AN EVALUATION OF MAGNETIC ION EXCHANGE (MIEX®) FOR NOM REMOVAL

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ABSTRACT

A new process for the removal of natural organic matter (NOM) was developed in Australia by Orica Watercare and South Australian Water Corporation. It employs a strongly basic anion exchange resin to remove NOM from water. In the first stage of the process, the (180 μm) MIEX® resin is mixed with the water to be treated and its small size encourages rapid removal of NOM. The resin beads also contain a magnetic component responsible for their rapid agglomeration and very efficient removal by sedimentation in the second stage of the process. A continuous process is achieved by recycling approximately 90% of the recovered resin and adding the remaining 10%, required for maintaining the resin concentration, as fresh (regenerated) resin. The remaining 10% of the recovered used resin is sent to a regeneration system where it is regenerated with 2M NaCl.

The MIEX® process was evaluated to determine how it might be best implemented for NOM removal and DBP reduction at the Saint Paul Regional Water Services (SPRWS). Batch and pilot plant studies were conducted to evaluate the MIEX® resin performance when it was applied before and after the lime softening. Measurements of TOC and ultraviolet absorbance (UVA) were made to characterize NOM removal. In addition, the impact of the MIEX® treatment on the chemical requirements for softening, and the DBP formation potential of the treated water, were also evaluated.

This paper provides an assessment of the MIEX® treatment process for NOM removal. Data on process performance, the impact of operating conditions, point of application, dosage, regeneration conditions etc., are presented and discussed.

INTRODUCTION

The Problem:

The St. Paul Regional Water Services (SPRWS) receives source water from a chain of impoundment reservoirs supplied by diversions from the Mississippi River and Rice Creek, as well as runoff from local watersheds. Groundwater is intermittently blended with the surface supply from a series of four deep wells tapping the Prairie Du Chien-Jordan aquifers. The lakes provide a retention time of about 144 days before the water is extracted from Lake Vadnais, just north of St Paul. This surface water supply generally has a high concentration of natural organic matter (NOM). The dissolved organic carbon concentration (DOC) in the source water can exhibit significant seasonal variations with DOC concentrations between about 6 and 10 mg/l during the course of the year. Traditional chemical softening of the water with excess lime and low dosages of metal coagulants is effective in providing 40 to 55 % DOC removal and results in a treated water with DOC concentrations that vary between 3 and 5 mg/l. These high residual DOC concentrations are a concern since they can impact disinfection by-product (DBP) formation and contribute to taste and odor problems in the treated water. The organic content of the water can also lead to water quality deterioration and corrosion problems in the distribution system. For these reasons, the Saint Paul Regional Water Services was interested in exploring alternative processes for improved NOM removal.

The objective of this study was to evaluate a novel magnetic ion exchange treatment process to determine if it would be effective and economical in removing DOC prior to disinfection.

Source Water Quality:

The inorganic quality of the source water and the treated water is shown in Table 1.

	Plant Influent	Plant Effluent
Turbidity (NTU)	1.2	0.07
Color	26.2	5.3
pH	8.1	9.1
Total Alkalinity (mg/L as CaCO3)	161.1	55.7
Carbonate Hardness (mg/L as CaCO3)	121.6	56.0
Non-Carbonate Hardness (mg/L as CaCO3)	19.4	26.6
Total Hardness (mg/L as CaCO3)	140.8	82.6
Total Phosphorus (mg/L)	0.045	0.022
Ammonia-N (mg/L)	0.327	0.857
Nitrate,Nitrite-N (mg/L)	0.35	0.27
TKN (mg/L)	0.92	1.03
TDS (mg/L)	187.1	153.4
Silicon (mg/L)	4.4	4.2
Fluoride (mg/L)	0.5	1.2
Sodium (mg/L)	10.5	12.8
Aluminum (mg/L)	0.0	0.039
Chloride (mg/L)	21.9	27.7
Calcium (mg/L)	39.7	23.4
Magnesium (mg/L)	10.2	5.8
Sulfur (mg/L)	5.3	7.1

Table 1: SPWRS Water Quality Data, 1997-1999 Averages

Although the Chain of Lakes is effective in equalizing and dampening the wider variations in water quality in the Mississippi River, it is apparent that the river dominates the source water quality. Two earlier studies Macko[1] (1980) and Semmens[2] et al (1983) characterized the NOM in the Mississippi and found largely similar results.

Approximately 40% of the NOM was hydrophobic and 60% hydrophilic. The hydrophobic fraction was predominantly acidic, while the hydrophilic fraction was largely neutral. The molecular weight distribution for the fractions <1K, 1-10K, 10-100K, and >100K was 23%, 50%, 10% and 17% respectively. The molecular size distribution varied somewhat with season.

Ion Exchange:

Earlier studies have shown that ion exchange is effective in removing NOM from Mississippi River water. In the neutral pH range, the negatively charged character of NOM allows these complex, polyanionic organic compounds to compete with inorganic anions for exchange sites. Although ion exchange is the dominant mechanism of NOM removal by ion exchange (IX), hydrophobic interactions between organic matter and the resin matrix can have a profound impact on selectivity. The most strongly bound organic ions are those in which the charged sites of the organic molecules can participate in electrostatic interactions with the fixed charged sites of resin while the non-ionized component physically adsorbs to the resin matrix.

The use of ion exchange provides similar levels of NOM removal to that achieved with granular activated carbon (GAC) (Semmens[2] et al, 1983). In addition, unlike GAC, ion exchangers can be regenerated in place with a brine, or caustic brine, solution; an attractive feature. Unfortunately, conventional resins become fouled by NOM since the regeneration process is not very efficient in removing the exchanged/adsorbed NOM. Ineffective regeneration is largely attributable to the slow kinetics of NOM release. The large molecular weight, polyanionic character of NOM means that it diffuses slowly through the water phase within the resin. During regeneration the high salt concentration causes conventional resins to contract and this “tightening” of the matrix, lowers the water content within the resin and makes the release of the NOM that much slower and more difficult to achieve during times typically allotted to regeneration.

There are several approaches that might be used to improve NOM removal kinetics during service and regeneration:

i. Design resins with a higher water content that do not contract significantly during regeneration with concentrated brine so that NOM diffusion within the resin is not restricted.

ii. Design the resin to reduce the opportunity for strong adsorption of the organic ions to the polymer matrix.

iii. Use resins with smaller bead sizes so that the NOM does not need to diffuse so far to get in or out of the resin.

Orica, an Australian Company, has incorporated some of these features into the design of a resin to allow rapid DOC adsorption and desorption kinetics. The MIEX® resin is very small measuring less than 80 mesh (180 μm) in size.

The MIEX® Resin Treatment Process:

To use such a small ion exchange resin in a conventional packed bed application would inevitably lead to high headlosses and problems with effective backwashing. For these reasons, Orica developed the resin specifically for continuous use in a stirred contactor, much like a flash mixer in a conventional water treatment plant. Once the resin has removed the NOM from the water, it is recovered from treated water by sedimentation. This patented process is illustrated below in Figure 1.

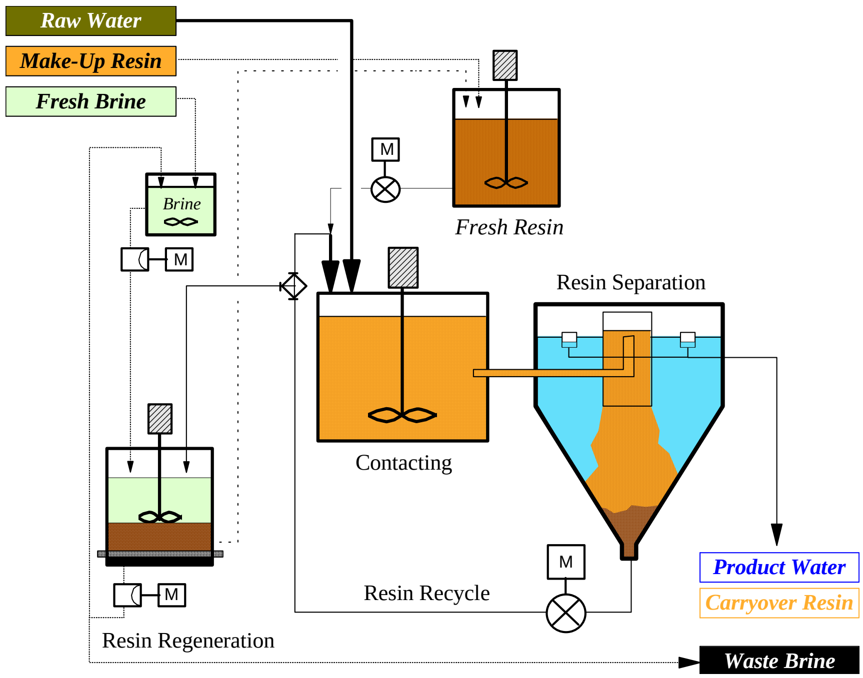

Figure 1: Schematic Illustration of the MIEX® Resin Treatment Plant[3]

Conventional ion exchange resins typically have a specific gravity around 1.1 and <80 mesh beads settle very slowly. To improve the separation of the resin from the water, Orica incorporated a magnetic component into the resin beads. This makes the resin beads heavier and their magnetic character encourages agglomeration of the resin beads during sedimentation. As a result, when the dispersed resin is passed to the settler, the fine resin beads rapidly agglomerate into larger, fast settling particles. Resin recovery rates of greater than 99.9% are achieved at settler rise rates of over 4 gal/ft^2 (10m/hr) (Bourke et al, 1999)[4].

Most of the settled resin collected from the separator is recycled back to the contactor as a concentrated suspension. A portion of the recycled resin stream is continuously diverted to a resin regeneration system. Usually the regeneration rate is 5 to 10 % of the resin recycle stream. In order to maintain ion exchange capacity in the system, the resin removed for regeneration is replaced by fresh resin. Resin lost due to carryover from the separator is also made-up by the feed of fresh resin.

Objectives:

The objective of this study was to evaluate the effectiveness of the MIEX® process for removing NOM and DBP precursors from the source water for the St Paul Regional Water Services. In addition, the studies were conducted to evaluate the impact of the MIEX® process when applied ahead of and after lime softening.

EXPERIMENTAL METHODS

From the spring of 1998 to January of 1999, jar tests were performed at the Saint Paul Regional Water Services (SPWRS) to determine the DOC removal effectiveness of ORICA's MIEX® resin. In the summer of 1999 and the winter of 2000 these tests were followed up by larger scale pilot plant experiments to determine if the results of the jar tests could be reproduced in conditions simulating full-scale treatment. This second round of experiments was again performed at the SPRWS. Orica provided the MIEX® resin separator and regeneration column (figures 2 and 3) and the equipment was used to retrofit a pilot plant designed to evaluate the influence of operating conditions during chemical softening. Two peristaltic feed pumps supplied the softened water from the treatment plant, or source water directly from Vadnais Lake to a rapid mix chamber and then to 4 flocculator compartments in series. The resin was added into flocculation compartments (ie. resin contactors) 3 and 4 initially and then into compartment 3 as each run continued. The resin/water suspension then flowed to the resin separator. The resin separator acted like a sedimentation tank with the MIEX® resin being collected as a concentrated slurry in the conical base while the treated, clarified water overflowed to the drain.

The trials consisted of 6 to 8-hour continuous runs at a constant 2 gpm flow rate to achieve 40 minutes contact time with the resin. To initiate a test-run, a calculated volume of resin was charged into contactors 3 and 4 (40% and 60% respectively). A fresh resin tank was previously prepared with the necessary resin concentration to maintain the desired dose at a 10% regeneration rate. Three peristaltic pumps were calibrated to pump 200 ml/min of the resin in water suspension. One of the pumps was set to recycle the resin from the separator back to contactor 3 for 90 seconds, while the other two pumped simultaneously the next 10 seconds to both replace fresh resin back into the system and send used resin to a regeneration column. The contactors and the fresh resin tank are continuously mixed to keep the resin suspended.

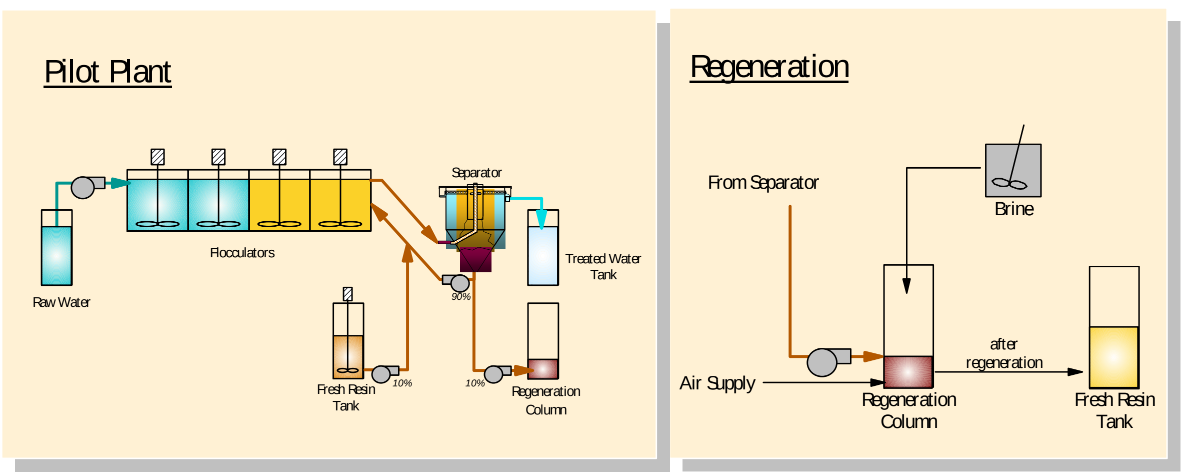

Figure 2: Schematic Illustration of SPRWS Pilot Plant and Regeneration Process

At the end of each run the used resin captured in the regeneration column is regenerated with 3BV of a NaCl brine (120 g NaCl per liter) for 45 minutes, followed by two 3BV rinses with effluent water for 5 minutes each. Air was used to mix the resin during the regeneration and rinsing. The regenerated resin was then poured back into the fresh resin tank for the next day run.

Measurements of total organic carbon (TOC) using a Phoenix 8000 Analyzer (Tekmar Dohrman). The ultraviolet absorbance (UVA) was measured with a HP 8453 UV-Visible Spectrometer (Hewlett-Packard, Waldbronn, Germany). The pilot plant was then operated to characterize the impact of MIEX® resin concentration on NOM removal and DBP formation potential of the treated water.

Figure 3: SPWRS Pilot Plant

Samples of influent and effluent water were taken in an hourly basis to determine TOC and UV-254 measurements. In addition, samples of the brine and rinse water after regeneration were taken and analyzed to calculate a TOC mass balance and predict the long-term resin performance and regeneration efficiency. Other basic water quality parameters like pH, temperature and alkalinity were also measured and recorded.

Two water sources, raw and softened water, were tested to evaluate the impact of MIEX® resin treatment on the current SPRWS scheme. Both water sources were tested in July and August of 1999 with resin concentrations 2, 4, 6 and 8 ml/l MIEX®. The raw water was tested again in March 2000 to evaluate the effect of water temperature on the MIEX® performance and to gather more data for the mass balance evaluation.

RESULTS

Reproducibility:

The first tests were conducted to evaluate the reproducibility of the test protocol for continuous flow operation. This study took place in the summer of 1999. A concentration of 6 ml/l and 90% recycle was repeated over a three-day period. The source water used for the test was piped directly to the pilot facility from the treatment plant influent conduit. The results indicated that approximately

65% of the TOC (SE[1]=1.47) and 79% of the UVA (SE[1]=0.37) could be removed from the untreated source water under the described operating conditions (Table 2). A second set of three pilot runs were conducted during March of 2000 investigating the reproducibility of earlier results and the performance of the MIEX® resins in cold water. This later pilot test involved treating raw water only. The cold water results (Table 3) showed a 56% removal of TOC (SE[1]=0.02) and a 78% reduction of UVA (SE[1]=0.58). The colder temperature appeared to reduce sorption by approximately 12%, while UVA removal was nearly identical to the earlier warm water tests.

Date of Experiment: m/d/y	Water Temperature: °C	Concentration: ml/l	Water Flowrate: Gpm	% TOC Removal:	% UVA Reduction:
7/12/1999	24.2	6.0	2.1	64.7	79.4
7/13/1999	24.0	6.0	2.1	67.4	NA
7/20/1999	23.1	6.0	2.1	63.5	77.9

Table 2: Raw Water MIEX® Pilot Trial Results, Summer 1999

Date of Experiment: M/d/y	Water Temperature: °C	Concentration: ml/l	Water Flowrate: Gpm	% TOC Removal:	% UVA Reduction:
3/13/2000	5.5	6.0	2.1	56.1	79.1
3/14/2000	6.0	6.0	2.1	55.7	76.8
3/15/2000	6.0	6.0	2.1	55.8	77.2

Table 3: Raw Water MIEX® Pilot Trial Results, Winter 2000

Softened Water Test:

In the summer of 1999 additional tests were conducted on softened water that was pumped from the recarbonation chamber upstream of the disinfection process. The softened water at this point had passed through softening, coagulation, and clarification processes, and the TOC content has been reduced by approximately 50%. In addition, the softening/coagulation process tend to reduce the hydrophobic portion of the raw water TOC as indicated by reductions in TSUVA[2] (average = 42%) following clarification. The MIEX® pilot tests on softened water effectively provided a further 39% reduction in TOC (SE=1.3) and a 51% (SE=1.9) reduction in UVA. This suggests that the resin can remove the lower molecular weight and more hydrophilic portion of the NOM that remains after conventional treatment. Earlier enhanced coagulation studies[5] using aluminum sulfate have shown removals of TOC following treatment at the St. Paul facility to be cost prohibitive requiring as much as 120 ppm of aluminum sulfate to remove an additional 1 ppm of TOC after softening/coagulation (normal dose ranges from 16-20 ppm).

Disinfection by-Products:

The intent of the investigation was to characterize the effectiveness of MIEX® resin in removing organic precursors that form disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) during the disinfection process, and to reduce the levels of these regulated compounds at the consumer tap. The promulgated Interim Enhanced Surface Water Treatment

[1] Standard Error

[2] TSUVA – specific UV absorbance (254 nm), i.e. measured UV absorbance x 100 / TOC

Rule (IESWTR) sets maximum contaminant levels (MCLs) for THMs and HAAs at 80 μg/l and 60 μg/l, respectively (Stage I 80/60 rule). The anticipated Long Term Surface Water Treatment Rule (LTSWTR) is expected to reduce the MCL to 40 μg/l for THMs and 30 μg/l for HAAs (Stage II 40/30 rule). The SPRWS finished water levels typically range from 14-39 μg/l for THMs and 25-39 μg/l for HAAs.

Figure 4 presents typical measured of THM formation potential values following MIEX® resin treatment in the pilot plant studies. The jar test data yielded very similar data. The data show significant reductions in the formation of THMs when compared to current SPRWS effluent concentrations. The typical free chlorine contact time during the treatment plant disinfection process is 4-6 minutes before the addition of ammonia. These data suggest that the use of MIEX® resin at the SPRWS would allow the free chlorine contact time to be extended more than 5 fold, greatly enhancing the inactivation of viruses and *Giardia*, while reducing the formation of undesirable by products by more than half.

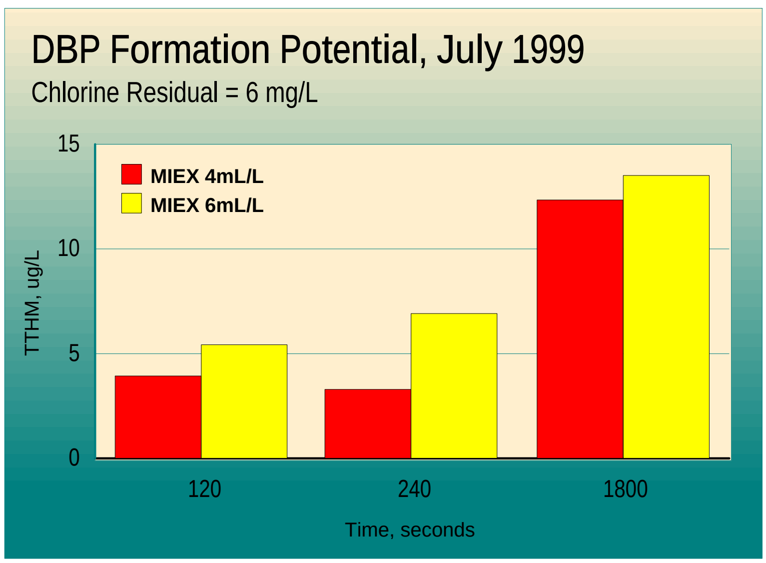

Figure 4: DBP Formation Potential Results, Pilot Trials, Summer 1999

Variable Resin Concentration:

Raw Water: Earlier jar tests comparing the performances of a series of resin concentrations ranging from 2 ml/l to 8 ml/l suggested an optimal concentration of 6 ml/l in 30-minute tests. These results agree with ORICA's recommended 6 ml/l standard concentration of the resin. Pilot studies on the raw water were also conducted to evaluate the impact of several concentrations of MIEX®: 2, 4, 6 and 8 ml/l when operated with a 90% recycle rate. As expected, the higher concentration of the resin resulted in higher percentage removal of TOC. It is clear from these experiments that even a 2 ml/l concentration provides a significant removal of TOC. Removal performance appeared to improve more significantly between 2 and 4 ml/l and there was no benefit to be gained by exceeding a resin concentration of 6 ml/l. The effect of resin concentration on TOC and UV-254 for raw water is illustrated in figure 5.

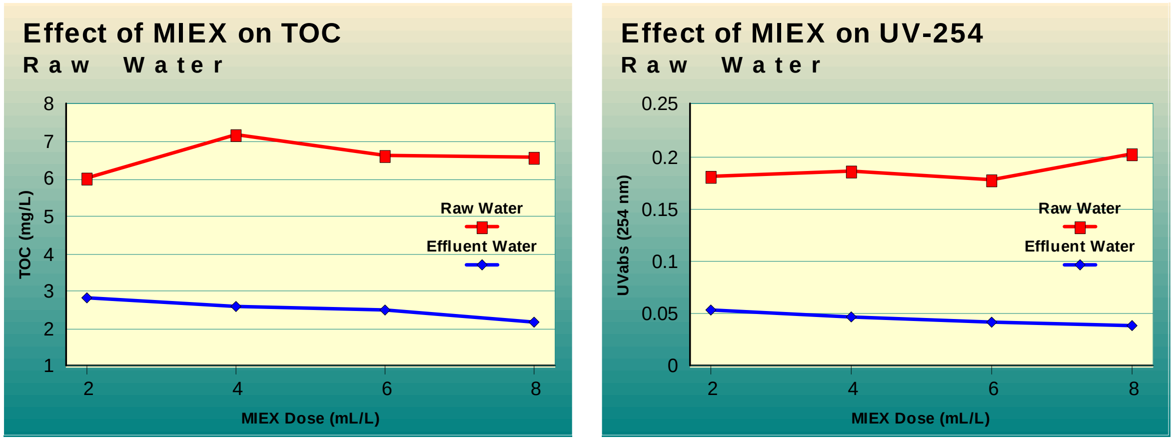

Figure 5: Effect of MIEX® on TOC and UV-254, Softened Water, August 1999

Figure 5 also shows the very similar results obtained for the removal of UVA. A resin concentration of 2 ml/l reduced UVA by 72%. Increasing the resin concentration to 4 and 6 ml/l of MIEX® only increased UVA removal to 74.6% and 76.8% respectively. There was little to be gained by exceeding 6 ml/l.

Softened Water: The impact of resin concentration on softened water was also evaluated. It is clear from Figure 6 that the final TOC an UVA of the water dropped with increasing resin concentration. However, all tested concentrations of the MIEX® resin removed approximately 40% of the TOC present in the softened water with only small fluctuations with resin concentration. Unfortunately, the feed softened water TOC and UVA values varied during the test period. It is apparent, that like the earlier tests on raw water, the 2 ml/l concentration removes a great deal of NOM and increasing the concentration provides only small incremental improvements in removal.

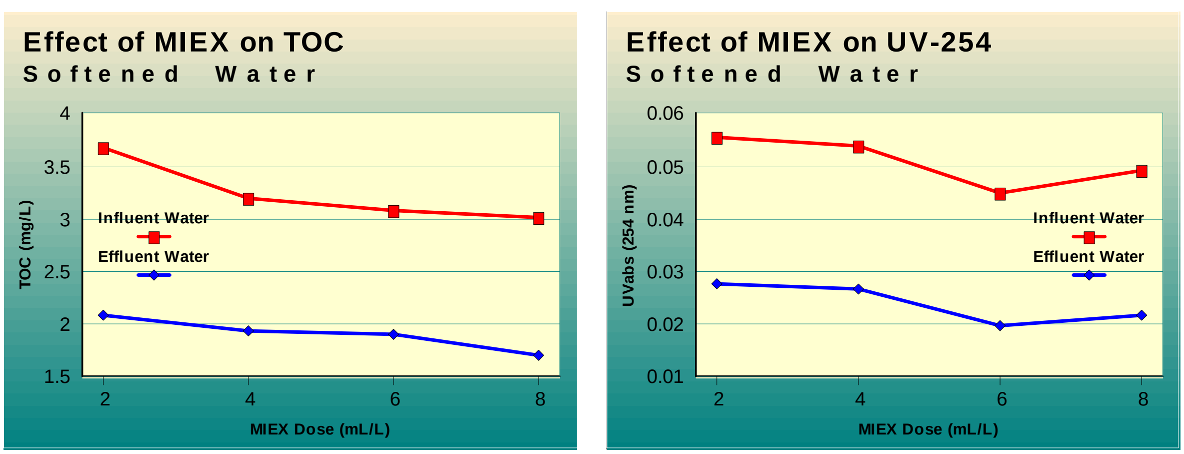

Figure 6: Effect of MIEX® on TOC and UV-254, Softened Water, August 1999

Water Quality Changes

Since the MIEX® resin is an anion exchanger we would expect that it might alter the carbonate/non-carbonate ion balance in the water. For this reason the change in alkalinity resulting from the MIEX® resin addition was monitored during pilot testing for both raw and softened water. Initial and finished alkalinity measurements were made with the raw water and softened water tests.

The results are shown in Figure 6. Slight reductions, <5 mg/l, in alkalinity were consistent with each of the four concentrations of MIEX®. The largest reduction occurred at the 2 ml/l concentration, but this was attributed to experimental error.

However, it was expected that the removal of NOM by the MIEX® resin would alter the chemical requirements for lime softening. The full-scale plant currently uses ferric chloride to "coagulate" the precipitated calcium carbonate and magnesium hydroxide. The dose of ferric chloride required is influenced to some degree by the NOM present in the water and its ability to complex metals, and interferes with the formation of a precipitate that settles well. Several experiments conducted so far to evaluate the impact of the MIEX® treatment on the chemical requirements for softening at SPRWS unfortunately produced inconclusive results.

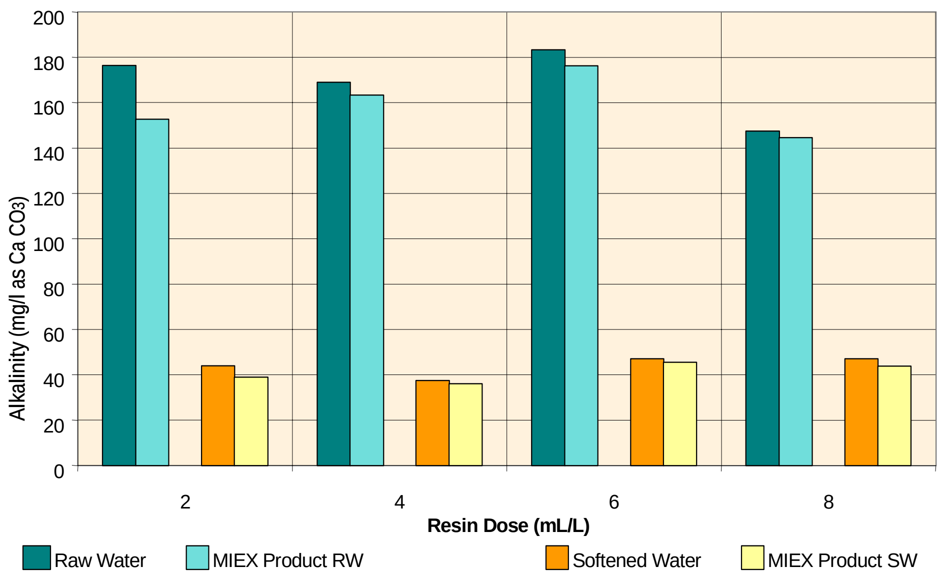

Figure 7: SPWRS Pilot Trial Alkalinity Results, Summer 1999

Regeneration

Mass balance calculations on TOC removal by the MIEX® resin and its recovery in brine during resin regeneration provide an effective and simple means of assessing the long-term performance of the resin or the practical life of the resin. The practical use of the resin in full-scale treatment will largely depend on the regeneration efficiency over time. Mass balances on TOC were performed on the system after steady state conditions were met. The pilot plant was operated at the 6 ml/l dose over a 3-day period to ensure that the whole resin inventory went through one full cycle and the system approached steady state.

The amount of TOC removed by the resin can be calculated simply based on the volume of water treated and the average DOC removal. The mass of TOC released during regeneration is easily calculated by measuring the total volume of regenerant brine and rinse water and the concentration of TOC in this volume. During the 3-day run the pilot plant was operated at 2.1 gpm (7.9 l/min) for 24 hours and the influent TOC of 7.97 was reduced to 3.52 mg/l. The mass of TOC removed was therefore calculated to be 51 g of TOC removed. The resin released 53.5g of TOC during regeneration and rinsing. This corresponds to a recovery of approximately 105%, but given the experimental uncertainty, it indicates that the TOC recovery was complete and the resin was regenerated effectively. This suggests that the MIEX® resin is not suffering from organic fouling and that it should be equally effective following regeneration and well suited to long-term use.

Finally, it is important to highlight the volume of water treated per unit volume of resin. At a resin concentration of 6ml/l and with 90% recycle, the effective resin concentration is 0.6 ml (0.0006 L) settled resin per liter of treated water. Expressed in terms of bed volumes (BV) of water treated per volume of resin regenerated, this would be 1/0.0006 = 1666 BV, i.e. the resin service was 1666 BV. A resin concentration of 2 ml/l with 90% recycle would correspond to a service run of 5000 BV. These numbers are impressive when compared to conventional ion exchange. For example, when Semmens[2] et al. studied the use of conventional ion exchange resins for TOC removal from Mississippi River water, they found that the fixed-bed resins were able to treat only 1630 BV (for a 2.5 mg/l final TOC).

CONCLUSIONS

The process for NOM removal based on the MIEX® resin is shown to be effective in reducing TOC and UVA content of the Saint Paul Regional Water Services source and softened water in continuous flow pilot studies. Even a low resin dosage of 2 ml/l gave dramatic improvements in NOM removal as measured by TOC and UVA. However, removals improved with resin concentration up to about 6 ml/l, which is in agreement with the manufacturer's recommendation. The resin performance dropped 14% during the colder winter months, which could have been the effect of either the colder temperatures or an altered NOM chemistry or both.

Removals of DOC were shown to reduce trihalomethane formation potential even when the free chlorine contact time was five times longer than the current period at the treatment plant.

The resin was regenerated effectively and with a 100% efficiency with just 3 bed volumes of 12% NaCl and appears well suited for long term use in surface water treatment.

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