

USE OF A MAGNETIC ION EXCHANGE RESIN FOR TOTAL ORGANIC CARBON (TOC) REMOVAL TO ALLOW COMPLIANCE WITH EPA DISINFECTION BY-PRODUCT RULE

Elizabeth Pyles, Barbara Martin, Orica Watercare, Watkins, Colorado

ABSTRACT

Ion exchange has been demonstrated to be an effective process for TOC removal. However due to the many limitation of conventional ion exchange processes this treatment method has not been widely accepted. The MIEX[®] process, a pre-treatment process, utilizing a magnetized ion exchange resin has been demonstrated to remove between 40 and 90 percent of source water NOM from a variety of water supplies while minimizing or eliminating inadequacies associated with conventional IX. The large reduction in TOC will in-turn reduce the formation of disinfection by-products upon chlorination. Many utilities are able to remain on free chlorine as the primary disinfectant, which has been shown to be a stronger disinfectant than chloramines.

The ion exchange process is applied as the initial treatment process in a surface or groundwater treatment plant. The removal of TOC at the beginning of the water treatment process results in many positive impacts on downstream processes, such as lower required doses of coagulant, pH adjusting chemicals, and disinfectant along with less sludge production. These reductions in chemical feed often result in improved filterability of the water for both conventional and membrane filters. The reduction in TOC also results in a decreased demand for disinfectant in the distribution system allowing for a stronger and longer lasting chlorine residual.

MIEX resin has been specifically targeted at the removal of dissolved organic carbon (DOC) compounds, such as humic and fulvic acids, from drinking water supplies in a continuously stirred reactor. The negatively charged DOC ions are removed from water by exchanging with a chloride ion attached to the resin surface. The resin has demonstrated the ability to remove the low molecular weight fraction of TOC that cannot be effectively removed by coagulation; therefore allowing much lower treated water TOC levels to be achieved than through coagulation treatment alone. This low molecular weight fraction of the TOC has also been associated with the formation of DBPs; hence the process tends to preferentially remove DBP precursor compounds from the water.

The MIEX resin has also been demonstrated to remove other problem anions, specifically, arsenic, chromium, perchlorate, bromide and nitrate. This paper presents information about the chemistry of the magnetic ion exchange treatment process, application of the process, case studies of facilities, in which the process is utilized, and bench and pilot scale test results from waters in New York and Pennsylvania

TOTAL ORGANIC CARBON AND ION EXCHANGE CHEMISTRY

TOC Chemistry and DBP Formation

Disinfection by-products (DBP) are chemical compounds that form as a result of disinfecting water in the presence of natural organic matter (NOM). While many disinfectants have the potential to form DBPs, the reaction of chlorine with dissolved organic carbon (DOC) can form halogenated organic compounds, such as total trihalomethanes (TTHM), haloacetic acids (HAA), haloketones (HK), and haloacetonitriles (HAN), some of which are regulated by the EPA Safe Water Act.

The Stage 2 DBP Rule, based on finding the highest DBP sites within a distribution system, will reveal many water systems in need of advance treatment options to adequately remove precursor materials. Removing additional TOC may be a daunting challenge for some water systems. The effectiveness of traditional TOC removal processes, such as coagulation, is highly dependant on water chemistry and the nature of the TOC species present in the water source.

TOC can be characterized in a variety of ways such as polarity, hydrophobicity and molecular weight. A more common description of TOC is SUVA. SUVA, or specific ultra violet absorbance is the absorbance, is a measure that relates the absorbance of the water at a wavelength of 254 nanometers to the concentration of DOC in the water. The calculation of SUVA is displayed in Equation [1] below.

$$[1] \quad SUVA = UV_{254}abs \text{ m}^{-1} / DOC \text{ mg L}^{-1}$$

These measurable TOC characteristics may be used in various ways in order to assess a water's potential to form DBPs. They may also be used to predict the effectiveness of TOC removal processes, such as coagulation.

It has been determined that coagulation preferentially removes TOC that is high in molecular weight, hydrophobic, and with large SUVA values (Pyles). Coagulation, even under acidic conditions, tends to be only marginally effective at removing the low molecular weight portion of the TOC. Coagulation is also not as effective at removing TOC that is hydrophilic or that has smaller SUVA values. However, it is this portion of TOC that can be a major contributor to DBP formation. Examining the character of a water's TOC may explain why some water systems have challenges in removing TOC using only coagulation methods. This may also explain why some water systems may remove a large portion of raw water TOC using conventional processes yet still experience high DBP yields upon chlorination. On the other hand, there are advanced TOC removal processes that preferentially remove additional portions of TOC. One of these is ion exchange. This paper examines the effectiveness of ion exchange as a TOC removal process, as well as the synergy that exists between the use of ion exchange and coagulation processes, in series, for TOC removal.

Ion Exchange for TOC Removal

Ion exchange is an effective means of TOC reduction for DBP control. MIEX[®] Treatment (abbreviation for Magnetic Ion EXchange) is an advanced ion exchange

process for DOC removal. The strong base anion exchange resin used in this process removes negatively charged DOC molecules from the water by exchanging them for chloride ions that are present on the resin. Examples of negatively charged DOC species include humic and fulvic acids, both of which are common DBP precursor compounds. Figure 1 illustrates the chemistry of the ion exchange process.

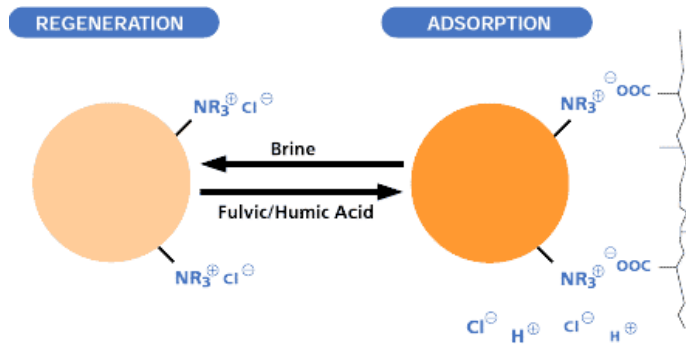


Figure 1: DOC Exchange

Many ion exchange resins consist of a polyacrylic skeleton with a quaternary amine functional group to which the chloride ion is attached. MIEX resin uniquely contains a magnetic component, iron based, which promotes attraction to one another, allowing the resin to agglomerate and settle quickly. This property tolerates the resin being used in a fluidized bed, rather than in a packed column configuration, which is described in more detail in the following section. The fluidized bed configuration has a number of application advantages that will also be described in detail in the following section. MIEX resin particles are small, on average 180 μm , which is about ten times smaller than conventional ion exchange resins. This size allows for a large ion exchange surface area in a small process footprint. The resin is more selective for DOC than for any other compound, and typically removes 40-90% of the raw water DOC, depending on the structure of the DOC present in the water and the overall water chemistry.

PROCESS APPLICATION

The magnetic ion exchange system is typically installed at the head of the water plant as either an open tank gravity vessel (Figure 2) or a pressurized tank, running off the pressure of the raw water pumps.

Raw water is fed to the base of the reactor vessel where the water is mixed with the magnetic resin in a fluidized bed fashion. By mixing the water with resin, rather than flowing through a packed column, the ion exchange process occurs very rapidly with minimal head loss. Water is fed at a minimum rate of 8-10 gal /min /ft² to keep the resin in suspension. An agitator operating at slow speeds keeps the resin/water suspension uniformly mixed. This results in a raw water contact time with the resin of between 4-6 minutes. Because of the fluidized bed approach, the process is unaffected by suspended solids in the raw water. Suspended solids from the raw water flow out of the vessel and into the downstream process.

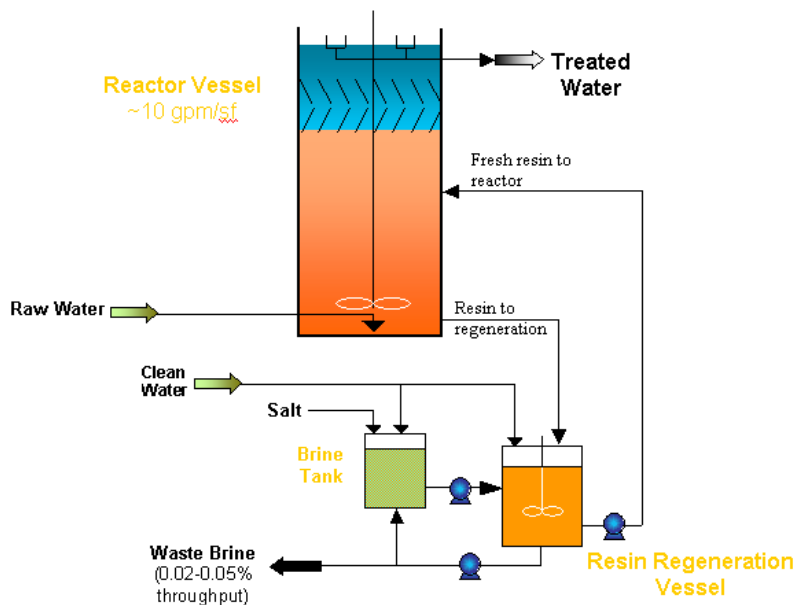


Figure 2: Open Tank High Rate MIEX® Process Schematic

A series of tube settlers at the top of the reactor vessel separate the resin from the water, and the treated water overflows into collection launders. The magnetic component of the resin allows for high separation efficiency in this separation zone. Treated water then flows by gravity to the next phase of the water treatment facility, with between 40 – 90 % of the raw water DOC removed. If the facility is a ground water plant with no other treatment units, treated water flows by pressure (from the raw water pumps) through a magnetic media polishing system to remove any resin particles that overflow the reactor vessel. A very small amount of resin, ranging from 1.0 to 2.0 gallons per million gallons of treated water flow, may be lost from the system. In order to maintain the resin concentration in the contactor vessel, a small amount of new resin is intermittently added to the system to replace the resin lost.

The magnetic ion exchange system is continuously running and is able to remain online during the periodic regeneration process. A small volume of resin is continuously withdrawn from the base of the reactor and sent to the regeneration vessel. Resin is accumulated and regenerated in small batches. Freshly regenerated resin is returned to the reactor in order to maintain a consistent ion exchange capacity, which results in a consistent treated water quality and prevents chromatographic peaking, a spike in the contaminant concentration.

This type of resin regeneration process results in a small waste stream. Typically 250-600 gallons of waste is generated, per million gallons of plant throughput, as a result of resin regeneration. A 10-12% brine solution or a saturated sodium bicarbonate solution can be used to regenerate the resin. Brine waste is typically disposed of to sanitary sewer. The optional bicarbonate regeneration waste solution can be disposed of to sanitary sewer or mixed with other plant residuals depending upon local regulations. The brine or bicarbonate waste generated by the process may also be treated on-site in order to remove organics from the waste stream and

recycle the regenerant solution, resulting in a system with essentially zero liquid discharge.

DOWNSTREAM BENEFITS

Reduction in Coagulant Dosage

The magnetic ion exchange process is most commonly applied as the initial treatment process in a surface water treatment plant. This is due to the fact that there are a number of downstream process benefits that occur as a result of removing DOC, particularly with regards to coagulation. Ion exchange tends to preferentially remove hydrophilic compounds that are low to medium molecular weight, which are the type of compounds that tend to be less effectively removed by coagulation. Removing these organic compounds by ion exchange prior to coagulation can reduce the coagulant dose required downstream. An example of this is presented in Figure 3.

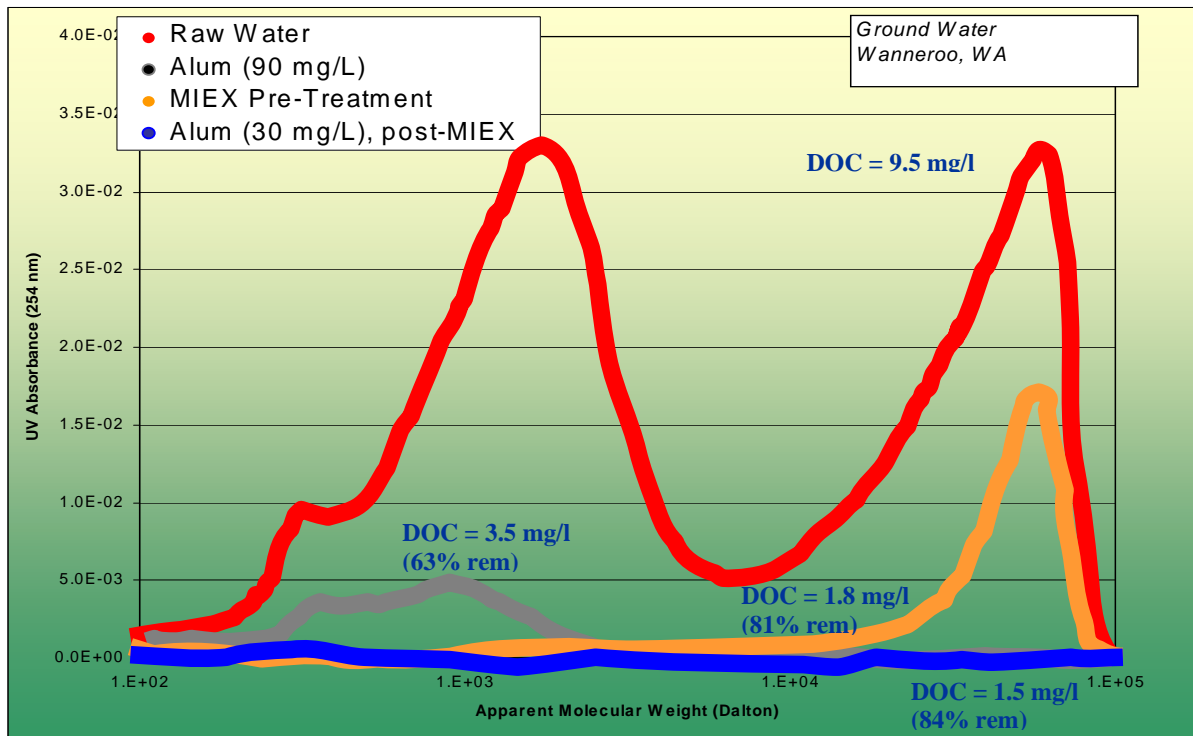


Figure 3: UVA Removal vs. Molecular Weight for a Groundwater from Western Australia

Figure 3 is a graph of the molecular weight profile of a water source from Western Australia based on UV absorbance at 254 nanometers, (UVA). As Figure 3 illustrates, the DOC in the raw water is 9.5 mg/L. The profile of the DOC indicates that it has a low molecular weight fraction of approximately 1000 Daltons. It also has a high molecular weight fraction greater than 10,000 Daltons. Coagulation with 90mg/L of alum removed 63% of the DOC; however, it preferentially removed the higher molecular weight fraction of the organics as indicated by the grey curve.

Magnetic ion exchange treatment alone removed 81% of the DOC. It tended to remove the low and mid-molecular weight portion of the organics, leaving the higher molecular weight compounds behind. The combination of magnetic ion exchange pre-treatment followed by a reduced dose of alum (30mg/L), removed 84% of the raw water DOC, with ion exchange removing the low molecular weight fraction of the organics and coagulation removing the high molecular weight fraction as indicated by the blue line.

This reduction in coagulant dose is experienced in full-scale installations, as the following case study illustrates. The ability to reduce coagulant dose results in many associated treatment benefits. In low alkalinity water where significant amounts of pH adjusting chemicals are added in addition to a coagulant, the amount of pH adjustment will be reduced along with the coagulant dose. These chemical reductions will also result in fewer solids being produced by the process and reduced requirements for solids handling. With less solids loading on the filters, plants may also experience longer filter run times and improved operability.

Organic Fractions Removed by Ion Exchange

It is also significant to note the fractions of the organic carbon that are removed through the ion exchange treatment process. Figure 4 illustrates the DOC profiles for raw water and various treatment processes run at the Lexton WTP (Australia) pilot plant, with respect to Very Hydrophobic Acids (VHA), Slightly Hydrophobic Acids (SHA), Charged Hydrophilic Acids (CHA), and Hydrophilic Neutral Acids (NEU).

As Figure 4 illustrates, magnetic ion exchange treatment removed 63% of the VHA, 57% of the SHA, and 75% of the CHA (Reyne). The hydrophilic neutral compounds, having no charged portion, cannot be removed using ion exchange. As would be expected. Microfiltration (MF) alone did not remove a significant amount of DOC from the raw water as would be expected.

As illustrated in these two examples, ion exchange removes portions of the DOC that are not effectively removed by conventional coagulation processes, yet can still be considered as DBP precursor compounds (Owen). There is a synergy between the two processes, increasing the overall DOC removal when both are used together and improving process performance downstream of the ion exchange.

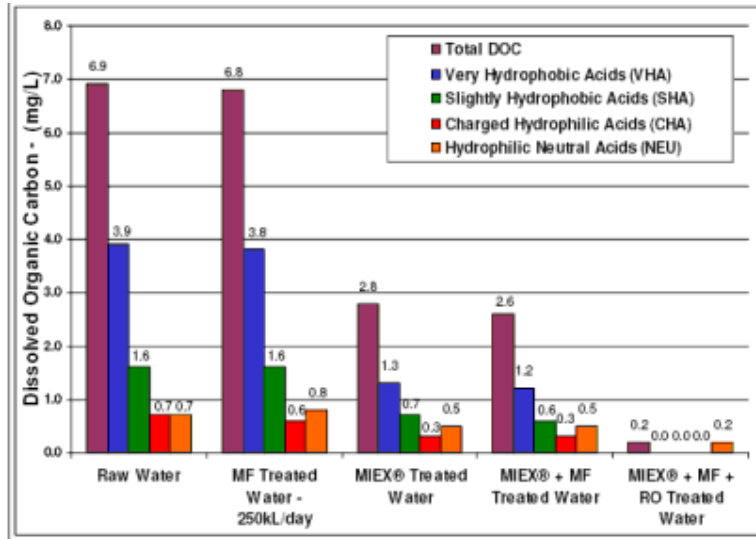


Figure 4: DOC Fractionation for Various DOC Removal Processes – Lexton WTP Pilot Plant (Australia)

CASE STUDY

City of Vallejo, California – Green Valley Water Treatment Plant

The City of Vallejo, California’s Green Valley Water Treatment Plant (WTP) is a 1 MGD system in which magnetic ion exchange treatment is installed as pre-treatment to conventional coagulation and filtration. The plant serves a rural area in the Napa Valley region of Northern California. Detention times of two to four weeks in the distribution system can occur due to low demand. For example, one 9-mile section of 24-inch pipe serves only 62 customers. The combination of free chlorine disinfection, the reactive nature of the raw water DOC, and a long detention time in distribution contributed to the formation of TTHM well in excess of the US EPA limit of 80µg/L. In 2005, after completing a year of quarterly sampling, the plant was required to issue violation notices for exceeding the regulatory limit for TTHM.

After considering and evaluating a number of treatment options for DBP control, magnetic ion exchange was selected and installed. The treatment system at the Green Valley WTP has been in operation since 2006, significantly improving the plant’s DOC removal. Prior to installation of the magnetic ion exchange process, raw water DOC removal from resulting from conventional coagulation averaged approximately 20%. The addition of magnetic ion exchange pre-treatment increased DOC removal to more than 60%, which has also resulted in a significant reduction in DBP concentrations in the distribution system. Since installation of the treatment system, the Green Valley WTP has remained in compliance with the US EPA requirements for TTHM and HAA5, with quarterly TTHM concentrations falling from a range of 100-120µg/L prior to system installation to a current range of 35-

40µg/L. Figure 5 demonstrates the dramatic change in distribution system TTHM concentrations before and after installation of the treatment system.

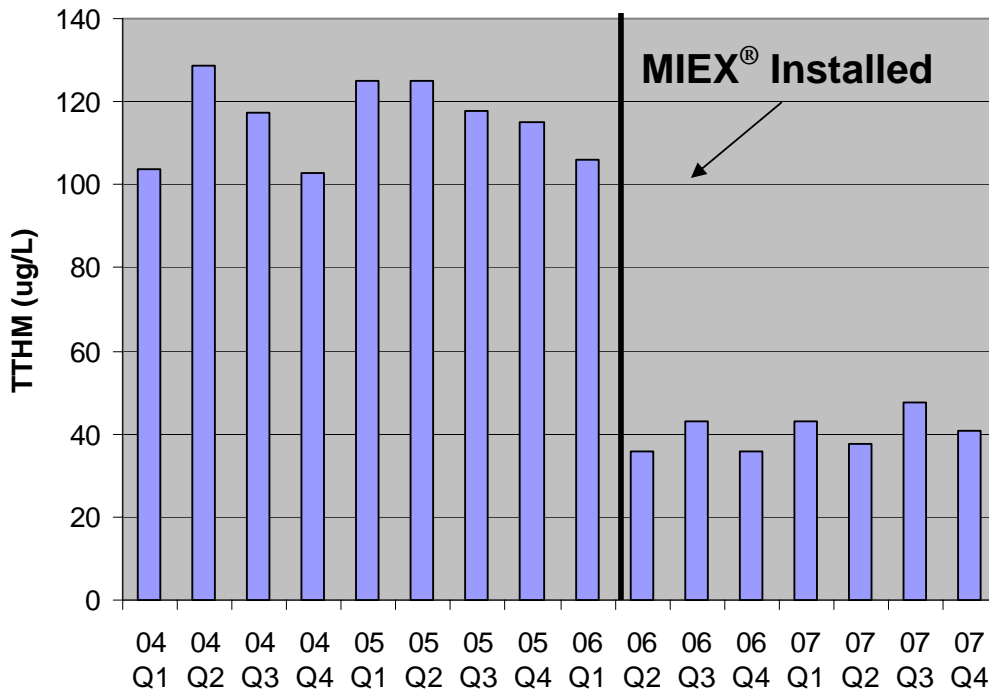


Figure 5: Green Valley WTP Quarterly TTHM Results Before and After Installation of Magnetic Ion Exchange Pre-Treatment

Additionally, the Green Valley WTP has realized many of the downstream benefits associated with magnetic ion exchange pre-treatment. The chlorine dose required for disinfection has been reduced by approximately 50% due to the reduction in chlorine demand that improved DOC reduction provides, and system operators report that it is easier to maintain a residual throughout the distribution system. Coagulant doses have also been reduced by more than 50%, resulting in decreased use of pH adjusting chemicals, and decreased solids loading on the filters.

RESULTS FROM NORTH EAST STUDIES

Results from New England Waters

Magnetic ion exchange treatment for DOC removal has also been studied at the pilot scale for a number of waters in the northeast. A major challenge in treatment of some waters from Massachusetts is the DOC swings in a given raw water sources (some ranging from 4 to an excess of 15 mg/L). The DOC, if not removed sufficiently, can result in high levels of DBP formation upon chlorination.

Table 1, below, summarizes the results of bench scale testing for DOC removal from various surface water sources in New England using magnetic ion exchange resin.

Table 1: MIEX[®] Treatment Pilot Results for Raw Waters From New England

Water	Raw DOC (mg/L)	Raw Color (PCU)	Raw UVA (cm¹)	MIEX[®] DOC (mg/L)	Finished¹ DOC (mg/L)	Finished Color (PCU)	Finished UVA (cm¹)	COAG Reduction
Water A Summer	10.5	208	0.552	4.67	1.99	1	0.034	81 %
Water A Winter	5.84	62	0.297	2.33	1.11	0	0.013	67%
Water B Spring	6.96	8	0.271	2.11	2.11	0	0.059	NA
Water C Fall	4.50	27	0.135	1.30	1.80	8	0.026	NA

1. Finished is MIEX treated followed by downstream coagulation or slow sand filtration
2. Sample A from Massachusetts, B from Rhode Island and C from Maine

As Table 1 shows, the greater the raw water DOC the greater the percent DOC removal can be achieved with ion exchange. In each case, a very low level of DOC remains after treatment. For water A, the large reduction in coagulant demand will make a substantial difference in the overall water plant performance. Notice also that water temperature does not affect the ion exchange DOC removal capability.

Ion exchange can also be highly effective in removing color from the raw water. Table 1 presents raw and treated absolute color values for each water. Removal of color is variable as noticed by water C. If the color is related to humic and fulvic material versus metallic or even heavy molecular weight organics, ion exchange removal values can be as high as 99%.

In many cases in the above table the removal percentage of UVA exceeds the removal percentage of DOC from the raw water. In fact, it has been demonstrated that UVA is a better indicator of DBP yield than DOC (Singer). The results above indicate that ion exchange treatment may preferentially be removing the DBP precursor compounds that absorb strongly at 254 nanometers.

A simulated distribution system DBP formation potential (SDS TTHMs and HAAs) analysis was run on water from Table 1. Both plant treated and MIEX[®] treated waters were spiked with sufficient chlorine to achieve a residual chlorine concentration of 0.3 mg/L after incubation (time varied for each location) at 25 degrees Celsius. Results of this study are presented in Table 2.

Table 2: SDS DBP FP for Waters A – C Control and MIEX[®] Treated

Sample	Plant Control DOC (mg/L)	Plant Control TTHM FP (µg/L)	Plant Control HAA FP (µg/L)	MIEX[®] Treated TTHM FP (µg/L)	MIEX[®] Treated HAA FP (µg/L)
Water A Summer	3.17	99.8	66.7	56.4	18.9
Water A Winter	1.90	65.2	32.8	28.5	7.9
Water B Spring	6.96	212	65	53.6	30.0
Water C Fall	4.50	128	55	34.9	25.5

Water B and Water C are from locations with slow sand filters only. It can be seen from the information presented above that ion exchange can have a big impact on DBP formation for these systems. If you look at the µg of TTHM formed per mg of DOC you will notice that for Water A, 31-34 µg of TTHM formed per mg of DOC and for the MIEX[®] Treated only 25-28 µg of TTHM are formed per mg of DOC. The result for Water B is 30 µg of TTHM formed per mg of DOC without any treatment and with MIEX[®] Treatment only 25 µg of TTHM formed per mg of DOC. For Water C, 28 µg of TTHM formed per mg of DOC as 19 µg of TTHM formed per mg of DOC for the MIEX[®] Treated. This data supports the idea that ion exchange preferentially removes DOC fractions that are more likely to contribute to DBP formation.

CONCLUSIONS

Magnetic ion exchange treatment is an anion exchange process for DOC removal that has the ability to reduce raw water DOC by up to 90%. It is typically applied as the initial process in a surface water treatment plant, due to the fluidized bed configuration of the process, which is not affected by the presence of suspended solids in the raw water. The process' preferential removal of low to medium molecular weight DOC compounds and the fractions that tend to be reactive with chlorine to form DBPs, results in significantly reduced formation of TTHM and HAA upon the addition of chlorine in the treatment plant. Additionally, the removal of these portions of the organic matter tends to complement conventional coagulation processes, which tend to preferentially remove different fractions of the organic matter. There is a synergy between the two processes, resulting in reduced dosages of coagulant required downstream of ion exchange treatment. Magnetic ion exchange has been applied successfully in a number of full-scale applications in the United States and throughout the world. Bench and pilot scale testing has been completed in Western Canada, with promising results on some challenging, high DOC waters.

REFERENCES

- Edzwald, J.K., W.C. Becker, and K.L. Wattier. (1985) Surrogate Parameters for Monitoring Organic Matter and THM Precursors. *Journ. Amer. Water Works Assoc.*, 7(4):122.
- Owen, D.M., G.L. Amy, and Z.K.Chowdhury. (1993) Characterization of NOM and its Relationship to Treatability. AWWA Research Foundation (AWWARF), Report no.90631, CO, USA.
- Pyles, E., (2008) Organic Matter Coagulation and the MIEX® Advantage: The Science Behind TOC Removal and Ion Exchange Pretreatment Benefits, 2008 American Water Works Association Conference, Coagulation and Filtration Workshop Proceedings.
- Reyne D., D. Dharmabalan, R.Van Merkestein, B. Murray. (2007) Retrofitting Small Water System to Meet New Regulations, Water Industry Operators Association of Australia, 70th Annual Victorian Water Industry Engineers and Operators' Conference, Proceedings.
- Singer, P. C., J. J. Barry III, G. M. Palen and A. E. Scrivner. (1981). Trihalomethane Formation in North Carolina Drinking Waters. *Journ. Amer. Water Works Assoc.*, 73(8):392.