

ENHANCED COAGULATION USING A MAGNETIC ION EXCHANGE RESIN

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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, 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 to determine its impact on subsequent coagulation of raw drinking water with alum and on subsequent DBP formation following chlorination.

Background

The MIEX[®] process is based on a new patented ion exchange resin developed by ORICA. The resin combines a number of anion exchange resin features intended to result in efficient removal of natural organic material. It has a polyacrylic, macroporous structure with a medium pore size and porosity. It also contains a high concentration of strong base, quaternary ammonia functional groups.¹

The MIEX[®] resin particle size is 2-5 times smaller than conventional resins, which are restricted to larger sizes because they tend to be used in fixed bed configurations where head losses need to be minimized. Smaller resins show higher rates of exchange because they have larger external specific surface areas. Accordingly, they have more active sites on the surface of the resin beads. As a result, the reliance on slow, intraparticle diffusion associated with active sites inside resin beads is correspondingly reduced.

A major feature of the resin that allows it to be used in a batch treatment mode is the high content of a magnetic 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.

It has been well established^{2,3,4} that, for most natural waters, the concentration of natural organic material (dissolved organic carbon [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 natural organic material (DOC), 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.

Procedures

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. Each water came from a utility representing a different element of the 3 x 3 matrix for enhanced coagulation as prescribed in the U.S. Environmental Protection Agency's Disinfectants/Disinfection By-Products (D/DBP) Rule.⁵ The utilities participating in this research are shown in Table 1.

Table 1. Enhanced Coagulation Matrix

Total Organic Carbon (TOC) Concentration mg/L	Alkalinity, mg/L as CaCO ₃		
	0-60	60-120	>120
2-4	Manchester, NH	Metropolitan Water District, CA	Austin, TX
4-8	Durham, NC	Hackensack, NJ	Indianapolis, IN
>8	Manatee Co., FL	TBS**	Sioux Falls, SD

** To be selected.

Upon receipt, the raw waters were characterized with respect to their turbidity, pH, alkalinity, TOC and DOC concentrations, and ultraviolet absorbance at 254 nm (UV254). A sample of water was also taken for subsequent chlorination and analysis of its trihalomethane (THM) formation potential (see below). All waters were refrigerated upon receipt and stored under refrigeration until use. All experiments were usually completed within two weeks of sample receipt.

Magnetic Ion Exchange Resin

The magnetic ion exchange (MIEX) resin 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 stored in a 10-L Nalgene plastic container with 4 L of deionized 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 ten minutes to settle. After this, a specific dose was administered by adding or removing resin from the

graduated cylinder with a glass pipette. For example, to dose 2 L of water with 6 mL/L of MIEX, two 10-mL graduated cylinders were filled with slurry and their settled volumes adjusted to be 6 mL of resin by volume. DOFW was then used to transfer each of the 6-mL volumes of MIEX to the 2-L container.

Preliminary MIEX Experiments

Preliminary experiments were conducted for each water to determine the optimal MIEX dose and mixing time. The range of MIEX doses tested was selected based on the TOC concentration of the raw water. For raw waters with TOC concentrations less than 4 mg/L, doses of 2, 4, and 6 mL/L of MIEX were used. For raw waters with TOC concentrations greater than 4 mg/L, MIEX doses of 6, 8, and 10 mL/L were used. The raw water was placed in 2-Liter square jars, dosed with the desired amount of the resin, and mixed at 100 rpm on a Phipps and Bird 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 a sampling port in the side of each jar at mixing times of 5, 10, 20, 30 and 60 min. The samples were filtered through pre-rinsed 0.45 µm membrane filters (Supor-450, Gelman Sciences) and stored in capped 40-mL glass vials. UV254 was measured for each of the samples. After 60 min of mixing, samples were also taken for TOC and DOC measurement. For the DOC measurements, the samples were first filtered through pre-rinsed 0.45 µm filter paper.

After the 60-min mixing period, the remaining water in the 2-L jars was allowed to settle for 30 min after which approximately 1 L of water from the sampling port of each jar was taken and stored for subsequent chlorination and analysis of THM formation potential.

Batch Treatment of Raw Water with MIEX

Approximately 12 L of raw water was 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 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. About 1 L of settled water was set aside for subsequent chlorination. Three to four liters of the settled water was transferred to a set of 500-mL beakers for subsequent small-scale 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 of the batch-treated water were also taken for measurement of UV254, TOC, and DOC, and for subsequent chlorination and analysis of THM formation potential.

Alum Coagulation of MIEX Pre-Treated Water

Jar testing of the pre-treated waters with alum was conducted in 500-mL beakers. Following the addition of alum, the waters were subjected to rapid mixing for 1 minute at 100 rpm, flocculation for 20 minutes at 35 rpm, and settling for 30 minutes, after which turbidity was measured.

After the optimal alum dose was determined based on turbidity removal, another 2 L of the MIEX batch-treated water was coagulated in 2-L square jars at the optimal alum dose using the same coagulation protocol as described above. After settling, one liter of the MIEX- and alum-treated settled water was withdrawn from the sampling port for analysis of UV254, TOC, and DOC, and for subsequent chlorination and analysis of THM formation potential.

As a control, the same coagulation procedure was applied directly to samples of raw water. Different doses of alum were added to a series of 500-mL beakers and the treated waters were rapid mixed for 1 min at 100 rpm, flocculated for 20 minutes at 35 rpm, and settled for 30 minutes. After selection of the optimal alum dosed based on turbidity removal, a larger quantity of raw water was coagulated at this alum dose in a 2-L square jar and analyzed for UV254, TOC, and DOC, and for its THM formation potential following subsequent chlorination.

Pre-Chlorination Studies

The chlorine demand of the product waters of each process train was determined prior to chlorination for measurement of its THM formation potential. The method used was based on the uniform formation conditions (UFC) procedure.⁶ Pre-chlorination studies were typically performed on the raw water, the alum coagulated water, and the water treated with the lowest MIEX dose that was mixed for 60 min and settled for 30 min. Preliminary experiments established that the same chlorine dose used for the lowest MIEX dose was also an appropriate choice for the other 60-min MIEX samples, as well as for the batch-treated water and the batch-treated water with subsequent alum coagulation. Five chlorine doses were typically selected for each process train. The chlorine doses were based on TOC and on UV254 measurements, and on the experience of the investigators.

The pre-chlorination experiments were conducted in 100-mL, chlorine-demand-free volumetric flasks. The flasks were filled with about 80 mL of the water to be tested, and a pH 8 phosphate buffer was added. An appropriate volume of chlorine was added from a freshly prepared and standardized 100 mg/L sodium hypochlorite stock solution, after which the flask was filled to the mark with the test water and capped. The chlorinated samples were stored for 24 hours in the dark, in an incubator set at 20°C. After 24 hours, the chlorine residual was measured with a HACH pocket colorimeter. The chlorine dose that yielded a 1 mg/L residual after 24 hours was the dose chosen for determining the THM formation potential of the water.

Chlorination to Determine THM Formation Potential

Raw water, alum-coagulated water, raw water treated with different MIEX doses and mixed for 60 min, raw water that was batch-treated with the optimal MIEX dose, and water treated with the optimal MIEX dose and then coagulated with the optimal alum dose were chlorinated in 300-mL glass bottles using the chlorine dose established from the chlorine demand experiments. The samples were buffered at pH 8 with a phosphate buffer prior to the addition of chlorine, sealed headspace-free, and incubated at 20°C in

the dark for 24 hours. After 24 hours, the chlorine residual was measured and the samples were quenched with ammonium sulfate.

Analytical Methods

Trihalomethane analysis

Trihalomethanes were extracted with pentane and analyzed by gas chromatography with an electron capture detector using Method 6232B.⁷ A Hewlett Packard 5890 Gas Chromatograph was employed for the measurement.

Total organic carbon and dissolved organic carbon analysis

TOC and DOC were measured using a Shimadzu 5000 Total Organic Carbon Analyzer. Standards in the range of 1-10 mg/L as C of potassium hydrogen phthalate 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).

Ultraviolet absorbance

UV absorbance measurements were made using 1 cm quartz cells and a Hitachi 2000 UV-Visible Spectrophotometer. Samples were first filtered through pre-rinsed 0.45 μm membrane filters.

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 percent of each other are reported.

Results and Discussion

Figures 1 and 2 show the impact of MIEX dose and mixing time on the removal of UV-absorbing natural organic material (assumed to be proportional to DBP precursors) for Indianapolis and Sioux Falls water, respectively. Indianapolis water had a lower initial TOC concentration (4.6 mg/L) and a lower initial UV absorbance (0.088 cm^{-1}) than Sioux Falls water (initial TOC = 8.7 mg/L, initial UV absorbance of 0.135 cm^{-1}), and therefore a lower range of MIEX doses were tested for this water. Both figures show that UV₂₅₄ decreased with increasing MIEX dose and mixing time, with most of the removal occurring within the first 20-30 min of mixing. For Indianapolis water, UV₂₅₄ values approached $0.02\text{-}0.03 \text{ cm}^{-1}$ after 60 min of mixing; for Sioux Falls water, UV absorbance approached $0.025\text{-}0.03 \text{ cm}^{-1}$ after 60 min. This corresponds to approximately 65-75% removal of UV-absorbing substances for Indianapolis and 75-80% removal for Sioux Falls. Similar removals were observed for the other waters examined, with MIEX doses increasing as the raw water TOC and UV absorbance increased. No changes in the pH of the water were observed as a result of the MIEX treatment.

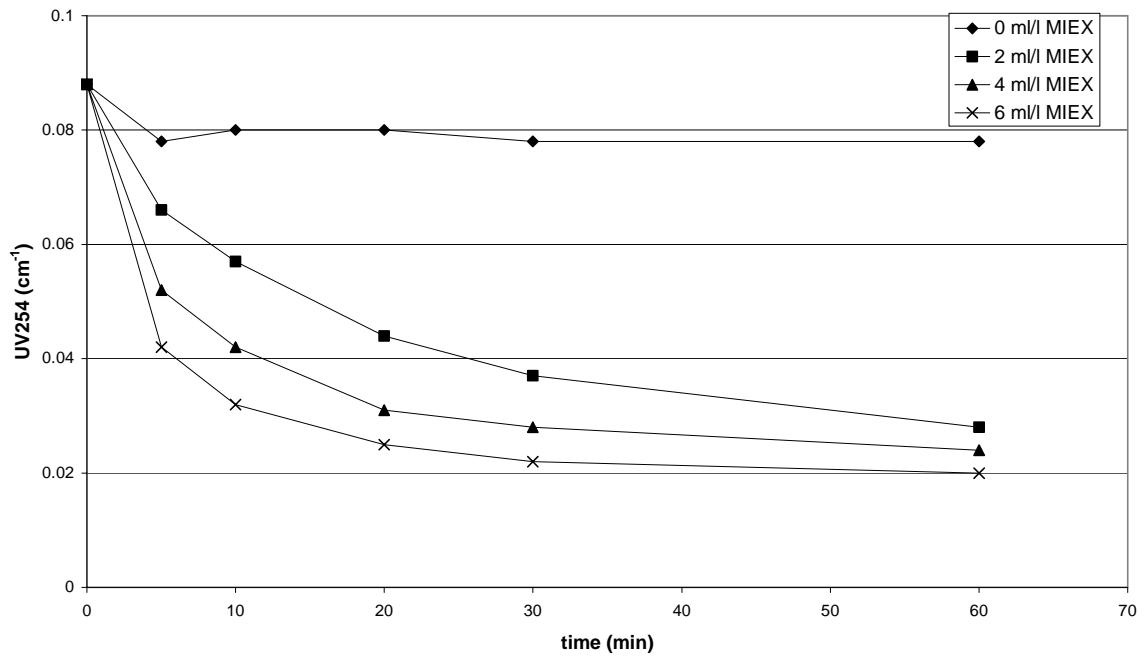


Figure 1. Ultraviolet absorbance as a function of mixing time for different MIEX doses added to raw water from Indianapolis, Indiana.

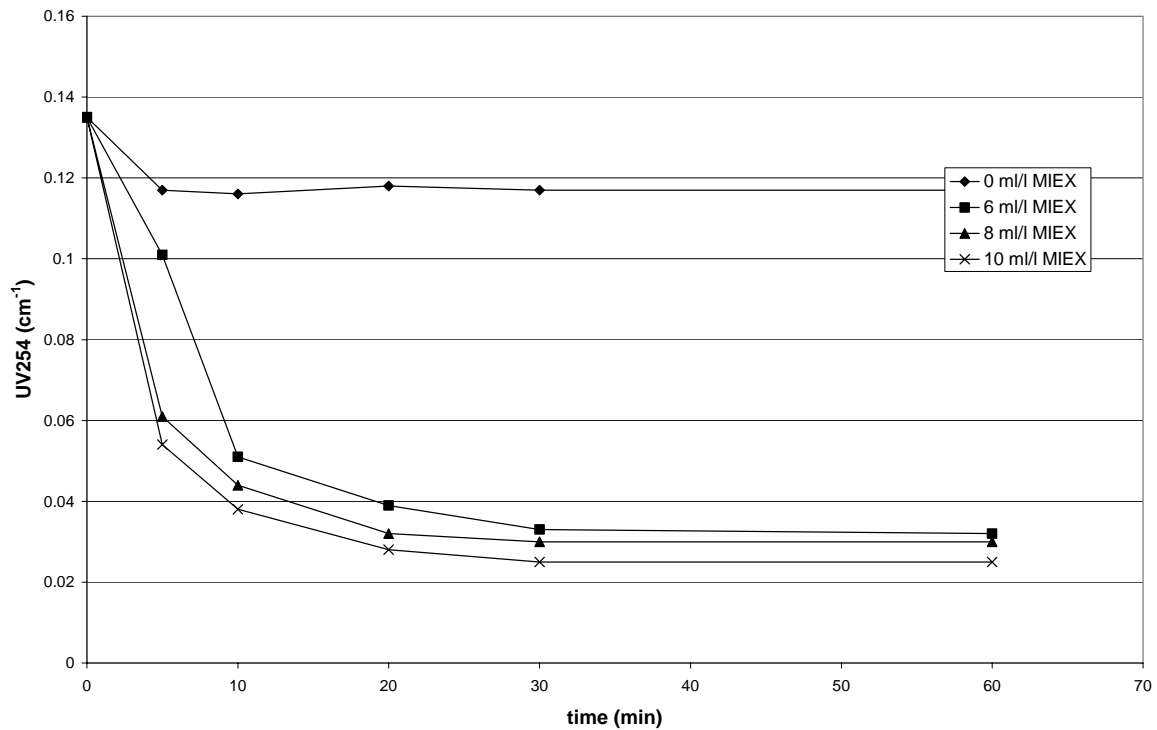


Figure 2. Ultraviolet absorbance as a function of mixing time for different MIEX doses added to raw water from Sioux Falls, South Dakota.

The impact of MIEX dose on the removal of UV absorbing substances and THM formation potential under uniform formation conditions is illustrated in Figure 3 for Sioux Falls. These samples were all taken after 60 min of mixing and laboratory filtration (0.45 μm) to remove the residual suspended MIEX resin. (Sioux Falls water is used here for illustration because it was the only water in which six doses [including zero] were examined.) As in the case of UV absorbance, the THM formation potential of the water decreased with increasing MIEX dose.

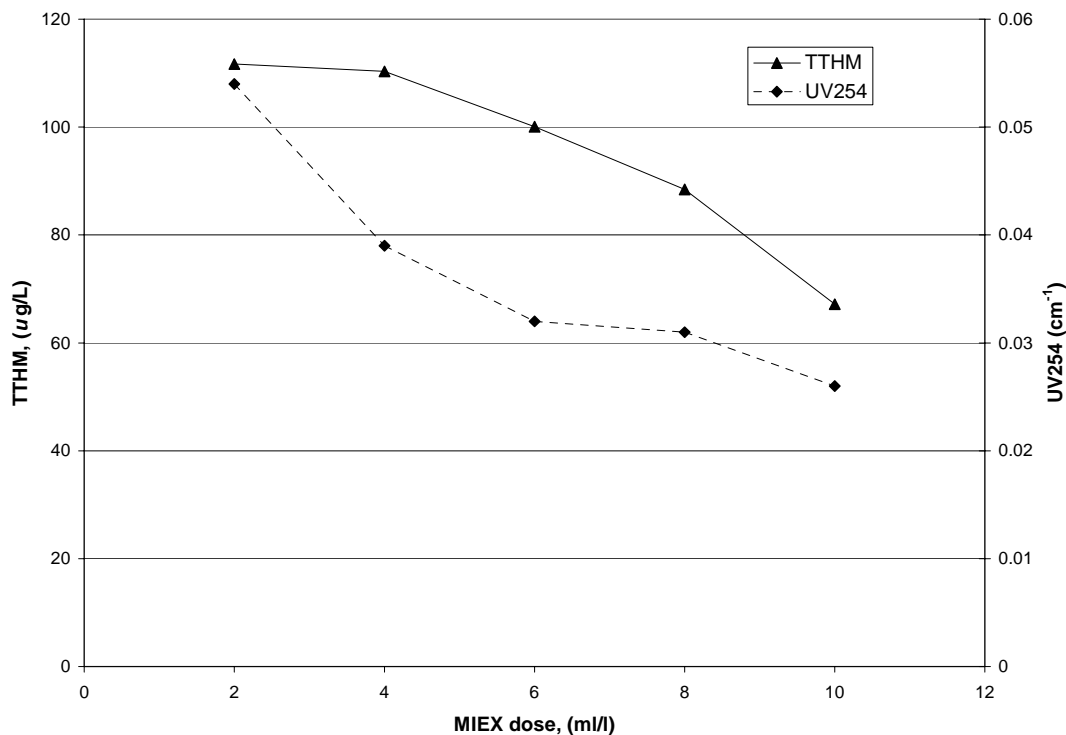


Figure 3. Ultraviolet absorbance and total trihalomethane concentration as a function of MIEX dose for Sioux Falls, South Dakota.

Figure 4 shows the reduction in THM formation after 60 min of mixing for three of the waters examined. For Hackensack water, the THM formation potential was reduced from 131 $\mu\text{g/l}$ to 25 $\mu\text{g/l}$ (81% reduction) with 4 mL/L of MIEX; for Durham water, the THM formation potential was reduced from 190 $\mu\text{g/l}$ to 60 $\mu\text{g/l}$ (68% reduction) with 4 mL/L of MIEX; for Sioux Falls, the THM formation potential was reduced from 239 $\mu\text{g/l}$ to 73 $\mu\text{g/l}$ (70% reduction) with 10 mL/L of MIEX.

The results illustrated in Figures 1-4 clearly demonstrate the capability of the magnetic ion exchange resin to remove DBP precursors. Removals approaching 70% and higher were achieved, depending upon the dose of resin used.

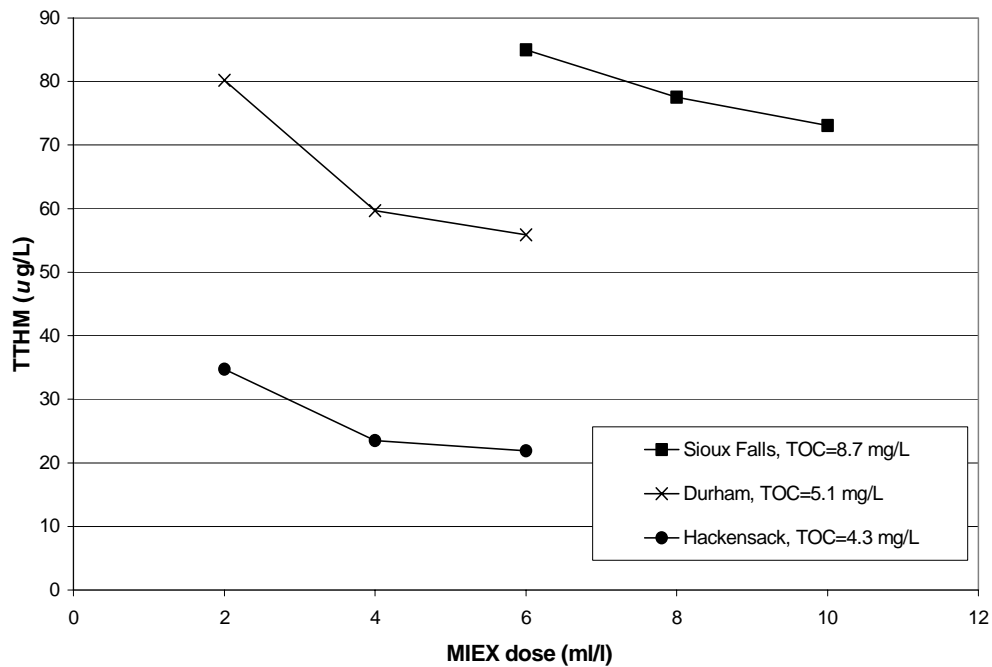


Figure 4. Total trihalomethane concentration as a function of MIEX dose for various surface waters.

Based upon the jar test results with the resin, an optimal MIEX dose and mixing time were selected for each water. Reduction of UV absorbance was used for selection of the optimal dose and mixing time. Each raw water was then batch-treated with that MIEX dose for the chosen mixing time and the resultant water, after settling, was subjected to conventional jar testing for coagulation with alum. A control set of jar tests was conducted in which alum was applied to the raw water without MIEX pre-treatment. Figures 5 and 6 illustrate the findings.

Figure 5 shows that, for Manatee County water, without MIEX treatment, 60 mg/L of alum was required to coagulate this low alkalinity, high TOC water (initial TOC = 10.6 mg/L) to achieve a settled water turbidity of less than 2 NTU. The pH's of the water before and after coagulation with 60 mg/L of alum were 7.33 and 6.08, respectively. Turbidity increased initially upon alum addition as a result of the formation of aluminum hydroxide particles which were stabilized by the dissolved organic carbon in the water, and the formation of organic aluminum complexes. After the coagulant demand of the organic material was satisfied, further addition of alum resulted in the formation of settleable floc, and coagulation of turbidity was observed. When the raw water was pre-treated with 8 mL/L of MIEX for 30 min, the TOC concentration was reduced from 10.6 to 1.6 mg/L. As a result of the lower TOC concentration, the coagulant demand of the water was lower and only 10 mg/L of alum was required to coagulate the turbidity to less than 2 NTU. The pH's of the water before and after enhanced coagulation with MIEX and alum were 7.14 and 6.92, respectively.

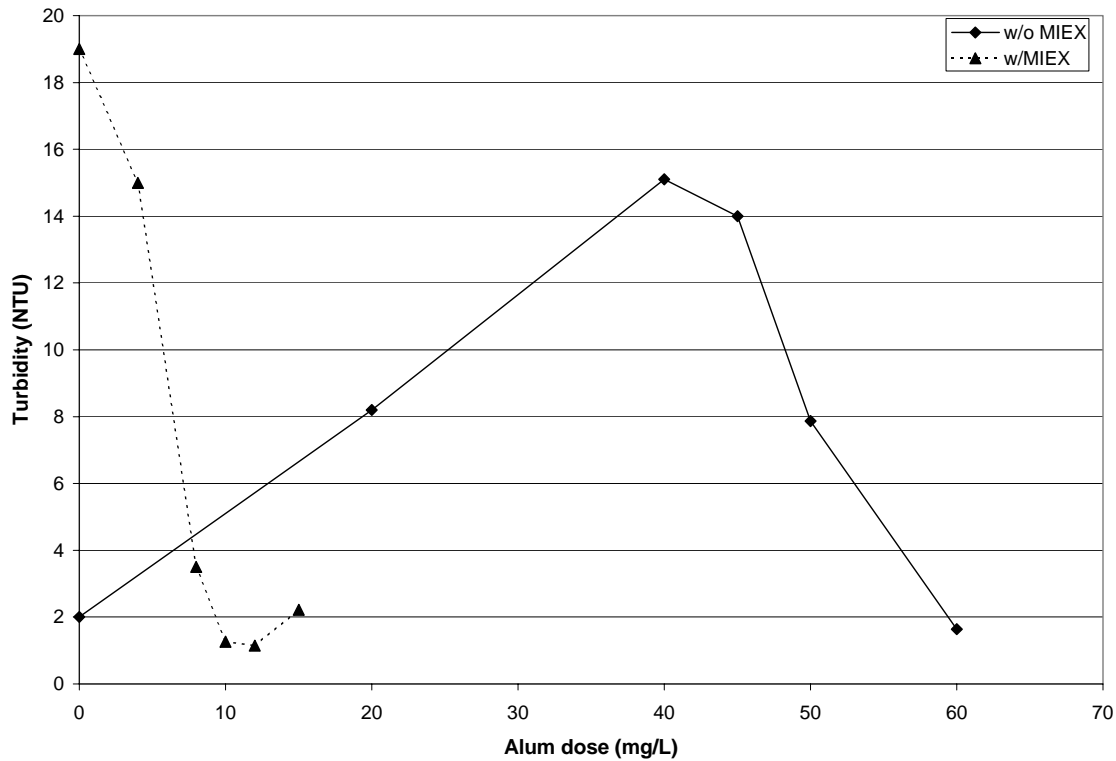


Figure 5. Turbidity as a function of alum dose with and without MIEX pretreatment for Manatee County, Florida.

Figure 6 shows similar findings for Sioux Falls water. With no pre-treatment, 45 mg/L of alum was required to coagulate the turbidity of this high alkalinity, hard water (initial TOC = 8.7 mg/L). (This water did not exhibit an increase in turbidity with the addition of alum as was the case for Manatee County water because of the higher pH of the water (pH 8.04) and the presence of high concentrations of hardness ions.) After pre-treatment of the raw water with 6 mL/L of MIEX for 30 min, the TOC concentration was reduced to 2.6 mg/L, and only 20 mg/L of alum was required to coagulate the turbidity to less than 2 NTU.

Similar findings were observed for the other waters examined. All exhibited a reduction in the requisite alum dose for turbidity removal as a result of the removal of organic carbon due to pre-treatment with the magnetic ion exchange resin, and all exhibited much lower formation of THMs with MIEX pre-treatment and alum coagulation than with alum coagulation alone. Table 2 is a summary of the findings for all seven waters tested at the time of this writing.

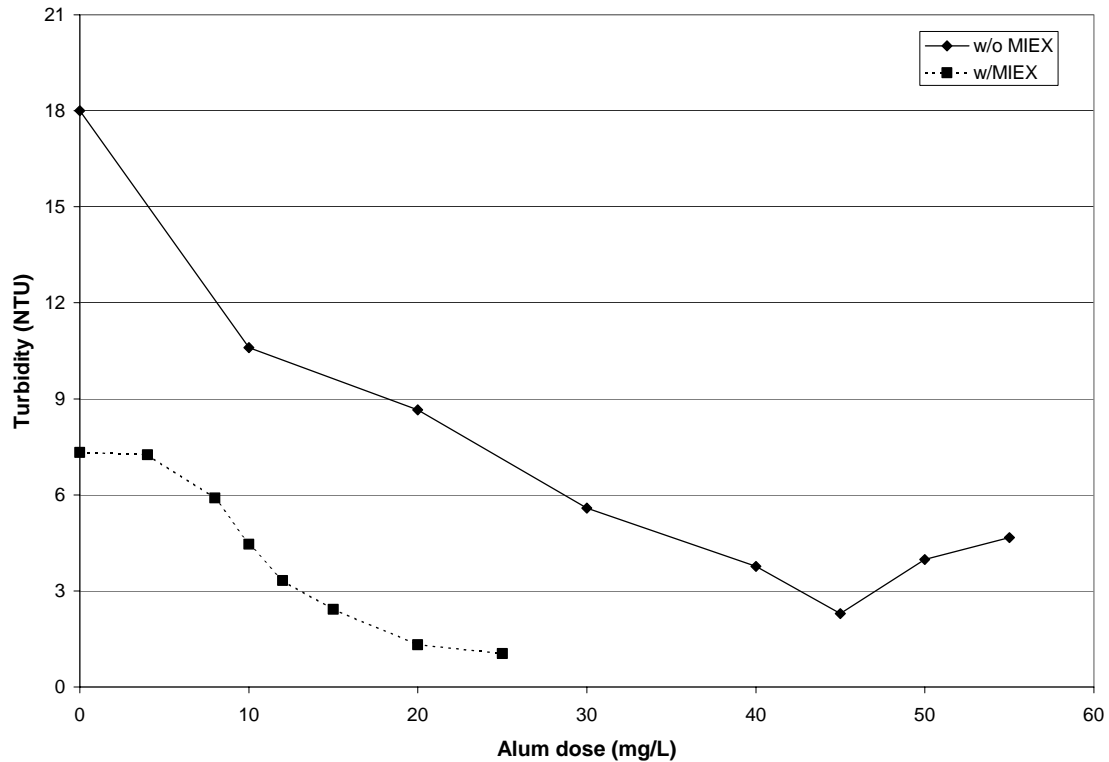


Figure 6. Turbidity as a function of alum dose with and without MIEX pretreatment for Sioux Falls, South Dakota.

Conclusions

Enhanced coagulation with the magnetic ion exchange resin was found to be very effective for removing THM precursors from the waters examined and for markedly reducing alum dosages for coagulation of turbidity. THM formation was reduced by more than 60%, 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.⁴ Residual TOC, UV absorbance, and THM formation potential were all substantially lower as a result of MIEX pre-treatment and alum coagulation compared to alum coagulation alone.

The findings of this research suggest that the MIEX technology represents another tool for potential use by water utilities to enhance the removal of natural organic material (DBP precursors) in drinking water beyond that achievable by coagulation alone.

Table 2. Summary of Results

Utility	Treatment	Turbidity (NTU)	TOC (mg/L)	UV254 (cm ⁻¹)	THMFP (ug/L)
Durham, NC	Raw	6.7	5.1	0.175	190
	30 mg/L alum	2.1	3.1	0.042	84.3
	6 mL/L MIEX, 30 min + 7 mg/L alum	1.7	1.2	0.014	36.3
Manatee Co., FL	Raw	4.3	10.6	0.477	335
	60 mg/L alum	1.6	5.3	0.106	222
	8 mL/L MIEX, 30 min + 10 mg/L alum	1.3	1.4	0.029	nr
Indianapolis, Indiana	Raw	2.7	4.6	0.088	nr
	30 mg/L alum	1.8	3.4	0.068	94.8
	6 mL/L MIEX, 30 min + 12 mg/L alum	1.6	nr	0.058	51.7
Hackensack, NJ	Raw	2.9	4.3	0.106	131
	40 mg/L alum	0.57	nr	0.058	84.7
	4 mL/L MIEX, 30 min + 12 mg/L alum	1.7	nr	0.020	23.6
Manchester, NH	Raw	1.9	2.6	0.030	73.4
	45 mg/L alum	1.0	2.0	0.029	58.0
	2 mL/L MIEX, 20 min + 10 mg/L alum	2.3	1.4	0.016	29.4
Sioux Falls, SD	Raw	55	8.7	0.135	239
	45 mg/L alum	2.3	4.9	0.100	167
	6 mL/L MIEX, 30 min + 20 mg/L alum	1.3	2.4	0.032	80.8
Metropolitan Water District, CA	Raw	7.7	2.8	0.081	na
	30 mg/L alum	0.79	2.0	0.048	na
	6 mL/L MIEX, 30 min + 10 mg/L alum	0.96	1.1	0.016	na

nr = not reported because the sample did not meet the quality assurance criteria

na = not available at the time of this writing

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