Evaluation of magnetic ion exchange resin (MIEX®) and alum treatment for formation of disinfection by-products and bacterial regrowth

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Abstract Four treatment options: (a) alum coagulation without pH adjustment; (b) alum coagulation at pH 6; (c) magnetic ion-exchange (MIEX®*) resin; and (d) combined alum/MIEX® treatment, were used to compare the removal of dissolved organic carbon (DOC) and treated water quality, particularly the formation of disinfection by-products and bacterial regrowth potential. Improved DOC removal was achieved with the inclusion of MIEX® treatment in the process. The DOC remaining after each treatment strategy was different in character. The molecular weight distribution results indicated that MIEX® treatment removed a broad range of compounds, whilst alum treatment targetted the removal of high molecular weight compounds. In addition, the DOC remaining after MIEX® treatment consisted of compounds with lower specific UV absorbance (SUVA). Including MIEX® in the treatment stream provided better DOC and bromide removal thus reducing chlorine decay and trihalomethane (THM) formation. The ability of the water to support bacterial growth as measured by bacterial regrowth potential (BRP) was the lowest after MIEX® treatment (option c) compared with the three other treatments (options a, b and d). In summary, laboratory tests show that including MIEX® in the treatment process can improve treated water quality. (*MIEX® is a registered trademark of Orica Australia Pty Ltd)

Keywords Bacterial regrowth potential; chlorine decay; coagulation; MIEX®, natural organic matter; trihalomethane formation

Introduction

In recent years, considerable effort has been made in drinking water treatment to develop methods which improved natural organic matter (NOM) removal from water. Reduction in the level of NOM before disinfection can minimise the formation of disinfection by-products and reduce the disinfectant residual required to control bacterial regrowth in the distribution system. This contributes to higher quality water delivered to consumers.

Conventional water treatment, employing coagulation/flocculation, sedimentation and filtration, has been the most common method for drinking water treatment mainly targetting turbidity and colour removal. With the requirement for higher quality drinking water from health authorities, there is a need to improve current treatment methods. The use of inorganic coagulants such as aluminium or iron-based salts remove only a portion of NOM. Research and development into improving treatment processes is therefore necessary.

The term "enhanced coagulation" refers to the modification of the coagulation process to achieve greater or maximum NOM removal (White *et al*., 1997). Higher doses of coagulant are used and the pH may be controlled during the coagulation/flocculation stage compared with conditions that maximise turbidity removal. The control of pH during coagulation is one of the most important factors controlling NOM removal (Semmens and Field, 1980; Crozes *et al*., 1995). Earlier studies using natural waters from southern Australia have demonstrated that the use of enhanced coagulation (controlled at pH 6) achieved greater removal of dissolved organic carbon (DOC) compared with conventional

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coagulation (without pH control) at the same alum dose (Chow *et al*., 1998; van Leeuwen *et al*., 1999).

When considering other technologies for NOM removal, ion-exchange processes have received significant attention. The MIEX® (magnetic ion exchange resin) process, jointly developed by the Australian Water Quality Centre, Orica Water Care and CSIRO, has been designed specifically for the removal of DOC from drinking water. The very small particle size of the resin (around 150 μm) provides a high surface area allowing rapid adsorption of DOC. The negatively charged DOC is removed by exchanging with chloride ions on active sites on the resin surface. The magnetised component assists in the resin recovery process (Morran *et al*., 1996; Slunjski *et al*., 1999).

The aim of this work was to develop treatment methods for improved NOM removal. Several characterisation techniques were applied to study the organic matter before and after treatment for the identification of the removable and non-removable components of the NOM.

Four treatment options were used in this study: a) alum coagulation without pH adjustment; (b) alum coagulation at pH 6 (pH adjusted to 6 during coagulation); (c) MIEX®; and (d) combined alum and MIEX®. The comparison focussed on the removal of dissolved organic carbon (DOC) and treated water quality, particularly the formation of disinfection by-products and bacterial regrowth potential. The impact on disinfectant stability was determined by monitoring chlorine decay over a period of 72 hours with periodic samples taken for disinfection by-product formation analysis and bacterial regrowth potential (BRP) measurement. The character of the residual organic compounds was examined using specific UV absorbance (SUVA) and high performance size exclusion chromatography (HPSEC) for molecular weight distribution.

Methods

Water sources
Waters were taken from two surface water storages (Hope Valley and Myponga) in South Australia to provide water of different characteristics.

Chemicals
Aluminium sulphate stock solution (20,000 mg/L as $Al_2SO_4 \cdot 18H_2O$) was prepared in Milli-Q® water using liquid aluminium sulphate (approximately 7.5% w/w Al_2O_3) from a local water treatment plant. MIEX® resin was obtained from Orica Australia Pty Ltd. Prior to testing, the MIEX® resin was loaded with NOM from natural waters and regenerated with 2M NaCl to produce resin similar to normal operating conditions. The NaCl was removed by rinsing with Milli-Q® water.

Experimental procedures
For all treatments, a FMS6V (SEM, Brisbane Australia) variable speed, six paddle gang stirrer with 7.6 cm diameter flat paddle impellers and Gator jars was used. The water samples collected from both reservoirs were treated using the treatment options stated below. Samples from treated and raw waters were analysed for DOC, UV absorbance at 254 nm, and molecular weight distribution. Chlorine decay, BRP and THM formation were monitored over 72 hours.

a) Alum coagulation without pH adjustment. Water samples (2 L) were placed on the gang stirrer and alum dosed over a range 20 mg/L–120 mg/L. The alum was added while stirring at 220 rpm and after 1 min. the speed was reduced to 25 rpm for 14 min. Formed floc was allowed to settle for 15 min. prior to gravity filtration through Whatman No.1 filter paper.

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The minimum alum dose that achieved the following treated water quality (turbidity < 0.5 NTU, colour < 10 HU, aluminium < 0.2 mg/L) was selected for comparison with the other treatment strategies.

b) Alum coagulation at pH 6. As above, except a predetermined amount of hydrochloric acid (0.2 M) was added prior to alum to give a coagulation pH of 6. The required alum dose was determined as the point where the exponential curve (residual DOC versus alum dose) began to flatten out. Beyond this dose only small increases in DOC removal were achieved with an increase in alum dose.

c) MIEX®. Water samples (2 L) were placed on the gang stirrer with MIEX® resin added while stirring at 100 rpm. The volume of wet MIEX® resin added was measured using a measuring cylinder. The amount of wet MIEX® resin added was between 2–12 mL/L. Samples were taken at specified time intervals for analysis. The optimum conditions for MIEX® treatment were determined based on the lowest dose and shortest contact time that achieved a 90% reduction of the removable DOC. Removable DOC was defined as the amount of DOC that was removed with the largest dose of resin (12 mL/L) reacted for the longest contact time used (30 minutes).

d) Combined alum coagulation (pH 6) and MIEX® treatment. Treated water from the alum coagulation was further treated with miex® as outlined in the MIEX® treatment. The required treatment conditions were selected as the minimum alum and miex® dose that resulted in achieving 90% decrease in the removable doc.

Analytical methods
All samples were filtered through a 0.45 μm membrane filter prior to simulated distribution system tests and analyses used to characterise the treated waters (except turbidity and aluminium).

Turbidity, colour and aluminium were determined following the methods described in *Standard Methods for the Examination of Water and Wastewater* (1998). DOC concentrations were determined with a total organic carbon analyser (Model 820, Sievers Instruments Inc., USA). UV absorbance at 254 nm was determined using a UV/VIS spectrophotometer (Model 918, GBC, Australia) with a 1 cm quartz cell. The specific UV absorbance (SUVA), UV/DOC × 100, was used to assess NOM.

The apparent molecular weight of the UV absorbing compounds was determined using high performance size exclusion chromatography (HPSEC). A Shodex KW-802.5 packed column (Shoko Co. Ltd., Japan) was used with a Waters 2690 separation module and 996 photodiode array detector. The procedure was based on the method described by Chin *et al*. (1994).

The trihalomethane formation potential (THMFP) is an indicator of the potential for THM formation under extreme conditions. The THMs were formed by reacting a buffered water sample (pH 7.4) at 35°C for 4 hours with an excess of chlorine (approximately 20 mg/L chlorine). The sample was subsequently quenched with ascorbic acid. THM components were determined using a gas chromatograph with a headspace autosampler, coupled with an electron capture detector.

BRP analysis was performed as described by Withers *et al*. (1999). A conversion factor calculated from standard acetate additions, allows the bacterial regrowth potential of a water to be expressed as μg acetate carbon equivalents (ACE) per litre.

Chlorine decay was determined by dosing 3 mg/L of chlorine into 1 litre of treated water stored in an amber bottle. At predetermined times 100 ml samples were taken for chlorine

analysis over a period of 72 hours. For each treatment a sample was incubated at $30 \pm 2°C$ and $10 \pm 2°C$ to represent conditions in summer and winter. Chlorine residual was determined using the DPD-FAS titrimetric method (*Standard Methods for the Treatment of Water and Wastewater*, 1998).

Simulated distribution system trihalomethane (SDSTHM) test was performed by chlorinating 60 mL of treated water at 3 mg/L in an amber bottle. After incubation at the above temperatures for 72 hours the sample was quenched with ascorbic acid and analysed for THMs using the method mentioned above.

Results and disucssion

Removal of NOM

Two reservoir waters: Hope Valley and Myponga, were selected based on the differences in the concentration and character of their NOM.

A comparison of the DOC removal and the character of the raw and treated waters under the selected treatment conditions is presented in Table 1. The relative effectiveness of each treatment for DOC removal was in the following order: combined alum/MIEX® ≅ MIEX® > alum (pH 6) > alum without pH adjustment. For both waters, the DOC concentration remaining after alum coagulation at pH 6 was approximately double that remaining after combined alum/MIEX® (option d) and MIEX® alone (option c). This shows a significant improvement in DOC removal can be achieved by including MIEX® in the treatment process. Using Myponga reservoir water as an example, treating the water with MIEX® resulted in an increase in DOC removal of 33% and 21% relative to alum coagulation without pH adjustment and alum coagulation at pH 6, respectively. MIEX® alone is capable of higher DOC removal than alum, with 2.3 (Hope Valley) and 1.4 (Myponga) times more DOC being removed by MIEX® than coagulation at pH 6. Based on these results there is no significant increase in DOC removal by including alum in the treatment process. However, MIEX® will not remove turbidity, so alum addition or some form of turbidity removal is essential to produce acceptable treated water. Including alum in the process can either lower MIEX® doses or contact times to achieve optimum DOC removal.

All four treatment options removed UV absorbing compounds to a greater extent than DOC. When considering the MIEX® (option c) and alum alone (options a and b) as treatment options, the character of the NOM remaining in the treated water was different. The ability to remove precursors for THM formation for each treatment option can be assessed by expressing the results as THMFP/DOC. Alum treated waters (options a and b) were similar to the raw water. This indicates that alum treatment did not selectively remove the main precursors of THM formation. Lower values for MIEX® treated waters (options c and d) were obtained compared with the raw water indicating that MIEX® treatment has the potential to remove precursors of THM formation.

Additional analysis of Myponga raw and treated waters for bromide showed that incorporating MIEX® into the treatment process removed bromide from the water. Alum alone was ineffective, while MIEX® alone (option c) and in conjunction with alum (option d) removed 61% (460 μg/L → 180 μg/L) and 52% (460 μg/L → 220 μg/L) of the bromide, respectively. These results indicate that bromide removal will depend on MIEX® dose and contact time. Removing bromide before disinfection decreases the formation of bromine substituted THMs.

Figure 1 shows the molecular weight distribution of Hope Valley water treated by the four treatment options. There is a certain degree of overlap of NOM removal between alum and MIEX®. UV absorbing compounds particularly greater than 2000 AMW were favourably removed by alum coagulation (options a and b). In contrast, compounds of the entire molecular weight range were removed by MIEX®, particularly those less than 2000

Table 1 Treatment conditions and water quality results for Hope Valley and Myponga reservoirs

Treatment	DOC (mg/L)	DOC removal (%)	SUVA (m⁻¹mg⁻¹L)	THMFP/DOC (µg/mg)
Hope Valley				
Raw water	5.8		2.4	30
(a) alum without pH adjustment				
30 mg/L alum	4.5	22	1.8	31
(b) alum coagulation at pH 6				
20 mg/L alum (pH 6)	4.2	28	1.8	32
(c) MIEX®				
6 mL/L MIEX® (15 min. contact)	2.1	64	1.2	27
(d) combined 20 mg/L alum (pH 6)/6ml/L MIEX®				
(10 min. contact)	2.1	64	1.2	22
Myponga				
Raw water	10.0		3.5	33
(a) alum without pH adjustment				
55 mg/L alum	5.9	41	2.2	31
(b) alum coagulation at pH 6				
60 mg/L alum (pH 6)	4.7	53	2.1	31
(c) MIEX®				
8 mL/L MIEX® (15 min. contact)	2.6	74	2.1	22
(d) combined 30 mg/L alum (pH 6)/6ml/L MIEX®				
(15 min. contact)	2.4	76	1.4	21

AMW that were not easily removed by alum. Similar trends were observed with Myponga reservoir water.

Combining the processes resulted in a treated water with no UV absorbing compounds >2000 AMW and a significant reduction in those <2000 AMW. After the combined alum/MIEX® treatment the treated waters from both reservoirs were similar in character (Table 1). This shows that similar compounds are present in both waters that are not removed by alum or MIEX®. In addition, the order of treatment had no effect on NOM removal (both concentration and character, results not shown) regardless of whether alum was dosed before or after MIEX®.

Impact of chlorination

Analyses for chlorine decay, THM formation, and BRP over 72 hours were performed to assess the impact of improved DOC removal when MIEX® treatment was included.

Chlorine decay and simulated distribution system THM test. Figure 2(a) shows that the chlorine profiles varied with the treatment strategy. The order of chlorine consumption
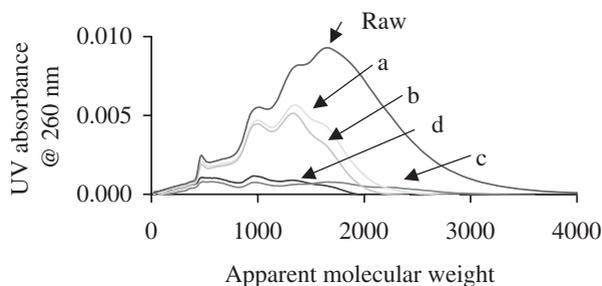

Figure 1 Molecular weight distribution of UV absorbing compounds present in raw and treatment Hope Valley reservoir water: (a) alum coagulation without pH adjustment; (b) alum coagulation at pH 6; (c) MIEX®; and (d) combined alum/MIEX®
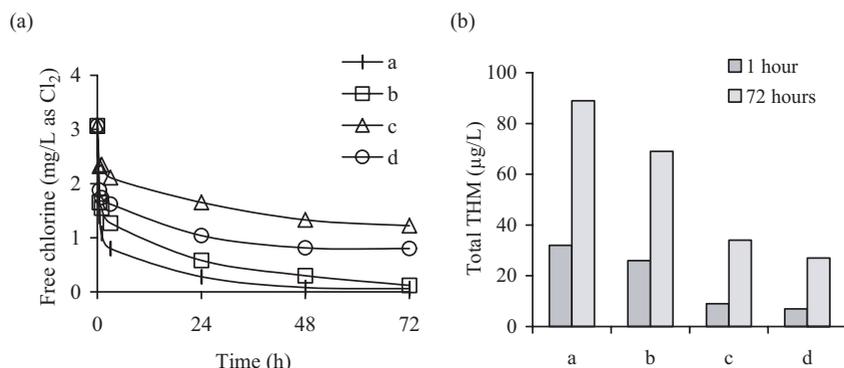
Figure 2 (a) Chlorine decay over a 72 hour period. (b) THM formation at 1 and 72 hours in treated waters. The experiment was performed at 10°C using Hope Valley reservoir water. (a) alum coagulation without pH adjustment; (b) alum coagulation at pH 6; (c) MIEX®; and (d) combined alum/MIEX®

was: alum coagulation without pH adjustment > alum coagulation at pH 6 > combined alum/MIEX® > MIEX®.

The slower chlorine decay for the MIEX® alone compared with the combined alum/MIEX® was likely due to a higher resin dose or longer resin contact time (Table 1). Additional experiments have confirmed the same chlorine decay rate was observed when the same MIEX® treatment conditions were used for both options. The MIEX® process removes the compounds that are more reactive to chlorine and are not removed by alum. Higher resin doses or longer contact times favour the removal of these compounds.

Similar trends were observed at 30°C with the only difference being faster chlorine decay. Incorporating MIEX® into the treatment scheme resulted in slower chlorine decay (reduced chlorine consumption) and lower THM formation. For Hope Valley water after 24 hours at 10°C, the amount of chlorine consumed was reduced with MIEX® and combined alum/MIEX® treatment by 1.0 and 0.5 mg/L, respectively, when compared with alum coagulation at pH 6. The amount of THMs formed after 72 hours was reduced by 35 and 42 µg/L for the above conditions (Figure 2b). Similar results were obtained with Myponga water.

Bacterial regrowth potential. The BRP of the two waters from the four treatment strategies was similar, with no consistent trends apparent for both waters. Although there was some indication that the BRP decreased after MIEX® treatment and increased with further alum treatment. After chlorination, BRP increased for all treatments in both waters. This is a result of larger compounds being oxidised and/or broken down to more assimilable compounds. The higher BRP in Hope Valley water after chlorination compared with Myponga water reflects the differences between the two waters. It appears that both before and after chlorination, MIEX® treated water yielded the lowest BRP. Generally, an increase in BRP occurs when high molecular weight compounds are removed, possibly caused by a release of more assimilable organic compounds previously complexed with high molecular weight compounds. Zhang and Wang (2000) reported the release of organics, which are absorbed and complexed by fulvic acid. This was also evident in this work where the MIEX® (option c) treated waters with a higher proportion of compounds >2000 AMW had a lower BRP than the combined alum/MIEX® (option d). Further investigation is required to understand the relationship between non-removable DOC and BRP.

Conclusions

This study compared four treatment options using water from two local reservoirs: Hope Valley and Myponga. They were selected based on the differences in the level and
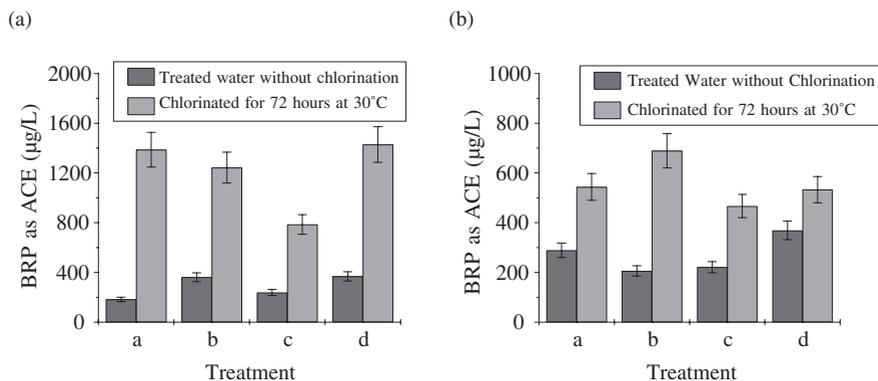
Figure 3 Bacterial regrowth potential: (BRP) expressed as µg acetate equivalents (ACE) per litre of treated and chlorinated waters from: (a) Hope Valley; (b) Myponga treated waters. (a) Alum coagulation without pH adjustment; (b) alum coagulation at pH 6; (c) MIEX®; and (d) combined alum/MIEX®

character of their dissolved organic matter. The results showed that including MIEX® in the treatment stream reduced chlorine decay and THM formation. The DOC remaining after each treatment strategy was different in character; this could be the result of different fractions of NOM being removed. From the HPSEC scans, compounds of higher molecular weight were preferentially removed by alum whilst compounds of broader molecular range were removed by MIEX®. When comparing the results of THMFP per DOC, alum did not selectively remove precursors for THM formation. The reduction in THM formation was due to the reduction of DOC concentration after the treatment. Unlike alum, the THMFP per DOC results showed THM precursors were selectively removed by MIEX®. The reduction in THM formation by incorporating MIEX® into the treatment strategy is due not only to greater NOM removal but also the removal of bromide.

Acknowledgements

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