every 10 samples. Results were unaffected by the high LOQ for chloride as the chloride concentrations reported on the study were significantly higher than the LOQ (40-260 mg/l). IC calibration curves were prepared from stock solutions of sodium chloride, potassium nitrate and sodium sulphate at a concentration of 1000 mg/l of the anion. The calibration curves were prepared from the stock solution at concentrations of 2, 10, 30, 60 and 100 mg/l for chloride; 0.5, 2.5, 7.5, 15 and 25 mg/l for nitrate; and 1, 5, 15, 30 and 50 mg/l for sulphate.

Bicarbonate concentrations were measured using 0.02 M HCl acid as a titrant and a combination of phenyl red and bromocresol green in methanol as the midpoint indicator. Samples were also checked for carbonates using the phenolphthalein method. Negative results showed that the overall alkalinity was due only to the presence of bicarbonate anions (Judd, 2019; HACH, 2020).

Samples were sent for LC-OCD analysis to the Het Water Laboratorium (Netherlands) for determination of the molecular weight distribution before and

after treatment with the SIX resins according to the method described by Huber et al (2011). Briefly, 1 ml of buffered sample was injected into a weak cation exchange column with a separation range of 0.1-10 kDa. The elution volume was set at 1.1 ml with a column bypass that was used as a reference for the total DOC of the sample. The difference between the DOC in the chromatograph and the total DOC of the sample is attributed to organic matter that remained on the resin (referred as hydrophobic organic carbon). For the remaining organic matter, elution time is inversely proportional to molecular weight. Detection and interpretation of the peaks was made by software (ChromCALC) that combines the signals obtained from the UV and DOC detectors. A Poisson distribution was fitted to the peak with the highest signal area (~1 kDa) and was used to determine the areas and boundaries of the remaining peaks. This method produces five distinct organic matter fractions: >10 kDa; 1 kDa; 550-350 Da; 350 Da acids and neutrals; and 350 Da neutrals. The limit of detection (LOD) and LOQ of this method are reported to be within the low ppb range (Huber *et al.*, 2011).

Charge density was measured by titration with polydiallyldimethylammonium chloride (PDADMAC) using zeta potential (Malvern Nano Series, Worcestershire, UK) as an indicator, following the method used by Finkbeiner *et al.* (2018). Zeta potential measurements were performed by transferring the sample to a polystyrene latex folded capillary cell which was equilibrated to 25°C, using a peristaltic pump and measured in triplicate with a minimum of 10 and a maximum of 100 runs.

The volume of sample per titration was 15 ml. The sample was adjusted to pH 7 using 1M HCl and NaOH of analytical reagent grade and titrated with PDADMAC at a concentration of 6.2 meq/l (diluting a 20% wt PDADMAC stock solution to 0.1% w/v) past the isoelectrical point (point of zero charge) using an auto titrator MPT-2 with a 3-channel degasser (Malvern). The charge load (amount of titrant required to achieve the isoelectrical point) was calculated by fitting a straight line of at least 3 measurements near the point of zero charge. The charge density was defined as the charge load divided by the sample DOC concentration.

DBP formation potential (DBP-FP) tests were performed on raw water and all SIX treated samples after 30 minutes contact time. A stock chlorine solution was prepared by diluting concentrated sodium hypochlorite (10-14% w/v) solution in UP water to a 1:100 ratio. The stock concentration was determined by further dilution of the working stock with UP water using a 1:1000 ratio. Free chlorine was measured with N, N-diethyl-p-phenylenediamine (DPD) by a Hach portable spectrophotometer.

Samples were diluted with ultrapure (UP) water to 1 mg/l DOC, spiked with 5 mg/l of free chlorine and incubated in 100 ml Pyrex glass bottles with no headspace and PTFE caps in the dark at room temperature for 7 days. Afterwards, the excess chlorine was quenched using sodium sulphite and ammonium chloride for THMs and HAAs, respectively. The DBP species were transferred to an organic solvent using liquid-liquid extraction and analysed by a gas chromatography with an electron capture detector (GC-ECD). Extraction an analysis of four THMs (bromoform (BF), dibromochloromethane (DBCM), dichlorobromomethane

(DCBM) and chloroform (CF)) and nine HAAs (monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dibromo acetic acid (DBAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), dibromochloroacetic acid (DBCAA), dichlorobromoacetic acid (DCBAA), trichloroacetic acid (TCAA) and tribromoacetic acid (TBAA) was performed following a modified methodology of the USEPA extraction method (551.1 and 552). The THM calibration curve was prepared from a 1000 ug/l stock solution of BF, DBCM, DCBM and CF. Dilutions were prepared at concentrations of 0, 25, 50, 75, 100, 200 ug/l. The calibration curve for HAAs was prepared similarly, with a stock solution of 1000 ug/l containing MCAA, MBAA, DBAA, DCAA, BCAA, DBCAA, DCBAA, TCAA and TBAA. For the different DBP species the LOQ was 1 μg/l, except for MCAA which was 2 μg/l.

To ensure the integrity of the measurements all the experiments were performed in duplicate, in addition to quality control checks for all types of analysis performed.

2.5 Bromine substitution factor

The bromine substitution factor (BSF) is defined as the ratio of the bromine incorporated into a given class of DBPs to the total concentration of chlorine and bromine in that class (Hua and Reckhow, 2012).

$$1)\quad BSF(\%) = \frac{\sum_{i=1}^{n} br_i * molar\ concentration\ brominated\ species_i}{\sum_{o=1}^{p} h_o * molar\ concentration\ DBP\ species_o}$$

With br_i defined as the number of brominated atoms in the DBP species, h_0 being the number of halogenated atoms (Br and Cl) in the DBP species, n is the number of brominated species and p the number of DBP species.

For THMs, the BSF is:

$$2)\quad BSF_{THM} = \frac{[BDCM]+2*[DBCM]+3*[BF]}{3*([CF]+[BDCM]+[DBCM]+[BF])}$$

For HAAs, the BSF is:

$$3)\quad BSF_{THM} = \frac{([BCAA]+[MBAA]+[BDCAA])+2*([DBAA]+[DBCAA])+3*[TBAA]}{([MCAA]+[MBAA])+2*([DBAA]+[DCAA]+[BCAA])+3*([DCBAA]+[DBCAA]+[TCAA]+[TBAA])}$$

2.6 Water corrosivity

The risk of corrosion was assessed by the Larson Index (LI) and the chloride to sulphate mass ratio (CSMR) as defined below:

The LI (Larson and Skold, 1958) is defined as the ratio between the sum chloride and sulphate milliequivalents divided by the alkalinity:

$$LI = \frac{[Cl^-] + 2 * [SO_4^{2-}]}{[Alk]}$$

The CSMR is the mass ratio between chloride and sulphate in mg/l:

$$CSMR = \frac{C_{Cl^-}}{C_{SO_4^{2-}}}$$

3. Results and Discussion

3.1 Impact of regenerant and resin age on organic matter removal

Understanding the changes in organic matter uptake derived from the regenerant change and resin age is important to predict the treatability of the source using SIX as an organic matter removal process. The influence of resin age on organic matter removal using SIX in chloride and bicarbonate form was firstly assessed from kinetics experiments (Figure 1).

Resin age and regenerant change had a limited impact on the DOC uptake and the removal of UV_{254} absorbing moieties, with comparable performance for all conditions considered. Results after 30 min resulted in DOC concentrations for the different aged resin samples of 3.4 ± 0.1 mg/l and 3.3 ± 0.2 mg/l for chloride and bicarbonate form resin, respectively. Equivalent figures for UV_{254} were 0.030 ± 0.002 for chloride form and 0.033 ± 0.001 cm^{-1} for the bicarbonate form resin, outlining the similarities between treatments. The use of SIX in either regenerant form was more effective at removing UV_{254} absorbing moieties than DOC, with relative removals of 50% and 80%, respectively. The increased UV_{254} reduction in comparison to DOC was attributed to the preferential removal by IEX of charged organic matter moieties such as humic and fulvic acids, that present a high degree of aromaticity (Mergen *et al.*, 2009; Huber *et al.*, 2011).

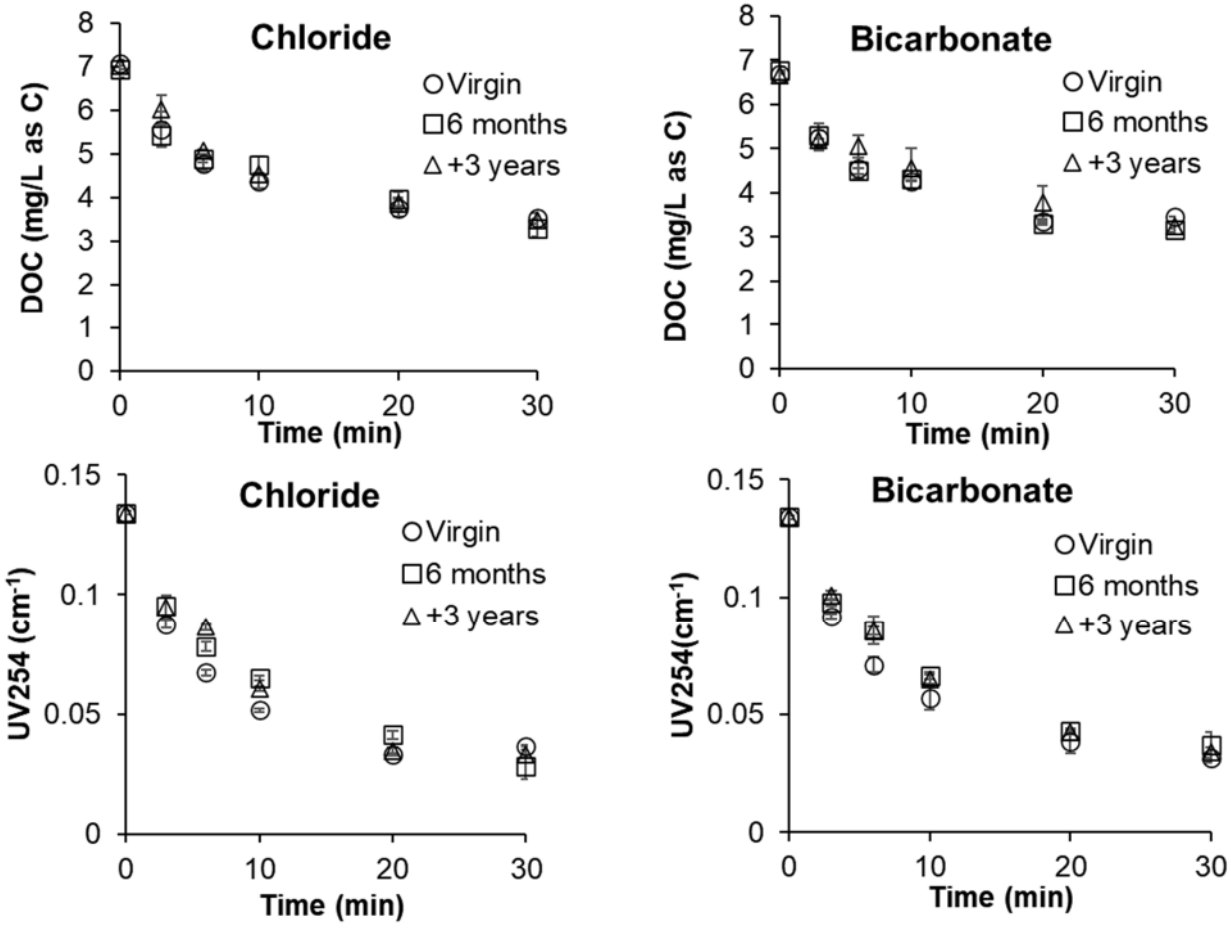


Figure 1. Impact of resin age and regenerant on DOC concentration and UV_{254} during SIX treatment.

A set of sequential batch experiments was performed over 15 cycles using virgin resin, where the resin was regenerated after every treatment cycle (Figure 2). The purpose was to evaluate the longer-term performance of bicarbonate under similar regeneration conditions. In agreement with the kinetic tests (Figure 1), DOC concentrations were similar with the chloride or bicarbonate form resin. Results after 15 cycles reduced the final DOC concentration from 6.5 ± 0.1 to 2.6 ± 0.1 mg/l and to 2.5 ± 0.1 mg/l for chloride and bicarbonate resin forms, respectively. Similarly, reducing the regenerant concentration from 1 to 0.5 M did

not have a significant impact on DOC removal. The similarities in removal were attributed to the reduced differences between the hydrated radius of bicarbonate (3.64 Å) (Kiss *et al.*, 2013) and chloride anions (3.32 Å) ~~(Marcus, 1988)~~ Richards et al., (2012), in addition to the high degree of charge of the organic matter in the source water (17.4 ± 2 meq/ g DOC). This is a result consistent with previous research (Walker and Boyer, 2011; Ness and Boyer, 2017).

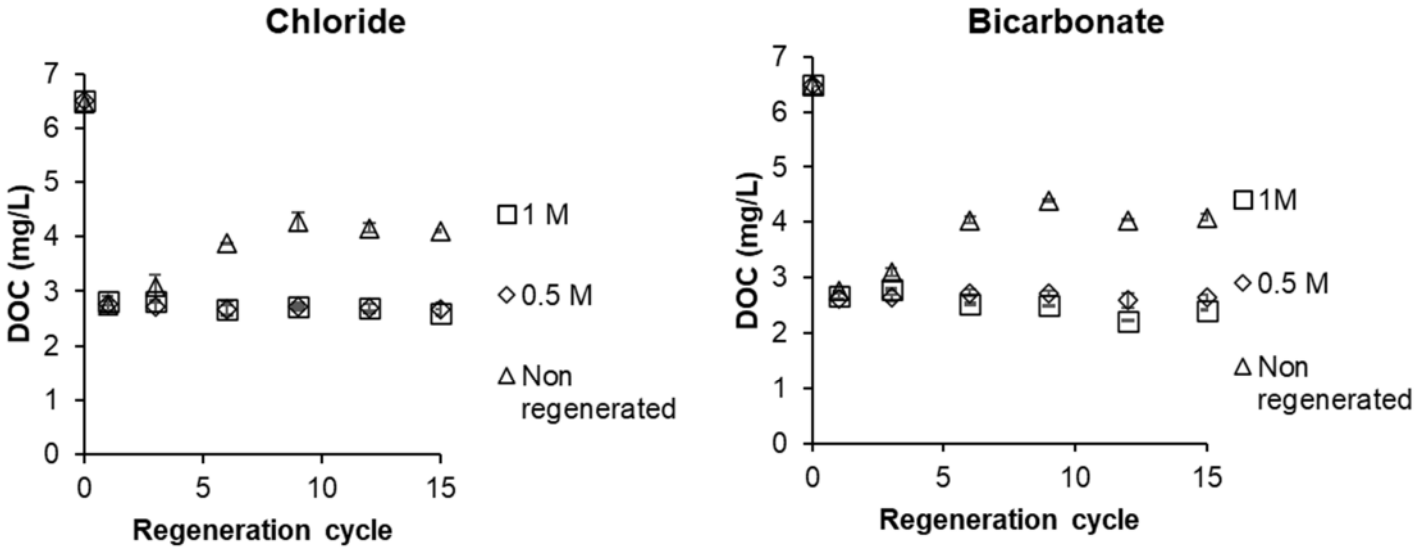


Figure 2. SIX treated water DOC concentration over 15 treatment cycles using chloride and bicarbonate form resins regenerated after every cycle at 0.5 M, 1 M and not regenerated.

A set of sequential batch experiments was also performed consecutively over 15 cycles without regenerating the resin between treatment cycles (Figure 2). Results were also comparable for both resin forms. There was an increase in the DOC treated effluent due to resin fouling in comparison to the regenerated samples that plateaued after cycle 9. DOC levels were consistently reduced from 6.5 ± 0.1 to 4 ± 0.1 mg/l from cycle 9 to cycle 15, despite regeneration not taking

place. It is considered that the stability in DOC removal after cycle 9 despite using the non-regenerated resin was caused by exchange of organic matter with previously exchanged inorganic anions (e.g. nitrate, chloride) in the so called secondary IEX (Edgar and Boyer, 2021), a hypothesis that is further explored later in the results.

A more in-depth approach to the influence of the regenerant change on organic matter removal was taken using LC-OCD analysis (Figure S1). The LC-OCD has both an improved precision in detecting organic carbon and is able to discriminate different molecular weight size ranges when compared to conventional DOC analysis (low μg/l range) (Huber *et al.*, 2011). This allowed for the identification of small differences in removal between the two different regenerants. In line with previous results (Mergen *et al.*, 2009; Caltran *et al.*, 2020), most of the organic matter removed by SIX was related to the 1 kDa and 0.5-0.35 kDa organic matter size bands. This was a consistent result for both regenerant forms, in agreement with data obtained from size exclusion chromatography (Rokicki, 2013).

The bulk of the differences between chloride and bicarbonate form IEX were seen in the removal of organic matter <0.35 kDa (45-55 retention time). This peak accounts for low molecular weight (LMW) acids and LMW humic substances. Huber et al. (2011) suggested that a UV signal at this retention time is indicative of the presence of LMW humic substances rather than LMW acids. In this case, the UV signal of the sample at the 45-55 retention time matched that of the OCD signal (Figure S2), supporting the idea that this peak mainly contained LMW humic substances rather than LMW acids.

A quantitative comparison was also performed (Figure 3). After fifteen cycles of regeneration, the use of SIX in bicarbonate form showed a positive effect on the uptake of higher molecular weight organic matter, with removals of 194 and 141 µg/l for bicarbonate form SIX regenerated with 1 and 0.5 M, respectively. Equivalent results with SIX in the chloride form were 60 and 27 µg/l removed for resins regenerated with 1 M and 0.5 M. These differences were not observed in the bulk DOC measurements (Figures 1 and 2) due to the higher limit of detection (LOD) of the TOC analyser (LODs within the low mg/l and low µg/l ranges for TOC and LC-OCD, respectively), showcasing the advantages of LC-OCD analysis to understand treatability of organic matter in terms of both analysis sensitivity and identification of organic matter fractions.

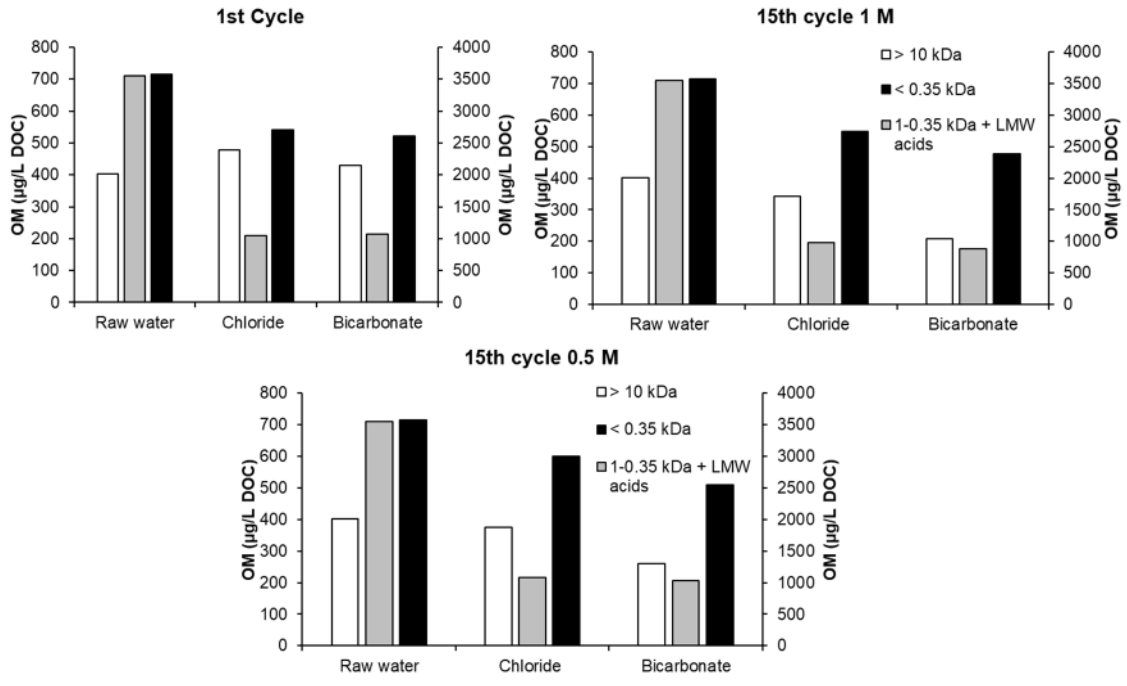


Figure 3. LC-OCD organic matter removal percentage before and after SIX treatment after 1 and 15 treatment cycles with 0.5 and 1 M regenerant concentration.

The differences in the amount of organic matter removed between 0.35-1 kDa after SIX treatment in the chloride and bicarbonate form increased with subsequent regeneration cycles. For example, the removed organic matter between 1-0.35 kDa was slightly higher for chloride (70.4%) than bicarbonate (69.8%) in the first cycle, evidenced from the observed peak at 45-55 min retention time (Figure 3). After fifteen regeneration cycles, the removed organic matter was 72.5% and 69.6% for 1 and 0.5 M using SIX in chloride form, respectively. Equivalent figures for bicarbonate form resin were 75.5% and 70.9%, showing the favourable effect of increasing regenerant concentration and using bicarbonate instead of chloride. Despite the peak at 45-55 min being higher with the bicarbonate-form resin, the improved removals observed between 30-45 min counteracted the increase with respect to the overall DOC removal. The differences observed in removal for the first and last cycles for organic matter >0.35 kDa were attributed to irreversible swelling of the resin (SenGupta, 2017). It was hypothesised that the pore size increased with subsequent regeneration, improving the overall organic matter amenability by SIX in either regenerant form.

For organic matter <0.35 kDa, the removal decreased when comparing the first (24.5%) and fifteenth cycles (23.5% and 15.9% using 1 M and 0.5 M, respectively) for SIX in the chloride form. This trend was not observed with the bicarbonate form resin, with results being 27.1% for the first cycle, and 33.3% and 28.8% for fifteenth cycle at 1 M and 0.5 M, respectively. It was considered that the reduced degree of charge of this fraction made it more susceptible to

changes in the resin such as from its continuous use or from the regenerant change.

For all organic matter sizes, the use of IEX in bicarbonate form provided increased removal in comparison to chloride form SIX. However, the differences were small and only detected from the data obtained from the LC-OCD. For example, the combined differences for bicarbonate and chloride were less than 0.3 mg/l of DOC. The differences observed with LC-OCD using bicarbonate form SIX were attributed to the slightly larger hydrated radius of bicarbonate (3.64 Å) (Kiss *et al.*, 2013) in comparison to chloride (3.32 Å) Richards et al., (2012). The larger the difference between the equivalent hydrated volume of the exchanged compound (i.e. organic matter) and the counter ion (bicarbonate or chloride), the higher the selectivity of the resin (Najid et al., 2021). This is due to the change in the degree of swelling in the exchanger, which affects the diffusivity of the exchanged compound.

The removal of inorganic anions was also assessed (Figure S3). There was a small increase in nitrate removal for the SIX treated effluents using bicarbonate-form resin in comparison to chloride. On average, bicarbonate regenerated resins, regardless of age, increased nitrate removal by 13% in comparison to chloride resins. On the other hand, sulphate removal was removed to a similar degree by both bicarbonate and chloride form resins at around 90% in all cases. This was attributed to the reduced equivalent hydrated volume of sulphate (0.19 nm) in comparison to nitrate anions (0.34 nm), which resulted in a larger

difference between the counter-ion (bicarbonate or chloride) and exchanged ion hydrated radius (sulphate), decreasing the resin's degree of swelling.

The influence of sequential batch regeneration on the uptake of ions was explored using both regenerants at 1 M and 0.5 M concentrations (Figure 4). In line with the initial batch tests, the use chloride or bicarbonate SIX at 1 M and 0.5 M removed sulphate by >90% for all the different cycles considered with little difference between regenerants. Sequential cycles without regeneration showed comparable trends in both cases following sigmoidal curves.

The concentrations of chloride and bicarbonate for their respective regenerant forms, were matched after cycle 9 (Figure 4). However, sulphate was removed until cycle 15, when treated water concentrations stabilised. These results were linked with the DOC data (Figure 2), where even after cycle 9 there was uptake of DOC as a result of secondary exchange with other adsorbed anions.

This can also explain the reduction in nitrate uptake after successive regeneration cycles by either resin form. After cycle 1, 50% nitrate removal was achieved on average using either regenerant. However, sequential regeneration reduced nitrate removal progressively until cycle 9, after which removal stabilised, with removal of 29 and 19% using chloride at 1 and 0.5 M, respectively. Improved nitrate uptake was seen by resin in the bicarbonate form, with removal of 37% and 29% with 1M and 0.5 M regenerant concentrations after cycle 9. The existence of a plateau after cycle 9 for samples with and without regeneration, suggest that there is a saturation of the active sites after 9 sequential cycles. Evidence for this was provided by the results showing that the initial

concentrations of the exchanged counterion matched the final concentration after cycle 9 (Figure 4). From this point onward, desorption was necessary to sustain organic matter removal, explaining the stability of nitrate after cycle nine in addition to secondary IEX as the main organic matter removal mechanism for the non-regenerated resins.

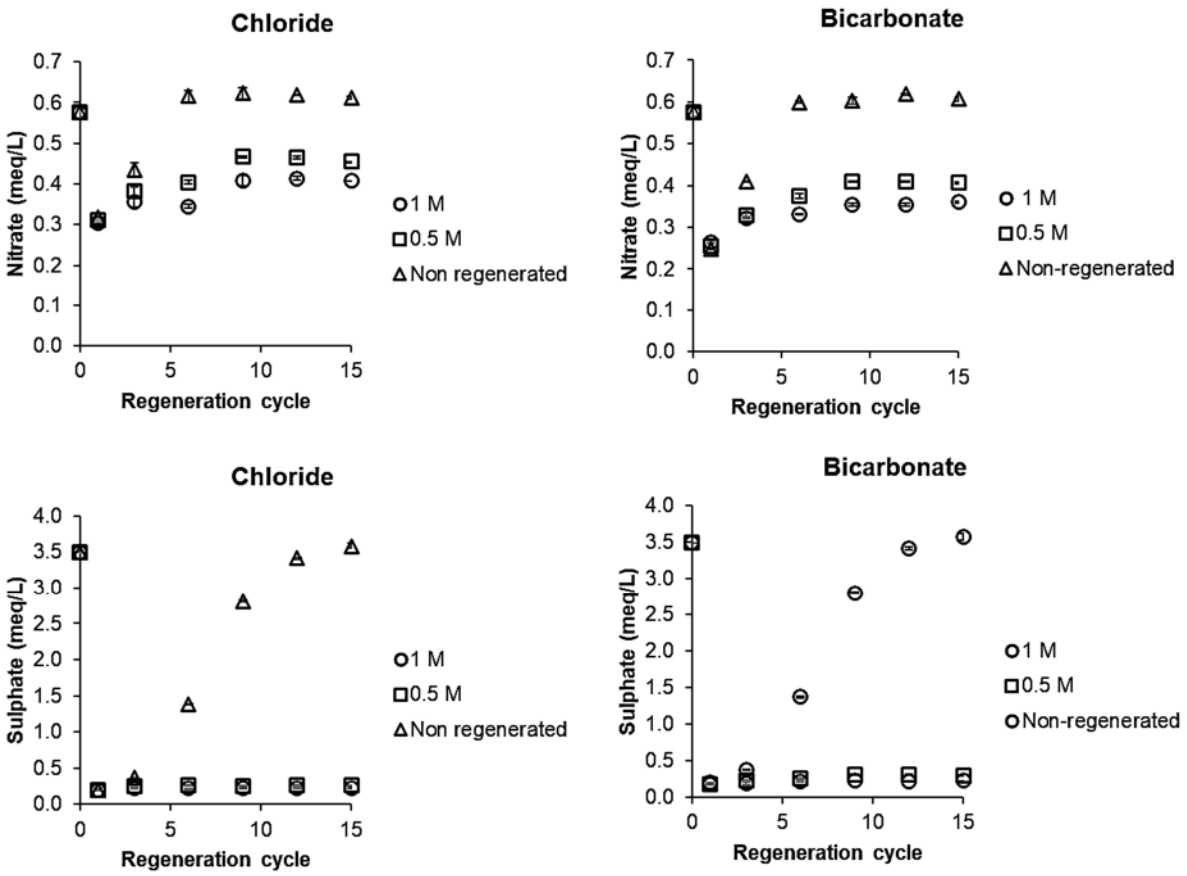


Figure 4. Nitrate and sulphate concentrations during fifteen sequential batch tests using different concentrations of chloride and bicarbonate regenerant on virgin resin.

Results for the non-regenerated cycles (Figure S4) showed desorption (concentrations higher than the raw water) for nitrate (both regenerants), chloride (bicarbonate regenerant) and bicarbonate (with chloride regenerant). Results confirmed secondary IEX as the main organic matter removal mechanism for the non-regenerated tests after 9 cycles, in agreement with the findings of Edgar and Boyer (2021).

Changes in the ion concentration affect the corrosivity of the water in the distribution network (Willison and Boyer, 2012). The Larson Index (LI) measures the degree of corrosiveness for a water source for cast iron surfaces with values above 0.8 related to pipe tuberculation (Larson and Skold, 1958). Chloride to sulphate mass ratios (CSMR) over 0.5 are related to increased lead galvanic corrosion due to the inhibition of the formation of a protective layer on the lead pipe's surface (Nguyen *et al.,* 2011a).

The LI was above one for the raw water as a result of the high concentration of sulphate in the source (171 ± 2 mg/l) (Figure 5). The use of SIX in chloride form increased the LI by a factor of 2-3, caused by the release of chloride and the uptake of sulphate and alkalinity. Positive synergies were observed with the use of bicarbonate form SIX, with LI values after fifteen sequential cycles being 5-10 times lower than the raw water (values < 0.5) using both 1 M and 0.5 M regenerant concentrations. A similar effect was observed for the CSMR where the ratio increased from 0.5 to >25 using SIX in the chloride form, whereas the resin in bicarbonate form achieved a CSMR of 4. These results showed the

positive influence of the regenerant change in the above-mentioned indices, limiting the corrosion potential of treated water.

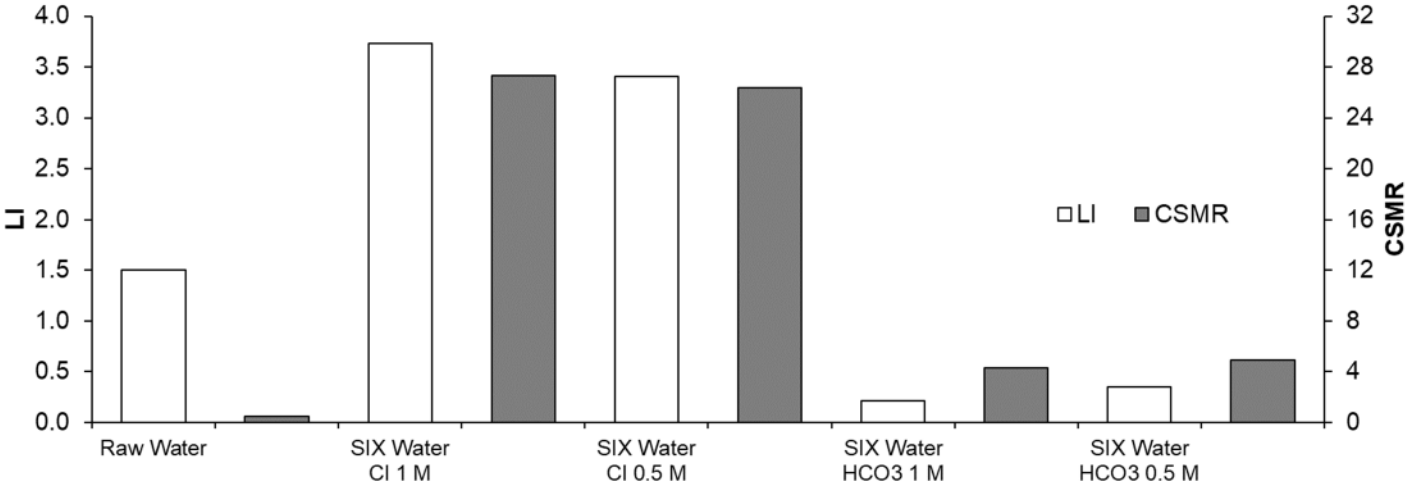


Figure 5. LI and CSMR for the raw and SIX treated waters after 15 cycles of sequential tests. The dotted line refers to the LSI limit (0.8) whereas the dashed line refers to the CSMR limit (0.5).

In summary, results showed that the use of bicarbonate as an alternative regenerant is feasible for the removal of organic matter. Similar organic matter removal performance was observed in both regenerant forms in terms of DOC, with LC-OCD results showing a small improvement with the use of SIX in bicarbonate form for the 0.35-1 kDa organic matter fraction. The following section addresses the changes in the DBP formation potential for the different resin samples caused by the regenerant change.

3.2 Impact of regenerant and resin age on DBP formation potential

The most effective manner to achieve DBP minimisation is the elimination of the organic matter precursors (Bond *et al.*, 2009; DWI, 2020). Previous studies

investigated the influence of the regenerant change from chloride to bicarbonate on organic matter removal with comparable performance on a DOC basis (Table S1). The use of LC-OCD showed that bicarbonate as an alternative regenerant had a small positive effect on the organic matter uptake. However, the influence on organic matter on the DBP formation, derived from the regenerant change and resin age, has not been previously studied.

Formation potential tests were performed on samples taken after 30 min contact time, from the kinetic tests and from the sequential batch regeneration experiments. Results obtained for the kinetic tests (Figure S5), were consistent with the DOC removal profiles (Figure 1). Resin age did not have a significant impact on THM-FP and HAA-FP using either regenerant. For example, SIX treatment, regardless of resin age in either regenerant form, reduced the THM-FP and HAA-FP on average by 71% and 72 %, respectively, in comparison to the untreated water. When the DBPs were considered as the formation potential yield, IEX reduced the treated water values by 44% and 47% for THMs and HAAs, respectively (Figure S6-S8). The similarities observed in the DBP yield reduction suggested an unselective removal of DBP precursors. In both cases, an efficient minimisation of the organic matter size band between 0.35-1 kDa was achieved by IEX, which made up the bulk of the raw water OCD signal (Figure 3) and was responsible for the reduction in DBP yield and concentration. The partial removal of the >10 kDa through adsorption on the resin surface also contributed to the reduction in the DBP yield, as suggested by Finkbeiner et al. (2018a). While there were reported differences in the removal of different molecular weight fractions

for bicarbonate and chloride form SIX, this did not translate to differences in the DBP formation potential indicating that there was no selectivity towards DBP precursors for the different regenerated resins. This is likely to be linked to similarities in the removal of organic matter that has a high potential to form trihalogenated HAAs and THMs, namely aromatic hydrophobic compounds such as humic and fulvic acids (Bond *et al.*, 2012). Dihalogenated HAAs, in particular DCAA, has been attributed to the presence of β-dicarbonyl structures (Jiang *et al.*, 2016). These compounds would be expected to appear in the 0.35-1 kDa size fraction, a fraction that was equally well removed by resins in both chloride and bicarbonate forms. Therefore, the reduction in DBP formation during SIX treatment of this lowland water source can be attributed to the efficient removal of the 0.35-1 kDa band and the organic matter molecules in this fraction, but also to the fact that this fraction is the largest and contributes to 40% of the organic content in this source.

The effectiveness of SIX in either regenerant form for reducing DBP formation was also explored after 15 sequential cycles (Figure 6). The results aligned closely to the X-Y diagonal line and were within the 95% confidence interval, indicating that the different forms of the IEX had similar removal of DBP precursors. Formation potential results for THMs and HAAs varied between 100-300 μg/l for the treated samples. In all cases, subsequent cycles caused an increase in the DBP-FP. However, this trend was not as pronounced for HAAs, as it was for THMs. For example, THM-FP increased from 130 μg/l from the first cycle to 230, 250 and 410 μg/l for the 1 M, 0.5 M and non-regenerated samples,

respectively after 15 cycles. Equivalent figures for HAA-FP were 190 µg/l on the initial cycle, and 165, 250 and 344 µg/l after 15 cycles using 1 M, 0.5 M and non-regenerated samples, respectively.

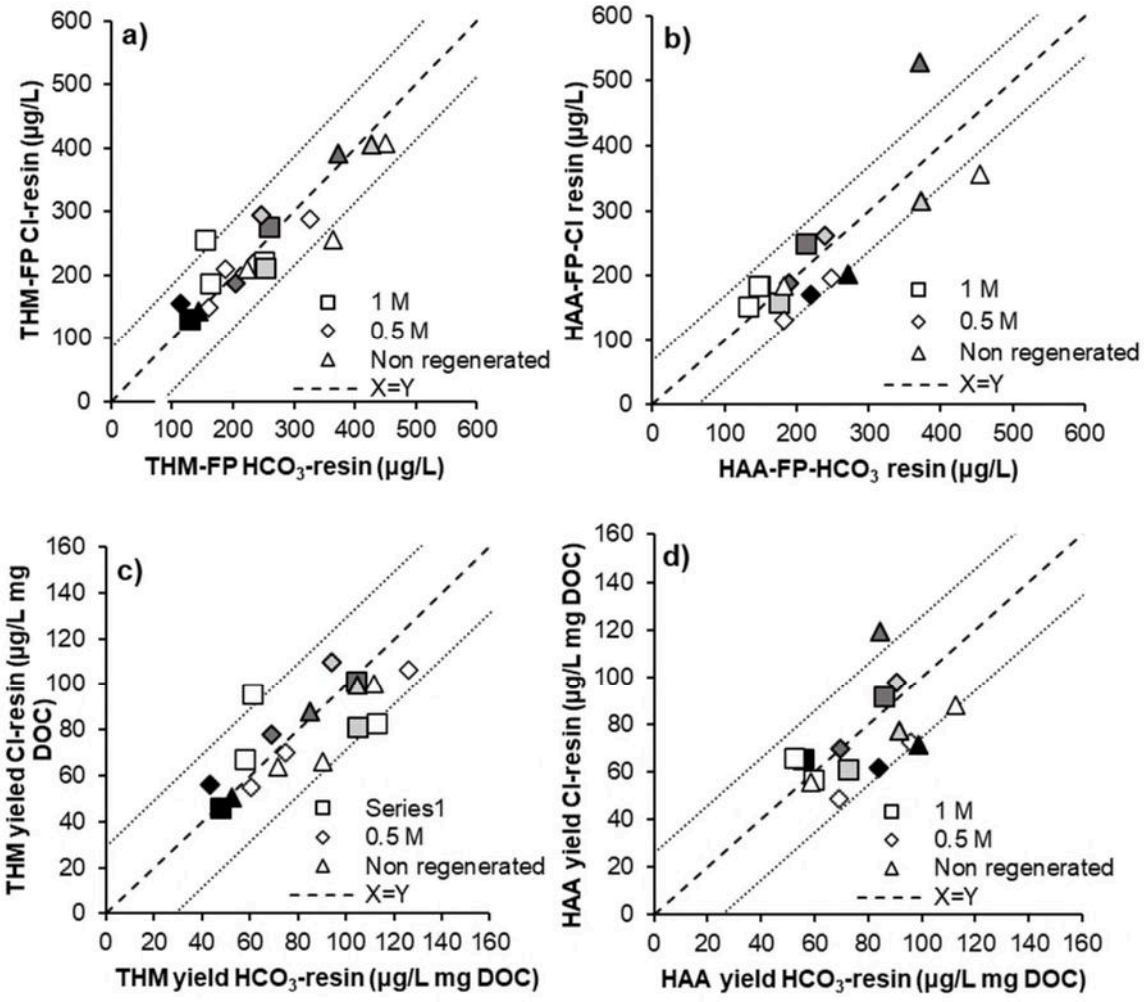


Figure 6. THM and HAA formation potential (a and b) and yield (c and d) for sequential cycles after SIX treatment with chloride and bicarbonate resins. Black, dark grey and light grey coloured samples refer to cycles 1, 9 and 15, respectively.

For samples with regeneration, the increase in the DBP-FP was caused by an increased reactivity of the organic matter in the treated samples, as the DOC

treated water after sequential cycles were stable (Figure 2). A possible explanation for the observed trends is that some of the THM/HAA precursors were not readily removed by IEX, resulting in an increase in their relative concentration with subsequent cycles.

For the non-regenerated cycles, DOC was reduced consistently from 6.5 ± 0.1 to 4 ± 0.1 mg/l, using the resin in both regenerant forms after cycle 9 (Figure 2). After fifteen cycles without regeneration, despite 2.5 mg/l of DOC being removed, THM-FP results were close to that of the raw water (417 ± 12 μg/l). Equivalent figures for HAAs were 344 ± 20 μg/l. These results evidenced the importance of regeneration for DBP precursors removal using SIX, despite secondary IEX effectively removing 40% of the incoming DOC. Further research is required for the identification of DBP precursors that were not readily removed by the treatment. The use of molecular level characterisation such as FT-ICR MS, NMR or ATR-FTIR could provide useful insights into the changes in organic matter performance and DBP formation with subsequent use of the resin.

The relative importance of brominated DBPs was assessed by the BSF (Hua and Reckhow, 2012). For THMs, the BSF increased from 5 to 10% when comparing virgin resin with used resins, resulting in similar BSF values seen for the untreated sample (12%) (Figure 7). For HAAs, the BSF increased for the older resins with BSF results of 4%, 6% and 7% for the virgin, 6 months used and + years used resins, respectively. From the sequential batch regeneration tests the final BSF was approximately 12% after 15 cycles, double the value obtained for the +3

years used resins. In all cases, the regenerant change did not influence the observed results.

The increase in the BSF was caused by higher concentrations of DBCM for THMs when comparing virgin resin to previously used resins, with values of 23.9 ± 2.8 μg/l for virgin resins and 36.7 ± 2.3 and 31.6 ± 6.7 μg/l for the 6 months and + 3 years used resins, respectively, in either regenerant form (Figure S5). For HAAs, the increases were related to BCAA with equivalent figures of 10.6 ± 1 μg/l for virgin resin, 17.0 ± 3.0 μg/l for 6 months used resin and 24.0 ± 11.1 μg/l for 3+ years used resin.

Previous studies have shown that high alkalinity levels limits bromide removal by IEX (Singer *et al.*, 2007; Metcalfe *et al.*, 2015). It was hypothesised that the increase in the brominated DBP species for used resins was caused by competition with other ions (e.g. sulphate, bicarbonate) and DOC, reducing the achievable removal yields for bromide by SIX in both regenerant forms (Hsu and Singer, 2010; Ding *et al.*, 2012). In other words, increased bromide concentrations relative to DOC in the water increased the proportion of brominated species for THMs and HAAs (Hua and Reckhow, 2012).

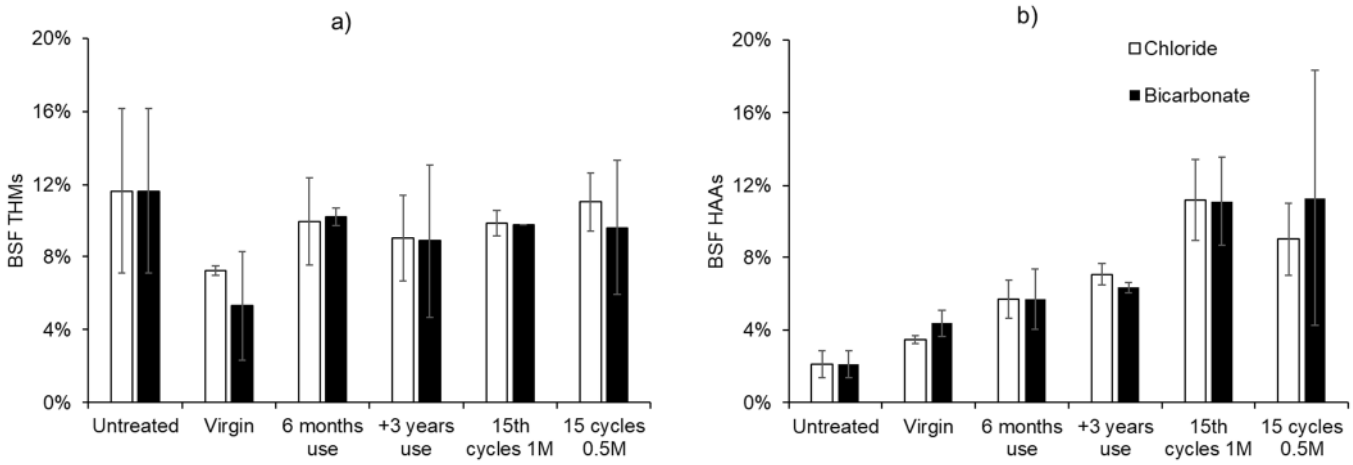


Figure 7. THMs (a) and HAAs (b) BSF for raw and SIX treated samples with chloride and bicarbonate regenerated resins.

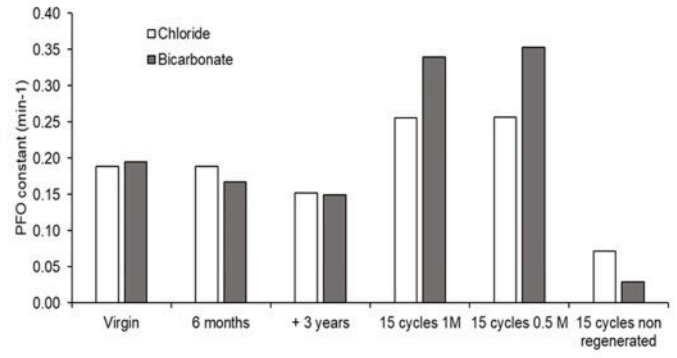
Kinetic and sequential regeneration experiments showed that the use of bicarbonate as an alternative regenerant does not have an observable impact on DBP formation. The similarities observed for DBPs were in alignment with the reported results for DOC, with comparable performance for both resin forms. LC-OCD results showed that bicarbonate regeneration increased slightly organic matter removal. However, this did not translate across to DBP-FP. Stable DOC removals of 40% were reported for the non-regenerated samples during sequential operation cycles, which were attributed to secondary-IEX. Nevertheless, THM-FP and HAA-FP increased threefold and twofold, respectively, when comparing cycles 1 and 15. Results evidenced that regeneration of the resin was essential to achieve DBP precursors minimisation. The comparable DBP reduction performance reported for SIX in chloride and bicarbonate form provided good evidence to support the use of bicarbonate as an alternative regenerant for organic matter treatment by IEX.

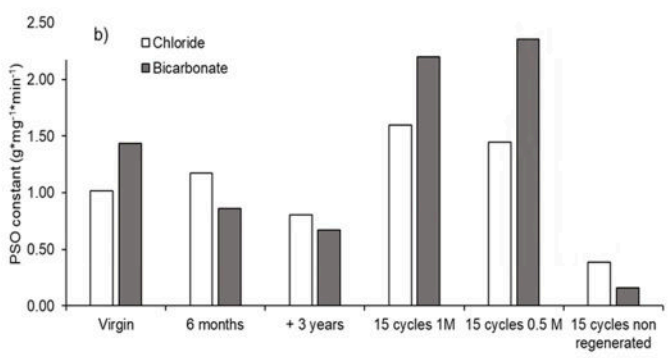
3.3 Organic matter adsorption kinetics and diffusion

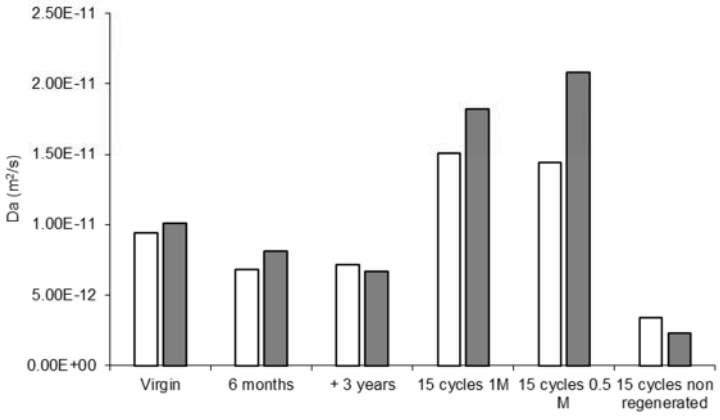
IEX is a diffusion controlled process (Sengupta, 2017). The overall mass transfer resistance is the sum of the resistances caused by the film, particle and the exchange of ions itself (SenGupta, 2017). The resin age and previous organic matter saturation can influence these factors, in turn affecting the uptake rate of organic matter (Finkbeiner *et al.*, 2020). It was hypothesised that pore blockage caused by continuous use could hinder the uptake of organic matter using resins of increasing age, despite frequent regeneration. In order to assess the influence of pore blockage with increasing resin age, experiments were reviewed using kinetic and mass transfer models.

Pseudo first order (PFO) and pseudo second order (PSO) models (Ho and McKay, 1999; Boyer et al., 2021) were used to fit the kinetic DOC data from experiments with different aged resins used for 15 sequential cycles (Figure 8). Both models provided relatively good fits to the empirical data (Figure S9 and S10, Tables S5 and S6). However, the PFO model was considered to better represent the data due to the increased similarity between the calculated and experimental uptake concentrations at equilibrium in comparison to the PSO model (Figure S9). There was a decrease of 20% in the PFO kinetic constants when comparing the virgin resin to +3 years used resin in both bicarbonate forms (0.19 to 0.15 min^{-1} for chloride form resin and 0.19 to 0.15 min^{-1} for bicarbonate form resin). Notwithstanding this, the decrease in the uptake kinetics was not sufficient to cause an observable change in DOC removal.

Sequential cycles increased PFO kinetic rate constants from cycle 1 to cycle 15 by 35% and 75% (0.26 and 0.34 min^{-1}) in comparison to the virgin resin in the chloride and bicarbonate form, respectively. It was considered that the improvement in the uptake kinetics with sequential batch operation was caused by irreversible swelling of the resin, improving the diffusion rates. Similarly, the increase in the organic matter uptake rates for the bicarbonate form resin were attributed to an increased degree of swelling in comparison to the chloride form, caused by the increased hydrated radius of bicarbonate in comparison to chloride. Regardless, the regenerant change did not cause an improvement in the uptake kinetics for the older resins. Despite the reported increase in the uptake rate, the overall DOC removed was not altered through subsequent cycles operation.







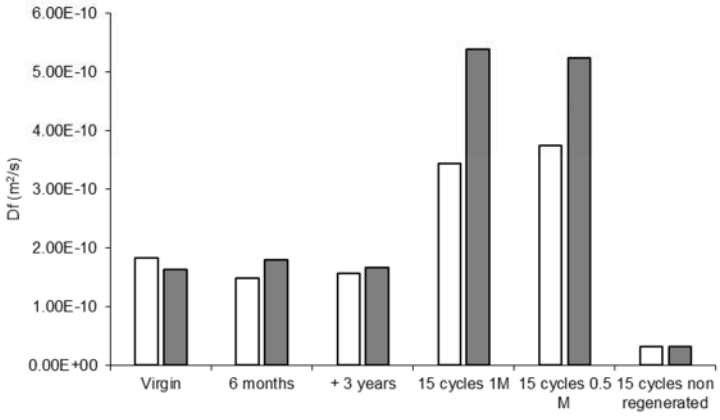


Figure 8. Influence of resin age and regeneration cycles on the PFO and PSO constants and pore and film diffusivities for the exchange of organic matter with chloride and bicarbonate IEX.

For the non-regenerated tests, neither the PFO nor the PSO models provided good fit for the data. Despite r^2 values being >0.85 for both models, the model fit was not representative of the process. For example, for bicarbonate form IEX, the uptake concentration at equilibrium was 0.08 mg DOC/g resin, whereas the calculated results were 0.17 and 0.19 mg DOC/g resin for the PFO and PSO models, respectively (Figures S9 and S10, Tables S5 and S6).

Competition with other inorganic anions (e.g., nitrate, sulphate) caused the PFO kinetic constants for organic matter to be 10-40 times lower in comparison to previous research using isolated systems (Bazri and Mohseni, 2016). The presence of other anions creates competition within the exchanger for the active sites, causing organic matter to diffuse further into the resin, decreasing the uptake rates. For example, Dixit *et al.* (2019) reported decreases in the PSO constants for the uptake of Microcystin-LR from 0.32 to 0.09 and 0.21 for experiments performed in deionised water (DI), DI with 5 mg/l of sulphate, and DI with 5 mg/l of nitrates respectively.

The use of the HPDM (Caetano *et al.*, 2009) allowed for examination of the changes in the diffusion rate limiting step derived from resin age and the use of bicarbonate as an alternative regenerant. The model assumes mass transfer only occurring on the phase of interest (film or particle), being the resistance to mass transfer determined by the diffusion coefficient (Helfferich, 1995). Resin age did

not affect the film diffusivities in either regenerant form (Table S8). It was considered that the high degree of turbulence in the mixing vessel on the jar tester improved the film diffusivity of the resin, explaining the similar results for the different resin ages. In contrast, a decrease of 30% was observed for the pore diffusivities from in the +3 years used resin in comparison to the virgin resin (from $9.4x10^{-12}$ to $7.1x10^{-12}$ for SIX in chloride form and from $1.0x10^{-11}$ to $6.6x10^{-12}$ for SIX in bicarbonate form) (Table S7). Reductions in the pore diffusivity agreed with the PFO constants, suggesting the possibility of pore blockage or change in resin bead structure occurring over time.

The mass transfer models also showed the positive impact of sequential batch regeneration on the organic matter uptake rates (Figure 8, Tables S7 and S8). Film diffusivities increased with resin age and sequential cycles by a factor of 2 ($3.4x10^{-10}$ and $3.7x10^{-10}$ for 1 M and 0.5 M) and 3 ($5.4x10^{-10}$ and $5.2x10^{-10}$ for 1 M and 0.5 M) with the resin in chloride and bicarbonate form, respectively. Equivalent results for pore diffusivities increased by a factor of 1.5 ($1.5x10^{-11}$ and $1.4\ x10^{-11}$ for 1 M and 0.5 M) with the resin in chloride form and 2 ($1.8x10^{-11}$ and $2.1x10^{-11}$ for 1 M and 0.5 M) if the resin was in the bicarbonate form.

In line with the reported results for the PFO and PSO models, the HPDM did not fit to the observable data for the non-regenerated results in either resin form (Figure S10). A possible explanation could be related to the secondary IEX being rate limiting. Further research is required to validate the mechanism of adsorption for resins that were non-regenerated. Additional research on the characterisation

of the resin, including the surface area, and equilibrium theory modelling can help understand the resin loading during the non-regenerated cycles.

The data from the diffusion models supported the hypothesis that irreversible swelling, consistent with the increased hydrated radius of bicarbonate, improved the uptake rates when using this regenerant. In all cases, the removals obtained after treatment, despite some differences in the kinetic constants, were similar. In all cases, film diffusivities were one order of magnitude higher than pore diffusivities, suggesting pore diffusion as the rate limiting step. These results were consistent with other studies on IEX for organic matter removal that have shown pore diffusion to be the rate limiting step (Bazri and Mohseni, 2016; Dixit *et al.*, 2019).

The implication of pore diffusion controlling the IEX process comes from the proportional increase of the uptake kinetic rate constant with increasing resin dose (Galjaard and Kamp, 2014). This is explained by the reduced distance that the target ion needs to diffuse inside the resin (Sengupta, 2017) with similar effects obtained by using resin with reduced size. Aside from the electrochemical forces that exist between the exchanger and the target ions, pore diffusion plays a significant impact on the ion-exchange process.

The use of SIX in bicarbonate form in comparison to chloride was shown to generally improve the selectivity of the resin as shown by the increased removals of organic matter as reported by LC-OCD and in the removal of nitrate. Comparable performance was seen for the minimisation of DBP precursors after SIX treatment for both regenerant forms.

4. Conclusions

The difference in organic matter removal for three different aged SIX resins was assessed using chloride and bicarbonate as regenerants. The influence of operational regenerant concentrations was investigated for 15 batch cycles of resin use with and without regeneration. In all cases, the use of bicarbonate and chloride regenerants showed comparable removal of bulk DOC regardless of resin. There was a strong affinity of the resin in either regenerant form towards organic matter that had a molecular weight of ~1 kDa, with removals of this fraction still observed after 15 operation cycles without resin regeneration. Bicarbonate-form SIX slightly improved the uptake of organic matter in comparison to chloride-SIX when comparing LC-OCD organic matter fractions. In addition, positive synergies were observed with nitrate removal and the use of SIX in bicarbonate form. The similarities in the DOC removal translated into comparable THM and HAA formation potential results for the resin in chloride and bicarbonate form, but increased resin age resulted in a higher BSF, which was more noticeable for HAAs.

The impact of resin age was also reflected in the organic matter uptake kinetics. There was a decrease of 20% in the PFO kinetic constants when comparing the virgin resin to +3 years used resin, although this decrease was not reflected in the bulk DOC concentrations, highlighting the significance of looking at organic

matter fractions. Mass transfer models showed pore diffusion was the limiting step, with resin age decreasing diffusivities by 30%.

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