Removal of algogenic organic matter by magnetic ion exchange resin pre-treatment and its effect on fouling in ultrafiltration
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ABSTRACT
Natural organic matter (NOM) fouling continues to be the major barrier to efficient application of ultrafiltration (UF) in drinking water treatment. Algogenic organic matter (AOM), the main contributor to total NOM levels in raw waters characterised by elevated algae levels, is currently the subject of much investigation. In this study, the effect of AOM on fouling of ultrafiltration and the effectiveness of magnetic ion exchange resin (MIEX®) pre-treatment for AOM removal and membrane fouling control was evaluated. The results showed that, the main species of algae in raw water were Chlorella vulgaris, which accounted for 80% of total algae. AOM was predominantly hydrophilic (50% or more) with a low SUVA (1.7 Lm⁻¹C0⁻¹mg⁻¹). Coagulation alone could not remove AOM effectively (less than 20%), however, when combined with magnetic ion exchange resin pre-treatment, more than 60% of AOM was be removed; pre-treatment followed by coagulation was observed to be very effective in controlling membrane fouling by AOM. The application of magnetic ion exchange resin technology at a bed volume treatment rate (BVTR) of 800 was observed to effectively eliminate fouling of UF membrane. Careful analyses of the molecular weight (MW) distribution of AOM and UV absorbance of treated water revealed that the effectiveness in membrane fouling control was the result of the changes in AOM molecular characteristics in treated water, namely a change in MW due to the preferential removal of high molecular proteins by coagulation and magnetic ion exchange resin pre-treatment. The results demonstrate that magnetic ion exchange resin followed by coagulation might be a new membrane pre-treatment option for UF membrane fouling control.

Key words | algogenic organic matter, magnetic ion exchange resin (MIEX®) pre-treatment, ultrafiltration

INTRODUCTION
Membrane processes, especially ultrafiltration (UF), are increasingly being used in drinking water treatment (Lee et al. 2004, Lee & Lee 2006). In spite of the various advantages UF systems offer, poor removal of organic matter and fouling of membranes are two major obstacles to broader application of UF in water and treatment (Laabs et al. 2006).

Algae are ubiquitous in lakes and reservoirs supplying drinking water treatment facilities. When algae populations increase, treatment processes can be adversely affected. For example, coagulant demand is increased, floc morphology and quality deteriorates and membrane fouling is increased (Her et al. 2004). This is a result of not only increased cell concentration but also in increase in associated algogenic organic matter (AOM) which can form a substantial component of the algae system. AOM arises extracellularly via metabolic excretion, forming extracellular organic matter...
(EOM) or intracellularly due to autolysis of cells, forming intracellular organic matter (IOM), and is known to comprise proteins, neutral and charged polysaccharides, nucleic acids, lipids and small molecules (Fogg 1983), of which polysaccharides can comprise up to 80–90% of the total release (Myklestad 1995). The IOM proportion increases with increasing age of the algae system. AOM provides a significant contribution to the heterogeneous mixture of compounds that forms dissolved organic matter (DOM) in algal systems.

AOM in drinking water sources is the major precursor of disinfection by-products (DBPs) when chlorine is used for disinfection (Scully et al. 1988). Therefore, removal of AOM is usually desired before chlorination. Unfortunately, UF membrane is generally ineffective in removing AOM because its molecules are typically smaller than the pores of UF membrane. Although pre-treatment for UF systems using conventional treatment processes such as coagulation/flocculation can partially remove AOM, the removal efficiency is low at low AOM concentrations. On the other hand, AOM is a major membrane foulant (Her et al. 2004). Membrane fouling results in reduction in membrane permeability, and hence decline of membrane permeate flux or increase in applied pressure, which leads to higher operating costs. Over time, fouling causes deterioration of membrane materials, resulting in compromised product water quality and ultimately shorter membrane life (Braghetta 1995). Although fouling can be reduced by utilizing low-fouling membrane materials (Lee et al. 2004), optimizing system operation (Childress & Elimelech 1996, Childress & Elimelech 2000), and chemically cleaning membrane units (Li & Elimelech 2004), fouling is inevitable as long as foulants exist in the membrane feed water. Therefore, development of effective pre-treatment methods to remove or transform NOM from membrane feed water is key to improving the cost-effectiveness of membrane systems and to broader application of membrane technology in water treatment.

Magnetic ion-exchange (MIEX®) resin has emerged as an effective technology for removing organic matters from raw water. Its use as a pre-treatment before coagulation has consistently shown a good removal effect of organic matters from drinking water. Depending on specific water characteristics, MIEX® pre-treatment can remove from 30% to over 70% of the DOC from the water (Tan et al. 2005; Mergen et al. 2008). The treated water therefore has a much lower coagulant demand allowing much lower doses to be applied when compared with conventional coagulation of the same raw water (Allpike et al. 2005; Boyer & Singer 2005). For example, Fearing et al. (2004) demonstrated that DOC and UV_254 removals (75% and 95%, respectively) were improved with a corresponding decrease in the coagulant dose from 14 to 5 mg L⁻¹ as Fe (ferric sulphate) when using MIEX pre-treatment (20 mL L⁻¹ for 20 min). Whilst the technology is currently used as a pre-treatment to MF and UF membranes systems in North America, Australia and Europe, the potential of the pre-treatment for controlling membrane fouling by AOM has not been fully explored. Importantly, comparing the different treatment stages indicates that the varying character of AOM from the different algae means that each species will cause a unique set of challenges restricting the ability to generalise about the treatment of algae.

In this study, the effectiveness of MIEX® pre-treatment for AOM removal and fouling control of UF membranes was evaluated. AOM removal effect as well as changes in AOM molecular and XAD fractionation characteristics during the pre-treatment was investigated to elucidate mechanisms of AOM removal and subsequent fouling reduction.

MATERIALS AND METHODS

Raw water, magnetic ion exchange resin system and membranes

Raw water was pumped from Hong-ze Lake, in middle China in August or late summer, during which time algae content reached 2000 × 10⁴ cells/L. AOM was characterized using techniques including dissolved organic carbon (DOC), specific UV adsorption (SUVA), hydrophobicity, molecular weight (WC). All analytical instruments were calibrated using the associated calibration procedure for the instrument prior to use.

A magnetic ion exchange resin pilot plant was used to treat raw water directly and without any pre-treatment. The UF membrane used in the evaluation was a cellulose acetate membrane with a molecular weight (MW) cut-off of 100 kDa. All membrane samples were stored in purified water at 4°C with water replaced regularly.
Analytical methods

Samples were analysed un-filtered for turbidity and zeta potential and were filtered using a glass fibre paper (0.45 μm pore size, Xin-ya, China) for DOC, UV_{254}.

_Ultraviolet absorbance_. UV_{254} and UV scan was measured using T6 spectrophotometer (Pu-xi Instruments Inc., Beijing, China).

DOC measurements. DOC was measured using a Shimadzu TOC-5000A analyser as the difference between total carbon and inorganic carbon. Each sample was analysed in triplicate with errors less than 2%. SUVA was calculated as UV_{254}/DOC.

Turbidity. Turbidity was measured using a Hach 2100N Turbidimeter (Hach Co., Loveland, CO).

XAD resin fractionation. Further characterisation work was carried out by fractionating raw waters using published methods (Goslan et al. 2002). During this process, 2 L of raw water was filtered through 0.45 mm glass fibre papers and acidified to pH 2. The water was then passed through three fractionation columns, the first containing 60 mL of XAD-8 resin, the second containing 60 mL of XAD-4 resin and the third containing 60 mL of IRA-958 resin. Effluent passing through all of the columns was the hydrophilic neutral fraction (HIN). Both the ion-exchange columns were back-eluted with 250 mL of 0.1 M NaOH. The eluate from the XAD-8 column was the hydrophobic fraction. The eluate from the XAD-4 resin was the hydrophilic acid fraction (HPIA). The eluate from the IRA958 resin was the hydrophilic neutral fraction (HIN). The fractions were filtered and analysed for DOC.

Molecular weight fractionation. Nitrogen gas at a constant pressure of 1bar was used to drive the AOM solution through ultrafiltration membranes (Millipore, Billerica, MA, USA) using the Amicon Stirred Cell (Model 8200) in series such that AOM was fractionated into portions of >30, 30~10, 3~10, 1~3 and <1 kDa. Each MW fractionation was repeated in triplicate.

Pilot plant description and operation

Orica Watercare, Melbourne, Australia provided a 90 L/min pilot plant and magnetic ion exchange resin. The pilot plant was set up at the water treatment plant in Huai-an, China, which treats surface water from Hong-ze lake. The pilot plant was operated in August 2008. Multiple raw water and pilot plant effluent (i.e. water treated by magnetic ion exchange resin) samples were taken daily and monitored for DOC, UV_{254}, pH, and turbidity. Additional raw water and effluent samples were collected periodically for molecular weight and XAD resin fractionation analysis, coagulation jar-tests and membrane filtration.

Membrane fouling experiments

The water before and after MIEX® pre-treatment, coagulation and MIEX® and coagulation were tested for membrane fouling potential. To avoid interference by flocs during fouling experiments, the treated suspension was filtered by a sand filter to remove the flocs in the water. The supernatant was collected and used as the feed solution for the membrane fouling experiments. Membrane fouling experiments were conducted in a bench-scale UF filtration instrument (a flow rate of 40 L/h). Raw water before and after treatment of coagulation and resin pre-treatment was filtered through the membrane to evaluate its fouling potential.

RESULTS

Raw water characterisation

The raw water presenting to the pilot plant was characterised throughout the duration of the investigation. As can be seen from Table 1, the physical and chemical characteristics of the raw water remained relatively constant over the course of the study. The raw water had a high turbidity of about 20.0 NTU as a result of this water containing high concentrations of algae. Microscopic examination identified that the dominant species in this water were green algae (Chlorella vulgaris), which account for 80% of the total algae cells.

Water hydrophobicity was measured in two ways. Firstly, the SUVA provided a quick indication of the nature of the organics present in the raw water. High SUVA (>4.0 Lm^{-1}C0^{-1}) values are indicative of a hydrophobic water while the low SUVA value (<4.0 Lm^{-1}C0^{-1}) are indicative of water containing mostly hydrophilic organics. The values of SUVA for the raw water were about 1.7 Lm^{-1}C0^{-1}, which accounts for 20% of the total algae cells.
mg L\(^{-1}\), which indicated the organic matters in the raw water were mainly hydrophilic. More detailed hydrophobicity characterisation was made using XAD resin fractionation (Figure 1). However, while the SUVA of the raw water suggested that there was a low hydrophobic content, 35\% of the water was determined to be hydrophobic after fractionation, indicating that this water contained a large proportion of non-UV\(_{254}\)-absorbing hydrophobic compounds that the SUVA measurement was not able to identify.

The MW distribution of AOM was dependent on the species of algae in raw water. The MW distribution of the AOM in raw water used in the experiment is shown in Figure 2. As seen from Figure 2, the AOM was of smaller MW and not bimodal with 21\% greater than 30 kDa, 40\% between 1 and 30 kDa, and 39\% less than 1 kDa, respectively. These observations are not in agreement with Lusse \textit{et al}. (1985), who demonstrated bimodal distributions for stationary phase green algae including \textit{Chlorella} sp., \textit{Scenedesmus obliquus} and \textit{Dictyospherrium} sp. and the cyanobacteria, \textit{Pseudanabaena catenata}, using 0.2 mm and \(<1.1\) nm (\(~2\) kDa) membranes. The reason may lie in the observation that the organic material in raw water was not exclusively AOM, rather there were some other organic contaminants present which altered the MW distribution. AOM arises extracellularly via metabolic excretion, forming extracellular organic matter (EOM) or intracellularly due to autolysis of cells, forming intracellular organic matter (IOM), and is known to include glycolic acids, carbohydrates, polysaccharides, amino acids, peptides, organic phosphorus, enzymes, vitamins, hormonal substances, inhibitors and toxins (Her \textit{et al}. 2004; Henderson \textit{et al}. 2006). Compounds such as polysaccharides and proteins have a higher MW than humic and fulvic acids, however, compounds such as uronic acid are typical of the charged, small MW.

### AOM removal effect

Figure 3 shows the removal effect of DOC, UV\(_{254}\) and COD\(_{Mn}\) by different processes.

As seen from Figure 3, only 20\% of DOC was removed during coagulation alone, similar to the results of previous study (Edzwald 1993). The reason lied in that hydrophilic water is generally assumed to have a low coagulant demand due to its low charge density and relatively low DOC removals can be anticipated on coagulation. In comparison,
DOC removals of 68%, 65%, 61% were observed upon magnetic ion exchange resin treatment applied at 500, 800 and 1200 bed volumes, respectively. Similar results were observed for the removal of UV254 and CODMn. The removal effect of DOC (above 60%) observed here is higher than former research on high-algae raw water (about 33%) (Mergen et al. 2008). This may relate to the inherent variability in AOM composition in source waters and the MIEX® operating conditions used. According to Boyer’s research, the consistently low NOM removals seen for high-algae, high AOM water may be explained by the combination of size exclusion and low charge. Many of these compounds tend to be uncharged and are therefore unlikely to have a strong affinity for exchange onto the resin (Allpike et al. 2005). However, it has been shown that algal-derived extracellular organic matter (EOM) is dependent on species. Algae such as *Chlorella vulgaris* produce EOM with a charge density 3.2 meq g⁻¹ DOC (Henderson et al. 2006). As *Chlorella* was one of the dominant algae in the water sampled here, some small MW AOM (charged compounds such as uronic acid) was removed from this water (Allpike et al. 2005). In addition, large polysaccharides and proteins exuded by microbes and algae have a higher MW than humic and fulvic acids, indicating that size exclusion may play a significant part in the poor removals seen from this water using the resin. However, by enhancing the dose of magnetic ion exchange resin and making full use of the mechanism of adsorption, the process has demonstrated it can effectively remove large polysaccharides and proteins, improving the removal of AOM.

Seen from Figure 4, MIEX® pre-treatment process not only improves the removal effect of organics but also enhance the coagulation process. Better turbidity removals by reducing the coagulant (PAC) dose from 32 to 16 mg L⁻¹ when using magnetic resin pre-treatment.

**Effect of magnetic ion exchange resin pre-treatment on AOM fouling of UF membranes**

Membrane fouling experiment was conducted using UF membranes. Raw water before and after different treatment by magnetic ion exchange resin as well as coagulation were used as the feed solutions to the membranes. The results obtained are shown in Figure 5a and b.

The membrane TMP measured with these feed solutions is presented in Figure 5b. The total fouling rate curves (Figure 5a) were obtained by plotting the slope of each of filtration cycles in Figure 5b against the filtration cycle number. From Figure 5a, the total fouling rate generally increased with the sequence of MIEX® + coag., coag., raw water. This was probably due to increased percentage of large sized NOM in the AOM fractions.

Similar results were reported by Fan *et al.* who concluded that the large MW fraction of NOM (> 30 kDa - most likely in colloidal state) was responsible for most of the flux decline. Fan *et al.* and Lahoussine *et al.* (1990) seemed to agree when...
they concluded that higher SUVA NOM contained a greater amount of colloidal NOM molecules (i.e. > 30 kDa) and caused greater fouling than lower SUVA NOM. Cho et al. found that large sized NOM components such as amino acids, polypeptides, proteins, colloidal NOM, and not the smaller sized humic substances were efficiently rejected by UF membranes. However, raw water used here has plenty of such substances due to the high algae levels. Therefore, membrane fouling is severe when raw water is loaded directly onto the membrane.

**Changes in AOM molecular characteristics**

NOM fractions of different molecular characteristics, e.g. hydrophobicity, MW, and aromaticity, have been found to foul membranes differently (Carroll et al. 2000; Cho et al. 2000; Fan et al. 2001). The experimental results presented above strongly suggest that NOM compounds were decomposed into intermediate products that have lower membrane fouling potential. Therefore, further characterization was carried out to understand such changes.

**Changes in UV scan.** UV$_{254}$ of NOM is an indicator of its aromaticity and hydrophobicity, which has been found to relate to membrane fouling by NOM (Hong & Elimelech 1997; Fan et al. 2001; Howe & Clark 2002). Meanwhile, a good correlation has been reported between trihalomethane and haloacetic acid formation and UV$_{254}$ of NOM (Laabs et al. 2006; Kim & Yu 2005). UV scan of all NOM samples could give more information on the NOM, so measured the UV scan of the samples, results shown in Figure 6a and b.

As can be seen in Figure 6, coagulation could achieve good removal of those compounds that had high adsorption at wavelength higher than 250 nm, i.e. high molecular and aromatic organics. In contrast, magnetic ion exchange resin pre-treatment was observed to very effectively remove organics absorbing UV across the entire spectrum applied. It is suggested that the ability of the resin to remove a wide range of organic material is its main advantage compared to other process used in drinking water. Since both coagulation and MIEX$^{\text{®}}$ pre-treatment could remove compounds that have adsorption at wavelength higher than 250 nm, both are likely to have the ability to materially reduce the fouling of UF membranes.

**Changes in molecular weight.** AOM MW distributions of samples were determined by molecular weight fractionation analysis. The results are presented in Figure 7. The raw water contained NOM consisted of organic compound with MWs ranging from a few hundred to over 30,000 Da.

It is clear from Figure 7 that large AOM compounds are preferably removed during the coagulation and magnetic ion exchange resin pre-treatment. The pre-treatment followed by coagulation was observed to result in very significant removal of AOM molecules larger than 5,000 Da with minimal removal observed for compounds smaller than 1000 Da.
In contrast, coagulation alone could remove compounds higher than 10,000 Da, and even then, the removal of sub 10,000 Da species was evidently lower than that of pre-treatment + coagulation. Many studies have reported that larger NOM molecules cause more serious membrane fouling (Lee & Lee 2006; Laabs et al. 2006). Therefore, the almost totally removal of large NOM compounds by the pre-treatment and coagulation is believed to be an important mechanism for its fouling control efficiency shown in Figure 6a and b.

The UV scan and molecular weight fractionation analyses revealed that the MIEX® pre-treatment reduced membrane fouling not only by reducing the DOC concentration but also by changing the molecular distribution of AOM – effectively magnetic ion exchange resin appears to preferentially remove those NOM fractions believed to be most responsible for membrane fouling. These findings indicate that a combined pre-treatment and coagulation process is a very promising pre-treatment method for the control of membrane fouling in UF systems.

**CONCLUSIONS**

It is shown in this study that magnetic ion exchange resin pre-treatment followed by coagulation is an effective treatment process for NOM (AOM) removal, although a small fraction of refractory AOM exists. The combined process could remove more than 60% of DOC. The reduction in membrane fouling is attributed primarily to the changes in NOM molecular characteristics resulting from preferential removal of high MW, hydrophobic NOM molecules, which are the major NOM fraction responsible for membrane fouling. Considering the highly efficient removal of NOM fouling potential, the MIEX® pre-treatment combined coagulation process is expected to find wide application as a pre-treatment for membrane fouling control.

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