

LABORATORY STUDY OF CONVENTIONAL ALUM TREATMENT VERSUS MIEX[®] TREATMENT FOR REMOVAL OF NATURAL ORGANIC MATTER

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EXECUTIVE SUMMARY

In recent years, considerable effort has been made in drinking water treatment research to develop methods with 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 residual required to control bacterial regrowth in the distribution system. This contributes to a higher quality water that is delivered to the consumers.

This paper describes a laboratory study using (a) conventional alum treatment (without pH control), (b) enhanced alum treatment (controlled at pH 6), (c) magnetic ion-exchange resin (MIEX[®]) and (d) alum and MIEX[®] combined treatment. 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.

Two reservoir waters, Hope Valley and Myponga, were selected based on the differences in the character of their dissolved organic matter. The SUVA values were $2.4 \text{ m}^{-1}\text{mg}^{-1}\text{L}$ and $3.5 \text{ m}^{-1}\text{mg}^{-1}\text{L}$ for Hope Valley and Myponga, respectively. The higher SUVA values for Myponga water indicate that the DOC is composed largely of aquatic humics and a relatively higher content of hydrophobic and aromatic components.

Removal of DOC under optimised treatment conditions indicated alum and MIEX[®] combined (Option d) was very similar to MIEX[®] alone (Option c) and much better than conventional or enhanced coagulation with alum. Combined treatment (alum and MIEX[®]) removed 2.3 and 1.4 times the DOC removed by enhanced coagulation with alum from Hope Valley and Myponga, respectively. The DOC remaining after each treatment strategy was quite different in character. The HPSEC plots of the treated waters show that with alum treatment (enhanced and conventional) all UV absorbing compounds greater than 2000 AMW were removed. Treatment with MIEX[®] alone resulted in a much greater removal of compounds which were less than 2000 apparent molecular weight (AMW) compared with the alum treatment. However unlike alum treatment there were compounds

greater than 2000 AMW remaining after MIEX[®] treatment. Combining the alum with MIEX[®] resulted in a significant reduction of UV absorbing compounds above and below 2000 AMW. The character of the dissolved organic matter of the treated water was the same regardless of whether MIEX[®] was dosed prior to or after alum.

Including MIEX[®] in the treatment stream reduced the chlorine decay and trihalomethane (THM) formation. Using MIEX[®] alone or combined with alum the amount of chlorine consumed was 50 percent and 80 percent of that obtained with conventional alum treatment (after 60 minutes). The ability of the water to support bacterial growth as measured by BRP was the lowest after MIEX[®] treatment (option c) compared with the three other treatments (Options a, b & d). In summary, laboratory tests show that including MIEX[®] in the treatment process can improve DOC removal, resulting in lower chlorine decay and THM formation.

*MIEX[®] is a registered trademark of Orica Australia Pty Ltd.

KEY WORDS

Natural Organic Matter, Coagulation, MIEX[®], Trihalomethane Formation, Chlorine Decay, Bacterial Regrowth Potential.

INTRODUCTION

Conventional water treatment, employing coagulation/flocculation, sedimentation and filtration, has been the most common method for drinking water treatment mainly targeting turbidity and colour removal. With the requirement for higher quality drinking water from health authorities, there is a need to improve the current treatment methods. The use of inorganic coagulants such as aluminium or iron based salts remove only a portion of natural organic matter (NOM). Research to find better treatment methods is a continuing process.

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 in 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 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 kinetics of DOC. The negatively charged DOC is removed by exchanging with a chloride ion 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. In order to study the treatment process in depth, 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) conventional alum treatment (no pH adjustment), b) enhanced alum treatment (pH adjusted to 6 during coagulation), c) MIEX[®], d) combined enhanced alum coagulation and MIEX[®]. Each of these options was assessed by comparing the character of the NOM remaining after treatment, chlorine decay profiles, simulated distribution system trihalomethane (THM) formation, and bacterial regrowth potential (BRP). These were used to assess whether MIEX[®] alone or combined with alum had any benefits over conventional and enhanced coagulation.

METHODS AND MATERIALS

Water Sources

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

Chemical

Aluminium sulphate stock solution (20000 mg/L) was prepared in Milli-Q[®] water using liquid aluminium sulphate (approximately 7.5% Al₂O₃) 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 simulate used resin. 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 @ 254 nm, colour and molecular weight distribution. Chlorine decay, BRP and THM formation were monitored over 72 hours.

a) Alum (conventional - no pH adjustment)

Water samples (2 L) were placed on the gang stirrer and alum dosed over a range from 20 mg/L to 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. The samples were allowed to settle for 15 min. The treated water samples were collected and filtered under gravity through Whatman No.1 filter papers. The dose used was the minimum dose required to achieve the following treated water quality: turbidity < 0.5 NTU, colour < 10 HU, aluminium < 0.2 mg/L.

b) Alum (enhanced coagulation pH =6)

As for (a) except a predetermined amount of hydrochloric acid (0.2M) 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 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 90 percent

decrease of the removable DOC. Removable DOC was defined as the amount of DOC that was removed with the largest dose of resin reacted for the longest contact time used (30 minutes).

d) Alum (enhanced coagulation pH =6) / MIEX[®] combined treatment

Treated water from (b) was treated with MIEX[®] as outlined in (c). The required treatment conditions were selected as the minimum alum and MIEX[®] dose that resulted in achieving 90 percent 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).

- **Dissolved organic carbon:** Concentrations were determined with a total organic carbon analyser (Model 820, Sievers Instruments Inc., USA).
- **UV absorbance @ 254 nm:** This was determined using a UV/VIS spectrophotometer (Model 918, GBC, Australia) with a 1 cm quartz cell.
- **Apparent molecular weight of the UV absorbing compounds:** This was determined using size exclusion chromatography (SEC). The column was a Shodex KW-802.5 packed column (Shoko Co. Ltd., Japan) and it was performed using a Waters 2690 separation module and 996 photodiode array detector. The procedure was based on the method described by Chin *et al.* (1994).
- **BRP analysis:** 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 acetate carbon equivalents µg/L.
- **Colour:** Colour was determined as described by Bennett and Drikas (1993).
- **Turbidity:** A Hach ratio turbidimeter (Model 2100AN) was used to give a direct reading of the turbidity of a sample in nephelometric turbidity units (NTU).
- **Chlorine Decay:** 1 litre of treated water was chlorinated at 3mg/L in an amber bottle. At predetermined times 100 ml was taken for chlorine analysis for the next 72 hours. For each treatment a sample was incubated at 30 ± 2 °C and 10 ± 2 °C to represent conditions in summer and winter. Chlorine residual was determined using the DPD-FAS titrimetric method (Standard Methods, 1998).
- **Simulated Distribution System Trihalomethane Test:** 60 ml of treated water was chlorinated 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. THM concentrations were determined using a gas chromatograph with a headspace autosampler and volatile compounds were detected by an electron capture detector (ECD).

RESULTS AND DISCUSSION

Removal of NOM

A summary of the treatment conditions chosen for each option is shown in Table 1. The relative effectiveness of each treatment for DOC removal was in the following order:

enhanced coagulation / MIEX[®] \cong MIEX[®] > enhanced coagulation > conventional coagulation. For both waters, the DOC concentration remaining after enhanced coagulation was approximately double that remaining after enhanced coagulation / MIEX[®] (Option d) and MIEX[®] alone (Option c).

Table 1 Treatment conditions for each strategy for Hope Valley and Myponga reservoirs.

Treatment	Treatment conditions	
	Hope Valley	Myponga
a (Conventional)	30 mg/L alum (without pH control)	55 mg/L alum (without pH control)
b (Enhanced)	20 mg/L alum (pH 6)	60 mg/L alum (pH 6)
c (MIEX [®])	6 ml/L MIEX [®] (15 min)	8 ml/L MIEX [®] (15 min)
d (Enhanced / MIEX [®])	20 mg/L alum (pH 6) / 6ml/L MIEX [®] (10 min)	30 mg/L alum (pH 6) / 6ml/L MIEX [®] (15 min)

This shows a significant improvement in DOC removal can be achieved by including MIEX[®] in the treatment process. Table 2 shows the percentage improvement in DOC removal between the various treatment strategies based on DOC data from Table 3. Using Myponga reservoir water as an example, treating the water with MIEX[®] resulted in an increase in DOC removal of 33 percent and 21 percent relative to conventional and enhanced alum coagulation respectively.

Table 2 Comparison of percentage DOC improvement of one treatment strategy over another

Treatment	Hope Valley Reservoir			
	Conventional	Enhanced	MIEX [®]	Enhanced/MIEX [®]
Conventional		6%	42%	42%
Enhanced			36%	36%
MIEX [®]				0%
Treatment	Myponga Reservoir			
	Conventional	Enhanced	MIEX [®]	Enhanced/MIEX [®]
Conventional		12%	33%	35%
Enhanced			21%	23%
MIEX [®]				2%

When considering the MIEX[®] (Option c) and alum alone (Options a & b) as treatment options, the character of the NOM remaining in the treated water was quite different. The NOM remaining after MIEX[®] treatment consisted of compounds with lower SUVA. HPSEC plots (Figure 1) show that alum coagulation (conventional or enhanced) removed all UV absorbing compounds greater than 2000 AMW, while the MIEX[®] removed a range of compounds of all molecular weights, particularly those less than 2000 AMW that were not removed by alum. Figure 1 shows the molecular weight distribution of the waters treated by the four treatment options, there is a certain degree of overlap for NOM removal between alum and MIEX[®]. Both treatments removed UV absorbing compounds to a greater extent than DOC (Table 3). This was prominent in the case of alum treatment. 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[®] over enhanced coagulation. Based on these results there is no significant increase in DOC removal from 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.

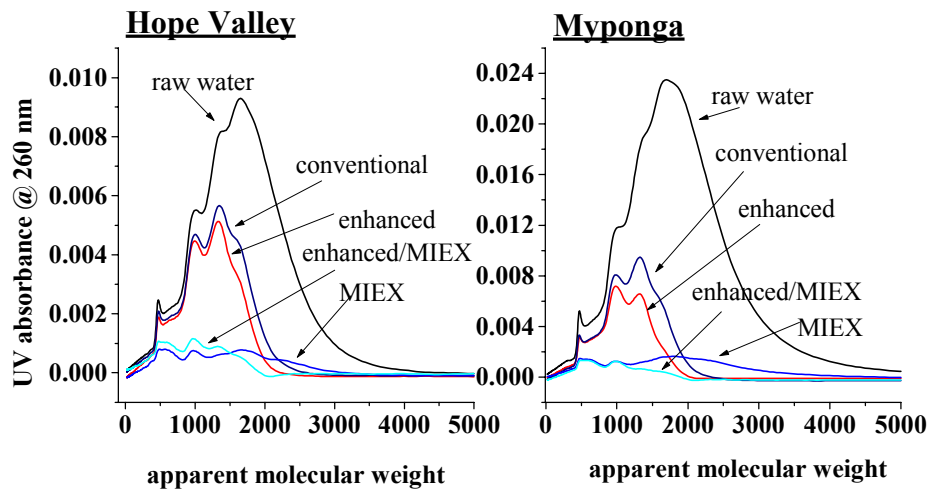


Figure 1 Molecular weight distribution of UV absorbing compounds present in raw and treated waters

Table 3 Character of NOM before and after treatment using different treatment conditions

Treatment	UV abs@254 nm (cm ⁻¹)	UV254nm % removed	DOC (mg/L)	DOC % removed	SUVA (m ⁻¹ mg ⁻¹ L)	Colour (HU)	Colour % removed
Hope Valley Reservoir							
raw water	0.137		5.8		2.4	14	
Conventional	0.082	40	4.5	22	1.8	7	50
Enhanced	0.074	46	4.2	28	1.8	6	57
MIEX [®]	0.025	82	2.1	64	1.2	2	86
Enhanced/MIEX [®]	0.025	82	2.1	64	1.2	2	86
Myponga Reservoir							
raw water	0.346		10.0		3.5	48	
Conventional	0.129	63	5.9	41	2.2	8	83
Enhanced	0.098	72	4.7	53	2.1	4	92
MIEX [®]	0.056	84	2.6	74	2.1	8	83
Enhanced/MIEX [®]	0.034	90	2.4	76	1.4	<1	100

Combining the processes resulted in a product water with no UV absorbing compounds > 2000 AMW and a significant reduction in those < 2000 AMW. After the combined treatment (enhanced / MIEX[®]) the product water from both reservoir waters was of similar character (Table 3). This shows that similar compounds are present in both waters that are not removed by alum or MIEX[®]. The order of treatment had no effect on NOM removal with NOM concentration and character the same after treatment regardless of whether alum was dosed before or after MIEX[®] (results not shown).

Impact of Chlorination

The results shown in the previous section have demonstrated the improvement of DOC removal using the treatment options studied compared with conventional alum treatment. Analyses for chlorine decay, THM formation, and BRP over 72 hours were performed to assess the impact of DOC removal.

Chlorine decay and simulated distribution system THM test

Figure 2 shown that the chlorine profiles of each treated water varied with the treatment strategy. The order of chlorine consumption for the treatments was conventional coagulation > enhanced coagulation > enhanced / MIEX[®] > MIEX[®]. The slower chlorine decay for the MIEX[®] alone compared with the enhanced / 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 removable 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 (Figure 2). Incorporating MIEX[®] into the treatment scheme resulted in slower chlorine decay (reduced chlorine consumption) and lower THM formation. For Myponga water after 24 hours at 10 °C, the amount of chlorine consumed was reduced with MIEX[®] and enhanced coagulation / MIEX[®] treatment by 40 percent and 26 percent respectively, when compared to enhanced coagulation. The amount of THMs formed was reduced by 47 percent and 71 percent for the above conditions. Similar results were obtained with Hope Valley water.

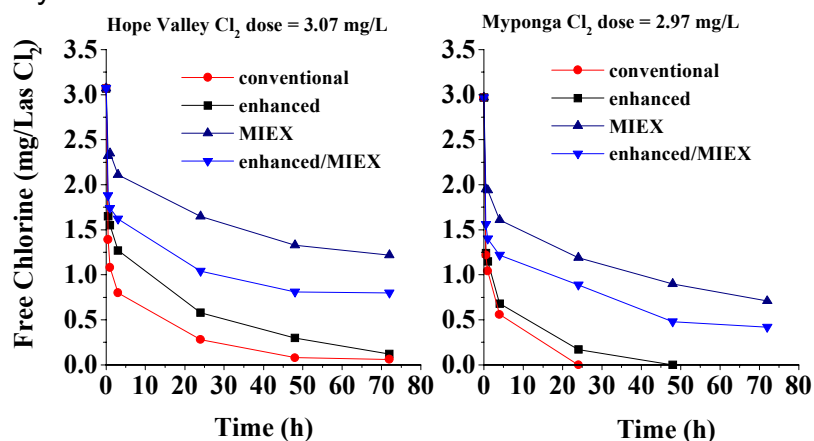


Figure 2 Chlorine decay in treated waters at 10 °C

Bacterial regrowth potential

There was a similar range for BRP of the treated waters from the four treatment strategies prior to chlorination.

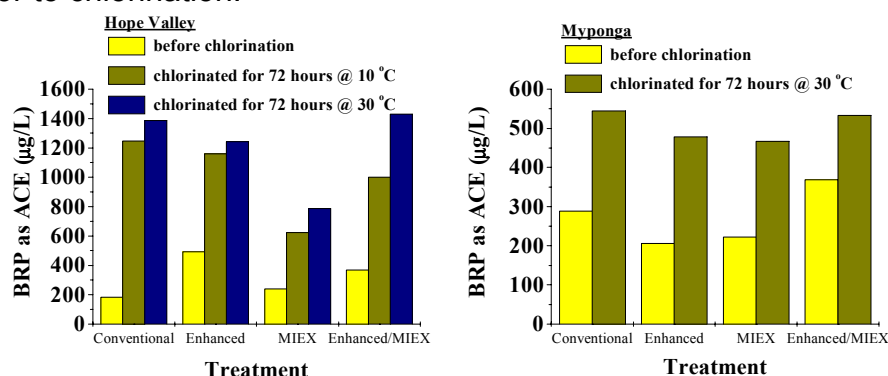


Figure 3 Bacterial regrowth potential (BRP) of treated and chlorinated treated waters.

The values ranged from 180-490 µg/L as acetate carbon equivalents (ACE) for Hope Valley and 200-390 µg/L ACE for Myponga. After chlorination the 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 by chlorine oxidation. An increase in BRP at

30 °C compared with 10 °C is likely due to more chlorine reacting with the NOM at the higher temperature. The higher BRP in Hope Valley water after chlorination compared with Myponga water reflects the differences between the two waters. 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[®] treated waters with a higher proportion of compounds >2000 AMW had a lower BRP than the MIEX[®]/enhanced and conventional treated waters had lower or the same BRP (Myponga) than enhanced coagulation.

CONCLUSIONS

This study showed that for Hope Valley and Myponga reservoir waters, enhanced coagulation improved DOC removal compared with conventional alum treatment at the same alum dose. Adding MIEX[®] to the treatment process either alone or combined with alum improved DOC removal resulting in decreased chlorine decay, lower THM formation and reduced BRP.

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