



Enhanced coagulation using a magnetic ion exchange resin

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Received 1 October 2001; accepted 1 February 2002

Abstract

The objective of this investigation was to examine the effectiveness of a magnetic ion exchange resin (MIEX[®]) to enhance the coagulation of disinfection by-product precursors in nine surface waters, each representing a different element of the USEPA's 3 × 3 enhanced coagulation matrix. The effect of MIEX-pretreatment on the requisite alum dose needed for subsequent coagulation of turbidity was also evaluated.

Enhanced coagulation with MIEX was found to be very effective for removing trihalomethane (THM) and haloacetic acid (HAA) precursors from the nine waters examined. THM and HAA formation potential was reduced by more than 60% in all of the waters studied; reductions approaching 90% were seen in the waters with the highest specific ultraviolet absorbance values. The residual total organic carbon concentration, ultraviolet absorbance, and THM and HAA formation potential were all substantially lower as a result of MIEX and alum treatment compared to alum coagulation alone. MIEX pre-treatment also lowered the coagulant demand of each of the waters substantially. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ion exchange; Disinfection by-products; Trihalomethanes; Haloacetic acids; Total organic carbon; Coagulation; Coagulant demand

1. Introduction

The objective of this investigation was to examine the effectiveness of a magnetic ion exchange resin (MIEX[®]) provided by ORICA Australia Pty Ltd. of Victoria, Australia to enhance the coagulation of disinfection by-product (DBP) precursors. The MIEX resin purportedly adsorbs natural organic material (NOM), thereby lowering the coagulant demand of the water, as well as lowering its DBP formation potential. Pre-treatment of raw drinking waters with MIEX was evaluated using bench-scale experimental procedures on nine surface waters to determine its impact on subsequent coagulation with alum and on subsequent DBP formation following chlorination.

2. Background

DBPs are formed when disinfectants such as chlorine are added to drinking water to inactivate pathogenic microorganisms. The disinfectants react with NOM in the water to produce a host of DBPs, many of which are halogenated compounds suspected of having adverse human health effects. Trihalomethanes (THMs) and haloacetic acids (HAAs) are the principal DBPs formed from chlorination of water [1–3]. Although THMs have been regulated in the US since 1979, the US Environmental Protection Agency (USEPA) recently promulgated Stage 1 of its Disinfectants and Disinfection By-Products (D/DBP) Rule establishing maximum contaminant levels (MCLs) for THMs and HAAs. The MCLs for total THMs (TTHMs) and five of the HAAs (HAA5) are 80 and 60 µg/L, respectively [4]. In addition, Stage 1 of the D/DBP Rule includes a requirement for “enhanced coagulation”. Enhanced coagulation is the practice of using a coagulant dose in excess of what is

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normally required for turbidity removal to achieve a specific reduction in the concentration of total organic carbon (TOC). The enhanced coagulation requirements mandate reductions in TOC concentrations based on the TOC and alkalinity of the source water as shown in Table 1. Water facilities treating water by conventional surface water treatment must achieve these percent removals prior to the application of a disinfectant. The purpose of the TOC removal requirements prior to disinfection, in addition to the specific MCLs set for THMs and HAAs, is to reduce the public's exposure to potentially harmful DBPs that have not yet been identified. Coagulation with alum or ferric salts is known to be effective for the removal of organic DBP precursors [3,5,6,7].

The subject of this investigation is a new magnetic anion exchange resin (MIEX[®]) capable of removing dissolved organic carbon (e.g. NOM) from raw water, thereby reducing THM and HAA formation potential (THMFP and HAAFP, respectively). Because of its anion exchange properties, the resin should be capable of removing both hydrophobic and hydrophilic acids. MIEX combines traditional strong base anion exchange properties, like quaternary ammonia functional groups, a polyacrylic, macroporous structure, and medium pore size and porosity, with several unconventional variations, such as making the particle size 2–5 times smaller than conventional resins (180 μm approximate resin diameter). Decreasing the particle size reduces the reliance on slow, intraparticle diffusion that is associated with active sites inside the resin beads. As a result, the rate of exchange between dissolved organic carbon (DOC) and the exchangeable ion (chloride) increases because the available external surface area for exchange increases.

A major feature of the resin is the high content of a magnetic iron oxide compound which is integrated into the resin structure. Because of this magnetic property, the resin beads can be recovered after they are allowed to separate from the suspending solution by gravitational settling at relatively high overflow rates, in excess of 10 m/h.

The MIEX process involves the application of the resin in slurry form to the raw water. The resin is mixed with the raw water in a mixing basin for contact times of 10–30 min, after which the suspension is treated in a

clarifier to remove the suspended resin. The supernatant water passes on to conventional coagulation and clarification, while the resin is collected and regenerated using 2% sodium hydroxide and 10% sodium chloride. After regeneration, the regenerated resin, along with fresh resin to make up for resin lost in processing, is returned to the plant influent, while the regenerant stream must be disposed of.

It has been well established [7,8–11] that, for most natural waters, the concentration of DOC tends to control the coagulant dosage required for effective turbidity (particle) removal. Hence, application of the MIEX resin prior to coagulation is expected to remove a substantial portion of this DOC (NOM), thereby lowering the coagulant demand of the water for subsequent coagulation of particulate material. In so doing, the application of MIEX is also expected to remove a substantial portion of the DBP formation potential of the water.

3. Procedures

3.1. Raw water

Raw water from nine different water utilities across the United States was collected and shipped to the Drinking Water Research Center laboratories at the University of North Carolina in Chapel Hill (UNC). Each water came from a utility representing a different element of the 3×3 matrix for enhanced coagulation shown in Table 1. The utilities that participated in this research are shown in Table 2.

Two 30-gal (0.114 m^3) plastic drums containing raw water drawn from the intake at each treatment plant, prior to any treatment, were shipped to the UNC laboratories. All waters were refrigerated upon receipt and stored under refrigeration at 4°C until use. The water samples were brought to room temperature prior to experimentation. All experiments were typically completed within two weeks of receiving the water.

The raw waters were characterized with respect to their turbidity, pH, alkalinity, TOC and DOC concentrations, and ultraviolet absorbance at 254 nm (UV254). The specific ultraviolet absorbance (SUVA) of each water was calculated as $\text{UV254}/\text{DOC} \times 100$, in units of L/mg-m. The SUVA of a water is believed to reflect its amenability to DOC removal by coagulation [7,9]. A sample of water was also taken for subsequent chlorination and analysis of its THMFP and HAAFP (see below).

3.2. General experimental approach

The general experimental approach is shown in Fig. 1. Raw water was initially treated with various doses of

Table 1
Stage 1 TOC removal requirements of the D/DBP Rule [4]

TOC concentration (mg/L)	Alkalinity, mg/L as CaCO_3		
	0–60	> 60–120	> 120
<2.0	No action	No action	No action
2.0–4.0	35%	25%	15%
> 4.0–8.0	45%	35%	25%
> 8.0	50%	40%	30%

Table 2
Sources of raw water

TOC concentration (mg/L)	Alkalinity, mg/L as CaCO ₃		
	0–60	> 60–120	> 120
> 2–4	Manchester Water Works (Manchester, NH)	Metropolitan Water District of Southern California (MWD) (La Verne, CA)	Davis Water Treatment Plant (Austin, TX)
> 4–8	Brown Water Treatment Plant (Durham, NC)	Haworth Water Treatment Plant (Hackensack, NJ)	White River Filtration Plant (Indianapolis, IN)
> 8	Manatee Water Treatment Plant (Manatee Co., FL)	Tampa Water Department (Tampa, FL)	Sioux Falls Water Purification Plant (Sioux Falls, SD)

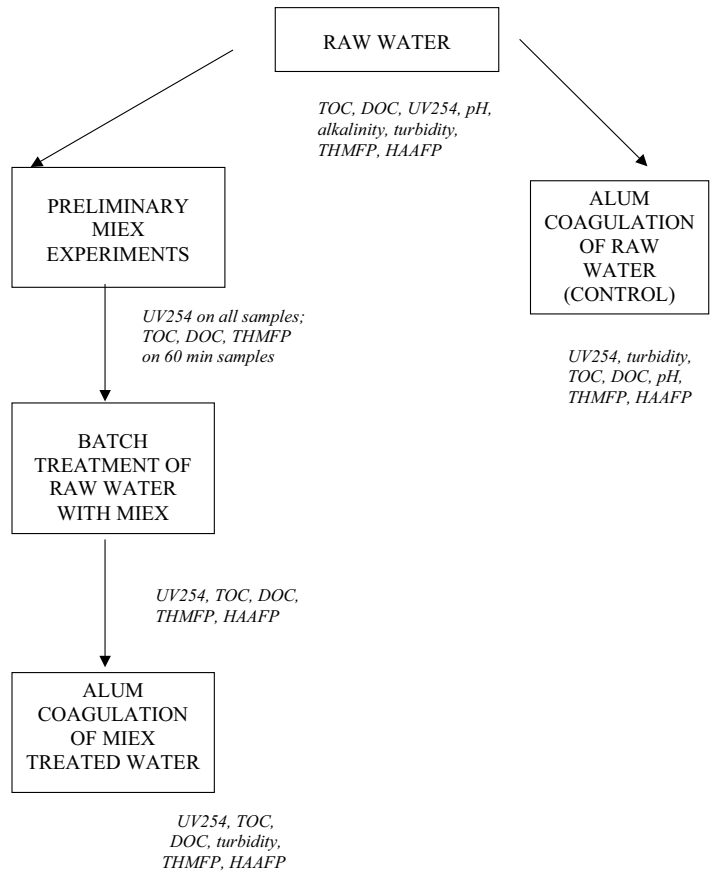


Fig. 1. General experimental approach.

MIEX and mixed for up to 60 min. Samples were collected at various times to determine the degree to which ultraviolet absorbing substances, measured as UV254, were removed as a function of MIEX dose and mixing time. UV254 was used as a surrogate for TOC (i.e. DBP precursors) because it is a much easier and quicker parameter to measure than TOC. From these results, an “optimal” MIEX dose and mixing time were

selected, where UV254 absorbance was observed to decrease very little with increased mixing time or MIEX dose. Twelve liters of raw water were then batch-treated with this optimal MIEX dose. Finally, alum was used to coagulate residual turbidity from the MIEX-treated water. Preliminary coagulation experiments were conducted to determine an “optimal” alum dose for turbidity removal, after which a large volume of the

MIEX-treated water was treated with this optimal alum dose. As a control (see right side of Fig. 1), raw water was coagulated with alum to determine an optimal dose without MIEX-pretreatment. A large volume of the raw water was then treated with this optimal alum dose. Chlorination studies were performed on each of the treated water samples and on the raw water, using uniform formation conditions (UFC; [12], see below). THM formation and HAA formation were then determined following chlorination.

3.3. *Magnetic ion exchange resin*

The MIEX was delivered in slurry form in four 1-L plastic containers. The plastic containers contained approximately 90% resin and 10% carrier water by volume. The four containers were emptied and the contents combined and stored in a 10-L Nalgene plastic container with 4 L of de-ionized organic-free water (DOFW). The container had a spigot at the bottom for convenient withdrawal of the resin slurry from the container.

MIEX doses were prepared by first vigorously shaking the Nalgene bottle and filling 10-mL glass graduated cylinders with the slurry. The slurry was given about 10 min to settle, after which a specific dose was prepared by adding or removing resin from the graduated cylinder with a glass pipette. DOFW was then used to transfer the MIEX to the water to be treated.

3.4. *MIEX treatment*

Preliminary experiments were conducted for each water to determine the optimal MIEX dose and mixing time. UV absorbance was monitored to determine these optimal conditions. The range of MIEX doses tested was selected based on the TOC concentration of the raw water. No pH adjustments were made to the raw water before or after MIEX treatment.

The raw water was placed in 2-L square jars, dosed with the desired amount of the resin, and mixed at 100 rpm on a Phipps and Bird (Richmond, VA) jar test apparatus. A jar containing raw water with no MIEX addition served as a control. While the samples were being mixed, aliquots were taken from the sampling port in the side of each jar at mixing times of 5, 10, 20, 30 and 60 min for UV absorbance measurement. The samples were filtered through pre-rinsed 0.45 μm membrane filters (Supor-450, Gelman Sciences, Ann Arbor, MI) and stored in capped 40-mL glass vials prior to measuring UV254. After 60 min of mixing and 30 min of settling, samples were taken for TOC and DOC measurements. For the DOC measurements, the samples were first filtered through pre-rinsed 0.45 μm filters (Supor-450, Gelman Scientific, Ann Arbor, MI).

After the 60-min mixing and 30-min settling period, approximately 1 L of the remaining water in each of the jars was withdrawn from the sampling port and stored for subsequent chlorination and analysis of THM and HAA formation potential. Samples were taken after 60 min of contact to assure that precursor removal had plateaued. The samples were stored in amber glass bottles in a refrigerator at 4°C. The samples were typically chlorinated within two weeks of treatment.

After conducting the preliminary MIEX experiments, UV254 was plotted as a function of mixing time for all of the different MIEX doses tested. Based on these results, an optimal MIEX dose and mixing time were selected.

Approximately 12 L of raw water were treated with the optimal MIEX dose and mixing time as determined from the preliminary MIEX jar test experiments. The batch treatment was performed in a 20-L glass carboy that was outfitted with a motorized paddle stirrer and a sampling port. The stirrer was designed to transfer a similar amount of energy to the water as was achieved in the jar test apparatus. After mixing, the water was allowed to settle for 30 min. One liter of settled water was set aside for subsequent chlorination and analysis of THMFP and HAAFP. Three to four liters of the settled water were transferred to 500-mL beakers for subsequent coagulation jar testing experiments with alum. Another 2 L of the settled, batch-treated water was set aside for subsequent coagulation at the optimal alum dosage. Samples were also taken for measurement of UV254, TOC, and DOC.

3.5. *Coagulation*

Jar-testing of the MIEX-treated water with alum ($\text{Al}_2(\text{SO}_4)_3 \cdot (14-16)\text{H}_2\text{O}$; Fisher Chemical Co., Fairlawn, NJ) was conducted in 500-mL beakers, each fitted with a sample port on the side. Following the addition of alum, the waters were subjected to rapid mixing for 1 min at 100 rpm, flocculation for 20 min at 35 rpm, and settling for 30 min, after which turbidity and pH were measured. No pH adjustment was made during alum coagulation of the MIEX-treated water.

After the optimal alum dose was determined based on turbidity removal, another 2 L of the MIEX batch-treated water was coagulated in a 2-L square jar at the optimal alum dose using the same coagulation protocol as described above. After settling, 1 L of the MIEX- and alum-treated water was withdrawn from the sampling port for analysis of turbidity, pH, UV254, TOC, and DOC, and for subsequent chlorination and analysis of THMFP and HAAFP.

As a control, the same coagulation procedure was applied directly to samples of raw water. For the control experiments, because higher doses of alum were evaluated, sodium bicarbonate (Fisher Chemical Co.,

Fairlawn, NJ) was added, if necessary, to prevent the pH from falling below 6. After selection of the optimal alum dose based on TOC, DOC, turbidity and UV254 removal, a larger quantity of raw water was coagulated at this alum dose in a 2-L square jar, and analyzed for turbidity, pH, UV254, TOC, and DOC, and for its THMFP and HAAFP following subsequent chlorination. The optimal alum dose was defined as the alum dose beyond which TOC and DOC were no longer appreciably removed with a 5–10 mg/L increase in alum dose, provided that settled water turbidities were less than 2 NTU and UV254 removal was beginning to plateau. If the turbidity was above 2 NTU, a higher alum dose that would meet this criterion was chosen.

3.6. Chlorination

The chlorine demand of the product water of each process train was determined using a modification of the UFC procedure [12]. Chlorination studies were typically performed on the raw water, the alum-coagulated water, and the water treated with the lowest MIEX dose. Preliminary experiments established that the same chlorine dose used for the lowest MIEX treatment was also an appropriate choice for the other MIEX samples, as well as for the MIEX batch-treated water and the MIEX batch-treated water with subsequent alum coagulation. Five chlorine doses were typically examined for each process train. The chlorine doses were based on TOC and UV254 measurements.

The chlorination experiments were conducted in 100-mL, chlorine-demand-free volumetric flasks containing a pH 8.0 borate buffer. After dosing with various amounts of sodium hypochlorite, the samples were stored in the dark, in an incubator set at 20°C. After 24 hour, the chlorine residual was measured with a Hach pocket colorimeter (Hach Chemical Co., Loveland, CO). The chlorine dose that yielded a 1 mg/L residual after 24 hour was the dose chosen for determining the THM and HAA formation potential of the water.

Raw water, alum-coagulated water, MIEX-treated water, and water treated with the optimal MIEX dose and then coagulated with the optimal alum dose were then chlorinated in 300-mL glass BOD bottles using the chlorine dose established from the respective chlorine demand experiments. The samples were buffered at pH 8 with borate buffer, dosed with chlorine, sealed headspace-free, and incubated at 20°C in the dark. After 24 hours, the free chlorine residual was measured with the Hach pocket colorimeter and aliquots were transferred to 40-mL screw-cap vials with TFE-lined silicone septa (Laboratory Supply Distributors Corp., Mt. Laurel, NJ) containing granules of ammonium sulfate (Mallinckrodt, Paris, KY) to quench the chlorine residual. The vials were filled headspace-free, sealed, and stored in the refrigerator at 4°C for up to 2 weeks. Extractions of

these chlorinated samples for THM and HAA analysis typically occurred within 3 days. Duplicate vials were stored for each analysis.

3.7. Analytical methods

3.7.1. Trihalomethanes

THMs were extracted with pentane (THM-Grade, Aldrich Chemical Co., St. Louis, MO) and analyzed by gas chromatography with an electron capture detector using Method 6232B [13]. A 5890A Series II Gas Chromatograph (Hewlett Packard Company, Cary, NC), equipped with an electron capture detector and a DB-1 fused silica capillary column (J&W Scientific, Folsom, CA) was employed for the measurement. Anhydrous sodium sulfate (certified ACS Grade, Mallinckrodt, Paris, KY) that was previously baked for 24 hours at 400°C was added to each sample to enhance extraction efficiency. THM standards were obtained from Supelco, Inc. (Bellefonte, PA); dilutions were prepared using high-purity THM-free methanol (Burdick & Jackson, Krackler Scientific, Muskegon, MI). An internal standard, 1,2-dibromopropane (Sigma Chemical, Bellefonte, PA), was also added. The THM concentrations of the samples were quantified based on their peak areas relative to the peak area of the internal standard compared against the relative peak areas of the calibration standards.

3.7.2. Haloacetic acids

Haloacetic acids were analyzed after derivatization with diazomethane using the micro liquid-liquid extraction gas chromatographic method (Method 6251B [13]). All nine haloacetic acids were analyzed. Magnesium sulfate was used as a drying agent (after [14]). Standards were obtained as a mixture of HAA6 in methanol, and as separate neat compounds of bromodichloroacetic acid, dibromochloroacetic acid, and tribromoacetic acid (Supelco, Inc., Bellefonte, PA). The standards were dissolved in methyl-tert-butyl ether (ultra resi-analyzed grade, J.T. Baker, Phillipsburg, NJ) and a calibration curve was prepared in a similar manner to the THM calibration curve. 1,2,3-Trichloropropane (Aldrich Chemical Co., St. Louis, MO) was used as the internal standard, and 2,3-dibromopropionic acid (Supelco, Inc., Bellefonte, PA) was used as a surrogate to assure the completeness of the derivatization. Unknowns were quantified by comparing their normalized peak areas to those of the calibration standards. A 5890A Series II Gas Chromatograph with an electron capture detector (Hewlett Packard Company, Cary, NC) was employed for the measurement.

3.7.3. Total organic carbon and dissolved organic carbon

TOC and DOC were measured using a Shimadzu 5000 Organic Carbon Analyzer (Shimadzu, Atlanta, GA).

Standards in the range of 1–20 mg/L as C of potassium acid phthalate (Nacalai Tesque, Inc., Kyoto, Japan) were used for calibration of the instrument. DOC measurements were made after filtering the samples through pre-rinsed 0.45 µm membrane filters (Supor-450, Gelman Sciences, Ann Arbor, MI).

3.7.4. Ultraviolet absorbance

UV absorbance measurements were made using 1 cm quartz cells and a Hitachi 2000 UV-Visible Spectrophotometer (Hitachi Instruments, Danbury, CT). Samples were first filtered through pre-rinsed 0.45 µm membrane filters (Supor-450, Gelman Sciences, Ann Arbor, MI). Filtered DOFW was used to calibrate the instrument.

3.7.5. Turbidity

A Hach 2100P turbidimeter (Hach Chemical Co., Loveland, CO) was used to measure turbidity. GEL-EX[®] Turbidity Standards (Hach Chemical Co., Loveland, CO) were used to calibrate the instrument.

3.7.6. Bromide

Bromide ion concentration was determined using a Dionex ion chromatographic (IC) system (Sunnyvale, CA) equipped with a Dionex AS12 IonPac analytical column, guard column, automated sampler, gradient pump, and chemical suppressor, after EPA Method 300.0 [15].

3.7.7. Quality assurance

All measurements were made in duplicate and the average of the two measurements is the reported value. Only duplicates that were within 10% of each other are reported.

4. Results and discussion

Table 3 summarizes the raw water quality characteristics for each water investigated. The TOC concentrations ranged from 2.6 to 26.4 mg/L, the UV absorbances ranged from 0.030 to 1.096 cm⁻¹, SUVA ranged from 1.4 to 4.5 L/mg-m, and the bromide concentrations ranged from 14 to 236 µg/L. pH varied from 6.1 to 8.2.

4.1. Removal of DBP precursors with MIEX

Figs. 2 and 3 show the effects of MIEX dose and mixing time on the removal of UV-absorbing material for Indianapolis and Sioux Falls water, respectively. Sioux Falls had a higher TOC concentration and UV absorbance than Indianapolis, and therefore higher MIEX doses were examined for Sioux Falls water. Both figures show that UV absorbance decreased as MIEX dose and mixing time increased. There was no observable change in pH as a result of MIEX treatment.

UV absorbance dropped to 0.020 cm⁻¹ for Indianapolis and to 0.026 cm⁻¹ for Sioux Falls. That corresponds to approximately 75% removal of UV-absorbing material for Indianapolis and 80% removal for Sioux Falls. UV254 decreases as MIEX dose increases because more surface area (exchange sites) is (are) being provided for a given amount of mixing time and, accordingly, more organic carbon is removed. Figs. 2 and 3 show that the majority of the UV254 removal occurred in the first 20–30 min of mixing. Orica suggests 30 min as a typical detention time for full-scale reactors [16]. According to Orica, 30 min of mixing allows easily removable hydrophobic and hydrophilic NOM to exchange with chloride ion without allowing significant adsorption of NOM on the resin to occur. By allowing ion exchange to dominate over adsorption as the

Table 3
Raw water quality characteristics

Location of participating utility	pH	Alkalinity (mg/L as CaCO ₃)	TOC (mg/L)	DOC (mg/L)	UV254 (1/cm)	SUVA (L/mg-m)	Turbidity (NTU)	Br ⁻ (µg/L)
Durham, NC	6.7	20	5.1	5.0	0.175	3.5	6.7	18.8
Manatee Co., FL	7.2	20	10.6	10.6	0.477	4.5	3.0	163
Indianapolis, IN	8.2	155	4.6	nm	0.088	1.9 ^a	2.7	38.1
Hackensack, NJ	7.7	95	4.3	3.9	0.106	2.7	7.1	42.5
Manchester, NH	6.1	4	2.6	2.1	0.030	1.4	1.9	13.7
Sioux Falls, SD	8.1	205	8.7	5.0	0.135	2.7	55	91.2
MWD, CA	7.8	73	2.8	2.7	0.081	3.0	7.7	215
Austin, TX	7.9	> 120	2.8	2.8	0.056	2.0	4.1	236
Tampa, FL	7.3	91	26.4	27.3	1.096	4.0	3.4	94.5

^aSUVA based on TOC for this sample.
nm = not measured.

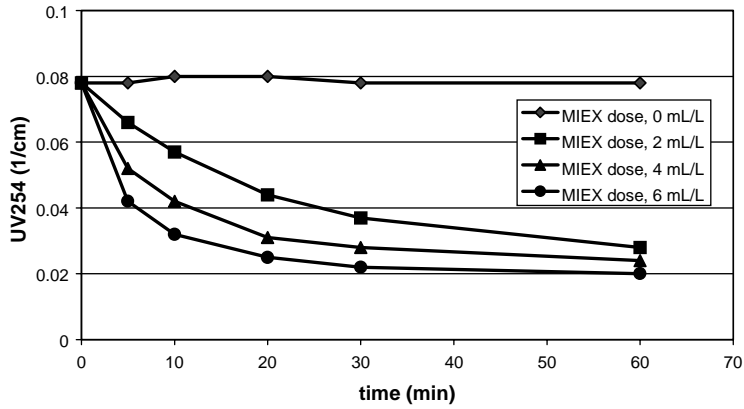


Fig. 2. Ultraviolet absorbance as a function of mixing time for different MIEX doses added to raw water from Indianapolis, IN.

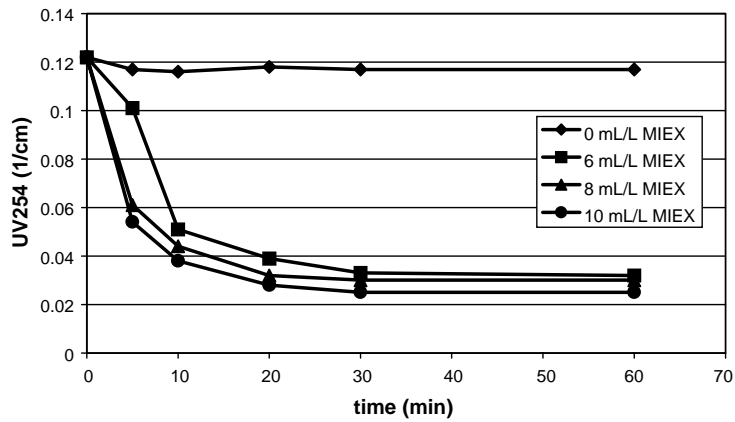


Fig. 3. Ultraviolet absorbance as a function of mixing time for different MIEX doses added to raw water from Sioux Falls, SD.

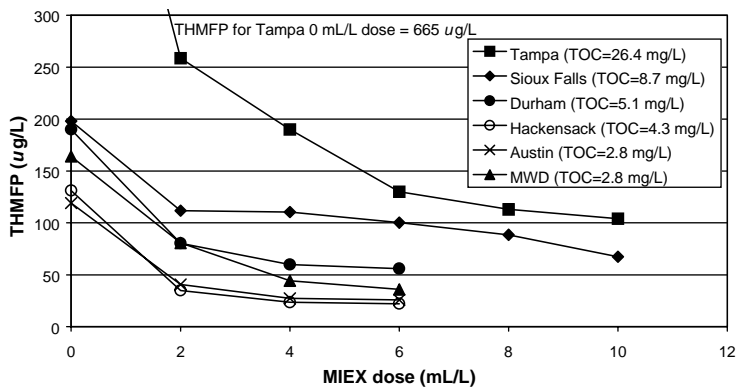


Fig. 4. THMFP as a function of increasing MIEX dose for several raw waters.

mechanism for NOM removal, the resin can be regenerated more easily.

Based on the UV findings, a reduction in THMFP and HAAFP with MIEX was expected. Indeed, Fig. 4

illustrates: (1) the concentration of THMs formed upon subsequent chlorination decreased as MIEX dose increased; and (2) after 60 min of mixing MIEX reduced THM formation potential by 84% for Tampa, 72% for

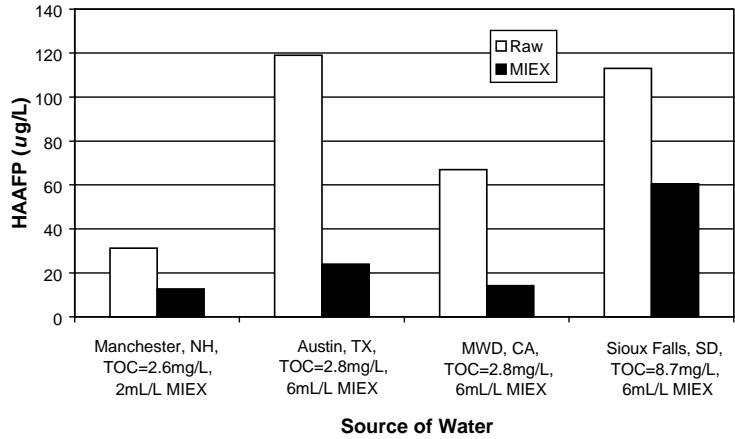


Fig. 5. Comparison of HAAFP in raw water and MIEX-treated water.

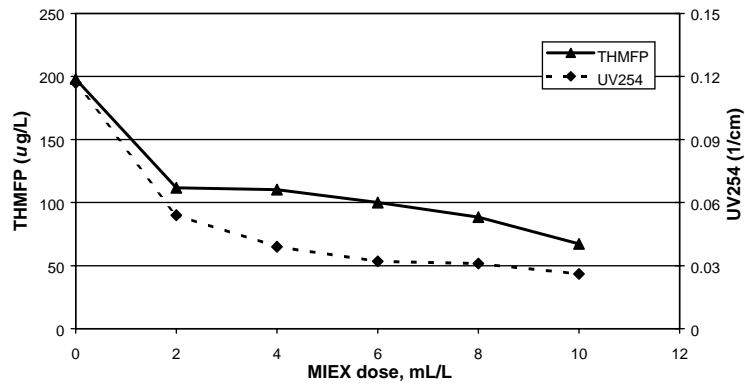


Fig. 6. UV254 and THMFP as a function of MIEX dose for Sioux Falls, SD.

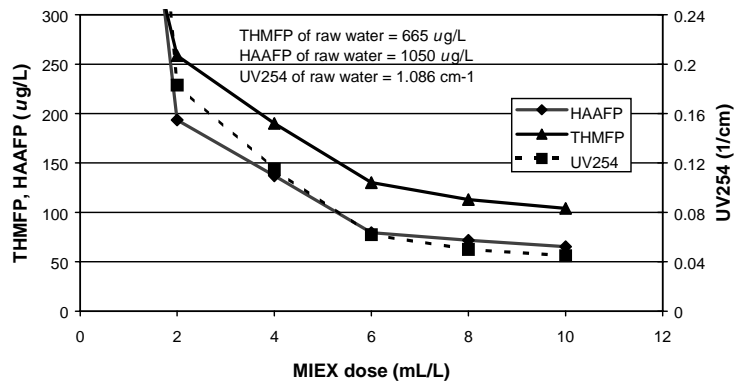


Fig. 7. UV254, THMFP, and HAAFP as a function of MIEX dose for Tampa, FL.

Sioux Falls, 71% for Durham, 78% for Metropolitan Water District, and 78% for Austin, for the highest MIEX doses tested. Fig. 5 shows comparable reductions in HAA formation potential with MIEX treatment, although fewer measurements of HAA formation potential were made.

Figs. 6 and 7 show that the removal of UV-absorbing substances for Sioux Falls and Tampa appears to track the decrease in THM and HAA formation potential. This is consistent with the published literature which indicates that UV254 is a good surrogate for THM formation potential (e.g. [17,18]). Similar trends were

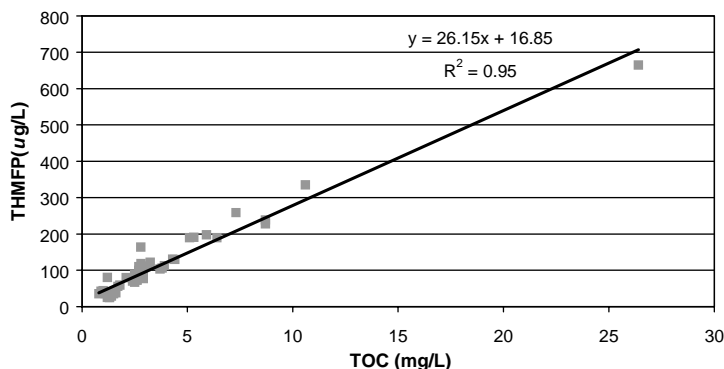


Fig. 8. THMFP as a function of TOC concentration for raw and MIEX-treated waters.

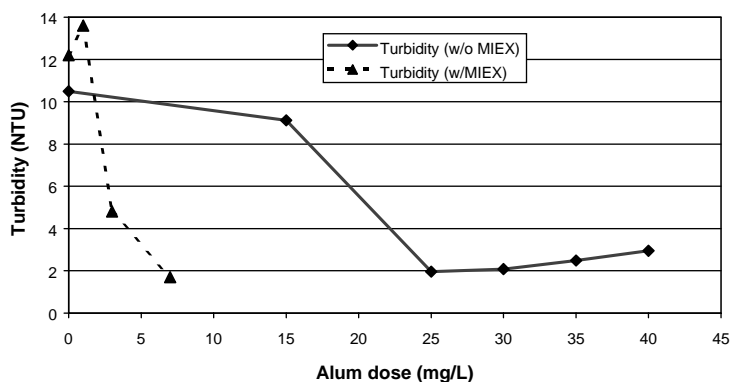


Fig. 9. Turbidity as a function of alum dose for Durham, NC with and without MIEX-pretreatment.

observed for THM and HAA formation potential in the other waters, although not all graphs showed as strong a trend as Figs. 6 and 7, and HAA results were more limited.

Fig. 8 illustrates the linear relationship between THM formation potential and TOC concentration for the nine waters examined. The R^2 value for Fig. 8 is 0.95, indicating that TOC is a useful surrogate for THM formation potential for these waters, regardless of the hydrophobic/hydrophilic carbon distribution in the different waters. This is consistent with the findings of other researchers (e.g. [5,6,17,19]). Some investigators have shown that hydrophobic carbon is more readily removed by certain treatment processes, e.g. by coagulation (e.g. [3,7,20]). This does not appear to be the case for MIEX treatment. The regression equation in Fig. 8 predicts a $26 \mu\text{g/L}$ decrease in TTHM formation for every 1 mg/L decrease in TOC concentration for the uniform chlorination conditions used here.

4.2. Impact of MIEX on coagulation of turbidity

MIEX treatment of raw water significantly reduced the amount of alum required for turbidity removal in all

nine waters. MIEX eliminates a significant portion of the coagulant demand in several ways, the most important of which is a significant reduction in TOC concentration. Fig. 9 compares the alum dosage required to remove turbidity from raw water and from MIEX-treated water for Durham, NC. Without MIEX treatment, 25 mg/L of alum was required to coagulate this low alkalinity, moderate TOC water (initial $\text{TOC} = 5.1 \text{ mg/L}$) to achieve a settled water turbidity of less than 2 NTU . The pH of the water before and after coagulation with 25 mg/L of alum was 6.77 and 5.78, respectively. When the raw water was pre-treated with 6 mL/L of MIEX for 20 min, the amount of alum required to lower the turbidity to less than 2 NTU was only 7 mg/L . The pH of the water before and after enhanced coagulation with MIEX and alum was 6.60 and 6.25, respectively. Suspended resin fines following MIEX treatment were observed to contribute to the residual turbidity prior to alum treatment.

Fig. 10 illustrates the impact of MIEX treatment on the coagulant demand for Manatee County, FL, a low alkalinity, high TOC water (initial $\text{TOC} = 10.6 \text{ mg/L}$). The requisite alum dosage was reduced from 60 mg/L without MIEX treatment to 10 mg/L with 8 mL/L of

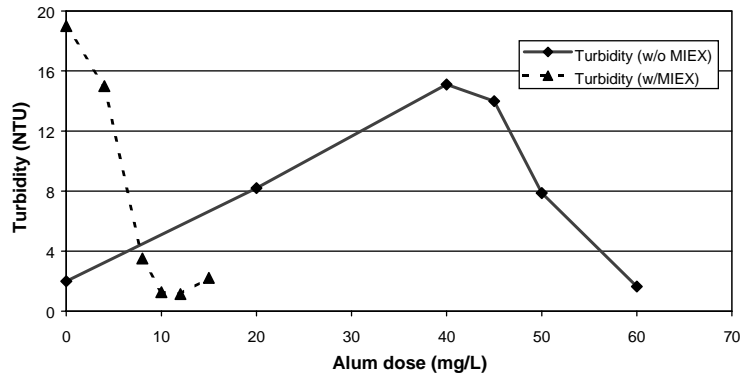


Fig. 10. Turbidity as a function of alum dosage for Manatee Co., FL with and without MIEX-pretreatment.

MIEX pre-treatment. The pH of the water before and after coagulation with 60 mg/L of alum was 7.33 and 6.08, respectively. The pH of the water before and after enhanced coagulation with MIEX and alum was 7.14 and 6.92, respectively. Without MIEX pre-treatment, turbidity increased initially upon alum addition as DOC in the raw water was converted to a non-settling particulate form at alum dosages below 40 mg/L. This phenomenon was not seen for the MIEX-treated water.

White et al. [7] found a linear correlation between the critical alum dose required to initiate turbidity and TOC removal and the raw water TOC concentration. Indeed, as TOC concentration for all of the waters examined decreased following MIEX treatment, so did the amount of alum required to coagulate turbidity. MIEX treatment alone tended to increase the turbidity of the waters because of the residual fine resin particles suspended in the water, but subsequent coagulation with alum lowered turbidity to levels comparable to turbidity levels in the raw waters treated with alum.

4.3. Removal of bromide by MIEX

Table 4 shows that, for some of the waters that were analyzed for bromide before and after MIEX treatment, the MIEX resin was capable of removing bromide from the raw water. Bromide removal with MIEX was an unexpected benefit due to the relatively low bromide ion concentration compared to the concentration of other dissolved anionic species, although removal decreased as the alkalinity of the raw water increased. Because of the high concentration of bicarbonate ions in the high alkalinity waters and the relatively low bromide concentrations, bromide is unable to compete effectively for the exchange sites on the strong base anion exchange resin. Nevertheless, some, and in the case of Manatee County appreciable, bromide removal was observed.

The removal of bromide by MIEX is significant as brominated DBPs are believed to be more harmful to

Table 4
Removal of bromide by MIEX

Utility	Treatment	Br ⁻ (µg/L)	Alkalinity (mg/L as CaCO ₃)
Indianapolis, IN	Raw water	38.1	155
	MIEX-treated	40.8	
Tampa, FL	Raw water	94.5	91
	MIEX-treated	54.1	
Manatee County, FL	Raw water	163	20
	MIEX-treated	<10	
Manchester, NH	Raw water	13.7	4
	MIEX-treated	<10	

public health than their chlorinated counterparts. Bromide has been shown to shift the speciation of THMs and HAAs toward the more harmful brominated forms (e.g. [6,21,22]), and to increase the absolute concentration of total THMs and HAAs. When raw water is coagulated with alum, the concentration of TOC decreases, but the bromide concentration tends to remain constant. Hence, the ratio of bromide ion concentration to TOC concentration increases, and therefore a greater fraction of brominated THMs and HAAs are produced upon subsequent chlorination [23,24]. This same phenomenon has been demonstrated following GAC and membrane treatment for TOC (NOM) removal. The apparent removal of bromide by MIEX negates this phenomenon.

4.4. Summary

Table 5 summarizes the findings for all nine waters in this study. TOC, UV254, THM formation potential, and

Table 5
Summary of results

Utility	Treatment	TOC (mg/L)	UV254 (1/cm)	THMFP ($\mu\text{g/L}$)	HAAFP ($\mu\text{g/L}$)	SUVA (L/mg-m)
Durham, NC	Raw water	5.1	0.175	190	40	3.4
	30 mg/L Alum	3.1	0.042	84	34	1.4
	6 mL/L MIEX + 7 mg/L Alum	1.2	0.014	36	nr	1.2
Manatee Co., FL	Raw water	10.6	0.477	335	264	4.5
	60 mg/L Alum	5.3	0.106	222	125	2.0
	8 mL/L MIEX + 10 mg/L Alum	1.4	0.029	nr	nr	2.1
Indianapolis, IN	Raw water	4.6	0.088	nr	59	1.9
	30 mg/L Alum	3.4	0.068	95	39	2.0
	6 mL/L MIEX + 12 mg/L Alum	nr	0.058	52	nr	nr
Hackensack, NJ	Raw water	4.3	0.106	131	81	2.5
	40 mg/L Alum	nr	0.058	85	54	nr
	4 mL/L MIEX + 12 mg/L Alum	nr	0.020	24	nr	nr
Manchester, NH	Raw water	2.6	0.030	73	31	1.2
	10 mg/L Alum	2.0	0.029	58	25	1.5
	2 mL/L MIEX + 10 mg/L Alum	1.4	0.016	29	13	1.1
Sioux Falls, SD	Raw water	8.7	0.135	239	113	1.6
	45 mg/L Alum	4.9	0.100	167	73	2.0
	6 mL/L MIEX + 20 mg/L Alum	2.4	0.032	81	46	1.3
MWD, CA	Raw water	2.8	0.081	164	67	2.9
	30 mg/L Alum	2.0	0.048	109	51	2.4
	6 mL/L MIEX + 10 mg/L Alum	1.1	0.016	35	14	1.5
Austin, TX	Raw water	2.8	0.056	119	119	2.0
	20 mg/L Alum	2.6	0.041	101	33	1.6
	6 mL/L MIEX + 10 mg/L Alum	1.3	0.012	25	24	0.9
Tampa, FL	Raw water	26.4	1.096	665	833	4.2
	150 mg/L Alum	9.3	0.219	196	180	2.4
	8 mL/L MIEX + 45 mg/L Alum	2.9	0.047	80	nm	1.6

nr = not reported because it did not meet our quality assurance criteria.

nm = not measured.

HAA formation potential all decreased as a result of enhanced coagulation with alum, and decreased to an even greater degree as a result of treatment with MIEX and alum, despite the fact that lower alum doses were used. Table 6 shows the percent removals for TOC, UV254, and THMFP achieved by alum treatment alone and by the combined MIEX and alum-treatment with respect to the raw water values. Specific UV absorbance (SUVA) values for each raw water are also shown. Table 6 demonstrates that the percentage of TOC, UV absorbance, and THMFP removed by MIEX and alum-treatment tended to increase with increasing SUVA values. Furthermore, whereas alum coagulation has been shown to preferentially remove UV-absorbing material and THM precursors compared to TOC (e.g.

[5,17,19]), MIEX tended to show little preference for removal of UV-absorbing material or THM precursors relative to removal of TOC. Instead, the percent removals of TOC, UV254, and THMFP tended to be similar for each water treated with MIEX and subsequently with alum. The fact that the TOC removals are as high as they are (46–87%) suggests that the resin removes both hydrophobic and hydrophilic material; hydrophobic material is typically 40–60% of the TOC content of most natural waters [25]. While the resin appears to remove both hydrophobic and hydrophilic acids, it cannot be stated unequivocally that there is no preferential removal of hydrophobic acids over hydrophilic acids. The fact that the resin gave greater TOC removals for the high SUVA waters

Table 6
Summary of percent removals achieved by alum and MIEX plus alum treatment

Utility	Raw water SUVA (L/mg-m)	Treatment	Reduction in TOC	Reduction in UV254	Reduction in THMFP
Manatee Co., FL	4.5	Alum	50%	78%	34%
		MIEX + Alum	87%	94%	89%
Tampa, FL	4.0	Alum	65%	80%	73%
		MIEX + Alum	86%	96%	88%
Durham, NC	3.5	Alum	39%	76%	56%
		MIEX + Alum	76%	92%	81%
MWD, CA	3.0	Alum	29%	41%	34%
		MIEX + Alum	71%	89%	79%
Hackensack, NJ	2.7	Alum	nr	45%	35%
		MIEX + Alum	nr	81%	82%
Sioux Falls, SD	2.7	Alum	44%	26%	30%
		MIEX + Alum	72%	76%	66%
Austin, TX	2.0	Alum	7%	27%	15%
		MIEX + Alum	54%	79%	79%
Indianapolis, IN	1.9	Alum	26%	23%	nr
		MIEX + Alum	nr	75%	nr
Manchester, NH	1.4	Alum	23%	3%	21%
		MIEX + Alum	46%	53%	60%

nr = not reported because it did not meet our quality assurance criteria.

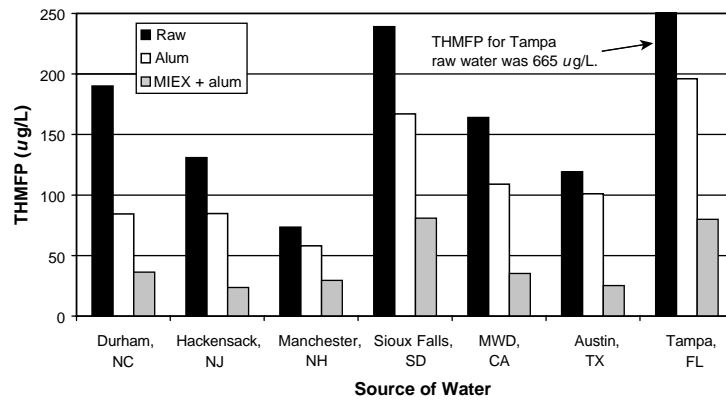


Fig. 11. THMFP for raw, alum-, and MIEX + alum-treated waters for different source waters.

suggests that this is the case, but the organic carbon in the waters was not fractionated before and after MIEX treatment.

The THMFP of raw, alum-, and MIEX and alum-treated waters for seven of the nine waters studied are compared in Fig. 11. (Manchester and Austin showed only a small difference between their raw and alum-coagulated THM formation potentials; both were low TOC waters with relatively low SUVAs.) Much less THM formation was observed for the waters treated with MIEX and alum as compared to the raw waters or to the waters treated by alum alone. The majority of the reduction in THMFP in the waters treated with MIEX and alum was attributable to the MIEX treatment; little

additional removal was achieved by the relatively low doses of alum. These findings complement the work of other researchers who have demonstrated that ion exchange is an effective tool for removing DBP precursors (e.g. [26,27]).

A similar trend was observed for HAA formation, as illustrated in Fig. 12. In this figure, it should be noted that the MIEX-treated sample refers to MIEX treatment alone, and not to MIEX and alum treatment combined. Alum coagulation by itself reduced HAA formation, as expected, but the removals of HAA formation potential by MIEX were much greater, i.e. 59% for Manchester, 59% for Sioux Falls, 79% for MWD, and 80% for Austin.

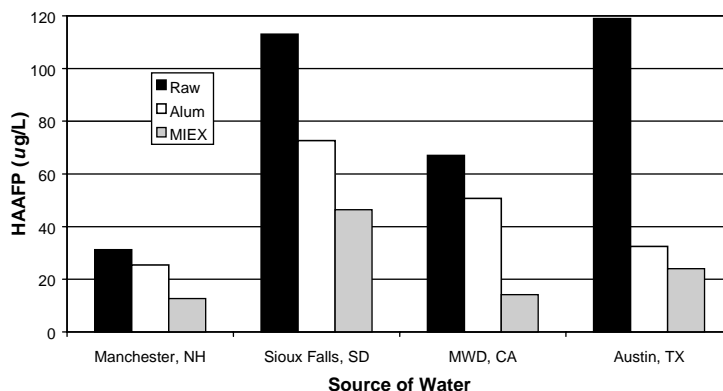


Fig. 12. HAAFP in raw, alum- and MIEX-treated waters for different source waters.

5. Conclusions

Enhanced coagulation with MIEX was found to be very effective for removing THM precursors from the waters examined, and for markedly reducing the coagulant demand of the waters and the corresponding alum dosages required for coagulation of turbidity. THM formation was reduced by 60–90%, even for waters with low TOC concentrations, low specific UV absorbance values, and high alkalinities—waters where coagulation of TOC is usually not very effective.

Residual TOC concentration, UV absorbance, and THM formation potential were all substantially lowered as a result of MIEX pre-treatment and alum coagulation as compared to alum coagulation alone. HAA formation potential was also substantially lowered as a result of MIEX pre-treatment. MIEX was also shown to be capable of removing bromide, particularly in waters with low alkalinity (low bicarbonate concentrations), thereby decreasing the potential formation of the more harmful bromine-containing DBPs.

The findings of this research suggest that MIEX technology represents another tool for potential use by water utilities to enhance the removal of NOM (DBP precursors) in drinking water beyond that achievable by coagulation alone. The resin appears to be effective for the removal of both hydrophobic and hydrophilic carbon.

Acknowledgements

The authors would like to thank Howard Weinberg, Christie Arlotta, Nichole Snider, and Carrie Delcomyn of the University of North Carolina at Chapel Hill for their laboratory assistance in conducting these experiments. The support of the participating water utilities is appreciated. This work was supported jointly by ORICA Australia Pty Ltd. of Victoria, Australia and

the US Environmental Protection Agency (USEPA) under cooperative agreement CR826342. Richard Miltner of the USEPA was the project officer.

References

- [1] Christman RF, Norwood DS, Millington DS, Johnson JD, Stevens AA. Identity and yields of major halogenated products of aquatic fulvic acid chlorination. *Environ Sci Technol* 1983;17(10):625.
- [2] Krasner SK, McGuire MJ, Jacangelo JJ, et al. The occurrence of disinfection by-products in US drinking water. *J Am Water Works Assoc* 1989;81(8):41.
- [3] Reckhow DA, Singer PC. The removal of organic halide precursors by preozonation and alum coagulation. *J Am Water Works Assoc* 1984;76(4):151.
- [4] US Environmental Protection Agency. National primary drinking water regulations: disinfectants and disinfection by-products. *Fed Regist* 1998;63(241):69389.
- [5] Babcock DB, Singer PC. Chlorination and coagulation of humic and fulvic acids. *J Am Water Works Assoc* 1979;71(3):149.
- [6] Stevens AA, Slocum CJ, Seeger DR, Robeck GG. Chlorination of organics in drinking water. *J Am Water Works Assoc* 1976;68(11):615.
- [7] White MC, Thompson JD, Harrington GW, Singer PC. Evaluating criteria for enhanced coagulation compliance. *J Am Water Works Assoc* 1997;89(5):64.
- [8] Edzwald JK, McIntyre J, Sanks RL, Semmens MJ, Taylor JS. Organics removal by coagulation: a review and research needs. *J Am Water Works Assoc* 1979;71(10):588.
- [9] Edzwald JK. Coagulation in drinking water treatment: particles, organics, and coagulants. *Water Sci Technol* 1993;27(11):21.
- [10] Randtke SJ, Jepsen CP. Chemical pretreatment for activated-carbon adsorption. *J Am Water Works Assoc* 1981;73(8):411.
- [11] Van Benschoten JE, Edzwald JK. Chemical aspects of coagulation using aluminum salts—I. Hydrolytic reactions of alum and polyaluminum chloride. *Water Res* 1990; 24(12):1519.

- [12] Summers RS, et al. Assessing DBP yield: uniform formation conditions. *J Am Water Works Assoc* 1996; 88(6):80.
- [13] American Public Health Association, American Water Works Association, Water Environment Federation. Standard methods for the examination of water and wastewater, 20th ed. Washington, DC: American Public Health Association, 1998.
- [14] Brophy KS, Weinberg HS, Singer PC. Quantification of nine halogenated acetic acids using gas chromatography with electron capture detection. In: Barrett SE, Krasner SW, Amy GL, editors. Natural organic matter and disinfection by-products: characterization and control in drinking water, ACS Symposium Series 761, American Chemical Society, Washington, DC, 2000. p. 343–55.
- [15] US Environmental Protection Agency. Methods for the determination of inorganic substances in environmental samples. US EPA, Cincinnati, OH, 1993.
- [16] Slunjski M, Bourke M, O'Leary B. MIEX[®] DOC PROCESS for removal of humics in water treatment. Presented at International Humic Substances Society Australian Chapter meeting, 2000.
- [17] Edzwald JK, Becker WC, Wattier KL. Surrogate parameters for monitoring organic matter and THM precursors. *J Am Water Works Assoc* 1985;7(4):122.
- [18] Singer PC, Barry III JJ, Palen GM, Scrivner AE. Trihalomethane formation in north Carolina drinking waters. *J Am Water Works Assoc* 1981;73(8):392.
- [19] Kavanaugh MC. Modified coagulation for improved removal of trihalomethane precursors. *J Am Water Works Assoc* 1978;70(11):613.
- [20] Croue JP, Debroux JF, Amy GL, Aiken GR, Leenheer JA. Natural organic matter: structural characteristics and reactive properties. In: Singer PC, editor. Formation and control of disinfection by-products in drinking water. Denver, CO: American Water Works Association, 1999. p. 65–93.
- [21] Cowman GA, Singer PC. Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of aquatic humic substances. *Environ Sci Technol* 1995;30(1):16.
- [22] Pourmoghaddas H, Stevens AA, Kinman RN, Dressman RC, Moore LA, Ireland JC. Effect of bromide ion on formation of HAAs during chlorination. *J Am Water Works Assoc* 1993;85(1):82.
- [23] Black BD, Harrington GW, Singer PC. Impact of organic carbon removal on cancer risks posed by drinking water chlorination. *J Am Water Works Assoc* 1996;88(12):40.
- [24] Krasner SK, Scilimenti MJ, Chinn R, Chowdhury ZK, Owen DM. The impact of TOC and bromide on chlorination by-product formation. In: Minear RA, Amy GL, editors. Disinfection by-products in water treatment: the chemistry of their formation and control. Boca Raton, FL: CRC Press, 1996. p. 59–90.
- [25] Harrington GW, Bruchet A, Rybacki D, Singer PC. Characterization of natural organic matter and its reactivity with chlorine. In: Minear, RA, Amy GL, editors. Water disinfection and natural organic matter. Adv. Chem Ser #649. Washington, DC: Amer Chem Soc., 1996. p. 138–58.
- [26] Kim PH-S, Symons JM. Using anion exchange resins to remove THM precursors. *J Am Water Works Assoc* 1991;83(12):61.
- [27] Rook JJ, Evans S. Removal of trihalomethane precursors from surface waters using weak base RESINS. *J Am Water Works Assoc* 1979;71:520.