Removal of multiple drinking water contaminants by combined ion exchange resin in a completely mixed flow reactor

Yue Hu and Treavor H. Boyer

ABSTRACT

This research evaluated the combined ion exchange (CIX) process to give drinking water treatment plants a new option for multiple contaminants removal. The CIX process uses anion exchange resin and cation exchange resin in a single vessel, which enables simultaneous removal of anionic and cationic contaminants. The novel aspect of the CIX process investigated in this research was its application in a small pilot, completely mixed flow reactor (CMFR) with resin recycle and resin regeneration thereby providing realistic performance data. A wide range of contaminants was tested for removal including dissolved organic carbon (DOC), calcium, strontium, nitrate, sulfate, sodium, and chloride, and sodium chloride (NaCl) and potassium bicarbonate (KHCO$_3$) were compared in terms of regeneration efficiency. The key results showed 50 to 80% removal of DOC, calcium, strontium, and sulfate, and less than 30% removal of nitrate, sodium, and chloride. In general, NaCl and KHCO$_3$ showed similar regeneration efficiency. Removal of sodium and chloride by CIX was only possible when KHCO$_3$ was used for regeneration due to the potassium and bicarbonate counterions.

Key words | calcium, DOC, groundwater, nitrate, regeneration, strontium

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INTRODUCTION

Conventionally, to remove multiple drinking water contaminants, ion exchange (IX) is operated as a two-stage process of anion exchange followed by cation exchange, or vice versa. Alternatively, anion exchange resin (AER) and cation exchange resin (CER) can be added to a single vessel, referred to as combined ion exchange (CIX), to achieve the same treatment goal as the two-stage process. The main advantage of the CIX process is the ability to remove anionic and cationic contaminants in a single unit process, as compared with multi-process treatment schemes such as anion exchange followed by cation exchange and coagulation followed by precipitative softening. In addition, the single CIX process results in a smaller process footprint, simpler operation, and single waste stream. To realize the benefits of the CIX process, however, it must be implemented in a suitable reactor configuration: namely, a fixed bed reactor (FBR) or a completely mixed flow reactor (CMFR). Although IX has traditionally been implemented in a FBR, there are advantages to implementing IX in a CMFR including the ability to treat water with high turbidity, lack of chromatographic peaking of contaminant ions, and lower salt usage for regeneration (Boyer & Singer 2006; Clifford *et al.* 2011; Amini *et al.* 2015). Accordingly, this research evaluated the CIX process in a CMFR (hereafter CIX/CMFR), which has not been previously documented in the literature.

Previous studies that have investigated CIX are mostly limited to bench-scale batch experiments. Apell & Boyer (2010) were the first to publish on CIX for drinking water treatment. They conducted single-loading (i.e., single use) jar tests in which magnetic AER and magnetic CER were combined in the same beaker. The results showed 70%

dissolved organic carbon (DOC) removal and >55% hardness removal by CIX treatment of groundwater, and NaCl solution was able to effectively regenerate the combined resins over three regeneration cycles (Apell & Boyer 2010). Other researchers have conducted multiple-loading jar tests in which AER and CER are combined in the same beaker and used to treat sequential batches of raw water (Comstock & Boyer 2014; Arias-Paic et al. 2016; Beita-Sandí & Karanfil 2017). The multiple-loading jar test procedure is designed to approximate a fluidized bed reactor where the results are expressed in terms of bed volumes (BVs) treated (Comstock & Boyer 2014; Arias-Paic et al. 2016). Ion exchange in a fluidized bed reactor is similar to IX in a CMFR depending on its design and operation (Boyer et al. 2010). Comstock & Boyer (2014) showed 70–87% DOC removal and >50% hardness removal by CIX treatment of three different groundwaters in composite samples corresponding to 1,000 BVs of AER and 250 BVs of CER. Arias-Paic et al. (2016) showed >70% DOC removal and >55% hardness removal by CIX treatment of four different groundwaters corresponding to 600 BVs of AER and CER treatment. Both Comstock & Boyer (2014) and Arias-Paic et al. (2016) evaluated NaCl regeneration at different concentrations and conditions.

Two studies have also evaluated CIX beyond the bench scale. Arias-Paic et al. (2016) evaluated CIX in an upflow pilot unit where AER and CER were fluidized and stratified in the same reactor. The CIX pilot was operated for approximately 1,000 BVs daily and showed approximately 75% DOC and 15% hardness removal (Arias-Paic et al. 2016). Arias-Paic et al. (2016) did not discuss why the CIX pilot was operated at low hardness removal. Locke & Smith (2016) documented the start-up testing of a full-scale (1 million gallons per day (MGD)) CIX fluidized bed contactor. The average performance over 6 days of testing was 67% DOC removal and 49% hardness removal (Locke & Smith 2016). Although the average hardness removal met the treatment target, the hardness concentration in the treated water varied from 24 to 340 mg/L as CaCO₃ (Locke & Smith 2016). Locke & Smith (2016) attributed the variable hardness removal to the regeneration process. However, DOC removal showed consistent performance so it appears that AER and CER were not being regenerated to the same extent. As with any new process or technology there are limitations to the previous research. Foremost, CIX has

not been evaluated in a true CMFR in which AER and CER are combined and mixed in the same contactor, treated water and combined resins are separated in a settler, the majority of combined resins in the settler are recycled back to the contactor, and a portion of the combined resins from the settler are regenerated together and returned to the contactor (Boyer & Singer 2006; Hu & Boyer 2017). Other aspects of CIX that have not be investigated include alternative salts to NaCl for regeneration and contaminants in addition to DOC and hardness (i.e., calcium) (Comstock & Boyer 2014; Arias-Paic et al. 2016; Beita-Sandí & Karanfil 2017).

Following from the gap in the literature, the goal of this research was to evaluate the performance of the CIX/CMFR process for multiple contaminants removal under different operating conditions. The contaminants studied in this research included problematic contaminants and contaminants common to groundwater. DOC and nitrate were studied because the Stage 1 Disinfectants/Disinfection Byproducts Rule and the nitrate maximum contaminant level are two of the most common violations in US water systems (Oxenford & Barrett 2016), and are problematic contaminants worldwide (Bhatnagar & Sillanpaa 2011; Li & Mitch 2018). Calcium was studied because it commonly co-exists with DOC in groundwater in Florida, and high calcium in water is problematic for aesthetic and economic reasons (Van der Bruggen et al. 2009). Strontium was studied because it can co-exist with calcium, and may be a concern for human health. Strontium has a life-time health advisory level and is being considered by the US EPA for regulation as a primary drinking water contaminant (USEPA 2014). Lastly, in coastal areas, surface water and groundwater can be impacted by seawater intrusion that can increase the concentration of sodium and chloride above secondary drinking water levels (Roehl et al. 2013; Saetta et al. 2015). Accordingly, the specific objectives of this research were to evaluate the CIX/CMFR process for: (1) removal of DOC and calcium at different resin doses using chloride-form AER and sodium-form CER; (2) removal of DOC and calcium at optimum resin dose comparing NaCl and KHCO₃ regeneration; and (3) treatment of multiple contaminants including DOC, calcium, strontium, and nitrate using chloride-form AER and sodium-form CER, and groundwater impacted by seawater intrusion

using bicarbonate-form AER and potassium-form CER. Although the co-existence of DOC and nitrate may not be frequently observed, the selection of multiple contaminants including those constituents is intended to demonstrate a worst case scenario.

MATERIALS AND METHODS

Test waters

Test waters were selected and prepared according to the research objectives. The test water for objectives 1 and 2 was from groundwater wells at the Cedar Key Water and Sewer District located in Cedar Key, FL, USA. The groundwater was collected after permanganate addition and settling in an equalization tank. The groundwater was transported to the laboratory for CIX experiments. Cedar Key groundwater has high DOC and calcium hardness. The DOC concentration was in the range of 7–9 mg/L and calcium was in the range of 100–120 mg/L. The raw water had a relatively low concentration of sulfate, about 25 mg/L and chloride, about 15 mg/L. The pH was about 8. The conductivity can fluctuate depending on rain events, and the conductivity was in the range of 600–800 μs/cm. The experiments in this study used Cedar Key groundwater as well as Cedar Key groundwater spiked with chemicals and blended with ocean water. Two different test waters were prepared for objective 3: (i) Cedar Key groundwater was spiked with strontium chloride ($SrCl_2$, CAS No. 10476-85-4) and sodium nitrate (NaNO3, CAS No. 7631-99-4) to create multiple anionic and cationic contaminants; and (ii) Cedar Key groundwater was blended with Atlantic Ocean seawater (collected from St Augustine, FL, USA) to mimic seawater intrusion into coastal groundwater.

Regeneration solutions

Two regeneration solutions were evaluated in this research: NaCl and $KHCO_3$. The solutions were prepared by dissolving the appropriate mass of salt, either NaCl (CAS No. 7647-14-5) or $KHCO_3$ (CAS No. 298-14-6) in deionized (DI) water to give a final salt concentration of 12% (m/v).

Ion exchange resins and preparation

For the majority of tests, the AER was MIEX and the CER was Plus, both provided by IXOM Watercare (Centennial, CO, USA). The same resins have been studied by previous researchers evaluating CIX (Arias-Paic *et al.* 2016; Beita-Sandí & Karanfil 2017). The MIEX AER has strong-base quaternary ammonium functional groups, macroporous pore structure, and polyacrylic composition. The ion exchange capacity of the AER is 0.52 meq/mL. The unique characteristics of the MIEX AER are the incorporation of magnetic iron oxide into the polymer matrix, and the smaller particle size (150–200 μm) compared with conventional AERs (550–810 μm) (Graf *et al.* 2014). The MIEX AER is produced in the chloride form. Bicarbonate-form MIEX AER was prepared in the laboratory by mixing the chloride-form AER with concentrated $NaHCO_3$ solution for 24 h. The Plus CER has strong-acid sulfonic acid functional groups, gel pore structure, and polystyrene composition. The ion exchange capacity of the CER is 1.9 meq/mL. The Plus CER has no magnetic properties. The CER is produced in the sodium form. Potassium-form Plus CER was prepared in the laboratory by mixing the sodium-form CER with concentrated KCl solution for 24 h. One test was conducted using A30 AER (Thermax) and C150 CER (Purolite). The A30 AER (capacity 0.7 meq/L) had the same resin properties as the MIEX AER but without magnetic iron oxide and a larger particle size. The C150 CER (capacity 1.8 meq/mL) had the same polystyrene composition as Plus CER but was macroporous instead of gel pore structure.

Experimental conditions

Description of CIX/CMFR process

A detailed description of the CMFR process is provided elsewhere (Hu & Boyer 2017); a brief description of how the CMFR process was operated in CIX mode is provided here. AER and CER were dosed together and mixed with raw water in the IX treatment contactor. The combined resins and treated water were separated in a settler, with the majority of the combined resins being recycled back to the IX treatment contactor and the treated water exiting the settler. Simultaneously, during recycle of the combined

resins, a side stream of freshly regenerated combined resins was pumped from the resin storage container to the IX treatment contactor, and the same amount of partially exhausted combined resins was pumped from the IX treatment contactor to the regeneration tank. One cycle of operation was performed in 6 h. During multiple cycles of treatment and regeneration, the regeneration step occurred at the end of the 6 h of treatment. The partially exhausted, combined resins that accumulated in the regeneration container were mixed with regeneration solution for 20 min. The volume of regeneration solution relative to the total volume of combined resins was 5 to 1. After regeneration, the combined resins were rinsed with DI water until the conductivity of the rinse water was <5 μS/cm. The freshly regenerated combined resins were transferred to the resin storage container for the next cycle of treatment. The multiple treatment/regeneration tests were performed three times in total.

Operating parameters and sampling

The volume ratio of AER to CER was 1 to 1 for all tests. The flowrate of all tests was about 150 mL/min. The resin regeneration ratio was 20% and the hydraulic residence time (HRT) was 12 min for all tests, giving a solids residence time (SRT) equal to 1 h. The SRT was calculated from the formula of the HRT divided by the resin regeneration ratio (Boyer et al. 2008). One hour was selected as the sampling interval to correspond to one SRT, and duplicate samples were collected from the treated water. One raw water sample was collected before starting each experiment. pH and conductivity were measured immediately after the sampling. Dissolved constituents were measured as described in the Analytical methods section. All samples were filtered through 0.45 μm membrane filters and stored at 4 °C.

Analytical methods

pH was measured using an Accument AB15 pH meter with Orion Dual Star pH electrode and conductivity was measured using an Oakton ECTestr 11 portable meter. DOC was measured using a Total Organic Carbon Analyzer (Shimadzu TOC-V$_{CPH}$) following Standard Method 5310 B (Eaton et al. 2005). Inorganic anions (chloride, nitrate, and

sulfate) and cations (calcium and sodium) were measured by ion chromatography using a Dionex ICS-5000 following EPA method 300.1 and Dionex Method (USEPA 1997; Thomas et al. 2002). Strontium was analyzed by inductively coupled plasma (ICP-OES) following EPA Method 6010C (USEPA 2007). Secondary standard solutions were used as external standards for DOC (Ricca Chemical Company), inorganic anions (Dionex Seven Anion Standard), and inorganic cations (Dionex Six Cation Standard). To monitor accuracy, the calibration points and external standards were analyzed at the end of each run, and one calibration point was analyzed after every 15 samples. The relative difference for calibration points and external standards was less than 10% difference at a concentration >2 mg/L and less than 20% difference at a concentration <1 mg/L. The majority of duplicate measurements for DOC, anions, and cations showed less than 10% difference.

RESULTS AND DISCUSSION

The experimental test plan is summarized in Table 1, and the raw water and treated water characteristics are summarized in Table 2.

DOC and calcium removal by CIX/CMFR process at varying effective resin dose

CIX/CMFR Tests 1–3 (Table 1) were conducted at different effective resin doses (ERDs) of 2, 4, and 6 mL/L to evaluate the impact of ERD on treatment performance and to determine the optimum ERD for subsequent testing. A single treatment (6 h) test without regeneration was performed at each ERD. The ERD is a concept that was created to calculate the fraction of resin in a CMFR that is available to undergo ion exchange (i.e., contains fresh ion-exchange sites), and is calculated by multiplying the total resin concentration in the contactor by the resin regeneration ratio (Boyer & Singer 2006; Boyer et al. 2008). The ERD concept can be applied to IX in a CMFR or fluidized bed reactor (Boyer et al. 2010), and in the latter case, the inverse of the ERD is equivalent to the BVs treated. Tests 1–3 used Cedar Key groundwater and combined resins consisting of chloride-form AER and sodium-form CER (for both MIEX

Table 1 │ Experimental plan for evaluating combined ion exchange resin in completely mixed flow reactor

Objective (#)	Test (#)	Operation cycle (#)	Test water	Type of resin AER	Type of resin CER	Regen. Ratio (%)	Contactor conc. (mL/L)	ERD[a] (mL/L)	HRT (min)
1	1	1	Groundwater	Chloride[b,c]	Sodium[d,e]	20	10	2	12
1	2	1	Groundwater	Chloride[b,c]	Sodium[d,e]	20	20	4	12
1	3	1	Groundwater	Chloride[b,c]	Sodium[d,e]	20	30	6	12
2	4	3	Groundwater	Chloride[b]	Sodium[d]	20	20	4	12
2	5	3	Groundwater	Bicarbonate[b]	Potassium[d]	20	20	4	12
3	6	1	Groundwater + $SrCl_2$ + $NaNO_3$	Chloride[b]	Sodium[d]	20	20	4	12
3	7	1	Groundwater + seawater	Bicarbonate[b]	Potassium[d]	20	40	8	12

AER, anion exchange resin; CER, cation exchange resin.
[a]Effective resin dose (ERD) calculated as resin dose (mL/L) in treatment contactor multiplied by regeneration ratio.
[b]MIEX AER.
[c]A30 AER.
[d]Plus CER.
[e]C150 CER.

Table 2 │ Summary of inffluent and effluent water quality for pilot plant tests evaluating combined ion exchange operation in completely mixed flow reactor configuration

Test (#)	Infl. pH	Infl. Conductivity (μS/cm)	Infl.DOC (mg/L)	Eff.DOC (mg/L)	Infl. Calcium (mg/L)	Eff. Calcium (mg/L)
1[a,b,c]	7.9, -	630, -	7.7, 8.2	3.6, 3.2	106, 111	72, 45
2[a,b,c]	7.7, -	777, -	8.0, 8.5	3.0, 2.3	111, 112	35, 15
3[a,b,c]	7.6, -	780, -	8.2, 8.9	3.0, 2.2	112, 110	34, 12
4	7.8	610	8.1	2.6	104	35
5	7.8	590	8.1	2.7	105	40
6[d]	7.6	933	7.7	2.9	89	30
7[e]	7.4	2267	8.6	2.5	115	48

[a]Cedar Key groundwater has DOC in range of 7-9 mg/L, calcium in range of 100 – 120 mg/L, sulfate about 25 mg/L and chloride about 15 mg/L.
[b]Test 1. a used MIEX/Plus at ERD level 2 mL/L, Test 2.a used MIEX/Plus at ERD level 4 mL/L, Test 3.b used MIEX/Plus at ERD level 6 mL/L.
[c]Test 1. b used A30/C150 at ERD level 2 mL/L, Test 2.b used A30/C150 at ERD level 4 mL/L, Test 3.b used A30/C150 at ERD level 6 mL/L. Influent pH and conductivity were not analyzed.
[d]Strontium and nitrate were spiked in Cedar Key groundwater. The final concentration in groundwater was 23 mg/L strontium and 31 mg/L as N nitrate. The concentration in effluent was 7.5 mg/L strontium and 22 mg/L as N nitrate.
[e]Atlantic Ocean seawater was blended with Cedar Key groundwater. The chloride concentration in blended groundwater-seawater was 503 mg/L chloride, 148 mg/L sulfate, 258 mg/L sodium, 89 mg/L calcium (223 mg/L $CaCO_3$ calcium hardness), and 12 mg/L potassium. The concentration in effluent was 390 mg/L chloride, 68 mg/L sulfate, 219 mg/L sodium, 48 mg/L calcium, and 160 mg/L potassium.

AER/Plus CER and A30 AER/C150 CER). The raw water contained 7–8 mg/L DOC and ~110 mg/L calcium. Average removal percentages are plotted in Figure 1(a) and dynamic (i.e., time-varying) concentrations are plotted in Figure 1(b). Figure 1(c) and 1(d) repeat Figure 1(a) and 1(b) for the combined resins A30 AER and C150 CER.

The concentration of DOC and calcium in the treated water decreased and the percent removal increased as the ERD increased (Figure 1(a) and 1(c)). This was expected behavior due to the increase in fresh ion-exchange sites available for contaminant removal. For example, the average DOC removal was 53%, 63%, and 63% at ERD of 2, 4, and 6 mL/L, respectively, and the average calcium removal was 32%, 69%, and 70% at ERD of 2, 4, and 6 mL/L, receptively (Figure 1(a)). Hence, an ERD of 4 mL/L was optimal based on the conditions tested. An ERD of 4 mL/L is equivalent to 250 BV, which is on the lower range of BVs treated for IX in a fluidized bed reactor with typical design being 600 to 1,000 BVs treated (Arias-Paic et al. 2016).
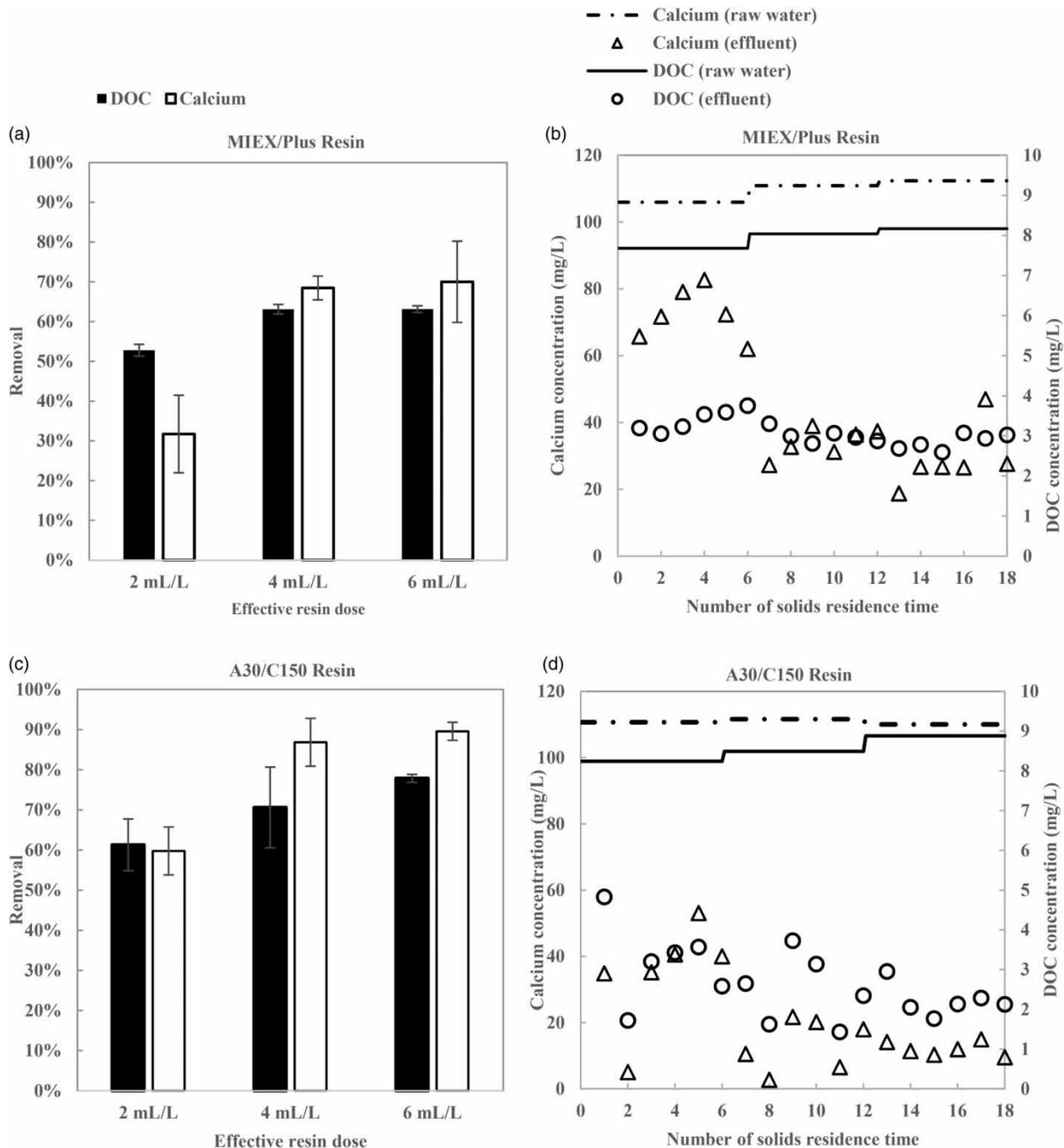
Figure 1 │ Simultaneous DOC and calcium removal under varying conditions of effective resin dose (ERD) using combined ion exchange resin in completely mixed flow reactor. (a) Percentage removal (mean ± 1 standard deviation) using MIEX anion exchange resin (AER) and Plus cation exchange resin (CER). (b) The dynamic concentrations corresponding to (a) with 2 mL/L ERD corresponding to 0–6 solids residence time (SRT), 4 mL/L ERD corresponding to 6–12 SRT, and 6 mL/L ERD corresponding to 12–18 SRT. (c) Percentage removal (mean ± 1 standard deviation) using A30 AER and C150 CER. (d) The dynamic concentrations corresponding to (c) following the same format as (b).

Figure 1(b) and 1(d) show the variation in DOC and calcium concentration in the treated water for each ERD. The variation in the treated water DOC concentration in this study was greater than has been observed in previous studies using a similar experimental set up. Both Boyer & Singer (2006) and Hu & Boyer (2017) showed that AER in a

CMFR achieved steady-state removal of DOC within three SRT and showed little variation in treated water DOC concentration. Although there was variation in the treated water calcium concentration in this study, it was not as wide ranging as observed in Locke & Smith (2016). This study evaluated the CIX/CMFR process in a small pilot unit (150 mL/min), whereas Locke & Smith (2016) evaluated CIX in a full-scale fluidized bed reactor (1 MGD), so there was more control of the process in this study. Nevertheless, the results in Figure 1(b) and 1(d) suggest that the variation in DOC and calcium concentration in the treated water is likely due to different proportions of AER and CER being recycled at different times. Ideally, both the AER and CER are well mixed throughout the IX treatment contactor such that the same proportion of AER and CER is continuously recycled. However, because the AER and CER have different particle size range and density, it is likely that the AER and CER were not uniformly mixed throughout the contactor. Furthermore, in Figure 1(b), the reason that the dynamic calcium concentration was more variable than the dynamic DOC concentration is because the Plus CER is larger than the MIEX AER, so it was not as well mixed and, therefore, the amount of CER being recycled varied at different times. A similar explanation applies to the dynamic DOC concentration in Figure 1(d) (using A30 AER), which shows more variability than the dynamic DOC concentration in Figure 1(b) (using MIEX AER) because the larger size of A30 AER makes its mixing, settling, and recycling less uniform than the smaller size MIEX resin.

DOC and calcium removal by CIX/CMFR process comparing different regeneration solutions

CIX/CMFR Tests 4 and 5 (Table 1) were conducted at the optimal ERD of 4 mL/L in order to compare NaCl and KHCO₃ regeneration solutions. Tests 4 and 5 were conducted for three treatment/regeneration cycles to observe the impact of regeneration on the subsequent contaminant removal. The three treatment/regeneration cycles corresponded to 0 to 6 SRT, 6 to 12 SRT, and 12 to 18 SRT. At the end of cycle 1 and cycle 2, either NaCl or KHCO₃ regeneration solution was used to regenerate the combined resins in the same vessel. Figure 2 shows the results in the same

manner as Figure 1 with average removal percentages and dynamic concentrations shown separately, and in the case of Figure 2, also separated by regeneration solution.

The percentage removal results (Figure 2(a) and 2(b)) showed DOC removal of 66–72% with $KHCO_3$ regeneration and 65–66% with NaCl regeneration. The comparable DOC removal indicates that bicarbonate counterion from AER can exchange with DOC as effectively as chloride counterion from AER. The consistent and comparable DOC removal also reflects that bicarbonate ion from $KHCO_3$ solution can desorb DOC as effectively as chloride ion from NaCl solution during regeneration. If $KHCO_3$ has lower regeneration, the DOC removal using $KHCO_3$ should be lower than using NaCl. Hu & Boyer (2017) showed a similar result comparing $NaHCO_3$ and NaCl regeneration solutions for removal of DOC by anion exchange in a CMFR. The 12% m/v $KHCO_3$ solution produced relatively consistent regeneration results in which DOC removal from cycle 1 to cycle 2 decreased by 5 percentage points and DOC removal from cycle 2 to cycle 3 decreased by 1 percentage point. The 12% m/v NaCl solution produced nearly identical regeneration results over three cycles with DOC removal changing by only 1 percentage point.

The calcium removal percentages (Figure 2(a) and 2(b)), 52–83% using $KHCO_3$ regeneration and 54–73% using NaCl regeneration, showed greater cycle-to-cycle variation for both $KHCO_3$ regeneration and NaCl regeneration than the corresponding DOC removal percentages. For example, calcium removal varied from 69% (cycle 1) to 51% (cycle 2) to 83% (cycle 3) using $KHCO_3$ regeneration solution. Based on the dynamic calcium concentrations in Figures 1 and 2, it is likely that the cycle-to-cycle variation in calcium removal percentage is due to the operation of the CIX/CMFR process (see discussion in previous section) and not the regeneration salts. This is supported by Maul et al. (2014), who showed similar regeneration efficiency for $KHCO_3$ and NaCl for CER exhausted with calcium.

The dynamic concentration results in Figure 2(c) and 2(d) show much greater variation in calcium concentration than DOC concentration similar to Figure 1. For example, the DOC concentration in the treated water had a coefficient of variation (CV) of 10% for $KHCO_3$ regeneration and 13% for NaCl regeneration, whereas the calcium concentration in the treated water had a CV
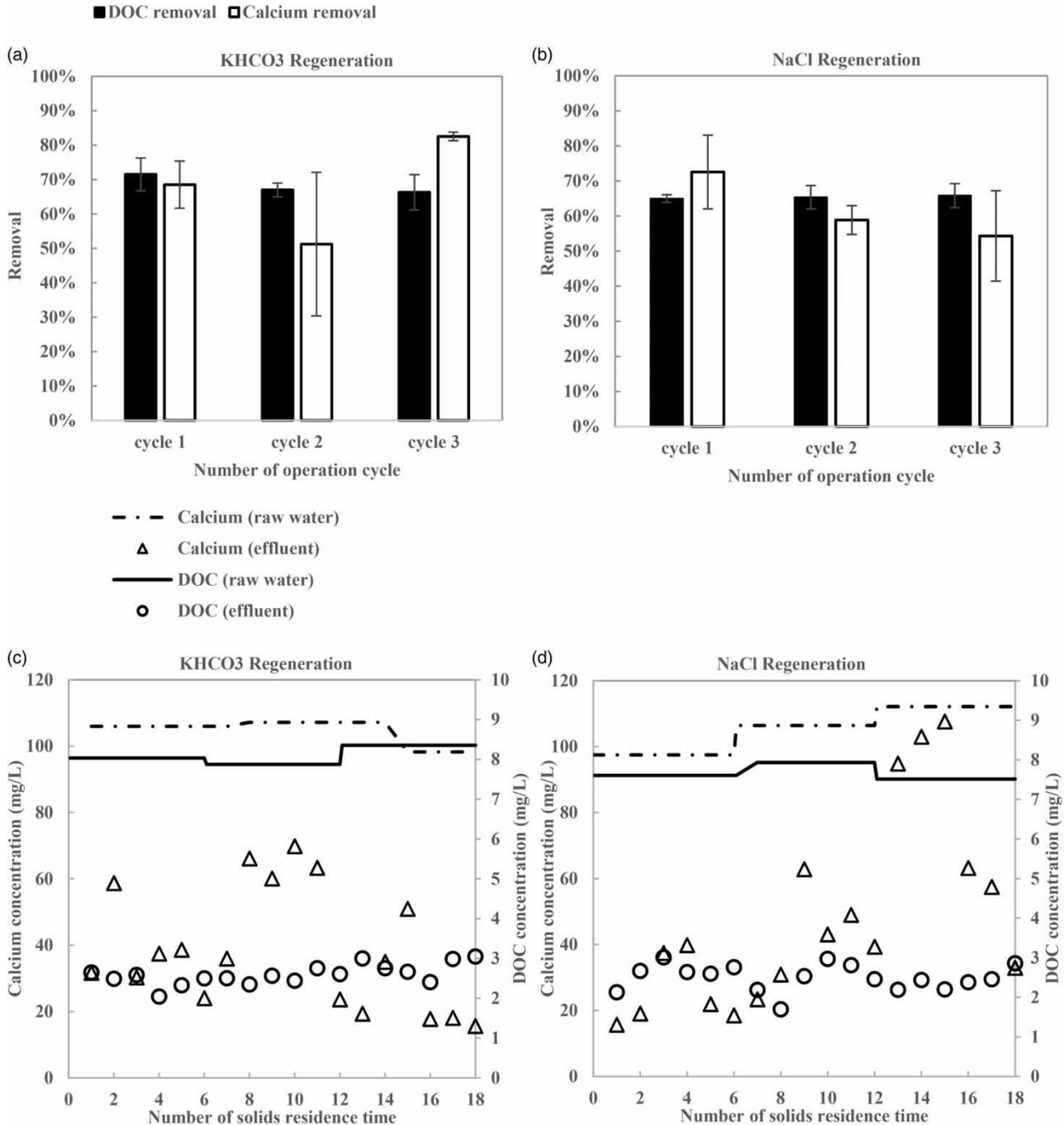
Figure 2 | Multiple cycle treatment and regeneration for simultaneous DOC and calcium removal using combined ion exchange in completely mixed flow reactor. (a) Percentage removal using bicarbonate-form anion exchange resin (AER) and potassium-form cation exchange resin (CER) with KHCO₃ regeneration (mean ± 1 standard deviation calculated from six samples collected at the last three solids residence time (SRT), two samples at each SRT). (b) Percentage removal using chloride-form AER and sodium-form CER with NaCl regeneration (mean ± 1 standard deviation calculated from six samples collected at the last three SRT, two samples at each SRT). (c) Dynamic concentrations (DOC and calcium) corresponding to (a) for three treatment/regeneration cycles with each cycle run for six SRT. (d) Dynamic concentrations (DOC and calcium) corresponding to (b) for three treatment/regeneration cycles with each cycle run at six SRT. (e) Dynamic concentrations (sodium, chloride, and sulfate) at the same conditions as (c). (f) Dynamic concentrations (sodium, chloride, and sulfate) at the same conditions as (d). *(Continued.)*
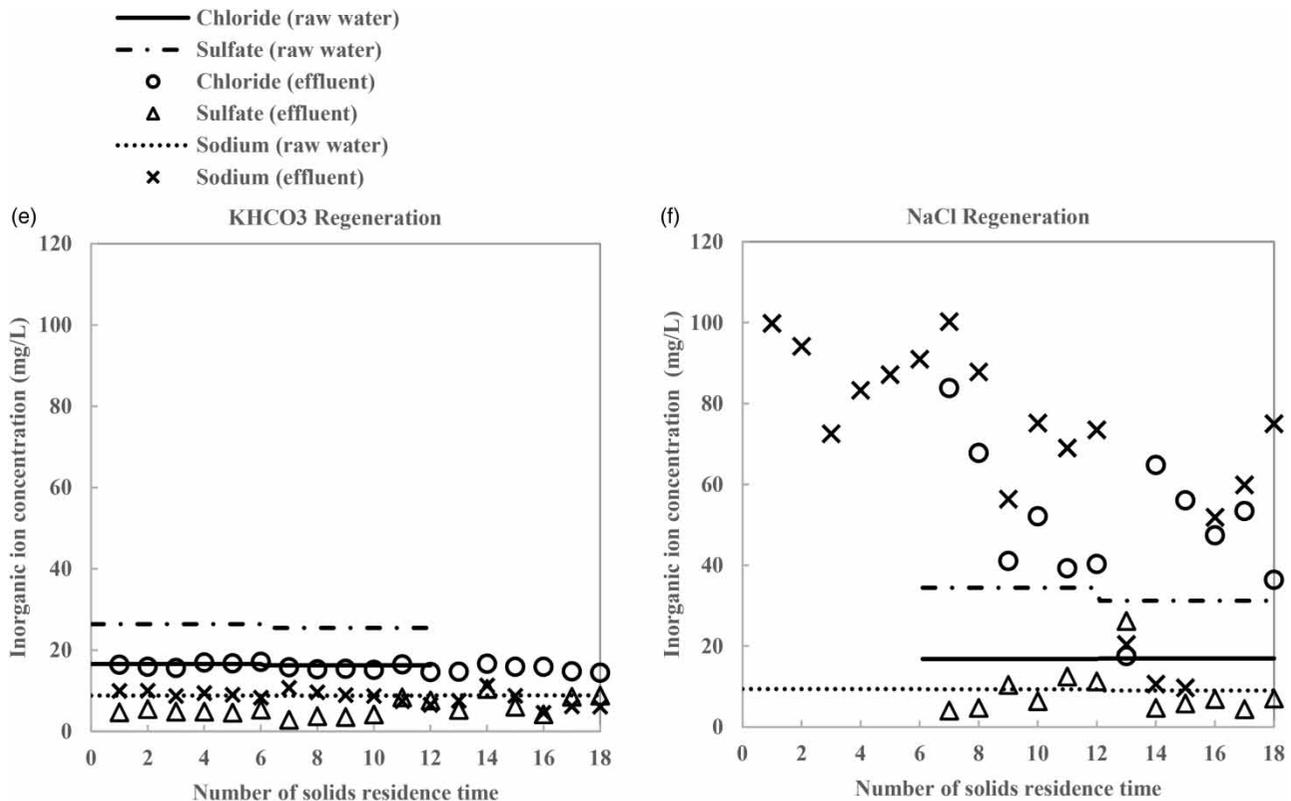
——— Chloride (raw water)
— · — Sulfate (raw water)
○ Chloride (effluent)
△ Sulfate (effluent)
········· Sodium (raw water)
✕ Sodium (effluent)

Figure 2 | Continued.

of 47% for KHCO$_3$ regeneration and 60% for NaCl regeneration. The CV was calculated as the standard deviation divided by the mean using data for each contaminant and regeneration solution for all three cycles. The reason for the high variation in calcium concentration in the treated water is discussed in the previous section and is inherent to the operation of a CMFR using combined resins with different physical characteristics. Figure 2(e) and 2(f) show dynamic concentrations of chloride, sulfate, and sodium and illustrate the potential benefit of using bicarbonate-form AER and potassium-form CER with KHCO$_3$ regeneration instead of chloride-form AER and sodium-form CER with NaCl regeneration. For example, both forms of AER remove sulfate but the bicarbonate-form AER is able to do this without increasing the chloride concentration, which is important because increasing chloride can make water more corrosive (Zhang & Edwards 2011; Willison & Boyer 2012). Likewise, both forms of CER remove similar amounts of calcium but the potassium-form CER does this without increasing the

sodium concentration in the treated water whereas the sodium-form CER increases the sodium concentration to approximately 100 mg/L (Figure 2(f)). Elevated concentrations of chloride and sodium in water can impart a salty taste, make the water more corrosive, and be unhealthy for individuals on a low sodium diet.

Treatment of multiple contaminants by CIX/CMFR process

Two scenarios were used to explore the potential applications of the CIX/CMFR process beyond DOC and calcium removal. The first scenario evaluated DOC, nitrate, calcium, and strontium removal by the CIX/CMFR process using chloride-form AER and sodium-form CER. The second scenario evaluated DOC, calcium, and seawater ions removal by the CIX/CMFR process using bicarbonate-form AER and potassium-form CER. The use of bicarbonate and potassium counterions in the second scenario allowed for partial desalination, as discussed below.

Removal of DOC, nitrate, calcium, and strontium

CIX/CMFR Test 6 (Table 1) was conducted at the optimal ERD of 4 mL/L in order to evaluate the removal of DOC, nitrate, calcium, and strontium. AER was used in the chloride form and CER was used in the sodium form corresponding to regeneration using NaCl; however, regeneration efficiency was not evaluated in Test 6. Figure 3 shows the results in a similar manner as Figures 1 and 2.

The average removals were 62% DOC, 31% nitrate, 67% calcium, and 67% strontium (Figure 3(a)). The results for DOC and calcium are in agreement with the results from Tests 2 and 4 (see Figures 1 and 2). The results for nitrate and strontium are explained by the properties of the AER and CER used in this study. The MIEX DOC AER has polyacrylic composition and macroporous structure, which

makes the resin selective for DOC (Bolto *et al.* 2002; Graf *et al.* 2014; Hu *et al.* 2016). Hu *et al.* (2016) discussed that AER with polystyrene composition and wider spacing of functional groups (e.g., triethylamine instead of trimethylamine) increases the selectivity of the resin for nitrate. Hence, effective removal of DOC and nitrate by ion-exchange requires AERs with diverse properties, which could be accomplished using the CIX/CMFR process using two different AERs instead of AER and CER. The Plus CER possesses strong-acid functional groups, polystyrene composition, and gel pore structure, which are the same properties as Purolite C100 CER studied by Foster *et al.* (2017) that had the selectivity sequence $Ba^{2+} > Sr^{2+} > Ca^{2+}$. Hence, the Plus CER is expected to be selective for strontium and achieve strontium removal equal to or greater than calcium removal, which is corroborated in
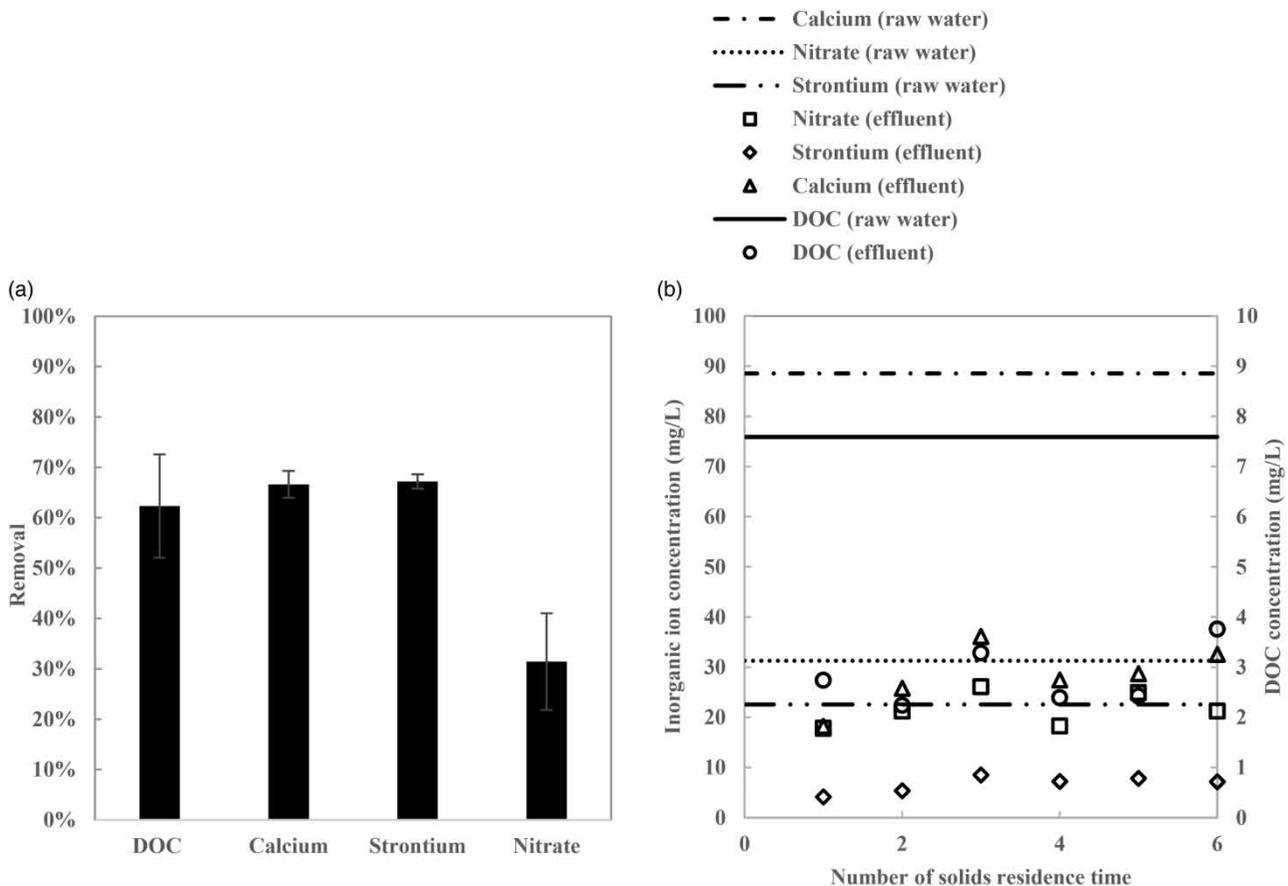

Figure 3 │ Simultaneous removal of DOC, calcium, nitrate, and strontium using combined ion exchange in completely mixed flow reactor using chloride-form anion exchange resin and sodium-form cation exchange resin. (a) Percentage removal (mean ± 1 standard deviation calculated from six samples collected at the last three SRT, two samples at each SRT) and (b) dynamic concentrations corresponding to (a).

Figure 3(a). Unlike anion exchange, it is possible to use one type of CER resin and achieve high removal of multiple cationic contaminants of concern including calcium, strontium, and barium.

The dynamic concentrations are plotted in Figure 3(b) and show similar trends as Figures 1 and 2. One advantage of IX in a CMFR is that chromatographic peaking does not occur with less selective contaminants (Clifford et al. 2011). For example, although the AER is more selective for DOC than nitrate, the resin is able to remove both DOC and nitrate without causing a spike in the nitrate concentration. Because the Plus CER is more selective for strontium than calcium (based on a similar resin in the literature), the variation in the concentration in the treated water was lower for strontium than calcium.

Removal of DOC, calcium, and seawater ions

CIX/CMFR Test 7 (Table 1) evaluated the removal of seawater ions, specifically sodium, chloride, and sulfate, in addition to DOC and calcium removal. An ERD of 8 mL/L was used for Test 7 based on doubling the optimum ERD determined in Tests 1–3 as a way of testing a high resin dose to account for the high concentration of ions in the test water. The basis for Test 7 was a seawater intrusion event that occurred in Cedar Key, FL, USA in which the groundwater became elevated in seawater ions (550 mg/L chloride, >160 mg/L sodium) in addition to the background DOC and calcium hardness (Saetta et al. 2015). The processes in place at the Cedar Key drinking water treatment plant were not capable of desalination. However, the plant did have a fluidized anion exchange process, so it is conceivable that the anion exchange process could be transformed into a fluidized CIX process (e.g., Locke & Smith 2016) and by using $KHCO_3$ for regeneration could be used to achieve partial desalination. In order to remove sodium and chloride ions in this study, the AER was used in the bicarbonate form and the CER was used in the potassium form corresponding to $KHCO_3$ regeneration; however, regeneration efficiency was not evaluated in Test 7. Figure 4 shows the results in a similar manner as Figures 1–3.

The average removals were 72% DOC, 54% sulfate, 23% chloride, 58% calcium, and 15% sodium based on initial concentrations of 8.6 mg/L DOC, 148 mg/L sulfate,

503 mg/L chloride, 115 mg/L calcium, and 258 mg/L sodium. The results show the effective removal of DOC, calcium, and sulfate, but lower removal of chloride and sodium. Many AERs are known to be selective for divalent sulfate so the effective sulfate removal was expected (Dron & Dodi 2011). AERs are also known to have a low selectivity for chloride, which is why chloride is typically used as the presaturant ion (Clifford et al. 2011), so the low removal of chloride was not unexpected. Cation exchange follows similar trends for calcium and sodium as anion exchange for sulfate and chloride, i.e., high selectivity for divalent calcium and low selectivity for monovalent sodium (Clifford et al. 2011). In addition to selectivity, the ion exchange capacity available for contaminant removal is an important consideration. Based on the ERD of 8 mL/L and the ion-exchange capacity of MIEX AER and Plus CER, the CIX/CMFR process consisted of 4.2 meq/L of anion exchange capacity and 15.2 meq/L of cation exchange capacity. For comparison, the concentration of chloride and sodium was 14.2 and 11.2 meq/L, respectively. Hence, because the MIEX AER has a low ion-exchange capacity, the anion exchange capacity of the process limited chloride removal to 23% not including DOC and sulfate. Therefore, the anion exchange capacity of the process may be the limiting factor. This problem may be addressed by using an AER resin with a higher capacity. For example, many conventional AERs have a capacity of approximately 1 meq/mL, which would double the anion exchange capacity of the process compared with MIEX AER. In contrast, the process had a high cation exchange capacity due to the high ion-exchange capacity of Plus resin. Assuming that Plus CER removes calcium selectively over sodium, there should be 9.4 meq/L of cation exchange capacity remaining for sodium removal, which corresponds to 84% sodium removal. Thus, ion-exchange capacity was not limiting sodium removal and, instead, the low selectivity of potassium-form CER for sodium is the most likely explanation. Increasing the selectivity of a CER for sodium is a more challenging problem than increasing the anion exchange capacity of the process.

The dynamic concentrations are plotted in Figure 4(b) and show similar levels of variation in the concentration of ions in the treated water as seen in Figures 1–3. The concentrations in the treated water were 2–3 mg/L DOC, 40–100 mg/L sulfate, 360–410 mg/L chloride, 40–60 mg/L
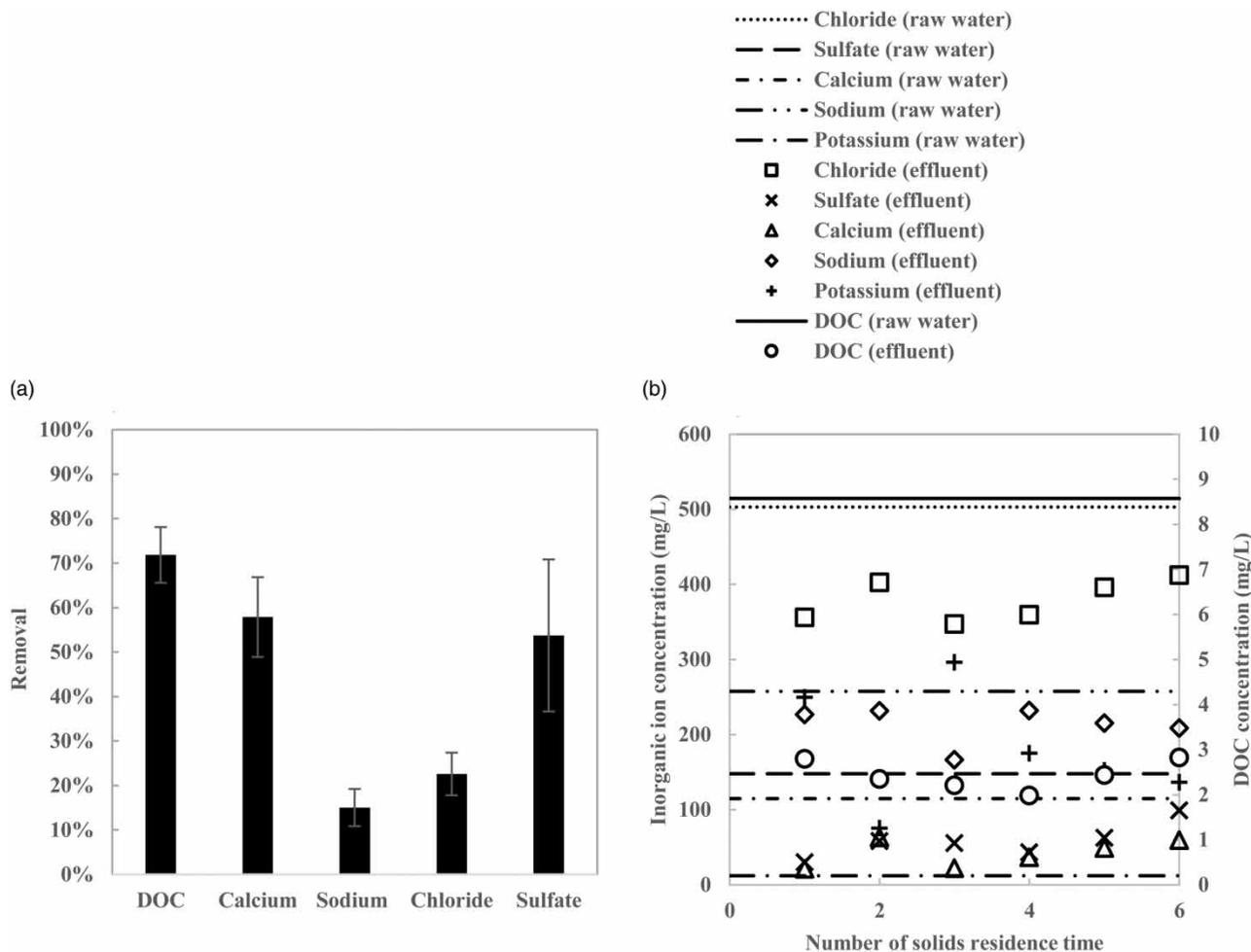
Figure 4 │ Simultaneous removal DOC, calcium, sodium, chloride, and sulfate using combined ion exchange in completely mixed flow reactor using bicarbonate-form anion exchange resin and potassium-form cation exchange resin. (a) Percentage removal (mean ± 1 standard deviation calculated from six samples collected at the last three SRT, two samples at each SRT) and (b) dynamic concentrations corresponding to (a).

calcium, and 210–230 mg/L sodium. The chloride and sodium concentrations would need to be reduced to less than 250 and 160 mg/L, respectively, to comply with aesthetic drinking water standard for chloride (i.e., salty taste) and health-based drinking water standard for sodium (FDEP 2018; USEPA 2018). One interesting result in Figure 4(b) is the potassium concentration in the treated water due to exchange with calcium and sodium. The potassium concentration varies from 75 to almost 300 mg/L. The US EPA does not provide guidance on the suitable potassium concentration in drinking water. However, there are detailed data available on dietary intake of potassium, in which the recommended intake for adults is 4.7 g potassium/d (IOM 2005). Assuming 300 mg/L potassium in the

treated water and water consumption of 2 L/d, the potassium intake from drinking water would be 0.6 g/d which is 13% of the recommended daily intake. Therefore, the concentration of potassium in the treated water from potassium-form cation exchange may not be a health concern, except for customers who have special potassium intake due to disease or other health effects. Although not measured, the treated water was elevated in bicarbonate due to exchange with DOC, sulfate, and chloride, similar to the potassium results (Rokicki & Boyer 2011). Elevated bicarbonate in treated water is beneficial in terms of making the water less corrosive (Nguyen *et al.* 2011; Zhang & Edwards 2011), so no problems are anticipated with bicarbonate-form anion exchange. Finally, the benefits of using

bicarbonate-form anion exchange and potassium-form cation exchange (e.g., partial desalination, less corrosive treated water) must be balanced with the increased cost of $KHCO_3$ relative to NaCl. Maul et al. (2014) reported that the cost of $KHCO_3$ was approximately 100× higher than NaCl from rock salt, which would be cost prohibitive for water utilities. However, the cost cited in Maul et al. (2014) was for food-grade $KHCO_3$ so it is possible that other, less expensive sources of $KHCO_3$ could be obtained. Otherwise, although more expensive than NaCl, CIX with $KHCO_3$ regeneration could be used temporarily to deal with a sudden change in water quality such as seawater intrusion.

CONCLUSIONS

The CIX/CMFR process can be used to remove multiple anionic and cationic contaminants from raw water including DOC, sulfate, nitrate, chloride, calcium, strontium, and sodium. The CIX/CMFR process was evaluated under varying resin dose conditions, which showed more than 60% DOC and 50% calcium removal. Using $KHCO_3$ as alternative chemical regeneration, the CIX/CMFR demonstrated over 60% DOC and 50% calcium removal, which is comparable to using NaCl for regeneration. Lastly, this new process was expanded to treat problematic water scenarios, which demonstrated removal of over 60% DOC, calcium, and strontium, and over 30% removal of nitrate, sodium, and chloride.

The novel part of this study is that the presaturant ions on the AER and CER can be altered to expand the range of contaminants that can be removed such as using bicarbonate-form AER and potassium-form CER for partial desalination. The types of resins used in the CIX/CMFR process can also be altered to target specific contaminants. With respect to anionic contaminants, resin properties play a key role in contaminant selectivity and it may not be possible to get high removal of all anionic contaminants with a single type of AER. In this case, the CIX process can be envisioned to contain two or more different types of AER for multi-anionic contaminant removal. Many cationic contaminants can be removed by the same type of CER, so multiple types of CER should not be necessary for multi-cationic contaminant removal. Using combined resins with different physical properties, such as size and density, can result in uneven recycling

of the resins which can lead to variations in contaminant concentrations in the treated water. In this research, both magnetically enhanced AER and conventional CER and conventional AER and CER were able to be used as combined resins in the CIX/CMFR process. Finally, the CIX/CMFR process can achieve consistent levels of contaminant removal over multiple treatment–regeneration cycles using salts that possess sodium or potassium and chloride or bicarbonate. Assuming that all salts achieve effective regeneration, the choice of salt should balance cost with impacts on the treated water, such as expended range of contaminant ions that can be removed and secondary water quality parameters like corrosion.

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