A pilot-scale evaluation of magnetic ion exchange treatment for removal of natural organic material and inorganic anions

Treavor H. Boyer*, Philip C. Singer

Department of Environmental Sciences and Engineering, School of Public Health, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-7431, USA

ABSTRACT

The objective of this research was to evaluate a magnetic ion exchange process (MIEX) for the removal of natural organic material (NOM) and bromide on a continuous-flow pilot-scale basis under different operating conditions and raw water characteristics. The most important operating variable was the effective resin dose (ERD), which is the product of the steady-state resin concentration in the contactor and the regeneration ratio. The raw water employed in this study had a moderate concentration of ultraviolet (UV)-absorbing substances and dissolved organic carbon (DOC), and a low turbidity, alkalinity, and concentration of competing anionic species. Experiments were conducted using the ambient raw water and raw water spiked with bromide, chloride, and sulfate. Substantial removal of UV-absorbing substances and DOC was achieved at ERDs as low as 0.16 mL/L. Moderate bromide removal was achieved, depending on the ERD. Increasing the sulfate concentration resulted in decreased removal of UV-absorbing substances, DOC, and bromide. Consistent results were observed between the continuous-flow pilot plant tests and batch equilibrium studies.

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1. Introduction

Anion exchange is a potential strategy for removing natural organic material (NOM) from raw drinking water to control the formation of disinfection byproducts (DBPs). The mechanism(s) of NOM removal, the affinity of resins for various fractions of NOM, important resin properties contributing to NOM removal, comparisons of anion exchange treatment with coagulation and activated carbon treatment, and the overall efficacy of anion exchange treatment for removal of DBP precursors have been investigated to varying degrees by several researchers (Boening et al., 1980; Fu and Symons, 1990; Kim and Symons, 1991; Croue et al., 1999; Bolto et al., 2002a, b; Humbert et al., 2005).

A magnetic ion exchange resin (MIEX) developed jointly by Orica Watercare, Commonwealth Scientific Industrial Research Organization, and South Australian Water Corporation was designed specifically to remove dissolved organic carbon (DOC) from natural water. MIEX is a strong base anion exchange resin with a macroporous polyacrylic matrix in the chloride form. Magnetic iron oxide is incorporated into the resin matrix to aid in agglomeration and settling. MIEX is designed to be used in slurry form in completely mixed continuous-flow reactors (i.e. contactors). A review of the literature pertaining to treatment with MIEX reveals it has the potential to remove a greater amount of DOC and ultraviolet (UV)-absorbing substances than coagulation, removes a wider range of molecular weight and organic acid fractions of DOC
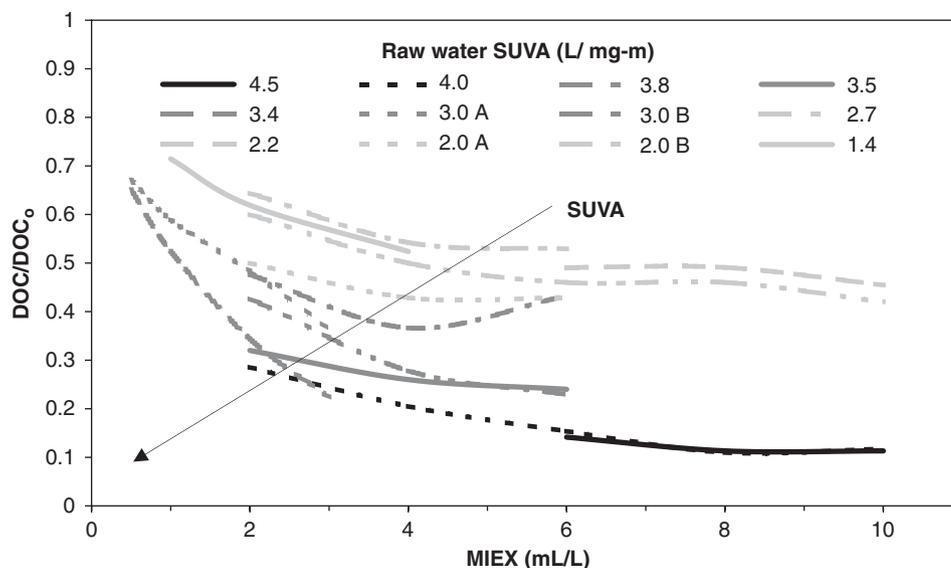

Fig. 1 – Illustrative example of batch-testing results using MIEX for various raw waters. Data from Singer and Bilyk (2002), Boyer and Singer (2005).

Table 1 – Illustrative pilot plant data

Location	DOC (mg/L)	SUVA (L/mg-m)	Sulfate (mg/L)	Alkalinity (mg/L as $CaCO_3$)	DOC removal (%)	Reference
New Port Richey, FL	1.9	5.6	18	200	65–77	Budd et al. (2005)
Charleston, SC	5.0	4.3	15	27	58–70	Budd et al. (2005)
Palmdale, CA	4.2	2.1	29–41	126	52–60	Fonseca et al. (2005)
Northern KY	1.8	4.6	75	113	47–61	Budd et al. (2005)
Southern NV	2.3	1.2	246	288	23–44	Budd et al. (2005)

than coagulation, and is capable of removing bromide (Singer and Bilyk, 2002; Drikas et al., 2003; Lee et al., 2003; Fearing et al., 2004; Johnson and Singer, 2004; Boyer and Singer, 2005). Fig. 1 is a summary of batch treatment studies illustrating the influence of specific UV absorbance (SUVA) on DOC removal by MIEX (data from Singer and Bilyk, 2002 and Boyer and Singer, 2005). SUVA is the ratio of UV absorbance at 254 nm (UV254) to DOC times 100, and is proportional to the aromatic carbon content of NOM. In general, high SUVA waters are characterized by hydrophobic NOM and low ionic strength, whereas low SUVA waters have more hydrophilic NOM. Fig. 1 shows a clear trend of increasing removal of DOC with increasing SUVA of the raw water, suggesting that MIEX resin has a greater preference for the types of aquatic NOM present in high SUVA waters, i.e., hydrophobic NOM.

Most of the published literature on MIEX performance is from batch treatment studies. There is less published information on the performance of MIEX treatment for the removal of DBP precursors on a continuous-flow basis. Table 1 summarizes the results from two continuous-flow pilot-scale

studies of MIEX treatment on several different raw waters (Budd et al., 2005; Fonseca et al., 2005). The highest DOC removals were seen in waters with a high SUVA and a low sulfate concentration. At Charleston, SC and Northern KY, where coagulation is practiced, pre-treatment with MIEX reduced the subsequent coagulant demand. Pilot testing by Hammann et al. (2004) and Mercer et al. (2004) reported substantial removal of DOC and reduction in subsequent coagulant demand. Morran et al. (2004) and Allpike et al. (2005) evaluated full-scale treatment with MIEX at the Mt. Pleasant Water Treatment Plant in South Australia and the Wanneroo Water Treatment Plant in Western Australia, respectively, and reported that pre-treatment with MIEX followed by coagulation was very effective at removing a wide range of molecular weight fractions of DOC and reducing the subsequent coagulant demand.

The objective of this research was to evaluate the performance of MIEX treatment for the removal of NOM and bromide on a continuous-flow pilot-scale basis under different operating conditions and for different raw water

characteristics. An advantage of working on a continuous-flow basis is the ability to run the resin to exhaustion in order to investigate regeneration effects, and to examine the competitive effects of inorganic anions. The operating conditions investigated in this research included the regeneration ratio and the steady-state concentration of resin in the contactors. The raw water source for this study was selected because it had a moderate DOC concentration and a low concentration of anions which afforded the authors an opportunity to spike the raw water with bromide, chloride, and sulfate to evaluate competition effects. The impact of MIEX treatment was analyzed based on removal of UV-absorbing substances, DOC, and bromide. Size exclusion chromatography (SEC) analysis, coagulation jar-tests, chlorine-demand studies, and equilibrium studies were also conducted on raw and treated water samples to complement the UV and DOC pilot-scale results.

2. Experimental procedures

2.1. Pilot plant description and operation

Orica Watercare of Watkins, CO provided a 7.6 L/min pilot plant and MIEX resin. The pilot plant was set up at the Brown Water Treatment Plant in Durham, NC, which treats surface water from Little River Reservoir. The pilot plant was operated from May 2004 to December 2004. Multiple raw water and pilot plant effluent (i.e. MIEX-treated water) samples were taken daily and monitored for DOC, UV254, pH, and turbidity. Additional raw water and effluent samples were collected periodically for SEC analysis, coagulation jar-tests, and chlorine-demand studies. Fig. 2 shows a process schematic of the pilot plant. Briefly, raw water and MIEX were combined in the first of two completely mixed contactors; the water with the suspended MIEX flowed through the two contactors in series. The water/MIEX suspension flowed from the contactors to an upflow clarifier where the treated water and resin were separated. Depending on the desired regeneration ratio, 85–99% of the settled resin was pumped back to the first contactor, and the remaining 1–15% of the settled resin was pumped to the batch regeneration tank and regenerated with a saturated sodium chloride solution.

Table 2 outlines the test plan for the pilot plant study (note: Run 9 was done in duplicate). For all tests, a constant hydraulic residence time (HRT) of 20 min was maintained while the regeneration ratio and the concentration of resin in the contactors were varied. The effective resin dose (ERD), in units of mL/L, is defined as the steady-state concentration of MIEX in the contactors multiplied by the regeneration ratio. To investigate the impact of competing anions on MIEX performance, a concentrated spiking solution was prepared and mixed with the raw water. Table 2 shows the concentration of bromide, chloride, and sulfate in the background raw water (Runs 1–5), and the target anion concentrations for the spiking studies (Runs 6–11). The spiking solutions were prepared by dissolving a predetermined mass of sodium chloride (low-bromide salt; Morton Salt International, Grantsville, UT), sodium bromide (Fisher Scientific, Fair Lawn, NJ), and sodium sulfate (Fisher Scientific, Fair Lawn, NJ) in the desired volume of tap water. The spiking solution was pumped (Masterflex L/S, Cole-Parmer Instrument Co., Vernon Hills, IL) to the first contactor, where it was mixed with influent raw water, recycled resin, and freshly regenerated resin. The flow rate of the spiking solution was controlled with a valved acrylic flowmeter (Cole-Parmer Instrument Co., Vernon Hills, IL).

2.2. Additional experiments

Coagulation jar-tests, MIEX jar-tests, and chlorine-demand studies were conducted as previously described by Boyer and Singer (2005). Equilibrium adsorption isotherm studies were conducted by dosing 0.2–4 mL/L MIEX to 250-mL French jars filled with raw Durham water from the Brown plant and continuously mixed for 12 days. Initial coagulation jar-tests, MIEX jar-tests, and all chlorine-demand and equilibrium studies were performed in duplicate to verify reproducibility. SEC was used to characterize the molecular weight distribution of DOC in raw and treated water samples. Samples for SEC analysis were transferred to 100-mL plastic bottles
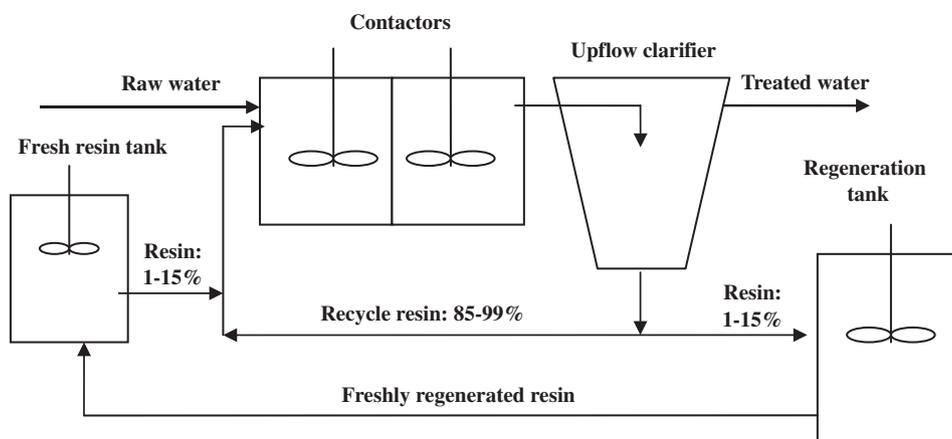

Fig. 2 – Schematic of MIEX pilot plant.

Table 2 – Pilot plant test plan

Run (#)	Regen. ratio (%)	Contactor conc. (mL/L)	ERD (mL/L)	HRT (min)	Infl. bromide (μg/L)	Infl. chloride (mg/L)	Infl. sulfate (mg/L)
1	1	15	0.15	20	Background <25	Background <10	Background <10
2	2	10	0.2	20	Background <25	Background <10	Background <10
3	2	15	0.3	20	Background <25	Background <10	Background <10
4	2	20	0.4	20	Background <25	Background <10	Background <10
5	5	15	0.75	20	Background <25	Background <10	Background <10
6	5	15	0.75	20	Spike to ≈200	Spike to ≈65	Background <10
7	10	15	1.5	20	Spike to ≈200	Spike to ≈65	Background <10
8	10	20	2	20	Spike to ≈200	Spike to ≈65	Background <10
9	15	20	3	20	Spike to ≈200	Spike to ≈65	Background <10
10	5	15	0.75	20	Spike to ≈200	Spike to ≈65	Spike to ≈50
11	10	20	2	20	Spike to ≈200	Spike to ≈65	Spike to ≈50

without any preservatives and sent by overnight carrier in coolers with ice packs to the University of Colorado at Boulder (see Lee et al., 2004). All samples requiring filtration were filtered through pre-rinsed 0.45 μm membrane filters (Supor-450, Pall Corp., Ann Arbor, MI) as described by Boyer and Singer (2005).

2.3. Analytical methods

2.3.1. Ultraviolet absorbance
UV254 was measured using either a Hitachi U-2000 spectrophotometer (Hitachi Instruments Inc., Danbury, CT) or a Hach DR 4000 spectrophotometer (Hach Co., Loveland, CO) as previously described by Boyer and Singer (2005).

2.3.2. DOC measurements
DOC was measured using a Shimadzu 5000 Total Organic Carbon Analyzer (Shimadzu Corp., Atlanta, GA) equipped with an ASI 5000 auto-sampler as previously described by Boyer and Singer (2005). All DOC samples were measured in duplicate. The reported value is the average of the duplicate values, provided the relative percent difference between duplicate samples and calibration check standards was ⩽ ±10%.

2.3.3. Turbidity
Turbidity was measured using a Hach 2100N Turbidimeter (Hach Co., Loveland, CO).

2.3.4. Inorganic anions
Bromide, chloride, and sulfate were analyzed using ion chromatography in accordance with Method 300.0 (USEPA, 1993). The samples were analyzed on a Dionex Ion Chromatograph Model AI-450v.3.32 using an IonPac AG4A-SC guard column and AS4A-SC analytical column (Dionex Corp., Sunnyvale, CA). Standards were prepared from the following ACS grade salts: sodium chloride (Mallinckrodt Baker Inc., Paris, KY), sodium bromide (Fisher Scientific, Fair Lawn, NJ), and potassium sulfate (Fisher Scientific, Fair Lawn, NJ). Quality assurance was monitored through matrix spike

recoveries, calibration check standards, and relative percent difference between duplicate samples.

2.3.5. Chlorine residual
A Hach Chlorine Pocket Colorimeter (Hach Co., Loveland, CO) was employed to measure low-level chlorine residuals from the chlorination experiments.

3. Results and discussion

3.1. Raw water characteristics

Raw water characteristics for Little River Reservoir over the duration of the study, as provided by personnel at the Brown Water Treatment Plant, are summarized in Table 3. The raw water temperature varied from 26 °C during the summer to 12 °C in December. Humbert et al. (2005) evaluated treatment with MIEX on a batch basis and showed that varying temperature between 6 and 26 °C had only a minor influence on DOC removal. Therefore, changes in raw water temperature were not expected to influence pilot plant performance appreciably. The alkalinity, hardness, conductivity, and chloride concentration indicate that the raw water had a low ionic strength. Between August and September, there was a noticeable increase in the amount of UV-absorbing substances and DOC present in the raw water. This made direct comparisons of results from May to August with results from September to December somewhat challenging, as is often the case with extended pilot plant studies. The SUVA values for the raw water indicate that the concentration of UV-absorbing substances and DOC increased proportionally (with the exception of December when the reservoir was undergoing turnover). This suggests that, for the most part, the physical and chemical characteristics of the aquatic NOM remained relatively constant over the course of the study. In general, based on previous research with Durham water, the raw water from Little River Reservoir was expected to be dominated by humic substances, be amenable to organic carbon removal by both coagulation and MIEX treatment, and

Table 3 – Raw water quality over duration of pilot plant study										
Month 2004	Temperature (°C)	Turbidity (NTU)	pH	Alkalinity (mg/L CaCO$_3$)	Hardness (mg/L CaCO$_3$)	Conductivity (µS/cm)	Cl$^-$ (mg/L)	UV254 (1/cm)	DOC (mg/L)	SUVA (L/mg-m)
May	21	2	6.9	25	27	97	8.8	0.151	5.0	3.1
June	24	4	6.8	25	29	102	9.9	0.136	5.0	2.7
July	26	2	6.8	27	29	104	10.5	0.148	5.1	2.9
August	26	3	6.8	27	30	105	10.4	0.182	5.2	3.5
September	24	5	6.6	22	27	81	8.3	0.237	7.0	3.4
October	21	3	6.8	23	27	87	9.3	0.246	6.7	3.7
November	17	4	6.9	24	29	91	8.8	0.225	6.3	3.6
December	12	11	6.8	20	30	91	10.0	0.318	7.2	4.4

have a high chlorine demand and subsequent DBP formation potential (Edzwald et al., 1985; White et al., 1997; Singer and Bilyk, 2002; Liang and Singer, 2003; Johnson and Singer, 2004).

3.2. Continuous-flow pilot-scale testing

3.2.1. Removal of DOC and UV-absorbing substances

In developing the experimental plan, the authors expected that increasing either the regeneration ratio or the concentration of MIEX in the contactors, both of which influence the ERD, would result in increased NOM removal, but it was uncertain to what extent varying these operating parameters would influence performance. Since previous researchers have shown that MIEX treatment was insensitive to contact times ranging from 5 to 25 min (Booth et al., 2004; Mercer et al., 2004; Fonseca et al., 2005), the ERD is the only operating parameter needed to compare pilot plant results. Based on previous MIEX pilot plant studies (Booth et al., 2004; Hammann et al., 2004; Mercer et al., 2004; Budd et al., 2005; Fonseca et al., 2005), the pilot plant was initially operated at a 20 min HRT, a 10% regeneration ratio, and a steady-state MIEX concentration of 20 mL/L (ERD = 2 mL/L). These operating conditions resulted in substantial removal of UV-absorbing substances (79%) and DOC (74%). Based on these preliminary results, it was decided to evaluate the performance of treatment with MIEX at lower ERDs. All continuous-flow experiments were conducted at a HRT of 20 min. All subsequent discussions will define the operating conditions based on the regeneration ratio, the concentration of MIEX in the contactors, and the ERD. Due to the configuration of the pilot plant, the lower limit for the regeneration ratio was 1% and the lower limit for the resin concentration was 10 mL/L.

Following preliminary testing, both the regeneration ratio and the steady-state MIEX concentration in the contactors were separately varied to investigate their impact on performance. For the first suite of tests (Runs 1, 3, and 5; see Table 2), the regeneration ratio was varied while the MIEX concentration in the contactors was maintained at approximately 15 mL/L. For the second suite of tests (Runs 2–4; see Table 2) the steady-state MIEX concentration was varied while a constant 2% regeneration ratio was maintained. Table 4 summarizes the duration of the tests, operating conditions, and average influent and effluent water quality characteristics. Average removals of DOC at a MIEX concentration of

15 mL/L and regeneration ratios of 1%, 2%, and 5% (ERDs of 0.16, 0.3, and 0.75 mL/L) were 64%, 67%, and 73%, respectively, with a coefficient of variation (CV) of less than 5% for each test. The average DOC removals at a 2% regeneration ratio and MIEX concentrations of 10, 15, and 20 mL/L (ERDs of 0.2, 0.3, and 0.4 mL/L) were 62%, 67%, and 69%, respectively, with a CV of less than 6%. These results illustrate that substantial removal of UV-absorbing substances and DOC was achieved at low ERDs (i.e. 0.16–0.4 mL/L). The substantial removal of NOM at these low ERDs was unexpected because previous studies have required operation at ERDs of 1–4 mL/L to achieve comparable removals (Booth et al., 2004; Hammann et al., 2004; Mercer et al., 2004; Budd et al., 2005; Fonseca et al., 2005). Table 4 also illustrates that, under the operating conditions investigated, the treated water SUVA was approximately equal to the raw water SUVA. The equivalence of raw and treated water SUVA suggests that treatment with MIEX on a continuous-flow basis removes proportional amounts of UV-absorbing substances and DOC for raw waters characterized by a relatively high SUVA (i.e. > 3 L/mg-m) and a low anionic strength. Similar results have been observed on a batch treatment basis (Singer and Bilyk, 2002; Johnson and Singer, 2004; Boyer and Singer, 2005).

Fig. 3 shows the impact of varying the regeneration ratio on the removal of DOC at a MIEX concentration of 15 mL/L. The symbols represent the individual measurements, while the lines represent the average value over the duration of the test. The run time at which individual samples were collected was normalized by the corresponding mean solids (resin) residence time (SRT) to present results on an equivalent temporal basis. The SRT was defined as the HRT divided by the regeneration ratio. Given a HRT of 20 min, the SRTs for 1, 2, and 5% regeneration ratios are 33, 17, and 7 h, respectively. Fig. 3 illustrates that steady-state operation, as indicated by a consistent effluent DOC concentration, was achieved after one SRT and was maintained over multiple SRTs. Because of the configuration of the pilot plant, testing at the 1% regeneration ratio posed operational challenges and resulted in more variable performance. Similar steady-state results were observed for the suite of tests where the regeneration ratio was held constant and the MIEX concentration was varied.

Fig. 4 displays SEC results for selected raw water and MIEX-treated effluent samples from the pilot plant. The raw water samples display two peaks corresponding to apparent mole-

Table 4 – Impact of regeneration ratio and steady-state resin concentration on removal of DOC and UV absorbance

Dates of operation	Regen. ratio (%)	Contactor conc. (mL/L)	ERD (mL/L)	Infl. DOC (mg/L)	Effl. DOC (mg/L)	DOC removal (%)	Infl. UV254 (1/cm)	Effl. UV254 (1/cm)	UV254 removal (%)	Infl. SUVA (L/mg-m)	Effl. SUVA (L/mg-m)
13–29 Sept. 04	1	16	0.16	6.7	2.4	64	0.213	0.062	71	3.2	2.6
16–20 Aug. 04	2	10	0.2	4.8	1.8	63	0.158	0.055	65	3.3	3.0
2–6 Aug. 04	2	15	0.3	4.9	1.6	67	0.158	0.055	65	3.2	3.4
19–30 July 04	2	20	0.4	4.5	1.4	69	0.129	0.036	72	2.9	2.5
9–13 Aug. 04	5	15	0.75	4.8	1.3	73	0.155	0.043	72	3.2	3.3

cular weights of approximately 10,000–20,000 Da (small peak; fraction 1) and 1000–2000 Da (large peak; fraction 2). Fig. 4 shows that treatment with MIEX effectively removed UV-absorbing substances and DOC corresponding to fraction 2. Treatment with MIEX had a negligible impact on fraction 1. It is probable that this high molecular weight fraction corresponds to colloidal humic material, in which case anion exchange would not be an effective removal process. In addition to this apparent colloidal residual, the DOC remaining after MIEX treatment appears to be of low molecular weight (<1000 Da) and has a low UV absorbance.

3.2.2. Anion spiking studies

Because Durham raw water had a moderate concentration of DOC and a low concentration of anionic species, it was an ideal matrix for examining the performance of MIEX under different anionic compositions. We examined bromide removal because bromide is an important precursor in the formation of brominated DBPs, and the impact of sulfate because anion exchange resins tend to have a high selectivity for sulfate and elevated sulfate concentrations tend to inhibit DOC removal by ion exchange (Fu and Symons, 1990; Kim and Symons, 1991; Budd et al., 2005). Chloride was spiked at 333 times the bromide spike to reflect conditions in natural waters with high bromide concentrations (Johnson and Singer, 2004). An initial set of tests was conducted at elevated concentrations of bromide and chloride, and a second set of tests was conducted at elevated concentrations of bromide, chloride, and sulfate. The targeted anion concentrations and operating conditions are shown in Table 2, Runs 6–11. The influent concentration of DOC varied from 5.1–6.5 mg/L during this portion of the study, making direct comparisons between results from some of the runs difficult.

Table 5 summarizes the impact of MIEX on the removal of organic matter and bromide under different operating conditions for the bromide-spiked feed (Runs 6–9; see Table 2). Table 5 shows results for ERDs of 0.8–3.0 mL/L. At an ERD of 0.8 mL/L, the effluent concentration of bromide was approximately equal to the influent concentration, whereas at ERDs greater than or equal to 1.5 mL/L, the effluent bromide concentration was reduced by 20–28% as a result of MIEX treatment. Budd et al. (2005) observed comparable bromide removal in Charleston, SC at ERDs of 1 and 2 mL/L. In general, Table 5 illustrates that a substantial amount of UV-absorbing substances ($>74\%$) and DOC ($>65\%$) were removed under the operating conditions investigated, indicating that the increased concentration of chloride that accompanied the bromide spike had a negligible impact on NOM removal.

Table 6 summarizes the impact of elevated levels of sulfate on the removal of organic matter, bromide, and sulfate under different operating conditions (Runs 10 and 11; see Table 2). Comparing the results in Table 6 to those in Tables 4 and 5, it is clear that increasing the sulfate concentration decreases the removal of UV-absorbing substances, DOC, and bromide. For an ERD of 0.75 mL/L and background sulfate conditions, removal of DOC ranged from 66% to 73%, but DOC removal decreased to 51% when the sulfate concentration was increased to approximately 50 mg/L. For ERDs greater than or equal to 1.5 mL/L, removal of bromide decreased from a high of 28% at background sulfate conditions to approxi-
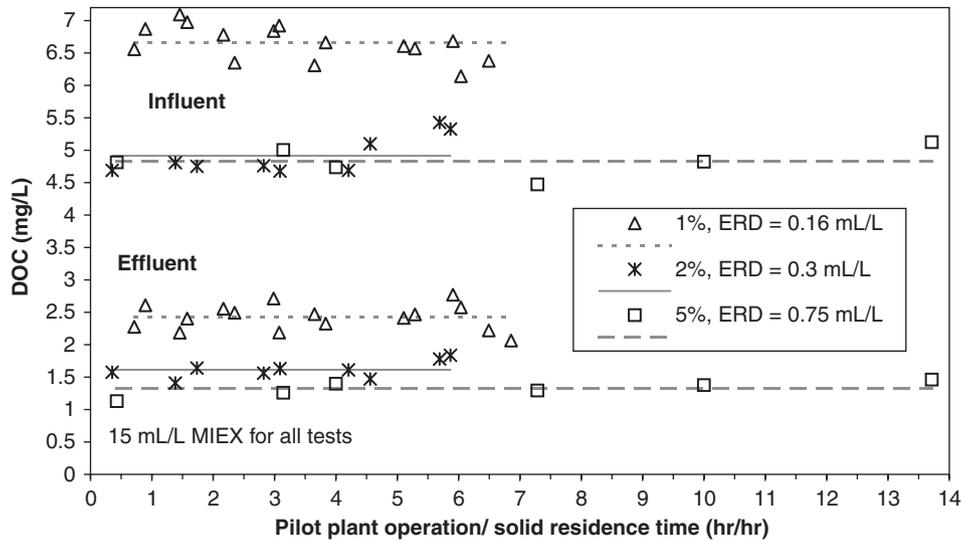
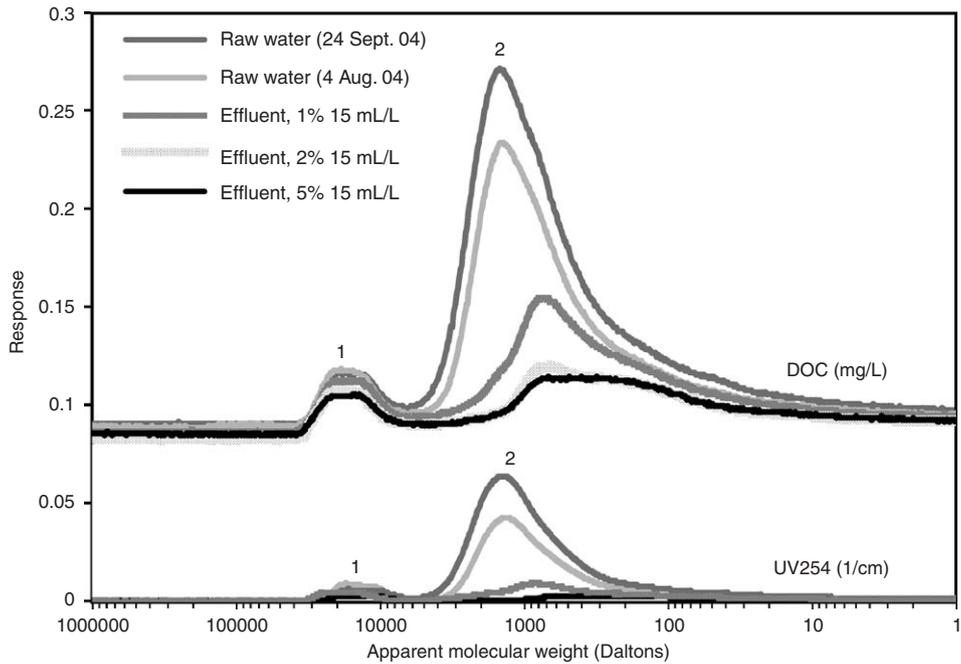Fig. 3 – Impact of regeneration ratio on the removal of DOC (15 mL/L MIEX).

Fig. 4 – Size exclusion chromatography results for selected raw water and effluent samples.

mately 5% when the sulfate concentration was increased to 50 mg/L. Sulfate removals were 29 and 46% at ERDs of 0.75 and 2.0 mL/L, respectively. Fonseca et al. (2005) reported similar results under comparable raw water conditions, e.g., TOC removals were 52 and 58%, bromide removals were 7 and 25%, and sulfate removals were 37 and 85% at ERDs of 1.4 and 3.4 mL/L, respectively.

3.3. Batch experiments

MIEX is designed to remove dissolved anions and not particulate material. In fact, depending upon the effectiveness of the solid–liquid separation process following the contactors, MIEX treatment can result in carry-over of resin

fines to downstream treatment processes. Therefore, a solid–liquid separation sequence, such as coagulation, flocculation, and clarification, is required following treatment with MIEX. Fig. 5 illustrates the impact of batch coagulation experiments with alum on settled water turbidity for untreated raw water and effluent samples from the MIEX pilot plant. Fig. 5 shows an approximate reduction in the coagulant dose of 67% following MIEX treatment which is attributable to the removal of a substantial amount of coagulant-demanding organic material by MIEX. Previous evaluations of MIEX pre-treatment on a continuous-flow basis have also reported substantial reductions in coagulant demand (Mercer et al., 2004; Morran et al., 2004; Budd et al., 2005).

Table 5 – Impact of regeneration ratio, resin concentration, and elevated levels of bromide and chloride on removal of DOC, UV absorbance, and bromide

Dates of operation	Regen. ratio (%)	Contactor conc. (mL/L)	ERD (mL/L)	Infl. DOC (mg/L)	Effl. DOC (mg/L)	DOC removal (%)	Infl. UV254 (1/cm)	Effl. UV254 (1/cm)	UV254 removal (%)	Infl. Br^- (µg/L)	Effl. Br^- (µg/L)	Br^- removal (%)
29 Sept.–6 Oct. 04	5	16	0.8	6.5	2.2	66	0.214	0.054	75	204	215	No removal
18–21 Oct. 04	10	15	1.5	5.8	1.8	69	0.175	0.046	74	217	156	28
8–12 Nov. 04	10	18	1.8	5.1	1.8	65	0.159	0.033	79	167	134	20
27 Oct.–2 Nov. 04	15	19	2.9	5.5	1.7	69	0.170	0.031	82	214	168	21
18–20 Nov. 04	15	20	3.0	5.9	1.6	73	0.173	0.034	80	218	165	24

Table 6 – Impact of regeneration ratio, resin concentration, and elevated levels of sulfate on removal of DOC, UV absorbance, bromide, and sulfate

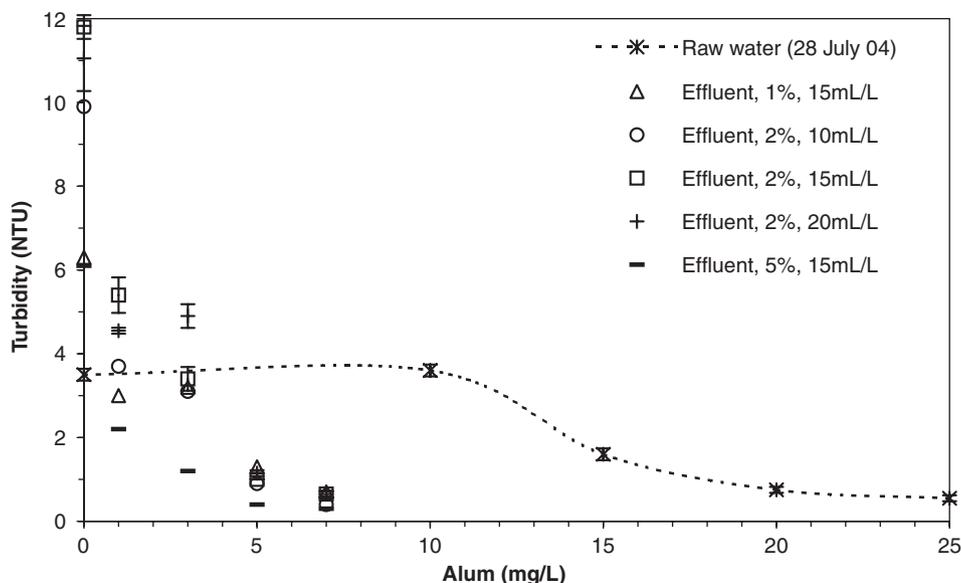| Dates of operation	Regen. ratio (%)	Contactor conc. (mL/L)	ERD (mL/L)	Infl. DOC (mg/L)	Effl. DOC (mg/L)	DOC removal (%)	Infl. UV254 (1/cm)	Effl. UV254 (1/cm)	UV254 removal (%)	Infl. Br^- (µg/L)	Effl. Br^- (µg/L)	Infl. SO_4^{-2} (mg/L)	Effl. SO_4^{-2} (mg/L)
13–17 Dec. 04	5	15	0.75	6.3	3.1	51	0.189	0.061	68	209	184	50.5	35.9
6–10 Dec. 04	10	20	2.0	6.2	2.8	55	0.184	0.055	70	231	216	52.3	28.0

Fig. 5 – Impact of coagulation with alum on settled water turbidity.

Because chlorine reacts with NOM to form halogenated organic DBPs, chlorine demand is a common surrogate for DBP formation potential. Fig. 6 displays the free chlorine residual for several raw water and MIEX effluent samples. All chlorine demand studies were conducted in duplicate with the average free chlorine residuals plotted; error bars represent one standard deviation. All chlorinated samples were incubated for 24 h in the dark at pH 8 and 20 °C. Fig. 6 shows that treatment with MIEX reduced the chlorine demand by approximately 50% compared with the raw water; this can be expected to translate to a similar reduction in trihalomethane and haloacetic acid formation.

3.4. Regeneration

Evaluating MIEX treatment on a continuous-flow basis allowed the authors to investigate the effectiveness of the regeneration process and to perform a mass balance on the DOC removed. Exhausted or partially exhausted anion exchange resins are typically regenerated by converting the resins back to their original chloride form. The exchange capacity of freshly regenerated MIEX, as measured by removal of UV-absorbing substances in batch treatment experiments, was periodically evaluated throughout the study to assess the effectiveness of regeneration. The recovery in ion exchange capacity of regenerated MIEX with respect to virgin MIEX was excellent, with a recovery of 92–106% ($n = 4$). The effectiveness of the regeneration process (i.e. essentially complete recovery in ion exchange capacity) indicates that the NOM was reversibly bound to the MIEX through electrostatic interactions, and strongly suggests that ion exchange accounts for the interactions between NOM and MIEX.

A mass balance, based on DOC, was performed on the pilot plant for every testing condition ($n = 12$) to further evaluate the regeneration process. The mass of DOC removed by MIEX treatment per regeneration cycle (M_T) was calculated according to

$$M_T = \frac{Q_{in} V_{FRT} (C_{infl} - C_{effl})}{Q_R R}, \tag{1}$$

where Q_{in} is the influent flow rate to the pilot plant, V_{FRT} is the initial volume of the water/MIEX slurry in the fresh resin tank, C_{infl} and C_{effl} are influent and effluent DOC concentrations, respectively, Q_R is the pumping rate of the regeneration pump, and R is the regeneration ratio. The mass of DOC recovered during each regeneration cycle (M_R) was calculated according to

$$M_R = V_B C_B + V_R C_1 + V_R C_2, \tag{2}$$

where V_B is the volume of brine used during regeneration, C_B is the DOC concentration in the waste brine, V_R is the volume of rinse water, and C_1 and C_2 are the DOC concentrations in the waste water from the first and second rinse, respectively. The ratios of DOC in the rinse waters to DOC in the waste brine were approximately constant ($C_1/C_B = 0.36$, CV = 3%; $C_2/C_B = 0.07$, CV = 11%). Fig. 7 shows the correlation between the mass of DOC recovered during regeneration (M_R) and the mass of DOC removed by MIEX treatment (M_T). The solid line corresponds to the theoretical 1:1 line (i.e. $y = x$) if all DOC removed by MIEX treatment was recovered during regeneration. In general, excellent closure is achieved for the mass balance. For the run at 1% regeneration and 15 mL/L MIEX, operational problems were encountered that resulted in only one brine sample being collected (solid square in Fig. 7). For all other testing conditions, multiple waste brine and waste rinse water samples were collected and analyzed (open squares in Fig. 7). For these samples, the average M_R is plotted with error bars representing one standard deviation. The results displayed in Fig. 7 confirm the effectiveness of the regeneration process, and further support the assertion that treatment with MIEX removes DOC via ion exchange.

3.5. Unifying considerations

Previous researchers' batch treatment experiments have shown that MIEX treatment is an effective process for
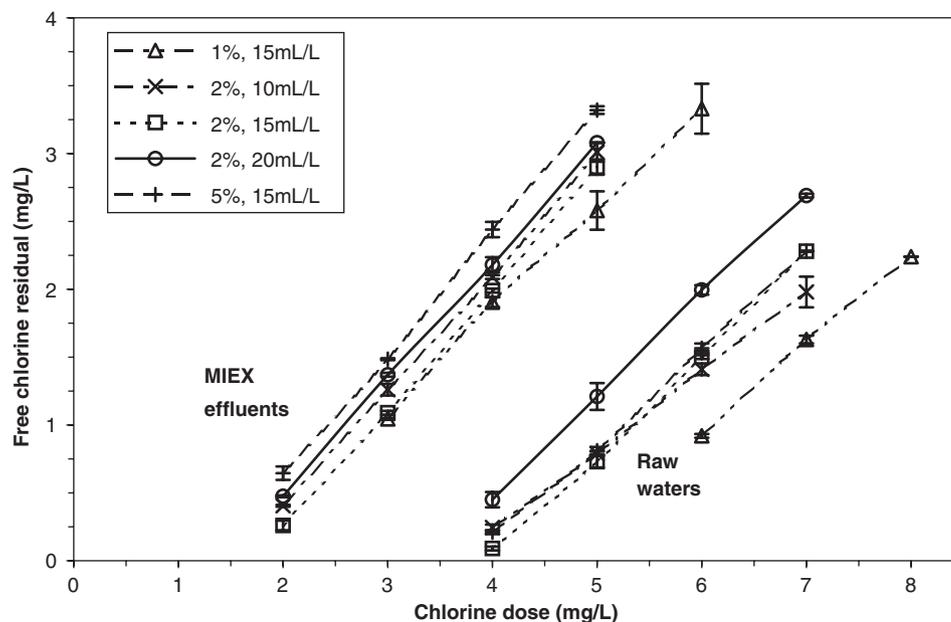
Fig. 6 – Illustration of reduction in chlorine demand for MIEX-treated effluents compared to raw waters.
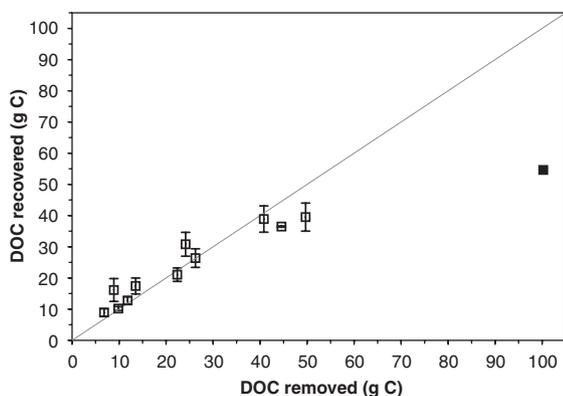

Fig. 7 – Illustration of mass balance between DOC removed by pilot plant and DOC recovered during regeneration.

removing DOC (Singer and Bilyk, 2002; Drikas et al., 2003; Lee et al., 2003; Fearing et al., 2004; Johnson and Singer, 2004; Boyer and Singer, 2005). To date, batch experiments have provided only minimal guidance for designing continuous-flow pilot-scale testing programs, i.e. choosing appropriate operating conditions such as regeneration ratios and resin concentrations. Previous researchers investigating MIEX treatment on a continuous-flow basis have made semi-quantitative observations relating process performance to operating conditions and raw water quality (Booth et al., 2004; Hammann et al., 2004; Mercer et al., 2004; Budd et al., 2005; Fonseca et al., 2005), but have not related their pilot-plant results to previous batch treatment results. Therefore, the authors of this study sought to unify batch and continuous-flow results to aid in future continuous-flow testing. The fraction of MIEX resin saturation, which represents the ratio of ion exchange sites occupied by DOC to total ion exchange sites, was found to be a useful concept in this regard.

The fraction of resin saturation was derived by starting with a general mass balance based on DOC removal as shown in the following equation:

$$C_{infl} - C_{effl} = q_{effl} \, \mathrm{ERD} \, \rho, \qquad (3)$$

where q_{effl} is the mass of DOC removed per mass of MIEX, ρ is the density of MIEX, and other variables are as defined previously. Since the interaction between MIEX and DOC was shown in the previous section to be dominated by ion exchange, the mass balance can be viewed in terms of equivalents of material exchanged. The equivalents of DOC loaded onto a mass of resin can be derived by combining Eq. (3) and the charge density of NOM:

$$f_{effl} = \frac{Z(C_{infl} - C_{effl})}{\mathrm{ERD} \, \rho}, \qquad (4)$$

where f_{effl} is the equivalents of DOC per mass of resin and Z is the charge density of NOM which was assumed to be 10 meq/g organic carbon at pH 7 based on work by Dempsey and O'Melia (1983). Anion exchange resins have a finite ion exchange capacity which is often expressed in units of equivalents of chloride per volume of resin. Therefore, the fraction of MIEX saturation can be expressed by normalizing Eq. (4) by the chloride exchange capacity of MIEX:

$$\frac{f_{effl}}{f_{max}} = \frac{Z(C_{infl} - C_{effl})}{Y \cdot \mathrm{ERD}}, \qquad (5)$$

where f_{max} is the equivalents of chloride per mass of resin and Y is an estimate of the chloride exchange capacity of MIEX as provided by Orica Watercare. Eq. (5) can be applied to both batch equilibrium data (from adsorption isotherm experiments) and continuous-flow pilot plant data. For batch equilibrium experiments, the ERD is equal to the MIEX dose.

The fraction of MIEX saturation as a function of the ERD is shown in Fig. 8. The open circles are for continuous-flow pilot plant data and the solid circles are for batch equilibrium data. Fig. 8 clearly shows that both continuous-flow and batch data
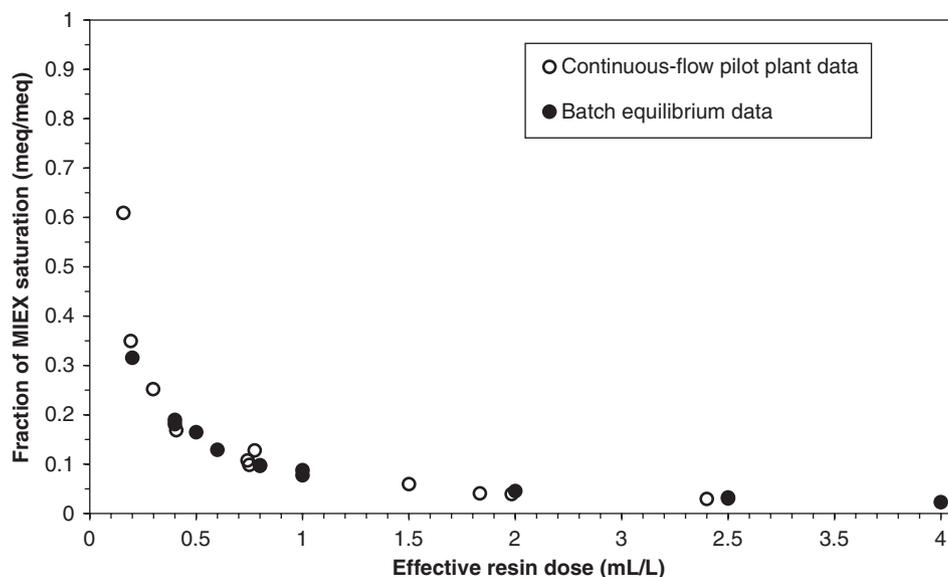
Fig. 8 – Impact of effective resin dose on fractional degree of resin saturation; comparison of batch equilibrium and continuous-flow pilot plant data.

follow the same trend. The concurrence of the data points in Fig. 8 is very interesting because it implies that batch experiments can be used to guide continuous-flow pilot testing. As a first approximation, Eq. (3) shows that the effluent concentration of DOC can be estimated based on raw water characteristics and results from batch isotherm tests. This can provide insight into whether pilot testing should be done at an ERD of 0.2 mL/L (e.g. 1% regeneration ratio and 20 mL/L MIEX) or an ERD of 4 mL/L (e.g. 20% regeneration ratio and 20 mL/L MIEX). Similar models predicting powdered activated carbon performance in completely mixed flow reactors have been developed based on batch equilibrium and kinetic experiments (e.g. Najm, 1996; Campos et al., 2000a, b). Fig. 8 also illustrates that as the ERD decreases, the fraction of MIEX saturation increases, e.g., the fraction of MIEX saturation increases from less than 5% to approximately 60% when the ERD decreases from 4 to 0.15 mL/L, and the resin approaches saturation with DOC. Recall, however, that at higher ERDs, a greater amount of organic material is removed. Therefore, Fig. 8 illustrates the optimization problem that must be considered between increasing the ERD to maximize NOM removal and decreasing the ERD to minimize the unused capacity of MIEX and lessen the quantity of waste brine associated with less frequent regeneration.

4. Conclusions

The primary objective of this research was to investigate the impact of operating conditions and raw water characteristics on continuous-flow MIEX treatment. The conclusions of this research are as follows:

- Substantial removal of NOM was achieved at ERDs as low as 0.16 mL/L, with additional NOM removal at higher ERDs.

- Bromide removal of 20–28% was achieved, but only for ERDs greater than or equal to 1.5 mL/L at background sulfate concentrations on the order of 10 mg/L sulfate.
- Increasing the sulfate concentration in the raw water to approximately 50 mg/L resulted in decreased removal of DOC, UV-absorbing substances, and bromide.
- Batch treatment experiments showed that pre-treatment with MIEX reduced the subsequent coagulant demand by approximately 67% and the chlorine demand by approximately 50% relative to the raw water.
- MIEX recovers its exchange capacity for DOC after regeneration with sodium chloride brine. The recovery in ion exchange capacity of regenerated MIEX was found to be 92–106%. Mass balance calculations showed that the mass of DOC recovered during regeneration was equal to the mass of DOC removed during treatment.
- The fraction of MIEX saturation was found to be a useful unifying concept linking batch treatment and continuous-flow pilot plant results. Batch treatment and continuous-flow experiments were found to give consistent DOC removals when viewed in terms of the fraction of MIEX resin saturation. The fraction of resin saturation increases with decreasing ERD.

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