A rapid fractionation technique to characterise natural organic matter for the optimisation of water treatment processes
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ABSTRACT

A rapid characterisation technique for natural organic matter (NOM), specifically designed to study water treatment processes, is reported. The organic carbon concentrations of four NOM fractions, very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), hydrophilic charged (CHA) and hydrophilic neutral (NEU), were determined.

Raw water and alum treated samples were analysed using this technique. A wide alum dose range (30–180 mg l⁻¹ alum) was selected to simulate the situation of underdosing, conventional alum treatment, enhanced coagulation and extreme overdosing. The variation of the residual dissolved organic carbon (DOC) concentration of each fraction was used to interpret the removal mechanism under different situations. The results showed that the NEU fraction was hardly removed by alum treatment. The CHA fraction was readily removed in the underdosing and extreme overdosing situations. In the alum dose range covering the conventional to enhanced coagulation, both the SHA fraction and the VHA fraction were preferably removed. This technique could be applied in the operation of the treatment plant and could potentially guide treatment operators to control and monitor the treatment processes in the most effective way for NOM removal.

Key words | characterisation, DOC, flocculation, fractionation techniques, NOM, water treatment

INTRODUCTION

Drinking water treatment involves the removal of turbidity and colour to make the water aesthetically acceptable to consumers. However, the issue of water quality goes beyond the physical appearance of water. The well-informed community now expects drinking water to be both chemically and microbiologically safe. One result of this demand for improved water quality is that considerable effort has been made recently in drinking water treatment to develop methods of improving natural organic matter (NOM) removal from water. Reduction in NOM before disinfection can minimise the formation of disinfection by-products and reduce the residual required to control bacterial regrowth in the distribution system, resulting in water of higher quality delivered to the consumers.

The removal of NOM by conventional water treatment utilising inorganic coagulants is affected by the character of the NOM and factors such as the pH and alkalinity of the raw water (Krasner and Amy 1995; Owen et al. 1995). To enable a better understanding of the types of organic compounds present before and after the treatment processes, a number of characterisation techniques, such as fractionation using resins and structural analysis using analytical instrumentation, have been developed worldwide. This has provided considerable knowledge of the impact of NOM on treatment processes. However, these techniques are often too complicated (time consuming and requiring a high level of skill) or the results are not in a form that can be interpreted easily by the treatment operators. The method reported in this paper focuses...
on bridging this gap by developing a rapid characterisation technique for both raw and treated waters. The technique can be applied to increase understanding of the treatment process and it is also potentially an analytical tool that can guide plant operators to optimise treatment processes.

This rapid characterisation technique was based on the full-scale fractionation scheme reported by Croue et al. (1994) and Bolto et al. (1999) for determination of the concentration of four organic fractions: very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), hydrophilic charged (CHA) and hydrophilic neutral (NEU). In an earlier alum flocculation study, using four fractions isolated from two Australian reservoirs, it was established that the removal efficiency is based upon the character of the fractions and the treatment conditions. Highest removal was achieved for the CHA fraction while the NEU fraction was hardly removed by alum flocculation (Chow et al. 2000). In this paper, jar testing with a wide range of alum doses was used to simulate various treatment conditions, including underdosing, conventional alum treatment, enhanced coagulation and extreme overdosing, and a pilot plant run was performed to simulate enhanced coagulation practice to demonstrate the applicability of this technique.

METHODS

Water sources

Raw water was taken from Myponga Reservoir, South Australia. The water is generally considered to be a high colour and high dissolved organic carbon (DOC) source. Three batches were used in this study, Batch 1 was used during the optimisation study and Batches 2 and 3 were used for the alum coagulation study.

Materials

Ultrapure water used in these experiments was obtained from a Milli-Q® purification system and was collected when the measured electrical resistance was higher than 16 MΩ cm⁻¹. Aluminium sulphate stock solution (20,000 mg l⁻¹ as Al₂(SO₄)₃·18H₂O) was prepared in Milli-Q® water using liquid aluminium sulphate (approximately 7.5% w/w Al₂O₃) from a local water treatment plant. DAX-8, XAD-4 and IRA-958 resins were supplied by Supelco (Belefonte, Pennsylvania). Sodium hydroxide, hydrochloric acid and sodium chloride solutions used for pH adjustment and cleaning/regeneration of resins were prepared from AR grade chemicals.

Experimental procedures

Jar testing

A FMS6V (SEM, Brisbane, Australia) variable speed, six paddle gang stirrer and Gator jars (B-KER², Phipps & Bird, USA) were used for jar testing. The test waters (2 l) were placed on the gang stirrer and six alum concentrations, 30, 60, 90, 120, 150 and 180 mg l⁻¹, were dosed. The treatment conditions were 1 min flash mixing, 14 min slow mixing and 15 min settling. The settled water samples were then filtered under gravity through Whatman No.1 filter papers to simulate the filtration process in a water treatment plant.

Pilot plant

An in-house designed pilot plant was used in this study to simulate the enhanced coagulation process. This plant contained a flash mixer, four stage flocculation chamber, a tube settler for sedimentation and a dual media filter filled with a 500 mm depth base of coarse gravel and 300 mm sand below a 400 mm depth anthracite layer. A digital console drive (Masterflex LS, Cole Parmer, USA) was used as supply pump to feed water to the plant at 600 ml min⁻¹. Two computer controlled variable-speed peristaltic pumps (Minipuls 3, Gilson, France) were used for alum and pH adjustment dosing. On-line pH measurement was performed using a pH/mV meter (940, Orion Research, USA). The acquired pH readings were used to form a feedback control loop to control the acid dosing system to maintain the coagulation pH at 6.2.

The duration of the pilot run experiment was 6 h. Three different alum doses, 60, 80 and 100 mg l⁻¹ alum, were selected and each dose was allowed a stabilising period of 1.5 h before sample collection.
Analytical methods

Water quality parameters, pH (pH 320, WTW, Germany), turbidity (2100AN, Hach, USA) and DOC (820, Sievers Instruments Inc., USA), were determined using the methods described in Standard Methods (1998). Colour was determined using the method described in Bennett and Drikas (1993).

The fractionation procedure was based on adsorption on to different adsorbent resins according to the method published by Croue et al. (1994) and Bolto et al. (1999) and resulted in four fractions: VHA (adsorbed by DAX-8), SHA (adsorbed by XAD-4), CHA (adsorbed by IRA-958) and NEU, which was not adsorbed on any of the ion exchange resins.

Virgin resins were wetted and pre-cleaned in beakers, with successive 1 h mixing in HPLC grade methanol, acetonitrile and finally Milli-Q water. Resin fines were removed by decantation of the pre-cleaning solutions from the settled resin bed. Three 20 cm (length) × 13 mm internal diameter (ID) glass columns for DAX-8, XAD-4 and IRA-958 resins, respectively, were set up in series. The sample, 500 ml filtered through a 0.45 µm cellulose nitrate membrane, was acidified to pH 2 with HCl and was passed through the DAX-8 column at 3.0 ml min\(^{-1}\) (0.2 bed volumes min\(^{-1}\)). The first two bed volumes (30 ml) were discarded and the remaining effluent (460 ml) was collected. A sub sample of 100 ml was collected for DOC analysis. The remaining effluent (360 ml) was passed through the XAD-4 column, the first two bed volumes (30 ml) being discarded. After sampling 100 ml for DOC analysis, the effluent from the XAD-4 column was adjusted to pH 8 with NaOH and was pumped through the IRA-958 column, the first two bed volumes (30 ml) again being discarded. All pH adjustments were performed using concentrated solutions to minimise dilution of the sample.

RESULTS AND DISCUSSION

Optimisation

The rapid characterisation technique is focused on maintaining small sample volume and short turnaround time for the analysis. Small sample volume is a key issue if this technique is to be implemented with the jar test procedure, as the recoverable treated water sample is usually approximately 1 litre. Although a larger sample volume can be obtained by repeating the jar test procedure, the preparation time will be increased substantially. The use of mini-columns reduced the required sample volume to 500 ml and maintained accuracy of the DOC analysis.

The analytical procedure was based on measuring the organic carbon concentrations of the raw, DAX-8 effluent, XAD-4 effluent and IRA-958 effluent. The organic carbon concentration of each fraction was calculated based on the subtraction of the organic carbon concentration before and after contact with the resin. The detail of the calculation is shown below:

\[
\begin{align*}
VHA &= \text{Raw} - \text{(DAX-8 effluent)} \\
SHA &= (\text{DAX-8 effluent}) - (\text{XAD-4 effluent}) \\
CHA &= (\text{XAD-4 effluent}) - (\text{IRA-958 effluent}) \\
NEU &= (\text{IRA-958 effluent})
\end{align*}
\]

Results can be presented either as actual DOC concentration in mg l\(^{-1}\) of each fraction or as a relative percentage (Table 1). From the results shown in Table 1, there was over 50% VHA, approximately 20% SHA, approximately 15% CHA and less than 10% NEU present in the Myponga Reservoir sample (Batch 1). The uncertainty of the analysis was determined using the systematic error of the DOC analysis, generally reported as 0.1 mg l\(^{-1}\). However, the calculation of the fractions (except NEU) involved subtraction of two DOC concentrations. Therefore the uncertainty of the concentration of VHA, SHA and CHA is 0.2 mg l\(^{-1}\) while that of NEU is 0.1 mg l\(^{-1}\).

To make this technique useful for water treatment operators, the turnaround time of the analysis is also an important factor. Sample throughput depends primarily on the flow rate. Reasonable contact time between sample and resin is required for reliable analysis. The recommended flow rate is 0.1 bed volumes per minute. Thus for 15 ml of resin a 1.5 ml min\(^{-1}\) flow rate is recommended and this will correspond to a total column run time of over
12 h. The selection of flow rate is critical and needs to be a compromise between reproducibility and sample throughput. In this study, doubling the flow rate to 3.0 ml min$^{-1}$ (0.2 bed volumes min$^{-1}$) reduced the analysis time, enabling the fractionation steps to be completed in 6 h. With good co-ordination with the DOC analysis, the complete fractionation result can be obtained in 7 h.

Duplicate analysis was undertaken at a flow rate of 1.5 ml min$^{-1}$ (Table 1). The result showed that good reproducibility was obtained within the experimental error of the DOC analysis. The use of a higher flow rate (3.0 ml min$^{-1}$) also showed good consistency and was therefore used for the rest of the test.

### Jar testing

Jar testing is one of the most commonly used techniques to simulate treatment processes. In this study, alum was chosen as the coagulant and a wide dose range was employed to demonstrate the effect of alum dose on the character of the non-removable organic compounds in treated water. Water quality parameters of both the raw and treated waters including pH, turbidity, colour and DOC are shown in Table 2. Based on these results, the alum dose range was separated into four regions: below 60 mg l$^{-1}$ (underdosing), 60–90 mg l$^{-1}$ (conventional alum treatment), 90–120 mg l$^{-1}$ (enhanced coagulation) and 150–180 mg l$^{-1}$ (overdosing region; pH below alum flocculation range).

pH is one of the major factors governing the effectiveness of the water treatment process utilising inorganic coagulants. Without pH control, an increase in the alum dose is expected to produce an accompanying reduction in the pH level of the treated waters (Table 2). In this particular study, the effect of different treatment conditions (alum dose and pH) on the character of the residual DOC in the treated water was determined by the fractionation analysis.

When considering NOM removal by coagulation, several mechanisms are involved. These mechanisms include: (1) charge neutralisation where the cationic metal interacts electrostatically with anionic NOM to form insoluble charge-neutral products; (2) adsorption of organics on the precipitate of metal hydroxide (solid); and (3) formation of insoluble metal hydroxides where NOM is removed by entrapment (sweep coagulation) (Edwards and Amirtharajah 1985; Jacangelo et al. 1995; Dennett et al. 1996; Gregor et al. 1997). The operational conditions for the various removal mechanisms are not the same (Gregor et al. 1997), and so the removal of NOM and turbidity may be maximised by control of these various mechanisms.

Maximum turbidity removal was achieved at 60 mg l$^{-1}$ of alum; a further increase in alum dose adversely affected turbidity removal. Colour removal did not
improve with an alum dose above 120 mg\ l^{-1}. Past experience using the same water source found the optimum pH for maximum DOC removal to be between pH 5 and 6 (Chow et al. 1998; van Leeuwen et al. 1999). In this study, maximum DOC removal was achieved using 120 mg\ l^{-1} alum at pH 5.9. There was a reduction of DOC removal when the alum dose increased to 150 mg\ l^{-1}. At 150 mg\ l^{-1} and 180 mg\ l^{-1} alum doses, the pH levels were reduced to 5.3 and 4.7, respectively, which were lower than the effective pH range for alum coagulation. The proposed fractionation technique has been aimed at providing additional characterisation information about NOM and this information can be utilised by the treatment operator together with the other water quality parameters, such as turbidity, to assess the impact of source water quality on treatment process.

The fractionation results of the treated waters presented in Figure 1 show that both the residual DOC concentration and character (distribution of the fraction) changed with different alum doses. The fractionation result showed that in the raw water there was 6.7 mg\ l^{-1} of VHA (51%), 3.2 mg\ l^{-1} of SHA (25%), 1.9 mg\ l^{-1} of CHA (15%) and 1.2 mg\ l^{-1} of NEU (9%) fractions, which made up a total of 13.0 mg\ l^{-1} DOC. In Figure 1, the residual DOC concentration of each fraction after alum treatment is presented. A reduction in DOC concentration with increasing alum dose was observed for both VHA and SHA fractions until the alum dose reached 120 mg\ l^{-1}. Further increase in alum dose reduced the removal of VHA and SHA. The region between 60 and 120 mg\ l^{-1} alum equated to conventional alum treatment and enhanced coagulation in this water suggesting that removal of VHA and SHA fractions is best under these conditions.

The residual DOC concentration of the CHA fraction did not follow a clear trend as in the case of the VHA and SHA fractions. Good removal was observed in the underdosing region (30 mg\ l^{-1} alum) and overdosing region (180 mg\ l^{-1} alum). When the dose was increased to 180 mg\ l^{-1} (extreme case), the pH was reduced to less than 5. At this pH, using alum flocculation to remove SHA and VHA fractions became less effective. However, at these low pH conditions, the removal of the CHA fraction became favourable. The residual DOC concentration of the NEU fraction did not decrease with an increase in alum dose, indicating that alum flocculation did not remove the NEU fraction.

The removal of each fraction is more clearly demonstrated by using percentage removal as shown in Figure 2. By comparing the percentage removal of each fraction after treatment with 30 mg\ l^{-1} of alum, the CHA fraction showed the highest removal of 58%. The CHA fraction also showed good removal, 95%, when the dose was increased to 180 mg\ l^{-1} despite the fact that the overall

### Table 2: Treated water quality parameters after coagulation using different alum doses

<table>
<thead>
<tr>
<th>Alum dose (mg l^{-1})</th>
<th>pH</th>
<th>Turbidity (NTU)</th>
<th>Colour (HU)</th>
<th>DOC (mg l^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (Raw)</td>
<td>7.5</td>
<td>0.74</td>
<td>70</td>
<td>13.0</td>
</tr>
<tr>
<td>30</td>
<td>6.9</td>
<td>1.21</td>
<td>27</td>
<td>9.9</td>
</tr>
<tr>
<td>60</td>
<td>6.6</td>
<td>0.07</td>
<td>11</td>
<td>7.0</td>
</tr>
<tr>
<td>90</td>
<td>6.4</td>
<td>0.08</td>
<td>6</td>
<td>5.5</td>
</tr>
<tr>
<td>120</td>
<td>5.9</td>
<td>0.11</td>
<td>4</td>
<td>3.8</td>
</tr>
<tr>
<td>150</td>
<td>5.3</td>
<td>0.33</td>
<td>4</td>
<td>4.4</td>
</tr>
<tr>
<td>180</td>
<td>4.7</td>
<td>0.33</td>
<td>3</td>
<td>4.6</td>
</tr>
</tbody>
</table>
DOC removal was reduced. A charge neutralisation mechanism was believed to be the main removal mechanism for the CHA fraction.

Using 60 mg l$^{-1}$ alum, the percentage removal of VHA and SHA was 48% and 56%, respectively, while the CHA was 47%. This indicates that the removal of each fraction is changed with treatment conditions. When the dose was increased to 90 mg l$^{-1}$, the VHA removal increased to 62%. Increasing the dose to 120 mg l$^{-1}$ (close to the enhanced coagulation region), further increased the percentage removal of the VHA fraction. The removal mechanism of sweep coagulation with alum is by adsorption to the solid precipitate, particulate matter being removed by enmeshment or entrapment within the solid.
precipitate (Dennet et al. 1996). This mechanism is likely to be effective for removal of the higher molecular weight compounds such as the VHA but is unlikely to be effective for removal of soluble compounds such as the CHA. Charge neutralisation may remove more of the soluble compounds (e.g. CHA) although conditions for this may not be optimal for removal of the higher molecular weight compounds (e.g. VHA). The operational conditions for the various removal mechanisms are not the same, and so the removal of NOM and turbidity may be maximised by control of these various mechanisms (Gregor et al. 1997).

Pilot plant study

The term ‘enhanced coagulation’ refers to the modification of the coagulation process to achieve greater or maximum NOM removal (White et al. 1997) where greater doses of coagulant are used and the pH may be controlled during the coagulation/flocculation steps compared with conditions maximised for turbidity removal. In this pilot plant study, the flocculation pH was controlled at pH 6.2 and a narrow range of alum doses, 60, 80 and 100 mg l\(^{-1}\) alum, was selected. In Figure 3a, DOC concentration was reduced with increasing alum dose and a similar trend was observed with the fractions except the NEU. The percentage removals shown in Figure 3b indicate that at pH 6.2 the CHA fraction was preferentially removed compared with the other fractions. This result demonstrates the feasibility of selecting the appropriate treatment condition to remove the majority of the NOM. In addition, this technique can be applied to analyse treated water, with a turnaround time of 7 h. It is possible to apply this technique to fine-tune the treatment process and potentially customise the treatment conditions to address a particular water character, and hence achieve the goal of maximum removal of NOM.

CONCLUSIONS

There has been an increasing emphasis on improved water quality and operators of water utilities have become more aware of the impact of NOM on their treatment processes. In order to achieve better water quality, a good understanding of the NOM character and its removal by various treatment methods is essential. The fractionation technique reported in this paper has been designed for this
purpose. The use of fractionation to link treatment conditions with the treatability of a particular fraction has been demonstrated. This technique is rapid allowing the water treatment operators to react quickly to water quality change or to use the result to fine-tune the treatment process. With the ability to determine organic fractionation concentration in treated waters, the application of this technique can be extended to study the link between organic character and disinfection by-products formation.

REFERENCES


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