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Assessment of a new combined fractionation technique for characterization of the natural organic matter in the coagulation process

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ABSTRACT

The application of a new combined fractionation technique (CFT) using high performance size exclusion chromatography (HPSEC) and rapid resin fractionation (RRF) for characterization of natural organic matter (NOM) in raw and post-coagulated water samples was assessed. Two natural water samples from Myponga and Hope Valley reservoirs, South Australia, respectively, were selected for this NOM removal by coagulation study. With the use of HPSEC and RRF individually, removal in the low molecular weight (LMW) organic region was observed by comparison of the HPSEC profiles of raw and treated waters and the removal of the hydrophobic organics was observed by comparing the RRF results. A new organic fractionation and characterization technique involving the sequential application of the two techniques, called RRF–HPSEC, was developed to provide additional analytical information particularly to determine the key control factor for the removal of LMW organics. The RRF–HPSEC results showed that good removal of LMW organics could be linked to the presence of high ratio of hydrophobic LMW organics compared with hydrophilic LMW organics. It was revealed, therefore, that the removal of LMW organics was achieved mainly through the reduction of hydrophobic fractions compared with hydrophilic fractions with the corresponding molecular weight.

Keywords: NOM characterization; Coagulation; HPSEC; Rapid resin fractionation; Hydrophobicity; Molecular weight

1. Introduction

Conventional treatment (coagulation/flocculation–sedimentation and filtration) was previously mainly used for removal of turbidity and colour from drinking water. With better understanding of the negative impacts of natural organic matter (NOM) on water quality, the concerns are being focused on NOM removal by coagulation. From the reported investigations, the removal of NOM by coagulation can be related to the organic character such as humic/non-humic, hydrophobicity/hydrophilicity, and the molecular weight of NOM constituents [1,2] and to treatment conditions [3]. Organics in highly coloured waters which are hydrophobic in character and higher in molecular weight can be removed by coagulation more effectively than for

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waters with non-humic character and low molecular weight (LMW) hydrophilic fractions. These are generally considered as non-removable organics and are primarily responsible for regrowth of bacteria and formation of disinfection by-products (DBPs) [1,4,5].

There are various techniques for characterization of organics in source and treated waters with simple to complex application, and with distinct advantages and disadvantages [6]. Simple techniques such as measurement of total organic carbon (TOC), dissolved organic carbon (DOC), UV absorbance at wavelength of 254 nm (UV_{254}) and the use of specific UV absorbance (SUVA), can provide simple but valuable information about NOM character. There is also a range of reported advanced organic characterization techniques including fluorescence [7,8], pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) [6,9–11], Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectroscopy [6,10–13], colloidal titration and the use of ultra-filtration (UF) procedures [14] and gel filtration [15]. Most of these methods have some disadvantages such as the need for sophisticated instrumentation and complex data analysis, considerable sample preparation and high cost.

Among the characterization techniques, high performance size exclusion chromatography (HPSEC) and rapid resin fractionation (RRF), reported by Chow et al. [16] are popular choices for separation of organics based on their molecular weight and hydrophobic/hydrophilic character, respectively. These are reported as specific characteristics of NOM [17,18]. HPSEC is known to be an informative technique for characterization of organics [19–22] that gives more information than traditional techniques on the molecular weight character of NOM in water [23]. It has been widely used for determination of molecular weights of organics [24] for the purpose of comparison of NOM before and after drinking water treatment [25–27], prediction of treatability [22,28] and optimization of treatment processes [29]. The RRF technique has been used in many investigations [30–33] for separation of organics into hydrophobic and hydrophilic fractions. The simplicity of RRF and its readily understandable results, its requirement of only a low volume water sample and the short time of the separation procedure of the organic fractions [16] are some of the advantages of this technique over others. Most of the fractionation methods—resin adsorption (RA), UF, HPSEC—were applied individually in previously reported investigations; and the influences of hydrophobicity and MW were rarely examined simultaneously. It became apparent that character and behaviour of NOM could not be revealed completely by using only one of the individual characterization methods. Therefore, in this study, a new combined fractionation technique (CFT) for characterization of NOM, referred to RRF–HPSEC, was developed and assessed. This new technique is used to study the removal of organics, especially LMW organics, by coagulation using two natural waters with different organic contents.

2. Materials and methodology

2.1. Water sources

Raw water samples were taken from Hope Valley and Myponga Reservoirs. Hope Valley, (3470 ML capacity) is located approximately 10 km north-east of Adelaide, South Australia. It is fed from two other reservoirs, Millbrook (16,500 ML) and Kangaroo Creek (19,000 ML) which in turn are supplied from the Murray River. Myponga Reservoir, with a capacity of 26,800 ML is located about 50 km south of Adelaide. It is the only natural catchment in South Australia that has not been supplied with any water from the Murray River.

2.2. Coagulant

Aluminium sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) or alum stock solution (20,000 mg/L) was used as a coagulant for jar testing. It was prepared by diluting 40.54 g liquid aluminium sulphate (approximately 7.55% w/w Al_2O_3 and 49.33% as $Al_2(SO_4)_3 \cdot 18H_2O$) obtained from a local water treatment plant in 1 L ultrapure water (Milli-Q water).

2.3. Jar testing

A variable speed PB-900™ programmable laboratory jar tester with a six paddle gang stirrer using 76 mm [3.0 in.] diameter flat paddle impellers, and Gator jars (B-KER^2, Phipps & Bird, USA) was used for this study. The jar tester can test six samples at a time. The water samples (2 L) were flash mixed at 200 rpm for 1 min, followed by 14 min slow mixing at 20 rpm. The samples were then allowed to settle for 15 min. The settled samples were gravity filtered through 11 μm pore size paper filters (Whatman International, UK) to simulate rapid sand filtration. This procedure has been used previously and quite effective in comparing treatment performance in the laboratory [25–27,30], Alum dose ranges of 15–90 mg/L and 50–180 mg/L were selected for Hope Valley and Myponga water samples, respectively. The dose range selection was based on our previous experience on the water sources and the pH of flocculation was controlled at 6 (optimum pH for removal of organics by alum).

2.4. Analyses and organic characterization techniques

The following parameters were measured for this investigation: true colour [34], UV_{254}, DOC, turbidity, alkalinity [35] and SUVA as the ratio of UV_{254}/DOC. The HPSEC method reported by Chow et al. [36] was used to determine the size distribution of organic compounds in the waters based on the UV absorption. The RRF technique was used for separation of different character fractions of organic matter: very hydrophobic acid (VHA), slightly hydrophobic acid (SHA), hydrophilic charged (CHA) and hydrophilic neutral (NEU) [16]. The concentration of each fraction of NOM separated by rapid fractionation was calculated based on the subtraction of DOC concentration of the influent and effluent of each column [16]:

- VHA = Raw – (DAX-8 effluent)
- SHA = (DAX-8 effluent) – (XAD-4 effluent)
- CHA = (XAD-4 effluent) – (IRA-958 effluent)
- NEU = (IRA-958 effluent)

The RRF–HPSEC organic characterization technique was based upon combination of the two organic characterization techniques, HPSEC and RRF. From this combination, molecular weight distributions of chemical character categories: VHA, SHA, CHA and NEU can be obtained. The new organic characterization technique was applied based on a similar subtraction approach to that above. The HPSEC profiles of both water samples before and after contact with each resin were determined and subtracted. By this approach, the molecular weight distribution of each fraction of organic matter was obtained.

In Fig. 1 the application of the RRF–HPSEC technique for determination of molecular weight distributions of fractionated organics (VHA, SHA, CHA and NEU) in the Myponga raw water sample are presented. Molecular weight distributions of organic fractions adsorbed to resins (VHA, SHA and CHA) were achieved using Excel software by subtracting point to point the UV_{260} values of samples after contact with resins from the ones prior to contact with resins. The UV_{260} values of the adsorbed sample were related to the apparent molecular weights of organics (Dalton).

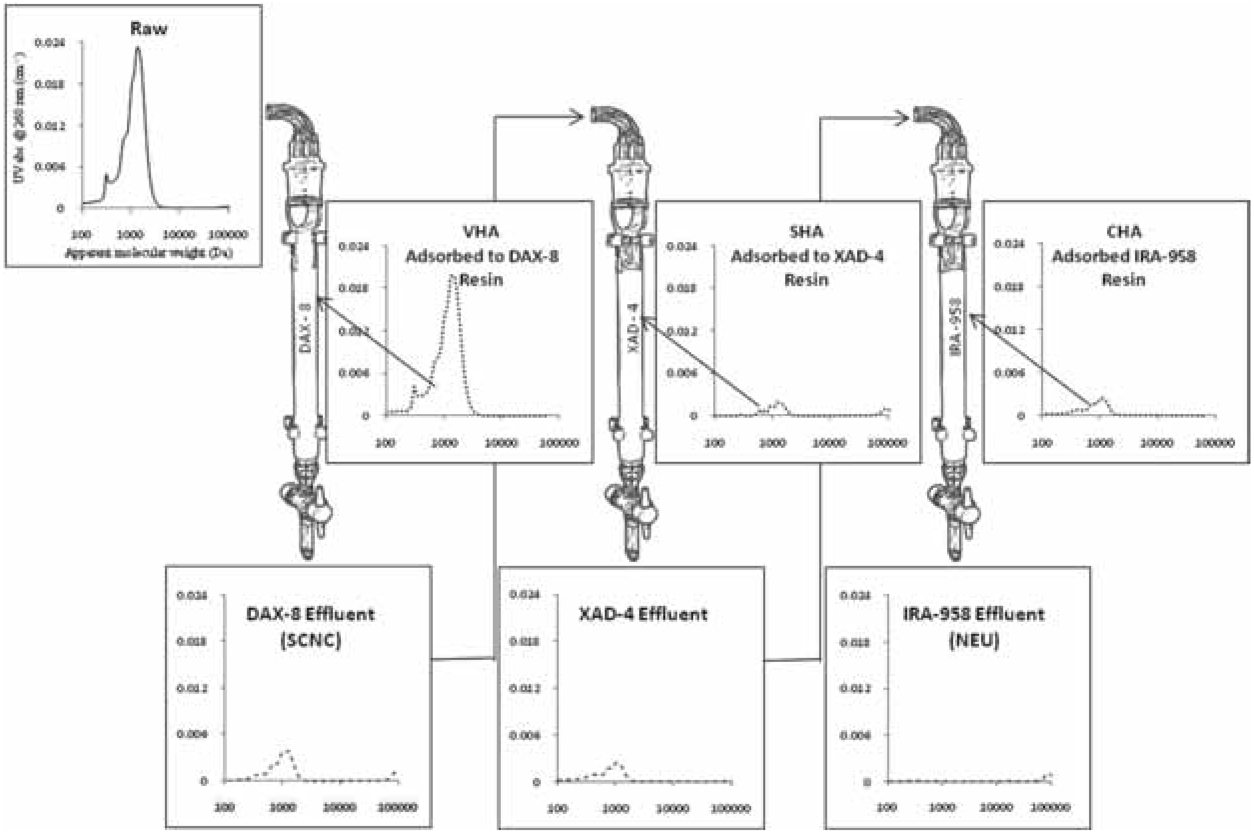

Fig. 1. Sequential steps in measurement of molecular weight distributions of fractionated organics in Myponga raw water, adsorbed by resins and before and after contact with resins.

3. Results and discussion

3.1. Water quality parameters of raw and post-coagulated waters

General water quality parameters, DOC, UV_{254}, true colour, alkalinity and turbidity of Hope Valley and Myponga raw (collected in October 2009 and April 2009, respectively) and treated water samples are presented in Table 1. The reason for selection of these water samples was related to their similarity of organic character which was shown by similar SUVA values. Considering the typically comparable organic character of Hope Valley and Myponga waters and double the concentration of organics in Myponga (Table 1), two jar test doses were selected for detailed comparison of organic removals in the Hope Valley water based on half of the doses selected for the Myponga water. The first dose was selected based on the criteria of reduction of treated water turbidity to less than 0.2 NTU and colour to less than 10 HU and the second dose was selected so that the DOC removal (mg) per alum (mg) was less than 5% (0.05 mg DOC/mg alum). Based on these criteria, 50 mg/L and 180 mg/L alum were selected for the Myponga water sample and 25 mg/L and 90 mg/L alum for the Hope Valley water sample.

For Hope Valley Reservoir water, the DOC removal increased from 47% to 57% and for Myponga Reservoir water, it increased from 41% to 62% with increased doses (Table 1). The selected doses resulted in removal of UV_{254} in the range of 60–75% for both water samples. High percentages of turbidity (more than 90%) were removed by applying selected doses of alum to these water samples followed by filtration (Whatman No. 1) (Table 1). Considering the percentage of DOC removed relative to the ratio of DOC removed per mg of alum used (Fig. 2), higher DOC removal for Myponga was obtained compared to Hope Valley when higher doses of alum were applied. The amount is higher for Hope Valley compared to Myponga at lower doses. This comparison is considered as an informative way to compare the effectiveness of coagulation for removal of NOM from waters with various initial DOC concentrations and the character of the organics.

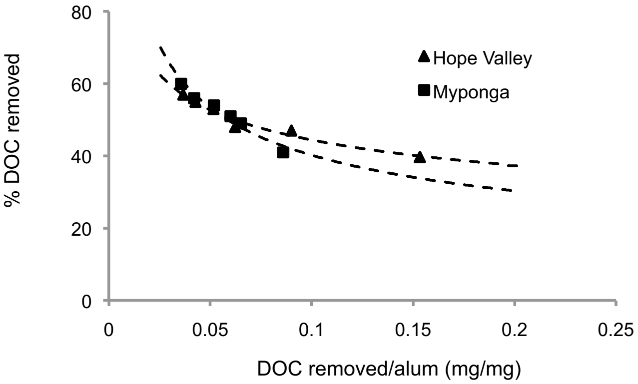

Fig. 2. Percentage DOC removed in post-coagulated water samples from Hope Valley and Myponga Reservoirs against DOC removed per consumed alum (mg/mg).

Physical and chemical characters of NOM defined by molecular weight and hydrophobicity of the organic matter were determined using the HPSEC and RRF techniques, respectively. HPSEC results for both Hope Valley and Myponga raw water samples (Fig. 3(a) and (b)) indicate the similarity of organic character in both waters. The overall shapes of their HPSEC profiles are similar, although the values for UV_{260} in Hope Valley are almost half those in Myponga. Characterization of organics by HPSEC on raw and treated water samples is presented in Fig. 3, which shows that in both the Hope Valley and Myponga water samples not only high molecular weight (HMW) components but also LMW

Table 1
Summary of water quality parameters related to raw and treated Hope Valley and Myponga water samples.

	Hope Valley					Myponga				
alum dose (mg/L)	0	25	90	% Removed		0	50	180	% Removed	
				25	90				50	180
Parameters										
DOC (mg/L)	5.8	3.1	2.5	47%	57%	10.6	6.3	4.2	41%	60%
UV abs @ 254nm (cm^{-1})	0.163	0.053	0.041	67%	75%	0.306	0.121	0.073	60%	76%
True colour (HU)	21	4	3	81%	86%	28	8	5	71%	82%
Turbidity (NTU)	2.5	0.14	0.2	94%	92%	2.07	0.16	0.19	92%	91%
SUVA (L mg^{-1} m^{-1})	2.8	1.7	1.6			2.9	1.9	1.7		
Alkalinity as mg/L $CaCO_3$	80					57				

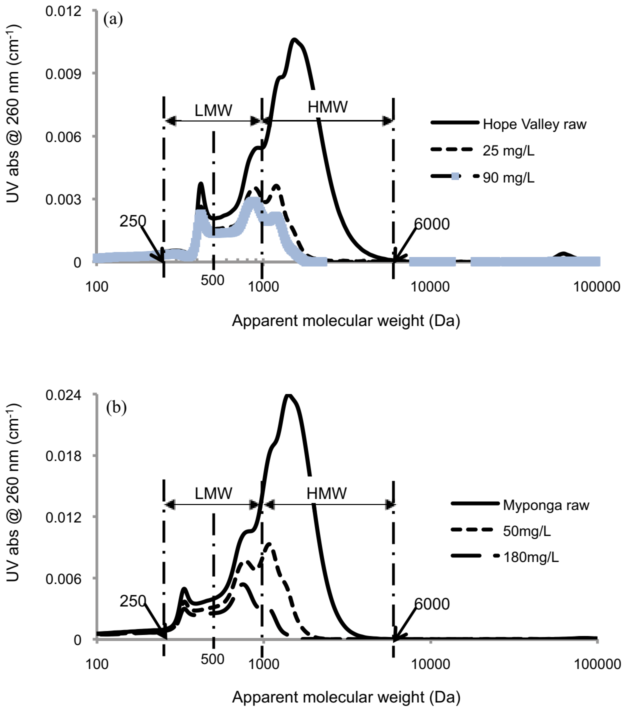

Fig. 3. Molecular weight distributions of organics present in raw and alum treated water samples (a) Hope Valley Reservoir (b) Myponga Reservoir.

organics (?1000 Daltons) can be removed by coagulation (Fig. 3). The removability of LMW organics by coagulation was unexpected from earlier reports [2,5].

The molecular weight of organics in Hope Valley and Myponga Reservoirs waters was distributed in the range from 250 Daltons to around 6000 Daltons. The LMW organics were studied in two ranges of 250–500 Daltons and 500–1000 Daltons which cover the first and the second peaks in the molecular weight distribution. These two ranges are shown in Fig. 3 between two vertical lines. The organics in the range of 1000–6000 Daltons in molecular weight were considered as HMW organics [36,37].

To compare the removal of LMW and HMW organics, the relevant area under the HPSEC profiles of raw and treated waters was calculated. Around the first peak (250–500 Daltons), 26% and 21% of organics was removed from Hope Valley and Myponga waters, respectively, by applying 25 mg/L and 50 mg/L alum. Applying 90 mg/L and 180 mg/L alum resulted in increasing these amounts to 36% and 34%, respectively. In the molecular weight range of 500–1000 Daltons, 33% and 45% of organics in Hope Valley Reservoir water which are considered as LMW were removed by applying the first and second dose, respectively. The removals for Myponga water were 32% and 58%, respectively. Overall, more than 50% of LMW (<1000 Daltons) organics were removed in both water samples. Therefore, the reduction of LMW organics by coagulation was confirmed. As expected removal of HMW organics (1000–6000 Daltons) was very efficient with coagulation. More than 85% and 95% of HMW organics were removed, respectively. The percentage removal results are presented in Table 2 for further comparison with the results of the RRF–HPSEC technique.

The chemical character of Hope Valley and Myponga raw water and treated water after coagulation was obtained by applying the RRF technique (Fig. 4). Although the DOC concentrations of the four categories of fractionated organics were different, the relative abundances of these fractions (VHA, SHA, CHA and NEU) were similar in both water samples. This confirmed the similar organic character of both water sources. The RRF results of treated water samples indicate that

Table 2
The area under HPSEC graphs of raw and treated waters from Hope Valley and Myponga reservoirs waters with two alum doses in three ranges of molecular weights. The percentage removal results determined from the original HPSEC are presented in brackets for comparison.

		Hope Valley			Myponga		
	MW range (Da)	250–500	500–1000	1000–6000	250–500	500–1000	1000–6000
Raw	% Hydrophobic	87	88	96	78	76	90
Hope Valley: 25 mg/L alum Myponga: 50 mg/L alum	% Hydrophobic removed	26(26)	59(33)	97(88)	46(21)	47(32)	88(85)
Hope Valley: 90 mg/L alum Myponga: 180 mg/L alum	% Hydrophobic removed	36(36)	72(45)	99(95)	41(34)	59(58)	97(97)

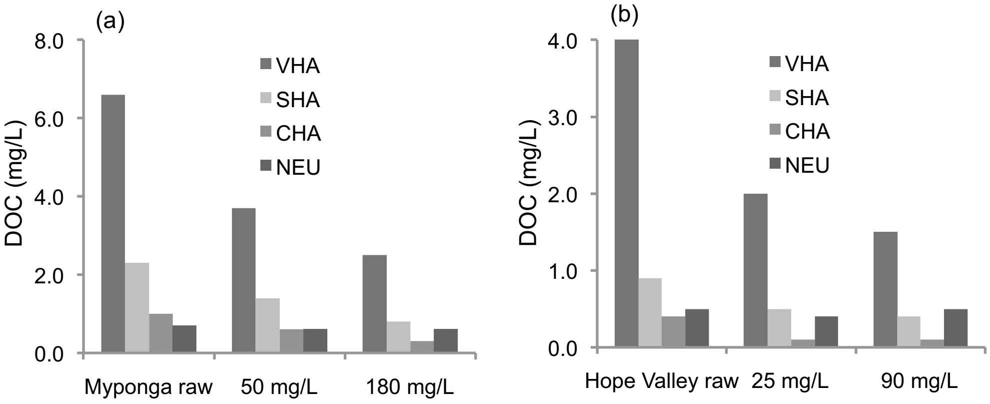

Fig. 4. Percentage DOC concentrations of fractionated organics in raw and treated (a) Hope Valley and (b) Myponga water samples.

the removal of organics happened through reduction of hydrophobic fractions mostly VHA which resulted in increase in the proportion of NEU fractions in treated water samples (Fig. 4).

The use of HPSEC and RRF techniques separately cannot provide a full understanding of the removal behaviour of LMW organics by coagulation. Therefore, this new organic characterization technique, RRF–HPSEC was developed to provide a wider range of information about the organic character of waters and specifically that of LMW organics. The RRF–HPSEC technique was applied to the Hope Valley and Myponga Reservoirs waters. Data on molecular weight distributions of VHA, SHA, CHA and NEU fractions of these water samples are presented in Fig. 5(a) and (b). The results show that the highest proportion of the organics in the raw water samples consisted of the VHA fraction and detection of UV_{260} absorbing compounds in SHA, CHA and NEU fractions was very low. This correlates with the results from RRF analyses and the DOC concentrations of each fraction (Fig. 4), where the relative abundance of the VHA fraction in the water samples was higher than those for the other fractions.

For better assessment of the molecular weight distributions of the fractionated organics and consideration of the low UV_{260} absorbance values detected for some fractions, the four graphs of VHA, SHA, CHA and NEU were reduced to two or less by mathematically combining some fractions. The graphs of the VHA and SHA, and CHA and NEU could be combined and their molecular weight distributions are presented in Fig. 5(c) and (d). The procedure of mathematically combining these graphs is similar to the subtraction approach described earlier. In this RFF–HPSEC and RRF technique, VHA and SHA were the organic fractions absorbed onto the first (DAX-8) and second (XAD-4) separation columns, respectively. Therefore, the combination of VHA and SHA should be achieved by deploying the first two columns of RRF.

The HPSEC results of VHA + SHA and CHA + NEU fractions presented in Fig. 5(c) and (d) show that the UV_{260} absorbance for the CHA + NEU fraction is still low. The highest portion of fractions of all water samples tested was of the VHA + SHA fractions. Considering that VHA + SHA fractions are the major organic fractions detected and combining these resulted in very similar molecular weight distributions to the raw water samples, another form of presenting the HPSEC results was required.

A further alternative method of presenting the molecular weight distributions of fractionated organics is based on two graphs, that of VHA (hydrophobic) and that of the combination of the three other fractions (SHA, CHA and NEU combined) referred to as collectively SCNC (hydrophilic). The results of applying the RRF–HPSEC technique for the raw water samples are shown in Fig. 5(e) and (f). These data were obtained by summation of SHA, CHA and NEU data together and using only the first column (DAX-8) of the RRF technique. The results of RRF–HPSEC for the VHA (hydrophobic) fraction were calculated based on the subtraction of the molecular weight distribution of the first column effluent from the raw water. The RRF–HPSEC result for the SCNC fraction is the molecular weight distribution of the DAX-8 effluent (Fig. 1).

3.2. Application of RRF–HPSEC to assess LMW organics removability by coagulation

The molecular weight distributions of fractionated NOM (VHA and SCNC) in both the Hope Valley and Myponga raw water samples, obtained by applying the RRF–HPSEC technique, are presented in Fig. 5(e) and (f). By applying RRF–HPSEC, the character of organics and specifically LMW NOM in both water samples

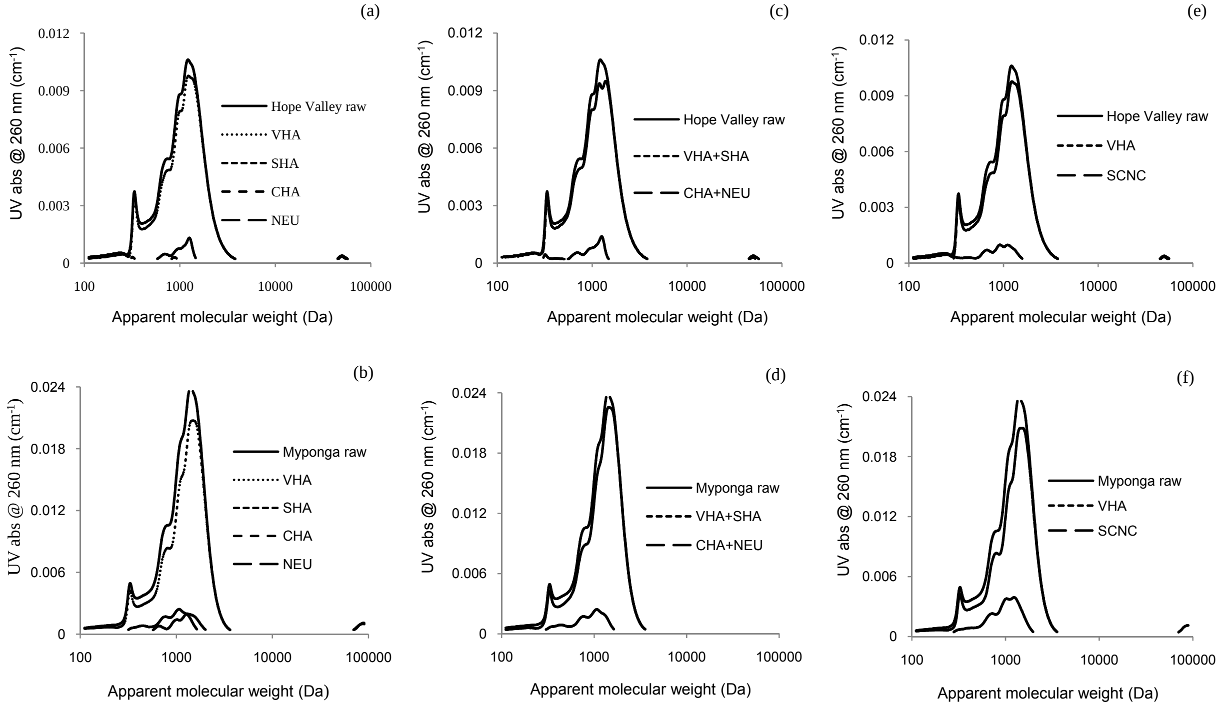

Fig. 5. Molecular weight distributions of fractionated organics present in raw Hope Valley Reservoir and Myponga Reservoir water samples.

could be studied. A significant part of the LMW fraction of each water samples was found to consist of hydrophobic organics (Fig. 5). For LMW organics in the range of 250–1000 Daltons, the removed fractions may also be hydrophobic and the removability of LMW parts of NOM in the Hope Valley and Myponga water samples may be attributed primarily to their hydrophobicity.

The impact of coagulation on removal of VHA (hydrophobic) and hydrophilic fractions of organics was also investigated by applying the RRF–HPSEC technique. The RRF–HPSEC results relating to treated water samples not only show the molecular weight distribution of various organic fractions of the NOM, but also directly show the removal behaviours of the molecular weight fractions under different doses of alum, especially the removal of LMW organics. The removal of LMW organics mostly happened through reduction of the VHA (hydrophobic) fractions (Fig. 6) compared

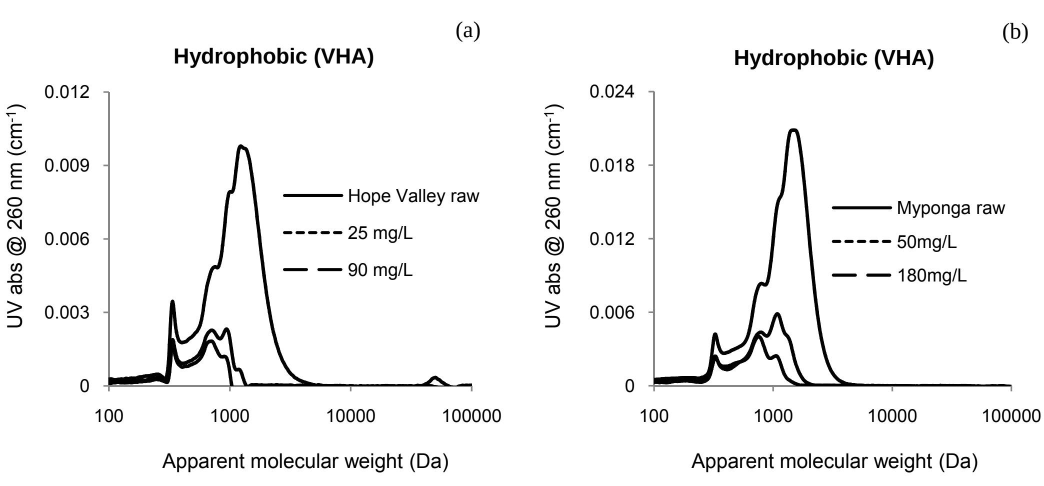

Fig. 6. Molecular weight distributions of VHA (hydrophobic) fraction of organics present in raw and alum treated (a) Hope Valley Reservoir and (b) Myponga Reservoir water samples.

to the hydrophilic fraction of organics. This was confirmed by calculation of the area under the graphs of the molecular weight distribution of the hydrophobic and hydrophilic fractions of treated organics in the ranges of 250–500, 500–1000 and 1000–6000 Daltons. These were compared with those of the raw waters. The results presented in Table 2 indicate that in the LMW region, the removal of organics happened through reduction of the hydrophobic fraction without significant removal of the hydrophilic fractions. The results also show that not all LMW hydrophobic organics can be removed by coagulation. When compared with the percentage removal results from the original HPSEC (discussed earlier), higher percentage removal of the hydrophobic compounds was observed.

4. Conclusion

This work described the use of the combined RRF–HPSEC technique to further characterize the removal behaviour of NOM. This combined technique has the benefit of providing information of the two key characters, hydrophobicity/hydrophicity and molecular size, of NOM with only minor alteration of the procedures by including an extra HPSEC run after each RRF step. The slight increase in the overall analytical cost is relatively minor in considering the additional information obtained compared with other more expensive organic characterization techniques. It was found that the LMW organics from the selected water sources showed a particular removability when the HPSEC profiles of the selected waters (Hope Valley and Myponga) were compared. Separate application of RRF or HPSEC technique cannot completely explain the reason for the removal of LMW organics from both these waters. The new combined fractionation and characterization technique (RRF–HPSEC) was then applied to reveal the reason, and the relative importance of hydrophobicity/hydrophilicity versus HMW/LMW fraction in terms of NOM removal by coagulation was assessed. It was revealed that the removable LMW organics from both selected waters are more hydrophobic in character than hydrophilic. Hence the determinative factor is based on the chemical character of NOM of the water sources. The LMW organics are generally considered as a non-removable fraction, but in this case, if the organics are hydrophobic, they can be removed, so that the chemical character of the organics is more determinative than physical character.

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