A 10-gpm pilot plant was operated for four to five weeks at each of four US water treatment plants to evaluate the effectiveness of a magnetic ion exchange (MIEX) process for the removal of disinfection by-product precursors. Variables examined were resin concentration, contact time, and regeneration frequency. Influent and effluent samples were taken on a regular basis and analyzed for ultraviolet (UV) absorbance at 254 nm, dissolved organic carbon (DOC), and bromide. Samples of the raw water and the MIEX-treated water were also subjected to hydrophobic/hydrophilic fractionation, molecular size characterization, and chlorination under uniform formation conditions to determine the trihalomethane (THM) and haloacetic acid (HAA) formation potential before and after MIEX treatment. Results indicated that the resin removed substantial amounts of DOC and UV-absorbing materials, except in one of the waters that had a high concentration of total dissolved solids and a low specific UV absorbance. The MIEX resin also removed bromide to some degree, depending on the presence of other competing anions in the raw water. Overall THM and HAA formation was decreased substantially as a result of MIEX treatment.

MIEX for removal of DBP precursors: Pilot-plant findings

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structure. The rate of exchange between DOC and the exchangeable ion (chloride in this case) increases because of the increase in available external surface area of the smaller particles, and the magnetic properties of the resin allow the beads to be readily and rapidly separated from the suspending solution by gravitational settling.

Batch laboratory studies have shown the MIEX resin to be effective for lowering the trihalomethane (THM) and halocarbon acid (HAA) formation potential in a number of waters (Boyer & Singer, 2005; Humbert et al, 2005; Singer & Bilyk, 2002). Removals of DOC and UV-absorbing substances have been shown to increase with increasing resin dose and tend to track each other relatively closely (Boyer & Singer, 2005; Johnson & Singer, 2004), suggesting that the resin effectively removes both hydrophobic and hydrophilic carbon. Under some circumstances, the resin is also capable of removing bromide (Fonseca et al, 2005; Johnson & Singer, 2004; Singer & Bilyk, 2002).

Although these earlier studies have been useful in demonstrating the capabilities of the MIEX resin to remove DBP precursors, the majority of them were limited to batch testing. Accordingly, the objective of this investigation was to evaluate the effectiveness of the MIEX process for the removal of DBP precursors (DOC and bromide) from drinking water on the basis of results from a continuous-flow pilot-plant study sponsored by the AWWA Research Foundation (Budd et al, 2005). The resin was evaluated for its effect on (1) removal of different fractions and molecular sizes of the natural organic material (NOM) comprising the DOC, (2) removal of bromide, and (3) lowering of overall THM and HAA formation potentials. Particular attention was focused on the speciation of the THMs and HAAs before and after treatment with the MIEX resin.

METHODS AND MATERIALS

Overview. The study was conducted on a 10-gpm MIEX pilot plant at four locations across the United States with varying raw water qualities. The pilot plant was designed to simulate full-scale operation of the MIEX process and was operated continuously for four to five weeks at each location. The pilot plant was initially run for several days to allow the resin to be exposed to several cycles of treatment and regeneration so that acclimated samples of regenerated and used resin could be acquired for bench-scale testing at doses matching pilot-plant operating conditions. The bench-scale testing provided dose–response information for various doses of the MIEX resin at different contact times.

Variables examined in the pilot-plant study were resin dose, contact time, and regeneration frequency. Influent and effluent samples were taken from the pilot plant on a regular basis and analyzed for UV absorbance at 254 nm (UV_{254}), DOC, bromide, and several other selected contaminants specific to the water being evaluated. Samples of the raw water and MIEX-treated water were also subjected to hydrophobic/hydrophilic fractionation, molecular size characterization, and chlorination under uniform formation conditions (UFC) to determine the concentration and speciation of DBP (THM and HAA) precursors.

Pilot-plant description and operation. The pilot plant (Figure 1) consisted of two mixed contacting tanks in series, each with a detention time of 7.5 min at a flow rate of...
of 10 gpm; detention time could be varied by changing the flow rate or bypassing one of the contactors. MIEX resin was continuously applied to the raw water to provide a steady-state concentration of 15–20 mL of resin per litre (mL/L) of water in the contactor. The resin was recovered in a gravity settler with an overflow rate of 1.8 gpm/sq ft, and the treated water was sampled and then discarded. Gravity separation of the resin was efficient because of the magnetic properties of the resin beads, which allowed them to agglomerate and settle against the rising water in the settling basin. The majority of the settled resin (90–95%) was recycled back to the contactor as a concentrated slurry, where it was combined with a stream of freshly regenerated resin (5–10%). The remaining 5–10% of the settled resin was sent to the regeneration tank where it was regenerated intermittently using a concentrated brine (sodium chloride) solution.

The regeneration system consisted of a brine storage tank containing a concentrated (10–12%) sodium chloride solution, a regeneration tank, and a tank for storing freshly regenerated resin. The regenerant solution was captured and reused over multiple regeneration cycles, and salt was periodically added to the regenerant solution to make up for chloride loss. Freshly regenerated resin was blended with recycled resin from the settler underflow to meet the target steady-state resin concentration in the contactor (15–20 mL/L). Virgin makeup resin was added, if necessary, to make up for resin loss. The plant was mounted on a skid with rollers for easy transport to the different test locations.

The four test locations were Tampa Bay Water’s Maytum Water Treatment Plant (TBW; Port Richey, Fla.), the Charleston Commissioners of Public Works Hanahan Water Treatment Plant (CCPW; Charleston, S.C.), the Northern Kentucky Water District’s Fort Thomas Water Treatment Plant (NKWD; Fort Thomas, Ky.), and the Southern Nevada Water Authority’s Alfred Merritt Smith Water Treatment Facility (SNWA; Boulder City, Nev.). At each location, the pilot plant was run for several days to allow the resin to be conditioned over several cycles of ion exchange and regeneration. Composite samples of regenerated and recycled resin were then collected from the contactor influent for bench-scale jar-testing. For each raw water, the bench-scale testing provided dose–response information at various contact times. In the bench-scale tests, the raw water was dosed at a variety of concentrations of the MIEX resin (5–20 mL/L from the contactor influent) for varying amounts of time (7.5–20 min). Following resin separation, each of the samples was analyzed for pH, UV$_{254}$, DOC, and bromide. On the basis of the UV$_{254}$ results, a resin concentration and a contact time were chosen for each weeklong pilot-plant test condition.

The first week of pilot-testing was conducted at the initially selected resin concentration and contact time as determined from the bench-scale tests. Thereafter, the resin concentration or percent resin regenerated was modified each week to assess the effects of varying operating conditions. The test conditions were 15–20 mL of resin/L of water in the contactor, contactor hydraulic residence times of 15–20 min, and regeneration ratios of 5–10%. Several raw and MIEX-treated samples were taken during each test and analyzed for UV$_{254}$, pH, bromide, and DOC.

After four weeks of pilot-plant operation, a final set of treatment conditions was selected, and the pilot plant
was operated under these conditions for one week. During the course of the run, raw and treated water samples were analyzed several times for UV\textsubscript{254}, pH, bromide, and DOC. At the completion of the test, samples of raw and treated water were subjected to hydrophobic/hydrophilic fractionation, molecular weight characterization, and DBP formation potential after chlorination under UFC (Summers et al, 1996).

Additionally, at the conclusion of the pilot-plant testing program at each site, samples of the regenerated resin were tested to evaluate the organics removal capacity of the regenerated resin compared with the capacity of fresh (virgin) resin. Both resins were examined in jar tests at four doses for select contact times using raw water from the subject utility as the test matrix. Following treatment, samples were analyzed for pH, UV\textsubscript{254}, and DOC.

**Analytical methods.** All reagents used in this study were American Chemical Society–grade quality.

**UV absorbance.** The procedures for UV absorbance measurements were in accordance with method 5910B (Standard Methods, 1998). Samples were prepared by filtering through 0.45-µm membrane filters,\textsuperscript{1} which were prerinsed with 500 mL of laboratory-grade water and 10 mL of the sample. UV\textsubscript{254} was measured using a spectrophotometer,\textsuperscript{2} and laboratory-grade water was used to zero the instrument. Measurements were made using a 1-cm quartz cell.

**DOC.** DOC concentrations were measured with a total organic carbon analyzer equipped with an auto-sampler.\textsuperscript{3} Analysis for DOC content was conducted according to the procedures dictated in method 5310B (Standard Methods, 1998), with one modification: 2 N hydrochloric acid rather than phosphoric acid was used to acidify the samples because the analyzer was sensitive to excess phosphoric acid. DOC samples
were first filtered through 0.45-µm filters that had been prerinsed with 500 mL of laboratory-grade water and 10 mL of the sample.

**Bromide.** At CCPW, NKWD, and SNWA, bromide samples were analyzed at the respective water utility’s onsite laboratory; bromide was not measured in the TBW raw water. The procedure used at all locations was US Environmental Protection Agency method 300.1A (USEPA, 1993). The minimum reporting level was 0.05 mg/L at CCPW and 0.01 mg/L at NKWD and SNWA.

**Nonionic resin fractionation.** Two nonionic resins (resin A\(^4\) and resin B\(^5\)) were used to fractionate the NOM in each of the raw and treated waters in accordance with the method of Thurman and Malcolm (1981). The resins were loaded into two 20-mL glass columns and the two columns were connected in series, with the resin B column following the resin A column; each column had a bed volume of 12 mL.

All samples were filtered through 0.45-µm filters, which were prerinsed with 500 mL of laboratory-grade water and 10 mL of the sample. The sample was then acidified to a pH of 2.0 with concentrated hydrochloric acid. One litre of the sample was passed through the resin A column by pumping the sample through the top of the column at a rate of 4 mL/min. The first bed volume (12 mL) of effluent was discarded. The rest of the sample was loaded onto the resin until the water level was just above the top of the resin bed so that the resin did not dry out. Resin A retains the hydrophobic acid fraction, allowing the transphilic acids and hydrophilic material to pass through. The resin A effluent was collected and then pumped through the top of the resin B column at a flow rate of 4 mL/min. The first bed volume (12 mL) of effluent was discarded. The sample passed through the resin until the water level was just above the top of the resin bed. Resin B retains the transphilic acid fraction. The effluent from the resin B column consisted of the hydrophilic acids.

Both resin beds were then back-eluted by pumping 100 mL of 0.1 N sodium hydroxide through the bottom of the column at a rate of 2 mL/min to elute the materials retained on the resin. The resin was then reacidified by pumping 0.1 N hydrochloric acid through the resin bed until the effluent was acidic.

The DOC concentrations of the feedwater, resin A effluent and eluent, and resin B effluent and eluent were analyzed. The fraction of hydrophobic, hydrophilic, and transphilic carbon in the water samples was determined on the basis of the measured DOC concentrations. UV measurements of each fraction were also taken.

**Ultrafiltration fractionation.** An ultrafiltration filter setup was operated at 55 psi using membranes with molecular weight cutoffs of 1,000, 10,000, and 30,000 D to fractionate the DOC of the raw and treated water. First, 70 mL of laboratory-grade water was filtered through the membranes and discarded, after which 70 mL of each sample was filtered through each membrane in parallel. The effluent from each of the three membranes was then analyzed for DOC and UV\(_{254}\) to determine the molecular weight fractions of each water sample.

**Chlorination under UFC.** A 4–6% solution of sodium hypochlorite was standardized on the day of each experiment by titration with a sodium thiosulfate standard in accordance with method 4500-Cl B (Standard Methods, 1998). Preliminary chlorination was performed on each sample of water to determine the 24-h chlorine demand.
The chlorination procedure was based on the UFC method suggested by Summers and co-workers (1996). Samples were chlorinated at pH 8.0 with sufficient chlorine to provide a free chlorine residual of 1.0 mg/L Cl₂ after storage at 20°C for 24 h. A series of 100-mL samples of each of the raw and treated waters was chlorinated in 100-mL volumetric flasks with a range of chlorine doses (1–2 mg Cl₂/mg DOC). The chlorine dose that produced a free chlorine residual of 1.0 mg/L after the 24-h incubation, plus an additional 1.0 mg/L of chlorine, was used for subsequent chlorinations to ensure a chlorine residual after three days.

Each water sample was then chlorinated in three 300-mL standard biochemical oxygen demand bottles with borate buffer to ensure that the pH would remain at 8.0. The bottles were sealed headspace-free. One of the bottles was removed from the incubator after 2 h, 24 h, and three days of storage in the dark at 20°C. Free chlorine residual and pH were measured, samples were transferred to 40-mL glass screw-cap vials with PTFE-lined silicone septa containing approximately 20 mg of ammonium sulfate (used to quench the residual chlorine), and samples were then set aside for THM and HAA analysis. Duplicate vials were prepared for each sample. In the HAA vials, 20 mL of 10-mg/L sodium azide was also added as a biocide. The THM samples contained 0.7 g of phosphate buffer to stabilize the pH of the samples between 4.8 and 5.5. The quenched samples were stored headspace-free and refrigerated at 4°C until analysis. All chlorinations were performed in chlorine demand–free glassware.

THMs. The samples generated by UFC chlorination were analyzed for all THM4 species—trichloromethane (TCM), bromodichloromethane (BDCM), chlorodibromomethane (CDBM), and tribromomethane (TBM). Analysis was performed using a liquid–liquid extraction gas chromatography (GC) procedure modified after method 6232B (Standard Methods, 1998) and method 551.1 (USEPA, 1995). Methyl-tertiary-butyl ether (MTBE) was used as the solvent, and 1,2-dibromopropane served as the internal standard. Sodium sulfate was added to each sample to aid in the extraction. Approximately 50 mg of anhydrous powdered magnesium sulfate was added as a drying agent to minimize the effects of water on the derivatization process (Brophy et al., 2000). The acids were extracted in MTBE before methylation. A surrogate, 2,3-dibromopropionic acid, was used to evaluate the efficiency of derivatization and extraction, and 1,2-dibromopropane served as the internal standard. Sodium sulfate was added to each sample to aid in the extraction. Approximately 50 mg of anhydrous powdered magnesium sulfate was added as a drying agent to minimize the effects of water on the derivatization process (Brophy et al., 2000). Derivatized sample extracts and standard extracts were analyzed by GCECD. Throughout the run, a standard was run after each set of 10 samples as a check to ensure that sample peaks were consistent; matrix spikes were used for purposes of quality assurance. All samples were analyzed in duplicate.

HAAs. All nine HAA species were analyzed using a micro liquid–liquid extraction procedure based on method 6251B (Standard Methods, 1998) and method 552 (USEPA, 1995), using diazomethane derivatization and GC/ECD direct injection analysis (Brophy et al., 2000). The acids were extracted in MTBE before methylation. A surrogate, 2,3-dibromopropionic acid, was used to evaluate the efficiency of derivatization and extraction, and 1,2-dibromopropane served as the internal standard. Sodium sulfate was added to each sample to aid in the extraction. Approximately 50 mg of anhydrous powdered magnesium sulfate was added as a drying agent to minimize the effects of water on the derivatization process (Brophy et al., 2000). Derivatized sample extracts and standard extracts were analyzed by GCECD. Throughout the run, a standard was run after each set of 10 samples as a check to ensure that sample peaks were consistent; matrix spikes were used for purposes of quality assurance. All samples were analyzed in duplicate.

Results indicated that magnetic ion exchange technology is an effective process that can be used by water utilities to achieve enhanced water quality.
RESULTS AND DISCUSSION

Water quality and operating conditions. Table 1 shows the average raw water quality characteristics for the final week of pilot-plant testing at each of the four utilities. The waters had a range of DOC concentrations, specific UV absorbance (SUVA) values, total dissolved solids (TDS) concentrations, alkalinitities, and bromide ion concentrations. The variation in SUVA is important because SUVA is a useful indicator of the DBP formation potential of the water (Croue et al., 1999; Edzwald et al., 1985).

Table 2 shows the operating conditions for the final week of pilot-plant testing at each site. The most common operating conditions were a steady-state resin concentration in the contactor of 20 mL/L, a hydraulic residence time in the contactor of 15 min, and a 5% regeneration ratio, except at SNWA where removals were less effective (discussed later).

Removal of DOC and UV-absorbing substances. The concentrations of DOC and UV-absorbing material were measured before and after MIEX treatment to assess the ability of the resin to remove NOM. Figure 2 summarizes DOC removal at all four sites; the values shown are for the final week of testing at each location. The MIEX process removed 71% of the UV-absorbing material at NKWD, 79% at CCPW, and 88% at TBW. SNWA had the lowest removal at 55%. Again, this likely was attributable to the relative low SUVA and high TDS concentration of the SNWA raw water.

As shown in Figure 3, the decrease in UV-absorbing substances paralleled that of DOC removal (Figure 2). Again, the values shown are for the final week of testing at each location. The MIEX process removed 71% of the UV-absorbing material at NKWD, 79% at CCPW, and 88% at TBW. SNWA had the lowest removal at 55%. Again, this likely was attributable to the rela-

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**TABLE 1** Average raw water quality at each utility during final week of testing

<table>
<thead>
<tr>
<th>Site</th>
<th>DOC (mg/L)</th>
<th>UV₂₅₄ cm⁻¹</th>
<th>SUVA L/mg m</th>
<th>Alkalinity mg/L as CaCO₃</th>
<th>pH</th>
<th>TDS (mg/L)</th>
<th>Bromide mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCPW</td>
<td>4.8</td>
<td>0.233</td>
<td>4.9</td>
<td>27</td>
<td>7.4</td>
<td>115</td>
<td>0.09</td>
</tr>
<tr>
<td>NKWD</td>
<td>1.4</td>
<td>0.066</td>
<td>4.7</td>
<td>69</td>
<td>7.9</td>
<td>207</td>
<td>0.04</td>
</tr>
<tr>
<td>TBW</td>
<td>1.8</td>
<td>0.139</td>
<td>7.7</td>
<td>188</td>
<td>7.8</td>
<td>233</td>
<td>NA</td>
</tr>
<tr>
<td>SNWA</td>
<td>2.5</td>
<td>0.031</td>
<td>1.2</td>
<td>133</td>
<td>7.8</td>
<td>610</td>
<td>0.09</td>
</tr>
</tbody>
</table>

CaCO₃—calcium carbonate, CCPW—Charleston Commissioners of Public Works (Charleston, S.C.), DOC—dissolved organic carbon, NA—not available, NKWD—Northern Kentucky Water District (Fort Thomas, Ky.), SNWA—Southern Nevada Water Authority (Boulder City, Nev.), SUVA—specific ultraviolet absorbance, TDS—total dissolved solids, TBW—Tampa Bay Water (Port Richey, Fla.), UV₂₅₄—ultraviolet absorbance at 254 nm

**TABLE 2** MIEX process operating conditions at each utility during final week of testing

<table>
<thead>
<tr>
<th>Site</th>
<th>Steady-state MIEX Concentration mL/L</th>
<th>Hydraulic Residence Time min</th>
<th>Regeneration %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCPW</td>
<td>20</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>NKWD</td>
<td>15</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>TBW</td>
<td>20</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>SNWA</td>
<td>20</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>

CCPW—Charleston Commissioners of Public Works (Charleston, S.C.), MIEX—magnetic ion exchange, NKWD—Northern Kentucky Water District (Fort Thomas, Ky.), SNWA—Southern Nevada Water Authority (Boulder City, Nev.), TBW—Tampa Bay Water (Port Richey, Fla.)

**TABLE 3** Effect of MIEX treatment on bromide removal during final week of testing

<table>
<thead>
<tr>
<th>Site</th>
<th>Raw Water Br Concentration mg/L</th>
<th>Treated Water Br Concentration mg/L</th>
<th>Alkalinity mg/L as CaCO₃</th>
<th>TDS mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCPW</td>
<td>0.09</td>
<td>&lt;0.05</td>
<td>27</td>
<td>115</td>
</tr>
<tr>
<td>NKWD</td>
<td>0.04</td>
<td>0.04</td>
<td>69</td>
<td>207</td>
</tr>
<tr>
<td>SNWA</td>
<td>0.09</td>
<td>0.09</td>
<td>133</td>
<td>610</td>
</tr>
</tbody>
</table>

Br—bromide, CaCO₃—calcium carbonate, CCPW—Charleston Commissioners of Public Works (Charleston, S.C.), MIEX—magnetic ion exchange, NKWD—Northern Kentucky Water District (Fort Thomas, Ky.), SNWA—Southern Nevada Water Authority (Boulder City, Nev.), TDS—total dissolved solids

**TABLE 4** Effect of MIEX treatment on BIF during final week of treatment

<table>
<thead>
<tr>
<th>Site</th>
<th>BIF for THMs</th>
<th>BIF for HAAs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before Treatment</td>
<td>After Treatment</td>
</tr>
<tr>
<td>TBW</td>
<td>0.086</td>
<td>0.453</td>
</tr>
<tr>
<td>CCPW</td>
<td>0.160</td>
<td>0.330</td>
</tr>
<tr>
<td>NKWD</td>
<td>0.150</td>
<td>0.460</td>
</tr>
<tr>
<td>SNWA</td>
<td>0.520</td>
<td>0.700</td>
</tr>
</tbody>
</table>

BIF—bromine incorporation factor, CCPW—Charleston Commissioners of Public Works (Charleston, S.C.), HAAs—haloacetic acids, MIEX—magnetic ion exchange, NKWD—Northern Kentucky Water District (Fort Thomas, Ky.), SNWA—Southern Nevada Water Authority (Boulder City, Nev.), TBW—Tampa Bay Water (Port Richey, Fla.)/THMs—trihalomethanes

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tively high TDS level and lower SUVA in the SNWA raw water. The SUVA value at each utility decreased with MIEX treatment because more UV-absorbing material was removed than DOC.

Hydrophobic/hydrophobic fractionation before and after treatment. Figure 4 summarizes the results of the hydrophobic/hydrophobic fractionation before and after MIEX treatment. Hydrophobic acids comprised the largest fraction of the organic matter at CCPW (53%), NKWD (40%), and TBW (62%). The hydrophobic acids at SNWA were only 31% of the DOC, consistent with the water’s lower SUVA value. TBW had the highest percentage of hydrophobic acids, consistent with its having the highest SUVA value among the four waters tested.

Because hydrophobic acids, hydrophilic acids, and transphilic acids are polyanionic in the pH range of natural waters, the anion exchange properties of the MIEX resin allowed it to remove each of these fractions of NOM, as shown in Figure 4. However, the hydrophobic and transphilic acid fractions generally were more effectively removed than was the hydrophilic fraction, which also included hydrophilic bases and neutral species. The MIEX resin removed substantial amounts (50–70%) of the hydrophobic and transphilic acid fractions at CCPW, NKWD, and TBW. Removal was lower at SNWA, but this was attributable to the lower overall removal of DOC as noted previously.

Molecular weight fractionation before and after treatment. Figure 5 shows the results of the molecular weight fractionation before and after MIEX treatment. At CCPW, a large portion of the DOC in the raw water (49%) had a nominal molecular weight (NMW) of 10–30 kDa. At
TBW and SNWA, however, the largest molecular weight fraction consisted of DOC in the range of 1–10 kD (46% at TBW and 48% at SNWA), with little of the DOC having a molecular weight range >10 kD. At NKWD, 39% of the DOC had an NMW in the <1-kD range.

Figure 5 shows that the MIEX resin was least effective in removing DOC with a molecular weight <1 kD and that removal increased in effectiveness as the NMW of the NOM increased. (The apparent increase in the >30-kD fraction is believed to be an analytical artifact associated with the sensitivity of the DOC measurement.) In light of the results for resins A and B discussed previously, the molecular weight removals shown in Figure 5 were not unexpected because the larger molecular weight DOC species corresponded to hydrophobic organic acids that were shown to be readily removed by the resin, whereas the smaller molecular weight fraction was associated with hydrophilic species that were shown to be less effectively removed.

**Bromide removal.** Table 3 shows that the MIEX process removed bromide to some degree at CCPW but did not affect bromide concentrations at NKWD and SNWA. (Bromide concentration was not measured at TBW.) Other research has shown that the MIEX resin removed bromide but that the removal decreased as alkalinity increased (Johnson & Singer, 2004; Singer & Bilyk, 2002). Because the MIEX resin is a strong-base anion exchange resin, water high in alkalinity offers more competition in ion exchange applications because of the high concentration of bicarbonate ions competing with bromide and DOC for the ion exchange sites. As shown in Table 3, the alkalinity of the SNWA water was relatively high, and therefore bromide removal equivalent to that at CCPW would not be expected. Additionally, the TDS concentration at SNWA was high (Table 3), with a relatively high concentration of sulfate (230–250 mg/L). Anion exchange resins are known to have a high selectivity for sulfate (Fu & Symons, 1990; Kim & Symons, 1989), so high-sulfate concentrations would be expected to limit bromide removal. The reason that no bromide removal was observed at NKWD may also be due to the relatively high TDS concentration compared with the low bromide concentration.

**Changes in DBP formation potential.** NOM is the principal precursor of DBPs, and DBP formation is directly proportional to the concentration and characteristics of the NOM. Given the decrease in DOC and UV-absorbing material observed with MIEX treatment, a decrease in both THM and HAA formation potential was expected. The THM and HAA formation potential of each of the waters did indeed decrease after MIEX treatment, as shown in Figures 6 and 7, respectively. (Values are shown in micromoles per litre because of the differences in molecular weights of each of the DBP species; presenting the findings in micrograms per litre might be misleading.) The formation potentials reported were observed after three days of contact with free chlorine. Removal of THM formation potential was 56% at CCPW, 59% at NKWD, 77% at TBW, and 38% at SNWA. Removal of HAA formation potential was 68% at CCPW, 64% at NKWD, 74% at TBW, and 44% at SNWA. Removals tended to mirror the decreases in DOC and UV-absorbing material shown in Figures 2 and 3.

**Effects of MIEX treatment on DBP speciation.** Previous research has shown that reducing organic carbon concentrations before chlorination reduces total THM and HAA formation (Liang & Singer, 2003; Edzwald et al, 1985; Babcock & Singer, 1979) but that the concentration of some of the bromine-containing THM and HAA species—which may be of greater health concern than...
their corresponding fully chlorinated counterparts (Linder et al., 1997; Pegram et al., 1997; Kroll et al., 1994)—can increase in waters that contain bromide (Black et al., 1996; Symons et al., 1993). Concentrations of bromine-containing THMs and HAAs that are formed during chlorination can increase as the DOC concentration of the water decreases because waters with lower DOC concentrations require a smaller chlorine dosage to achieve desired chlorine residuals. Therefore, the bromide-to-chlorine ratio increases with decreasing organic carbon concentration—more bromine is formed relative to DOC—shifting the distribution of THMs and HAAs to more-brominated forms (Black et al., 1996; Cowman & Singer, 1996; Symons et al., 1993).

Figure 8 shows the THM speciation of chlorinated CCPW water before (part A) and after (part B) MIEX treatment. TCM was the dominant THM species in the raw water, and the brominated species constituted <15% of the total THMs. In the MIEX-treated effluent, total THM formation after three days of contact with free chlorine decreased from 401 to 185 µg/L (54% decrease), but brominated THM species constituted 35% of the total THMs. TCM levels dropped from 323 to 121 µg/L (63% decrease), and BDCM concentrations decreased from 70 to 49 µg/L (30% decrease), whereas CDBM concentrations increased from 7.8 to 15 µg/L. The shift would likely have been more pronounced if the bromide concentration had not been decreased as a result of MIEX treatment (Table 3). Similar findings were observed for the other three test sites.

The corresponding effects of MIEX treatment on the dihalogenated acetic acid (DHAA) and trihalogenated acetic acid (THAA) concentrations in CCPW water are shown in Figures 9 and 10, respectively. (Results for the monohalogenated acetic acids are not shown because the concentrations measured were too close to the detection limits for these analytes.) The MIEX process decreased the overall concentration of DHAA and THAA concentrations to similar degrees, but as with the THMs, the speciation shifted to the more heavily brominated forms. Dibromoacetic acid and bromodi-chloroacetic acid concentrations increased in the treated water relative to the raw water, although the values were not very high. Again, the shift would likely have been more pronounced if the bromide concentration had not been decreased as a result of treatment. Similar findings were observed for the other three pilot-plant locations.

The bromine incorporation factor (BIF) is a measure of the extent of bromine incorporation into the different classes of DBPs and represents the average number of moles of bromine in the THMs or HAAs per mole of THM4 or HAA9, respectively. It is calculated by dividing the sum of the molar concentration of bromine in each species by the total molar concentration of all species and is used to quantitatively describe the degree of bromine substitution in the THM or HAA distribution (Miles et al., 2002; Chang et al., 2001; Ko et al., 1996). Table 4 shows the change in the BIF before and after MIEX treatment for THM and HAA species at each of the test sites. The BIF increased as a result of treatment, consistent with the results in Figures 8–10 and the observation that DOC is removed by the MIEX process to a greater degree than bromide.

Comparison of regenerated resin and virgin resin. For each study site, jar tests were performed to compare the behavior of regenerated resin that was collected when the pilot plant was initially started up and regenerated resin that was collected at the end of the five-week test period with virgin resin. Raw water at each of the sites
was used as the test matrix for all three samples of resin. The purpose of these tests was to determine whether the effectiveness of the resin for the uptake of organics changed over multiple regeneration cycles using a common raw water sample. Several doses of each resin sample were added to the test water, and after it was mixed for 30 min and settled, the residual DOC and UV absorbance were measured. Tests confirmed that despite repeated regeneration, there was essentially no change in the effectiveness of the resin with respect to its ability to remove DOC and UV-absorbing substances.

CONCLUSIONS

In a pilot-plant study conducted on four waters from locations across the United States, MIEX resin was shown to remove DOC, UV-absorbing substances, and bromide to varying degrees. The effectiveness of removal depended on the characteristics of the raw water. Figure 11 summarizes the pilot-plant findings.

Results indicated that MIEX technology is an effective process that can be used by water utilities to achieve enhanced water quality. In general, it is more effective for the removal of DBP precursors than is enhanced coagulation (Boyer & Singer, 2005; Singer & Bilyk, 2002), which tends to remove primarily hydrophobic DOC, whereas the MIEX resin removes hydrophobic as well as hydrophilic acids. Results from these four pilot-plant studies yielded the following conclusions:

- MIEX treatment is effective at removing DOC and UV-absorbing materials when the raw water does not have a high TDS concentration or a very low SUVA. In three of the four waters tested, removals in excess of 45% were achieved for DOC and in excess of 70% for UV-absorbing substances.
- The MIEX resin removed DOC with a wide range of molecular weights, but the higher-molecular-weight fraction (10–30 kD) was removed to a greater degree. DOC with molecular weights <1 kD was removed least effectively.
- The MIEX resin removed DOC with a wide range of polarity, but hydrophobic and transphilic fractions were removed to a greater extent than was the hydrophilic fraction.
- MIEX treatment also removed bromide to some degree, depending on raw water quality and operating conditions. Bromide removal is dependent on the presence of other competing anions in the raw water, e.g., bicarbonate and sulfate, and is likely to be more challenging in waters with a high TDS concentration, particularly when a multivalent anion such as sulfate is present.
- MIEX-treated water has appreciably lower THM and HAA formation potentials compared with the corresponding raw water, but DBP speciation after MIEX treatment tended to shift from the fully chlorinated THM and HAA components to their more highly brominated counterparts as a result of the limited removal of bromide relative to DOC and the corresponding increase in the bromide-to-carbon ratio.

This work demonstrated that anion exchange—particularly the MIEX process that was the subject of this research—is an effective process for the removal of DBP precursors and can claim a place in the water treatment

REFERENCES


toolkit along with nanofiltration, granular activated carbon adsorption, and ozonation/biofiltration.

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FOOTNOTES

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2U-2000 UV-visible spectrophotometer, Hitachi Instruments, Danbury, Conn.
4Amberlite XAD-8, Rohm and Haas, Philadelphia, Pa.
7Warner Scientific, Fair Lawn, N.J.
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