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Zhang, X, Fan, L and Roddick, F 2014, 'Feedwater coagulation to mitigate the fouling of a ceramic MF membrane caused by soluble algal organic matter', Separation and Purification Technology, vol. 133, pp. 221-226.

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http://dx.doi.org/10.1016/j.seppur.2014.06.053

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Feedwater coagulation to mitigate the fouling of a ceramic MF membrane caused by soluble algal organic matter

Xiaolei Zhang, Linhua Fan*, Felicity A. Roddick

School of Civil, Environmental and Chemical Engineering, RMIT University,

GPO Box 2476, Melbourne, VIC 3001, Australia

* Corresponding author. Tel: +613 9925 3692; fax: +613 9639 0138.

E-mail address: linhua.fan@rmit.edu.au

Abstract:

Soluble algal organic matter (AOM) resulted from the cyanobacterial blooms in water catchments can cause severe fouling of ceramic membranes in water treatment. The effect of feedwater coagulation using alum, aluminium, ACH, ferric sulphate and ferric chloride for reducing the fouling of a commercial ceramic MF membrane (ZrO_2-TiO_2) caused by the AOM released from *Microcystis aeruginosa* was investigated. At their optimum dosages (i.e., 5 mg Al^{3+}/L and 10 mg Fe^{3+}/L), all coagulants could significantly mitigate the membrane fouling, with the hydraulically reversible and irreversible fouling resistance reduced by over 90% and 65%, respectively. ACH, ferric chloride and ferric sulphate performed similarly in reducing the flux decline, and considerably better than alum did. The reduction in AOM fouling of the membrane was primarily due to the effective removal of the very high MW biopolymers (>>20,000 Da). There were much greater removals in carbohydrate (74 - 77%) than protein content (15 - 28%) by the coagulation. The hydrophobic compounds in the AOM solution were more susceptible to the coagulation treatment than the hydrophilic and transphilic compounds. Among the tested coagulants, ACH appeared to be more cost-effective in maintaining the permeate flux and minimising the irreversible fouling for the ceramic MF membrane.

Keywords: Microfiltration; algal organic matter; ceramic membrane; fouling; water treatment

1 Introduction

Ceramic microfiltration (MF) and ultrafiltration (UF) membranes are increasingly utilised in water and wastewater treatment due to their inherent advantages such as high mechanical stability, chemical stability and high hydrophilicity over conventional low-pressure polymeric membranes [1, 2]. However, membrane fouling due to the attachment of aquatic organic matter on the surface and/or inner structures of the membranes remains a major issue limiting the efficiency of ceramic membrane water treatment systems [3].

Blooms of cyanobacteria (also referred to as blue-green algae) occur frequently in many drinking water catchments and result in the release of a substantial amount of soluble algal organic matter (AOM) to the downstream water treatment systems, causing great concerns about water quality and treatment efficiency [4]. The predicted increase in average temperature due to climate change is likely to lead to a higher frequency of cyanobacterial blooms in the future [5]. The AOM released from the cyanobacteria is usually hydrophilic in nature and comprises mainly proteins and polysaccharides [6] which have been demonstrated to have high fouling potentials for both polymeric and ceramic water treatment membranes. The membrane fouling caused by AOM led to severe permeate flux decline in constant transmembrane pressure filtration or significant pressure increase in constant flux mode [6-9]. A recent study on the AOM fouling of a commercial ceramic MF membrane revealed that the majority of the flux decline was attributed to the very high molecular weight (MW) biopolymer compounds, which resulted in the formation of an outer fouling layer of high filtration resistance [7].

Feedwater pre-treatment is a common approach to transform/remove the high fouling potential components, and consequently mitigate their propensity to foul the water treatment membranes [8]. Among the various pre-treatment methods, chemical coagulation with aluminium based salts or ferric based salts is widely used for the removal of high molecular

weight organics from water and waste water [9, 10]. The effectiveness of organic removal through coagulation can be strongly affected by the characteristics of the feedwater, and the type and dose of the coagulant [11]. A previous study showed alum and ACH could improve the filterability of a biologically treated municipal wastewater containing the AOM derived from *Microcystis aeruginosa* for a polymeric MF membrane [12]. However, comparison of the effect of the most commonly used water treatment coagulants (such as aluminium and iron based coagulants) in reducing AOM fouling for ceramic membranes has not been documented.

The aim of the present study is to evaluate the fouling mitigation effect of four widely used water treatment coagulants, i.e., alum, ACH, $Fe_2(SO_4)_3$ and $FeCl_3$, on the water containing AOM using a lab scale ceramic MF membrane system. The AOM used in the work was extracted from stationary growth phase cultures of *Microcystis aeruginosa* which is the most prevalent cyanobacterium worldwide [13]. The effect of the coagulation on membrane fouling was characterised in terms of reduction in reversible and irreversible fouling resistance, dissolved organic carbon, carbohydrate and protein contents. Advanced organic characterisation techniques including size exclusion chromatography (SEC) using liquid chromatography with organic carbon detection (LC-OCD), fluorescence excitation-emission matrix (EEM) spectra and fractionation using resin adsorption chromatography were also employed, with a view to obtaining better insights into the effect of coagulation on fouling mitigation.

2 Experimental

2.1. Cultivation of cyanobacteria, AOM extraction and preparation of feed solutions

M. aeruginosa (CS 566/01-A01) was purchased from the CSIRO Microalgae Research Centre (Tasmania, Australia). The algal cultures were grown in 5 L Schott bottles using MLA medium [14] under humidified aeration. The cultures were placed in an incubator

at the temperature of 22 °C under illumination for 12 h/day. The AOM was extracted from cultures harvested after 35th day of growth (stationary growth phase) by centrifugation (3270 × g for 30 mins) of the cell suspensions, and the subsequent filtration of the supernatant using 1 µm membranes (Whatman® Grade GF/A). To mimic the presence of AOM in drinking water, the extracted AOM was diluted to a DOC concentration of 4.3 ± 0.2 mg/L with tap water (1.4 ± 0.05 mg DOC/L) to make the feedwater for the coagulation or MF tests. The pH of the AOM solution was adjusted to 8.0 ± 0.2 using 1 M HCl or 1 M NaOH prior to the coagulation tests.

2.2. Microfiltration tests

A 7-channel tubular ceramic ZrO_2-TiO_2 MF membrane with a nominal pore size of 0.1 µm (CeRAM™ INSIDE, TAMI Industries) was used in the filtration experiments and operated under dead-end mode. The ceramic membrane surface layer was made of ZrO_2 and the support layer was made of TiO_2. This membrane surface was considered as hydrophilic (ZrO_2 based membrane usually has a contact angle less than 20°) due to the presence of surface hydroxyl groups [15]. All filtration runs were carried out at a constant transmembrane pressure (TMP) of 70 ± 1 kPa at room temperature (22 ± 2 °C) for 90 min. After each MF test, the membrane was backwashed for 2 minutes with tap water. The same membrane was used for all MF runs, and after each run the membrane was restored by Cleaning in Place (CIP) by using 0.05 M NaOH and 0.05 M HNO_3 solution until the permeate flux reached 170-180 LMH.

The reversible and irreversible fouling resistance were determined with the following equations:

$$J = \frac{\Delta P}{\mu R_{total}} \quad (1)$$

$$R_{total} = R_{reversible} + R_{irreversible} + R_{membrane} \quad (2)$$

Where ΔP is the transmembrane pressure; J stands for the permeate flux and μ is the water viscosity at 22 ^{o}C (0.955×10^{-3} Pa s). R_{total} refers to the total resistance after MF of an AOM solution, which can be calculated using the permeate flux at the end of the filtration. $R_{reversible}$ is associated with the hydraulically reversible fouling resistance, and can be determined using the flux before and after backwash with tap water. $R_{membrane}$ is the resistance of a clean membrane, which was determined by the tap water flux prior to the filtration test with an AOM solution. $R_{irreversible}$ is the hydraulically irreversible fouling resistance, and can be calculated by deducting $R_{reversible}$ and $R_{membrane}$ from R_{total}.

2.3. Coagulation conditions

Coagulation using ACH (aluminium chlorohydrate, Megapac 23, 40% w/w), alum, ferric chloride and ferric sulphate were investigated as the pre-treatment for AOM solution. Coagulation was conducted at room temperature (20 ± 2^{o}C) in a laboratory jar tester unit (Phipps and Bird, PB-700) with rapid mixing for 1 min at 200 rpm, followed by slow mixing for 20 min at 30 rpm. A range of dosages (1-20 mg Al^{3+}/L or 1-20 mg Fe^{3+}/L) was tested to determine the optimal dosage for organic removal. After the jar tests, the resultant treated water samples were immediately filtered with 5 µm filter (Advantec) to remove the flocs in the coagulated solution and the pH of the filtrate was adjusted to 8 prior to being fed to the ceramic membrane MF rig.

2.4. Analytical methods

DOC and UV absorbance at 254 nm (UVA_{254}) were determined using a Sievers 820 TOC analyser and a UV/Vis spectrophotometer (UV2, Unicam), respectively. pH was measured with a Hach Sension 156 pH meter. The phenol-sulphuric method was used to determine carbohydrate content [16] with D-glucose used as the standard carbohydrate substance. Protein content was measured using the bicinchoninic acid (BCA) method for which the QPBCA QuantiPro™ BCA Assay Kit (Sigma Aldrich) was utilised. Bovine serum albumin (Sigma Aldrich) was used as the standard protein substance.

Fluorescence excitation-emission matrix (EEM) spectra were obtained using a fluorescence spectrometer (LS 55, PerkinElmer) at an excitation and emission wavelength range of 200–550 nm. An interpolation method [17] was used to remove the first-order Rayleigh scattering. The second-order Rayleigh scattering was limited by using a 290 nm emission cut off filter. The fluorescence spectra of deionised water were subtracted from all EEM spectra to remove the Raman scattering and other background noise.

The apparent molecular weight distribution of the AOM was determined by SEC with LC-OCD at the Water Research Centre of the University of New South Wales, Sydney, Australia. The LC-OCD system (LC-OCD Model 8, DOC-Labor Dr. Huber, Germany) utilised a SEC column (Toyopearl TSK HW-50S, diameter 2 cm, length 25 cm) and the chromatograms were processed using the Labview based program Fiffikus (DOC-Labor Dr. Huber, Germany). The details of this technique are described by Huber et al. [18].

Nonionic macro-porous resins (DAX-8 and XAD-4) were employed to separate the organics into hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) fractions. More details of the organic matter fractionation procedure can be found elsewhere [19]. All filtration tests were duplicated and analyses triplicated, and reported in terms of mean value and error/standard deviation.

2.5. Membrane fouling analysis using classic filtration models

Hermia's constant pressure filtration models including complete blocking, standard blocking, intermediate blocking and cake filtration have been widely used to interpret the filtration behaviour of dead-end membrane filtration systems [20]. The detailed description of these models can be found from Shen et al. [21]. The equations for these models are shown in Table 1. The identification of the key fouling mechanism in this study was conducted

by fitting the experimental data to the equations (Eqs. 3-6). The resulting *R*-squared (R^2) value was used to indicate the goodness of the fit.

Table1. Equations for classic filtration models [22].

Law	Equation	
Complete blocking	$J_0 - J = aV$	(3)
Intermediate blocking	$1/J - 1/J_0 = bt$	(4)
Standard blocking	$t/V = ct + d$	(5)
Cake filtration	$1/J - 1/J_0 = eV$	(6)

Where V is the cumulative volume of permeate at time t, J and J_0 represent flux and initial flux respectively. *a, b, c , d, e* are the model parameters, which could be obtained from data fitting.

3. Results and discussion

3.1 Optimum coagulant dosages

For the two aluminium based coagulants, the organic matter removal increased significantly with increasing the Al^{3+} dosage from 1 to 5 mg/L, with 70% and 65% of DOC reduction for ACH and alum at 5 mg Al^{3+}/L, respectively (Fig. 1a). On increase of the dosages from 10 to 20 mg Al^{3+}/L, there was no further increase in DOC reduction for ACH but a considerable decrease for alum. For the iron based coagulants, the DOC removal increased with increasing iron dosage and was maximium at about 10 mg Fe^{3+}/L, with approximately 70% of DOC was removed by the coagulation with the two coagulants. The optimum coagulant dosages in terms of DOC reduction for the AOM solutions were therefore determined as 5 mg Al^{3+}/L for ACH and alum, and 10 mg Fe^{3+}/L for $Fe_2(SO_4)_3$ and $FeCl_3$. Coagulation with ACH did not significantly alter the pH of the AOM solutions, and the pH of

the coagulated water was maintained at around 7 for all dosages (Fig. 1b). Coagulation with alum, $Fe_2(SO_4)_3$ and $FeCl_3$ at their optimum dosages greatly reduced the solution pH. As the solution pH could affect the MF performance, the pH of all coagulated solutions was adjusted to 8 prior to all filtration tests for the purpose of a better comparison.

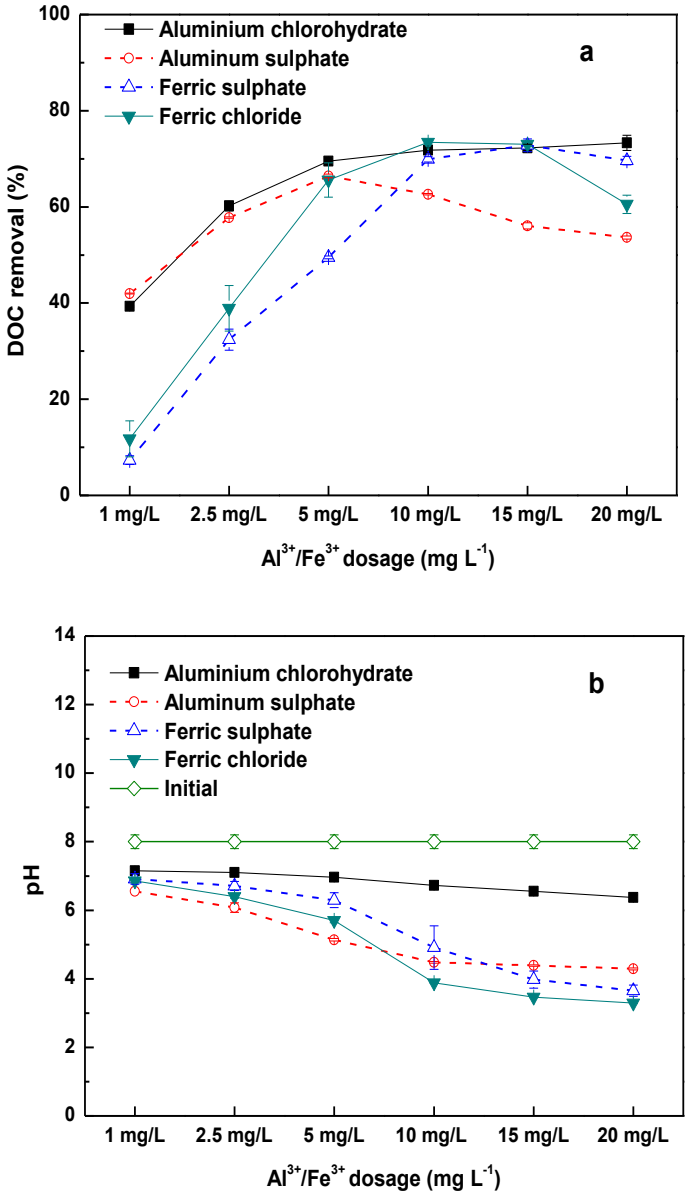
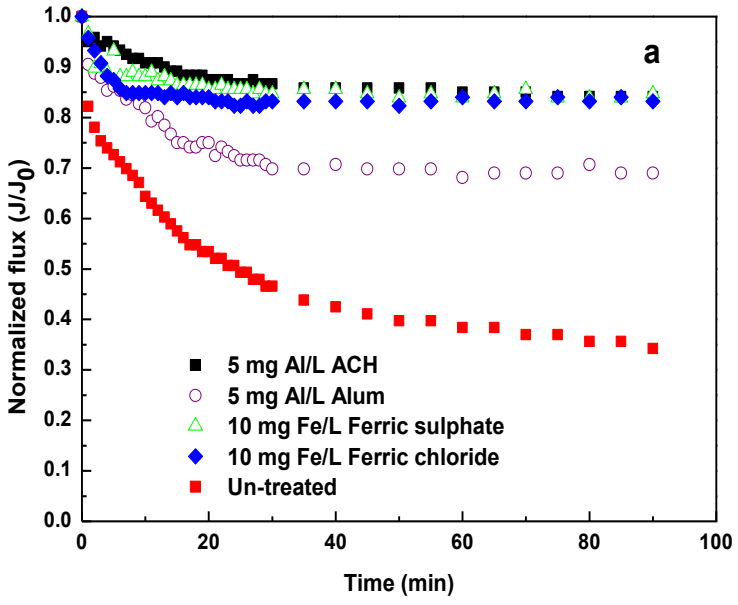


Fig.1 Comparison of DOC removal and pH change for the four coagulants: a) DOC removal, b) pH of the coagulated AOM solutions

3.2 Microfiltration tests

The AOM solution without pre-treatment caused rapid and severe flux decline, with approximately 55% reduction in flux at the end of the filtration (Fig. 2a). Feedwater pre-treatment by coagulation reduced the flux decline significantly for all coagulants tested, indicating the foulant causing severe flux reduction was effectively removed through the coagulation process. Coagulation with ACH at 5 mg Al^{3+}/L resulted in a slightly higher flux compared with ferric chloride and ferric sulphate at 10 mg Fe^{3+}/L in the initial 20 min of filtration. After that the extent of flux reduction for the three coagulants became comparable and approximately 15% of flux decline was obtained at the end of the filtration. Coagulation with alum at 5 mg AL^{3+}/L gave less flux improvement compared with other coagulants, with around 25% of flux decline at the end of the filtration. Fouling resistance results indicated both reversible and irreversible resistance were reduced markedly due to the coagulation of the feedwater (Fig. 2b). The reduction in hydraulically reversible fouling was comparable for the four coagulants (91-95%), whereas ACH and $Fe_2(SO4)_3$ performed considerably better than alum and $FeCl_3$ in reducing the irreversible fouling.



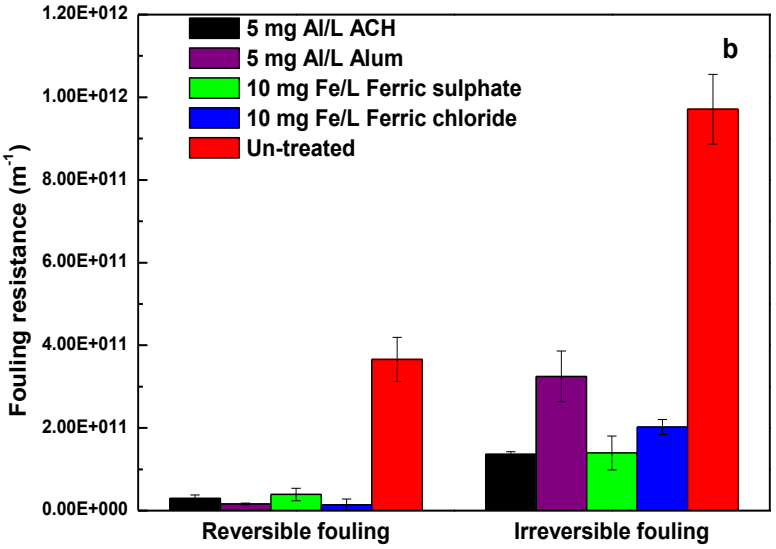


Fig.2 Comparison of (a) flux decline and; (b) fouling resistance in the MF of the un-coagulated and coagulated AOM solutions

3.3 Characterising the effect of coagulation by EEM spectra

Fluorescence EEM spectra have been employed as a useful tool in characterising aquatic organic matter including AOM [23]. EEM spectra can be divided into five regions. Regions I (Ex/Em: 220-270 nm/280-330 nm) and II (Ex/Em: 220-270 nm/330-380 nm) correspond to aromatic proteins (AP), and region III (Ex/Em: 220-270 nm/380-540 nm) is associated with fulvic acid (FA)-like substances. Regions IV (Ex/Em: 270-440 nm/280-380 nm) and V (Ex/Em: 270-440 nm/380-540 nm) represent soluble microbial products (SMPs, e.g., proteins and polysaccharide-like materials) and humic acid (HA)-like materials, respectively. The fluorescence regional integration (FRI) method was used to quantify the changes in the fluorescent organic species before and after the coagulation treatment [24]. All four coagulants gave greater reductions in HA-like (58-77%) and SMP (62-78%) substances than AP (25-41%) and FA-like (49-62%) substances (Fig. 3). Since the HA-like substances in AOM were shown to have less impact on the flux decline for the ceramic MF membrane compared with SMPs and AP [25], the results suggested the flux improvement in this study was primarily due to the removal of the SMPs. The removal in the SMPs by ACH

(77%) and $FeCl_3$ (78%) was greater than for alum (63%) and $Fe_2(SO_4)_3$ (62%), which was consistent with the resultant higher flux for the ACH and $FeCl_3$ treated water. Although relatively a lower SMP removal was observed for $Fe_2(SO_4)_3$ compared with ACH and $FeCl_3$, the $Fe_2(SO_4)_3$ treated water exhibited a similar permeate flux as the water treated by ACH and $FeCl_3$ (Fig. 2a). This was likely attributed to the better removal of AP (41%) and FA (62%) removal for $Fe_2(SO_4)_3$ than the other coagulants, since these organic substances also have high fouling potentials for the ceramic MF membrane [25] .

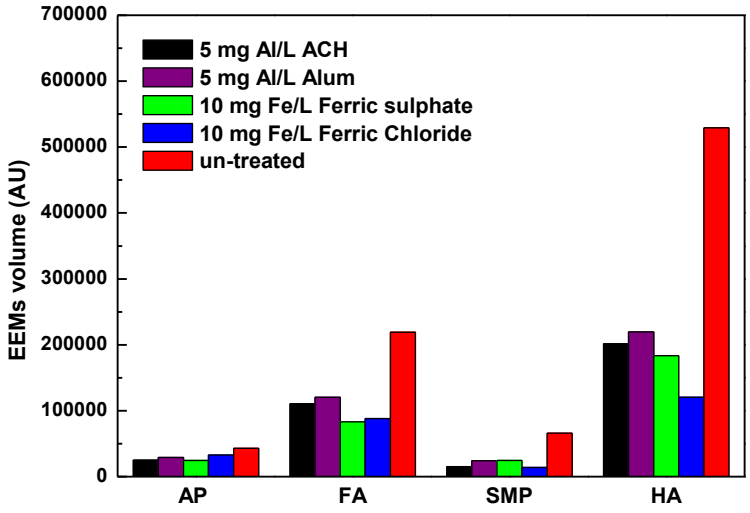


Fig.3 EEM spectra volumes for the AOM solutions before and after coagulation

3.4 Effect of coagulation on molecular weight of AOM

The apparent molecular weight distribution of the AOM before and after coagulation treatment was examined using SEC with LC-OCD (Fig. 4). The untreated AOM solution contained significant amounts of very high molecular weight (MW) biopolymers (>> 20,000 Da), including two peaks which appeared between 20 and 40 min retention time, medium-MW components (i.e., humic-like substances, ~1,000 Da and building blocks, 350-500 Da), and low-MW substances (< 350 Da). The organics associated with the second biopolymer peak (at around 38 min retention time) were likely mainly comprised of relatively lower MW

biopolymers such as small polysaccharides, polypeptides and polyamino acids in the AOM solutions [5].

According to the LC-OCD data, over 90% of the very high MW biopolymers were removed by the coagulation treatments. The iron based coagulants tended to remove more humic-like compounds than the aluminum based coagulants (e.g., ~ 50% for $Fe_2(SO_4)_3$ and $FeCl_3$ compared with 42% and 23% for alum and ACH). The results were consistent with some published studies in which it was observed coagulation tended to remove more macromolecules (such as biopolymers) than medium MW molecules (such as humic-like substances) from the biologically treated municipal wastewater [9, 26]. The significant reduction in flux decline after the coagulation treatment was therefore attributed to the effective removal of the macromolecules, which helped to mitigate the formation of the high-resistance outer fouling layer on the membrane [5].

The greater removal of the high MW biopolymers during the coagulation was related to the properties of these molecules. The high MW biopolymers mainly consist of polysaccharides and proteinaceous materials [4]. The high MW polysaccharides (such as transparent exopolymer particles) and proteins contained in AOM are reported to be very surface active, as the metal-binding functional groups (such as carboxyl and hydroxyl groups) in these organics are abundant [27]. Hence they could have strong potential to bind with trivalent metals (such as Al^{3+} and Fe^{3+}) to form larger size complexes [28, 29]. However, other coagulation mechanisms (such as sweep-floc and charge neutralization) may also have contributed to the removal of the biopolymers during coagulation. This would be due to the negatively charged AOM molecules (measured as -27 mV under the experimental conditions), the coagulant dosage and solution pH (4-7) used, which are likely to lead to the removal of the high MW molecules through these mechanisms [30].

It was observed that there was an increase in organic compounds with low MW (<350 Da) after the coagulation, this was probably due to the breaking down of macromolecules or the formation of some metal-organic complexes [31]. These compounds were not likely to be retained by the ceramic MF membrane due to these molecules being significantly smaller than the pore size of the membrane.

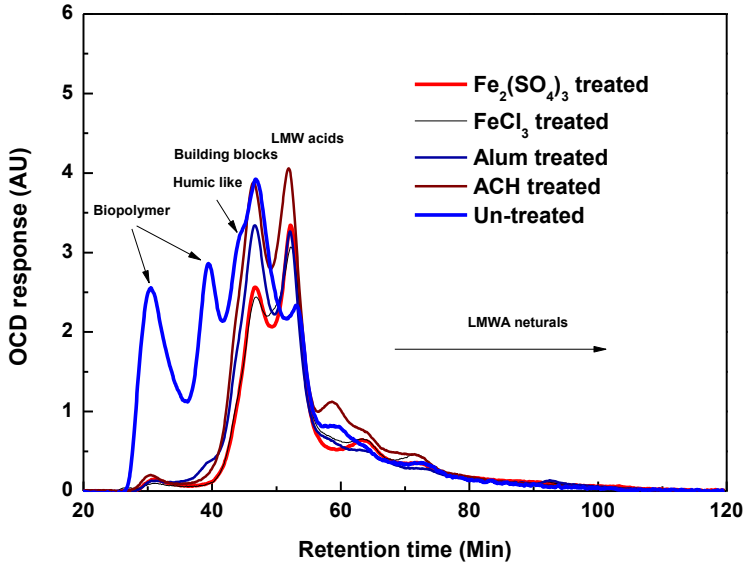


Fig.4. Comparison of LC-OCD chromatograms for the AOM before and after coagulation.

3.5 Effect of coagulation on carbohydrate and protein removal

As the biopolymers such as polysaccharides and proteins played an important role in the membrane flux decline, the carbohydrate and protein content of the AOM before and after the coagulation was analysed. The carbohydrate removal was similar for all types of coagulant, with the removal efficiency of 74 - 77% (Fig. 5). However, the protein removal efficiency for all types of coagulant was markedly lower (15-28%). The results suggested the very high MW and high MW molecules removed by coagulation (as indicated in LC-OCD chromatograms) were mainly consisted of carbohydrates (such as polysaccharides) instead of proteins. Hence it appeared that the carbohydrate compounds in the AOM were more susceptible to coagulation treatment. The relatively lower protein removal was probably

because some of the protein molecules had the capacity to form small complexes with coagulants, which inhibit the coagulation efficiency [32].

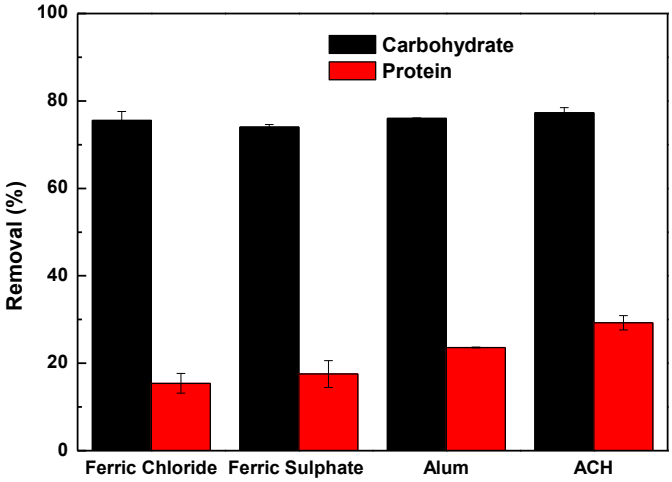


Fig.5 Removal of carbohydrate and protein content from the untreated and coagulated AOM. (The initial carbohydrate and protein concentration in un-treated solution was 5.2 ± 0.4 mg/L and 2.0 ± 0.1 mg/L, respectively.)

3.6 Characterising the effect of coagulation by organic matter fractionation

The AOM before and after coagulation was fractionated into different organic groups based on their hydrophobicity using resin adsorption chromatography. Our previous study showed the HPO and HPI fractions of the AOM had significantly higher fouling potentials than TPI in increasing flux decline and irreversible fouling resistance [25]. All coagulants achieved significant reductions in all three fractions (Fig. 6). Coagulation tended to reduce the HPO more than the TPI and HPI, with the average removal efficiencies of 78% for HPO, 70% for TPI and 52% for HPI. $FeCl_3$ and $Fe_2(SO_4)_3$ gave 85% and 81% reduction in HPO compounds, which were considerably higher than ACH (77%) and alum (69%). It appeared the iron based coagulants were more effective in removing the HPO compounds compared with the aluminum based coagulants, whereas the HPI removal by the four coagulants was fairly comparable (<5% difference). Although coagulation with ACH gave a considerably lower removal in HPO compounds compared with the iron based coagulants, it led to a

similar reduction in permeate flux decline as $FeCl_3$ and $Fe_2(SO_4)_3$. This might suggest that the hydrophilic compounds played a more important role in determining the flux performance for the ceramic membrane, since hydrophobic interaction between the organic compounds and membrane materials would not be significant due to the highly hydrophilic nature of the ceramic membrane [5].

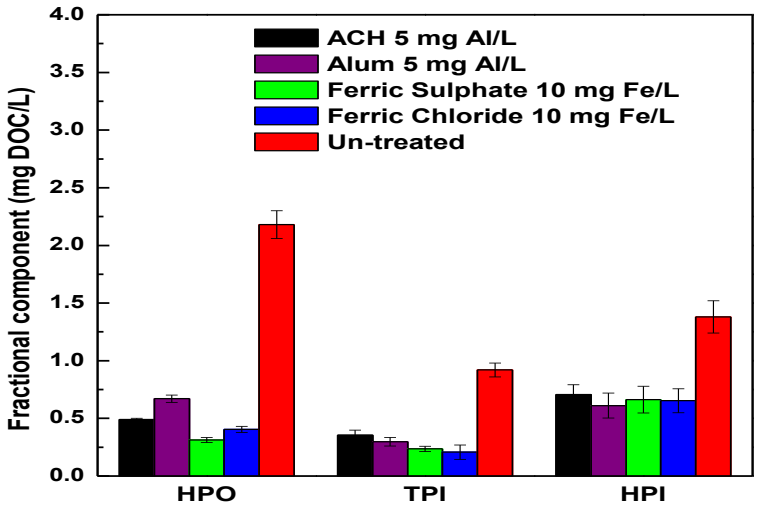


Fig.6 AOM fractions before and after coagulation.

3.7 Membrane fouling analysis

In order to investigate the influence of coagulation on the fouling of the ceramic MF membrane in the filtration of the AOM solutions, the classic filtration models were fit by the experimental flux data. The R^2 values obtained by fitting the flux data were used to indicate the major fouling mechanism for the AOM feed solutions with and without coagulation pre-treatment (Table 2).

The best fit (with the highest R^2 value) of the experimental data for the non-coagulated AOM solution was the cake filtration model. This was consistent with our previous study that the majority of flux decline during the MF of AOM with the ceramic membrane was attributed to the formation of a cake layer on the membrane surface [7]. The highest R^2 values for the coagulated AOM feed solutions were given by the intermediate blocking model, except for

the alum-treated solution. The shift of filtration mode before and after coagulation was most likely attributed to the removal of large MW biopolymer molecules during the coagulation process. Therefore, the improved flux resulting from the coagulation with ACH, $Fe_2(SO_4)_3$ and $FeCl_3$ would be due to the mitigation of the formation of a cake layer by the high MW molecules [7].

The best fit for the alum-treated AOM feed solution was cake filtration. One possible explanation is that the alum-treated AOM solution contained a greater amount of HPO compounds (as shown in Fig.6) compared with the solutions treated with the other coagulants. These HPO compounds may aggregate together on the membrane surface via hydrophobic interaction during the MF process. This mechanism is supported by our previous findings that the HPO compounds played a very important role in cake layer formation on the membrane surface [7]. However, due to the high MW compounds being largely removed from the AOM solution during the coagulation process, the cake layer would be lower in thickness compared with the un-treated AOM solution, resulting in the substantially improved flux.

Table 2 Summary of the R^2 values for the AOM solutions with and without coagulation pre-treatment.

Model	Non-coagulated	ACH	Alum	Ferric sulphate	Ferric chloride
Complete blocking	0.9195	0.8808	0.8626	0.6296	0.7931
Intermediate blocking	0.9559	0.9268	0.9003	0.8932	0.9437
Standard blocking	0.9869	0.6654	0.7488	0.6332	0.7154
Cake filtration	0.9884	0.9107	0.9176	0.6705	0.9007

4 Conclusions

The effect of the four commonly used water treatment coagulants (i.e., alum, ACH, ferric sulphate and ferric chloride) on mitigation of the fouling of a ceramic MF membrane caused by the AOM released from *Microcystis aeruginosa* was investigated. Treatment of the AOM solutions with the four coagulants led to marked reductions in both the reversible and irreversible fouling for the ceramic MF membrane at the optimal coagulant dosages. ACH, ferric chloride and ferric sulphate performed similarly in reducing the flux decline, while alum gave a considerably lower reduction in flux decline. Organic matter characterization using LC-OCD, fluorescence EEMs as well as carbohydrate and protein quantification indicated that the enhanced membrane performance was primarily due to the effective removal of the very high MW biopolymers (>> 20,000 Da) and hence the mitigation of the formation of the thick cake layer on the membrane surface. Although the cost of ACH, ferric chloride and ferric sulphate was fairly comparable (i.e. $ 0.03, $ 0.02 and 0.04 kL^{-1}, respectively), the iron-based coagulants caused a drastic drop in pH for the feed water, which would lead to a considerable increase in the treatment cost due to the necessary pH adjustment. As such, ACH appeared to be a more cost-effective coagulant in maintaining the performance of the ceramic MF membrane systems during cyanobacterial bloom events. It is suggested that further investigations should be conducted in order to gain a better insight into the key mechanism controlling the removal of the high MW biopolymer molecules, with a view to further optimizing the coagulation process.

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