The impact of recalcitrant organic character on disinfection stability, trihalomethane formation and bacterial regrowth: An evaluation of magnetic ion exchange resin (MIEX®) and alum coagulation

Mary Drikas, Christopher W. K. Chow and David Cook

ABSTRACT

Two South Australian reservoir waters, Hope Valley and Myponga, were selected in this study based on the differences in the character of their organic matter. 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. Removal of DOC under optimised treatment conditions indicated combined alum and MIEX® treatment was very similar to MIEX® alone but much better than conventional and enhanced coagulation with alum. Combined treatment (alum and MIEX®) removed 2.3 and 1.4 times the DOC of enhanced coagulation with alum from Hope Valley and Myponga respectively.

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 targeted 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 & d). In summary, laboratory tests show that including MIEX® in the treatment process can improve treated water quality.

Key words | bacterial regrowth potential, chlorine decay, coagulation, MIEX®, natural organic matter, trihalomethane formation

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INTRODUCTION

In recent years, considerable effort has been made in drinking water treatment to develop methods with greater 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 improved water quality delivered to consumers.

Conventional water treatment, employing coagulation/flocculation, sedimentation and filtration, has been the most common method for drinking water treatment targeting mainly turbidity and colour removal. With the requirement for drinking water quality from

health authorities, there is a need to improve current treatment methods. The use of inorganic coagulants such as aluminium or iron based salts removes 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. The control of pH during coagulation is one of the most important factors controlling NOM removal (Semmens & 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 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®[1] (magnetic ion exchange resin) process, jointly developed by the Australian Water Quality Centre (AWQC), Orica Advanced Water Technologies and Commonwealth Scientific and Industrial Research Organisation (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 evaluate treatment options 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 (recalcitrant) 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 coagu-

lation); (c) MIEX®; (d) combined alum and MIEX®. The comparison focused on the removal of DOC and treated water quality, particularly the formation of disinfection by-products and bacterial regrowth. The impact on disinfectant stability was determined by monitoring chlorine decay over a period of 72 h with periodic samples taken for disinfection by-product formation analysis using trihalomethane (THM) and bacterial regrowth using 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.

EXPERIMENTAL

Water sources

Waters for this study were taken from two storages (Hope Valley and Myponga) in South Australia to provide different raw water characteristics. Hope Valley Reservoir, located approximately 10 km north-east of Adelaide, South Australia, has a holding capacity of 3,470 Ml. This system is further supplied with water from the Murray River. Myponga Reservoir is located about 50 km south of Adelaide and has a holding capacity of 26,800 Ml with 124 km^2 of catchment area. The water in this reservoir generally has higher colour and DOC concentration compared with Hope Valley Reservoir.

Chemicals

Aluminium sulphate stock solution (20,000 mg l^{-1} 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 2 M NaCl to produce resin similar to normal operating conditions. The NaCl was removed by rinsing with Milli-Q® water.

Procedures

For all treatments a FMS6V (SEM, Brisbane, Australia) variable speed, six paddle gang stirrer with 7.6 cm

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

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 h.

Alum coagulation without pH adjustment

Water samples (2 l) were placed on the gang stirrer and alum dosed over a range from 20 mg l^{-1} to 120 mg l^{-1}. 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. The minimum alum dose that achieved the following treated water quality: turbidity <0.5 NTU, colour <10 HU, aluminium <0.2 mg l^{-1} was selected for comparison with the other treatment strategies.

Alum coagulation at pH 6

As for (a) except a predetermined amount of hydrochloric acid (0.2 M) was added prior to alum addition 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.

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 and 12 ml l^{-1}. 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^{-1}) reacted for the longest contact time used (30 min).

Combined alum coagulation (pH 6) and MIEX® treatment

Treated water from (b) was further treated with MIEX® as outlined in (c). The required treatment conditions were selected as the minimum alum and MIEX® dose that resulted in a 90% decrease in the removable DOC.

Analytical methods

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

A Hach ratio turbidimeter (Model 2100AN) was used to give a direct reading of the turbidity of a sample in nephelometric turbidity units (NTU). Colour was determined as described by Bennett & Drikas (1993) and measured using a UV/VIS spectrophotometer (Model 918, GBC, Australia) with a 5 cm cell. Aluminium was determined following the methods described in Standard Methods 3500 (*Standard Methods* 1998). Bromide was determined using ion-chromatography following the USEPA Method 300.1 (USEPA 1997). 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 the character of the NOM. The pH of the samples was measured using a portable WTW pH meter with a combined pH electrode. Calibration was carried out with pH 6.86 and pH 9.18 buffers.

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 carrier solvent was a 0.1 M phosphate buffer

solution (pH 6.80) adjusted to an ionic strength of 0.1 M with sodium chloride. The flow rate was 1 ml min^{-1}. Calibration was performed using polystyrene sulfonate (PSS) standards (Polysciences Inc., Massachusetts) of molecular weights 35,000, 18,000, 8,000 and 4,600. Detection was based on UV absorbance (260 nm cm^{-1}). 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 h with an excess of chlorine (approximately 20 mg l^{-1} 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.

The BRP analysis was performed as described by Withers *et al.* (1999). Samples were collected in glass bottles, stored at 4°C and analysed within 24 h. All glassware was sterile and washed in sodium hydroxide solution. The water sample was filtered through pre-rinsed glass fibre filters to remove large particulate matter. All filters used were pre-rinsed with 1 l of Milli-Q® water to prevent the leaching of DOC into the water samples. An inorganic nutrient salt solution was then added to the water sample in the ratio 1:11, to ensure that assimilable organic carbon was the limiting nutrient. The sample was sterile filtered through pre-rinsed polycarbonate membranes (0.2 μm Poretics). A 250 ml aliquot of sample was placed in the 300 ml cuvette and inoculated with the bacteria, which were washed off the polycarbonate membrane and resuspended in isotonic saline solution. The volume of inoculum was determined by turbidity measurements and the ideal bacterial concentration was between 1×10^4 and 5×10^4 cells ml^{-1}. Each cuvette received the same volume of inoculum. The samples were then incubated at 20°C for a minimum of 72 h with turbidity measurements taken every 30 min. Turbidity was measured at 12° forward scattering. 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^{-1} 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 h. 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 ferrous titration method. N,N-diethyl-p-phenylenediamine (DPD) was used as an indicator in the titration procedure with ferrous ammonium sulfate (FAS) (*Standard Methods* 1998).

Simulated distribution system trihalomethane (SDSTHM) test was performed by chlorinating 60 ml of treated water at 3 mg l^{-1} in an amber bottle. After incubation at the above temperatures for 72 h the sample was quenched with ascorbic acid and analysed for THMs using the method described above.

RESULTS AND DISCUSSION

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 water sample from Hope Valley Reservoir has a lower DOC concentration, UV absorbance and colour compared with the sample from Myponga Reservoir. The SUVA can be used to characterise organic compounds; a SUVA value of 2.4 m^{-1} mg^{-1} l was found for Hope Valley Reservoir sample and a higher value of 3.5 m^{-1} mg^{-1}l was found for the sample from the Myponga Reservoir. The HPSEC analysis using UV detection indicated that the average molecular weight of UV-absorbing compounds present in the water of Hope Valley Reservoir was approximately 1200 Da while that of the Myponga Reservoir was higher (1600 Da). The higher molecular weight and SUVA values for Myponga water suggest that the DOC is composed largely of aquatic humics and a

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

| Treatment	DOC (mg l⁻¹)	DOC removal (%)	UV@254 nm (cm⁻¹)	UV@254 nm removal (%)	SUVA (m⁻¹ mg⁻¹ l)	Colour (HU)	Colour removal (%)	Colour/DOC (HU mg⁻¹ l)
Hope valley								
Raw water	5.8		0.137		2.4	14		2.4
(a) Alum without pH adjustment 30 mg l⁻¹ alum	4.5	22	0.082	40	1.8	7	50	1.6
(b) Alum coagulation at pH 6 20 mg l⁻¹ alum (pH 6)	4.2	28	0.074	46	1.8	6	57	1.4
(c) MIEX® 6 ml l⁻¹ MIEX® (15 min contact)	2.1	64	0.025	82	1.2	2	86	0.9
(d) Combined 20 mg l⁻¹ alum (pH 6)/6 ml l⁻¹ MIEX® (10 min contact)	2.1	64	0.025	82	1.2	2	86	0.9
Myponga								
Raw water	10.0		0.346		3.5	48		4.8
(a) Alum without pH adjustment 55 mg l⁻¹ alum	5.9	41	0.129	63	2.2	8	83	1.4
(b) Alum coagulation at pH 6 60 mg l⁻¹ alum (pH 6)	4.7	53	0.098	72	2.1	4	92	0.9
(c) MIEX® 8 ml l⁻¹ MIEX® (15 min contact)	2.6	74	0.056	84	2.1	8	83	3.1
(d) Combined 30 mg l⁻¹ alum (pH 6)/6 ml l⁻¹ MIEX® (15 min contact)	2.4	76	0.034	90	1.4	< 1	100	< 0.4
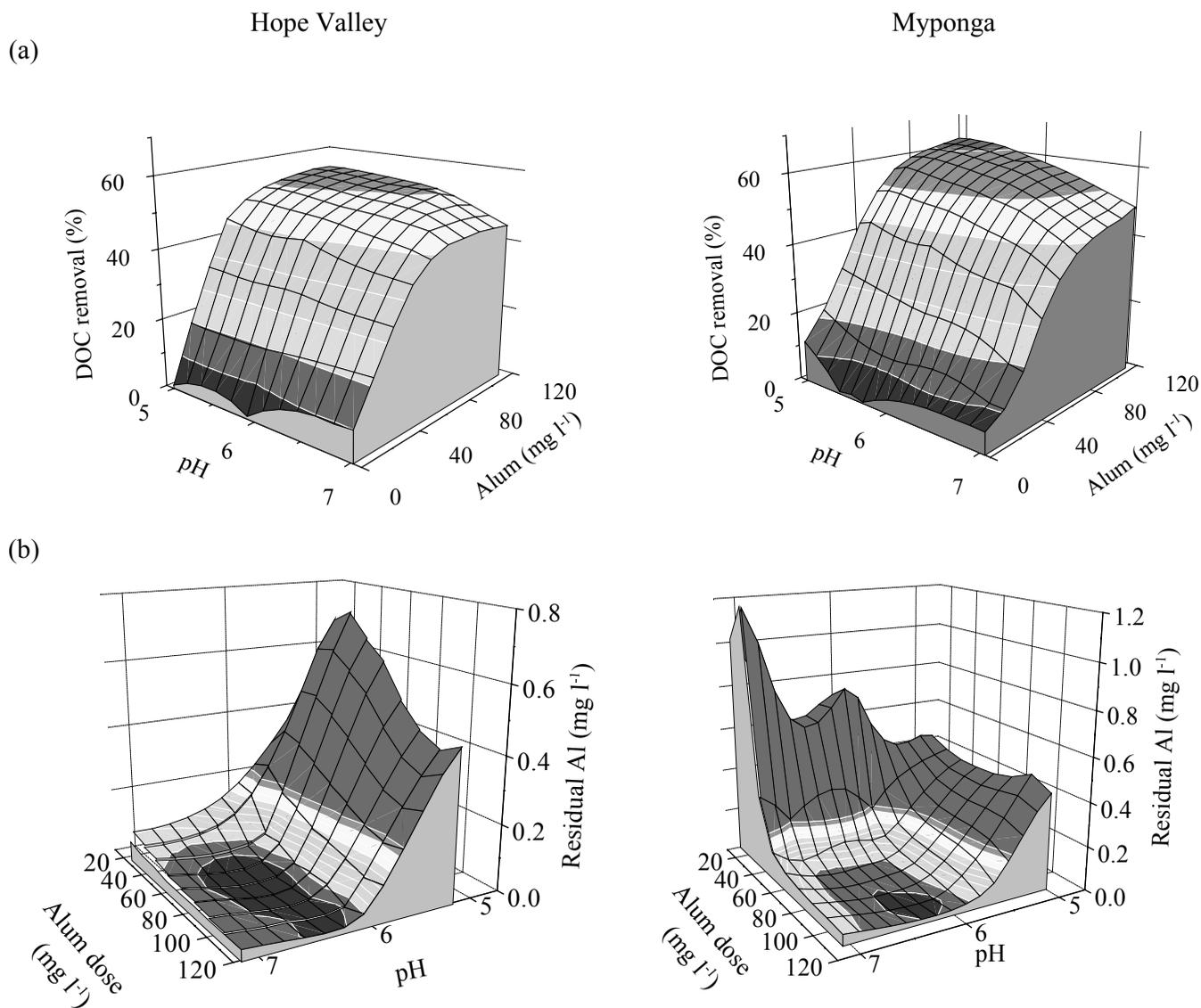
Figure 1 │ The surface plots of the relationship of residual (a) dissolved organic carbon (DOC) and (b) aluminium with pH and alum dose. The 3-D graphs were constructed based on the results of three pH controlled jar tests (pH 5, pH 6 and pH 7) and alum doses of 20, 40, 60, 80, 100 and 120 mg l^{-1} were used for each jar test.

relatively higher content of hydrophobic and aromatic components (Edzwald 1993).

The initial optimisation trial for alum coagulation at controlled pH is shown in Figure 1a. From the dose–response curves of residual DOC concentrations at pH levels ranging from 5 to 7, it was found that the percentage DOC removal increased with the higher alum doses and levelled off at the maximum alum dose applied, particularly at pH 5 and 6. From these curves it was evident that

there were DOC fractions in the waters that were very difficult to remove by this type of treatment. At pH 7, higher concentrations of residual DOC remained even at the higher dosing levels (100–120 mg l^{-1}). Treatment options to reduce the concentration of residual DOC in the water either using much higher alum doses or pH reduction to between 5 and 6 would be necessary. Further reduction in pH below 5 also reduced the efficiency of DOC removal (Chow *et al.* 1998; van Leeuwen *et al.* 1999).
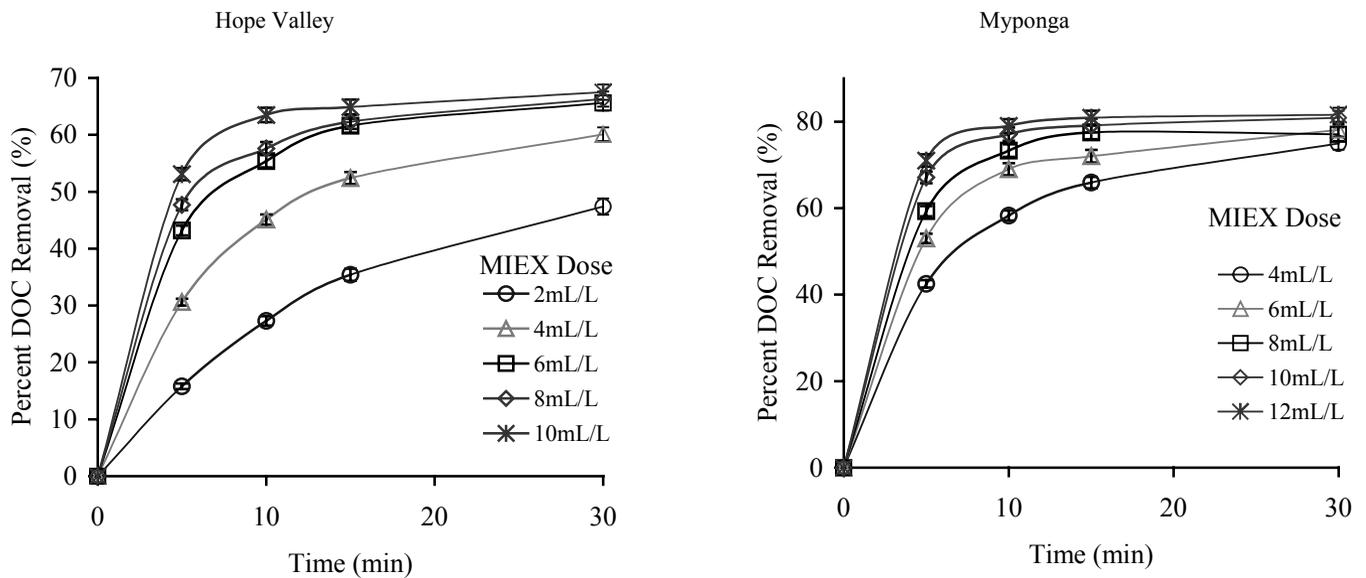
Figure 2 │ Dissolved organic carbon (DOC) removal as a function of contact time with different dose rates for Hope Valley and Myponga reservoirs. Error bars were determined using the standard deviation of the triplicate measurements.

For both waters, maximum DOC removal was found at pH 5.

Residual aluminium concentrations following alum treatment at pH levels ranging between 5 and 7 are shown in Figure 1b. Although maximum NOM removal occurred at pH 5, the residual concentrations of aluminium at that pH exceeded the guideline value of 0.2 mg l^{-1} (colour coded in Figure 1b). Minimum aluminium residuals occurred between pH 6 and 7 for a particular alum dose. Between pH 5.5 and 6 the aluminium concentrations were still below the guideline value. It is worth mentioning that the high aluminium residual in Myponga Reservoir at low alum doses was caused by poor coagulation, a common observation of underdosing of coagulant. For both waters it would appear that treatment at pH values between about 5.5 and 6 would result in a concurrent minimisation of the residual DOC and an acceptable aluminium residual in the treated water.

The optimisation of the MIEX® treatment process requires the determination of both the dose rate and the contact time. Time series percentage DOC removal graphs at various MIEX® dose rates are presented in Figure 2. The optimum conditions for both waters were found to be quite similar with the contact time between 10 and 15 min and

dose rate of 6–8 ml l^{-1}. The maximum DOC removal achieved was approximately 65% and 80% for Hope Valley and Myponga, respectively. In the alum treatment discussed above, the maximum DOC removal for the same batch of water was 50% and 60% for Hope Valley and Myponga, respectively. MIEX® treatment process demonstrated better DOC removal under the experimental conditions.

The treatment conditions were selected based on the criteria described in the procedure section. 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; 2.3 (Hope Valley) and 1.4 (Myponga) times more DOC
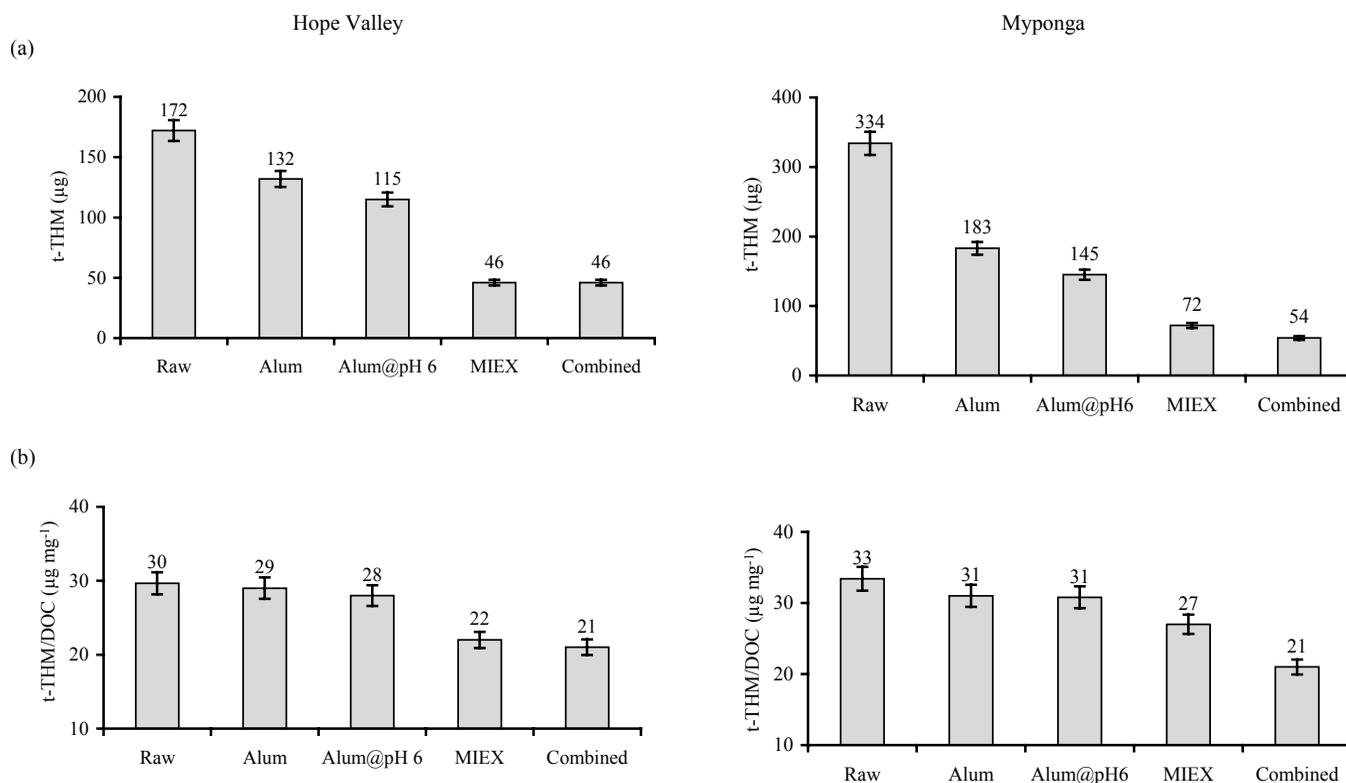
(a)

(b)

Figure 3 │ (a) Total trihalomethane formation potential and (b) total trihalomethane formation potential normalised against dissolved organic carbon concentration in waters after various treatments for Hope Valley and Myponga reservoirs. Error bars were determined using the standard deviation of 5 repeat measurements of the same sample during analytical method validation.

was removed by MIEX® than by 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 lower either 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. All four options reduced THM formation in the treated waters (Figure 3a). The ability to remove precursors for THM formation for each treatment option can be assessed by expressing the results as THMFP/DOC (Figure 3b). 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 for 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 for 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 (c) and in conjunction with alum (d) removed 61% (0.46 mg l^{-1}→0.18 mg l^{-1}) and 52% (0.46 mg l^{-1}→0.22 mg l^{-1}) of the bromide, respectively. These results indicate that bromide removal will depend on MIEX® dose and contact time. Reducing the bromide concentration before disinfection will reduce the formation of brominated THMs and hence total amount of THMs formed (Oliver 1980; Minear & Bird 1980; Amy

Table 2 | The formation potential of the trihalomethane species and bromide incorporation factor (BIF) for Hope Valley and Myponga reservoirs under the selected treatment conditions

Treatment	$CHCl_3$	$CHCl_2Br$	$CHCl_2Br_2$	$CHBr_3$	BIF
Hope Valley					
(a) Alum without pH adjustment 30 mg l⁻¹ alum	44	48	34	6	0.8
(b) Alum coagulation at pH 6 20 mg l⁻¹ alum (pH 6)	33	43	33	6	0.9
(c) MIEX® 6 ml l⁻¹ MIEX® (15 min contact)	17	17	10	2	0.7
(d) Combined 20 mg l⁻¹ alum (pH 6)/6 ml l⁻¹ MIEX® (10 min contact)	18	17	9	2	0.7
Myponga					
(a) Alum without pH adjustment 55 mg l⁻¹ alum	50	72	53	8	0.9
(b) Alum coagulation at pH 6 60 mg l⁻¹ alum (pH 6)	31	57	48	9	1.1
(c) MIEX® 8 ml l⁻¹ MIEX® (15 min contact)	22	30	18	2	0.8
(d) Combined 30 mg l⁻¹ alum (pH 6)/6 ml l⁻¹ MIEX® (15 min contact)	14	22	16	2	0.9

et al. 1991; Krasner *et al.* 1994). The speciation of the THMs after treatment with chlorine was examined by calculating the bromine incorporation factor (BIF) as described by Gould *et al.* (1980). This value will range from 0 to 3; an increase in BIF represents an increase in the formation of brominated THMs with 3 representing 100% bromoform. Table 2 shows the formation potential of the THM species for each of the treated waters. After incorporating MIEX® into the treatment process, the concentration of the brominated THM species was reduced compared with the alum treatment alone.

Figure 4 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 2,000 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 2,000 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 >2,000 AMW and a significant reduction in those <2,000 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 application (MIEX® prior to alum or alum prior to MIEX®) had no effect on NOM removal (both concentration and character; results not shown).

Impact of chlorination

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

Chlorine decay and simulated distribution system THM test

Figure 5 shows that the chlorine profiles varied with the treatment strategy. The order of chlorine consumption was: alum coagulation without pH adjustment>alum coagulation at pH 6>combined alum/MIEX®>MIEX®.
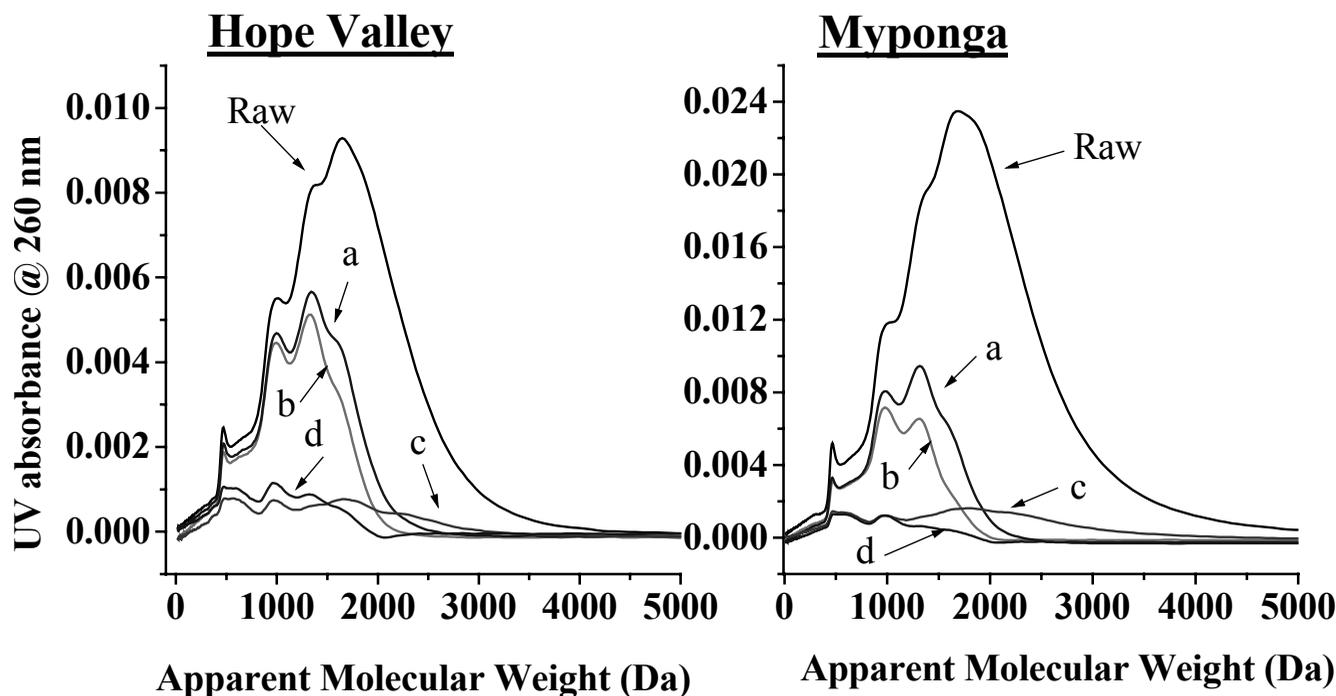
Figure 4 │ Molecular weight distribution of UV-absorbing compounds present in raw and treatment Hope Valley and Myponga waters: (a) alum coagulation without pH adjustment; (b) alum coagulation at pH 6; (c) MIEX®; (d) combined alum/MIEX®.

The slower chlorine decay for the MIEX® alone compared with the combined alum/MIEX® was probably due to a higher resin dose or longer resin contact time used with MIEX® alone (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; the only difference was 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 h 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^{-1}, respectively, when compared with alum coagulation at pH 6. The amount of THMs formed after 72 h was reduced by 35 and 42 μg l^{-1} for the above conditions

(Figure 6). Similar results were obtained with Myponga water (Figures 5 and 6), except a lower total THM value was observed after 72 h for option (a) (alum treatment). However, this was caused by the chlorine level dropping to almost zero in less than 24 h (Figure 5), which limited the THM formation. Based on these results, to maintain a chlorine concentration such as 0.5 mg l^{-1} at the end of the distribution (72 h), the chlorine dose rate can be reduced when including MIEX® as part of the treatment and this can further reduce THM formation.

Bacterial regrowth potential

The BRP of the two waters from the four treatment strategies was similar, with no consistent trends apparent for both waters (Figure 7), 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
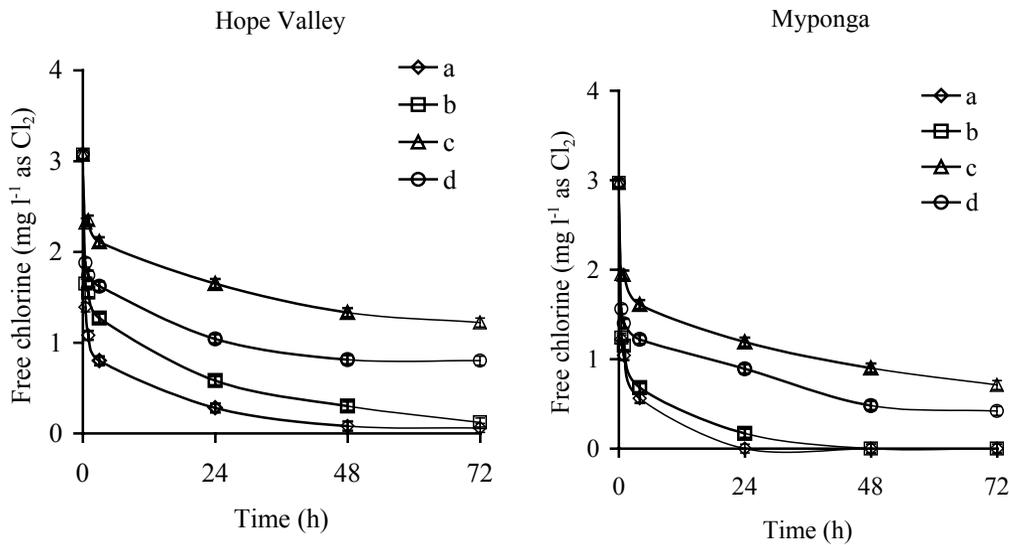
Figure 5 │ Chlorine decay over a 72-h period in treated waters. The experiment was performed at 10°C using Hope Valley and Myponga reservoir water: (a) alum coagulation without pH adjustment; (b) alum coagulation at pH 6; (c) MIEX®; (d) combined alum/MIEX®. Error bars were determined using the standard deviation of the triplicate measurements.

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 is apparent that the organics remaining in the Hope Valley water are of higher apparent molecular weight than those of Myponga (Figure 4) and might be expected to be more susceptible to oxidation to form biodegradable compounds as evidenced by the higher BRP produced.

It appears that both before and after chlorination, MIEX® treated water yielded the lowest BRP. From our past experience, an increase in BRP occurs when high molecular weight compounds are removed. Logically there should be either no change in BRP if the organics are non-biodegradable, or a decrease in BRP if the organics are biodegradable. The observed increase may be caused by removal of higher molecular weight compounds that
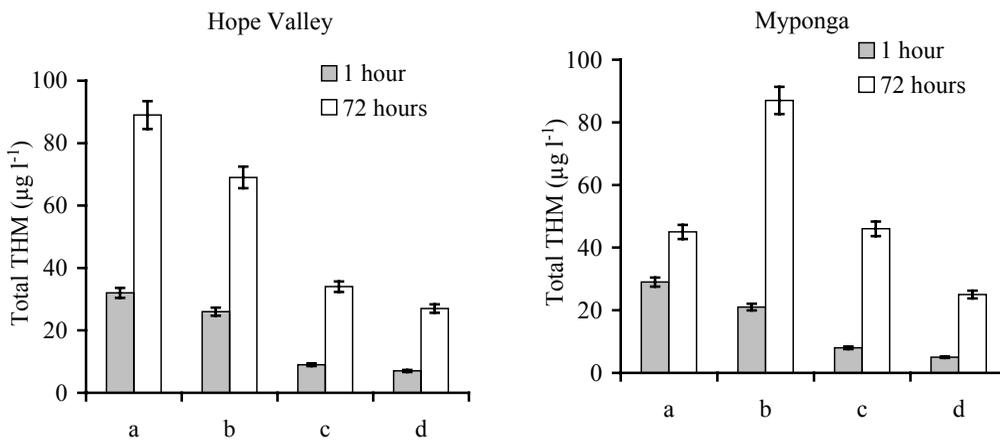

Figure 6 │ Trihalomethane formation at 1 and 72 h in treated waters. The experiment was performed at 10°C using Hope Valley and Myponga reservoir waters: (a) alum coagulation without pH adjustment; (b) alum coagulation at pH 6; (c) MIEX®; (d) combined alum/MIEX®. Error bars were determined using the standard deviation of 5 repeat measurements of the same sample during analytical method validation.
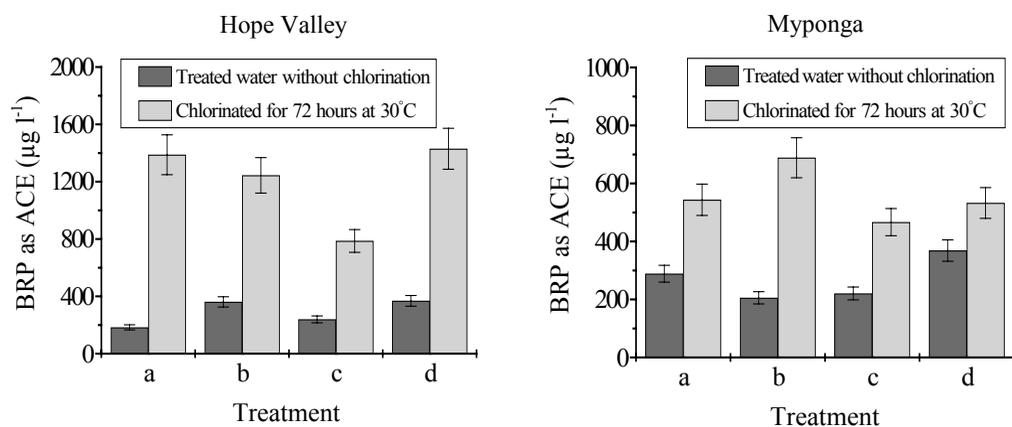
Figure 7 | Bacterial regrowth potential (BRP) expressed as μg acetate equivalents (ACE) per litre of treated and chlorinated Hope Valley and Myponga treated waters: (a) alum coagulation without pH adjustment; (b) alum coagulation at pH 6; (c) MIEX®; (d) combined alum/MIEX®. Error bars were determined from the standard deviation of the duplicate measurements.

are complexed to smaller, more biodegradable components. During the coagulation process when higher molecular weight compounds are removed these bonds are broken making the more biodegradable components accessible to bacteria, resulting in an overall increase in BRP of the water. Zhang & Wang (2000) reported the release of organics after coagulation, which are absorbed and complexed by fulvic acid. In this work the MIEX® (c) treated waters with a higher proportion of compounds >2,000 AMW had a lower BRP than the combined alum/MIEX® (d). This seems to confirm that as MIEX® removes both low and high molecular weight compounds it decreases BRP significantly but then further alum treatment may again release further biodegradable organics resulting in an increase in BRP. Further investigation is required to understand the relationship between recalcitrant 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 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 alum 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 to the removal of bromide.

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