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Characterisation of the influence of algal organic matter on the fouling of a ceramic MF membrane

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ABSTRACT

Blooms of blue-green algae such as *Microcystis aeruginosa* in natural waters or treated wastewater can result in substantial algal organic matter (AOM) entering downstream water treatment/recycling facilities. The influence of the characteristics of AOM on the fouling of a 7-channel tubular ceramic MF membrane (0.1 *μ*m) was investigated under dead-end filtration mode at a constant pressure of 70 kPa. The AOM (~ 3 mg DOC/L) extracted from a *M. aeruginosa* culture at different phases of growth all caused severe flux decline, but showed different fouling potentials, with 35 (stationary phase) > 20 > 10 days. The major components responsible for the fouling were identified as soluble microbial products such as proteins and polysaccharides, and humic substances.

For the AOM at stationary phase, greater flux decline and hydraulically irreversible fouling were observed for 0.45 and 1 *μ*m pre-filtered feed compared with 5 *μ*m pre-filtration. The non-pre-filtered feed (with algal cells) caused the greatest flux decline at the later stage of the filtration (specific permeate volume > 40 L/m^2). The addition of calcium to the feed led to reduced membrane fouling due to AOM-calcium interactions, implying that chemical coagulation may be an effective approach to mitigate the AOM fouling of the ceramic MF membrane.

Keywords: Algal organic matter (AOM); ceramic membrane; fouling; characterization; *Microcystis aeruginosa*

1. INTRODUCTION

Low pressure membrane (LPM) processes such as microfiltration (MF) and ultrafiltration (UF) are now widely used in drinking water and wastewater treatment due to their high cost-effectiveness (Lee 2004). The use of ceramic MF and UF membranes for water treatment has become popular in recent years as the ceramic membranes possess many advantages over the conventional polymeric LPMs, including higher

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selectivity, higher mechanical and chemical stability, and higher hydrophilicity (Hofs 2011). However, membrane fouling is commonly regarded as a major drawback for LPM processes, since it can lead to substantial loss of product water flux over time and consequent reduction in the efficiency of the water purification system (Bacchin 2006).

Blooms of blue green algae (also termed cyanobacteria) caused by eutrophication of aquatic systems have become a serious environmental issue worldwide. Blooms in natural surface water and treated wastewater can result in large amounts of algal organic matter (AOM) entering downstream water treatment/recycling systems (Fang 2010). The algal organic compounds are dominated by hydrophobic proteins and hydrophilic polysaccharides (Her 2004; Pivokonsky 2006; Henderson 2008), which have been widely regarded as responsible for the significant fouling issues in membrane filtration processes (Chiou 2010). It has been demonstrated that the presence of AOM associated with natural organic matter in surface water or effluent organic matter in wastewater can further reduce the filterability of polymeric MF/UF membranes (Lee 2006; Goh 2010; Goh 2011). Some efforts have been made since to characterise the AOM fouling of polymeric MF/UF membranes, with a view to understanding the fouling mechanisms. Qu et al. (2012a,b) investigated the impacts of interfacial characteristics of extracellular organic matter (EOM) extracted from *Microcystis aeruginosa* including surface charge, molecular size and hydrophilicity on fouling of UF polymeric mebranes. They also compared the impacts of dissolved EOM and cell surface EOM on fouling of the membranes. It was concluded EOM caused more serious flux decline than algal cells due to greater pore plugging and less porous cake layer formed by the EOM. It was found in a further study by the same research group that EOM could cause more severe flux decline and less irreversible fouling on the membranes than cell surface EOM as a result of more surface charge and stronger hydrophilicity (Qu 2012c). In another study by Huang et al. (2012), it was observed that different AOM compositions due to different nutrient conditions had different impacts on fouling of polymeric MF membranes. The high fouling potential of AOM was attributed to the high molecular weight polysaccharide-like and protein-like substances.

Although attention has been drawn to the application of ceramic membranes, information regarding to AOM fouling of ceramic membranes has not been documented to date. A better understanding of AOM fouling of ceramic membranes (which are significantly different from polymeric membranes in terms of physical, chemical and mechanical properties) is essential for effective operation of ceramic membrane based processes. As such, the purpose of this study was to characterise the impact of AOM fouling on a ceramic MF membrane using a lab-scale rig. The influence of the AOM from different phases of *M. aeruginosa* growth, AOM pre-filtraion, and the presence of calcium ions on the AOM fouling of a ceramic MF membrane was investigated.

2. MATERIALS AND METHODS

2.1 Cultivation of algae, AOM extraction and preparation of AOM solutions

M. aeruginosa (CS 566/01-A01) was purchased from CSIRO Microalgae Research

Centre (Tasmania, Australia). The algal cultures were grown in 5 L Schott bottles at 22 ^{o}C using MLA medium (Bolch 1996) under humidified aeration. A16/8 hour light/dark cycle was used to simulate natural light condition. According to several reports, algae have high absorbance at 684 nm (Zhang 2006a,b, Rajasekhar 2012). Optical density (OD) of the algal cell suspension was therefore used to measure *M. aeruginosa* cell concentration in this work. The OD was measured using an UV/vis spectrophotometer (UV2, Unicam). The correlation between OD_{684} and cell count (5 ×10^3 to 5 × 10^6 cells mL^{-1}) was validated as indicated by a strong linear relationship (R^2 > 0.99) (data not shown).

Algal cultures were harvested at the 10th, 20th and 35th day (stationary phase) of growth. Centrifugation (3269 × g for 30 mins) and the subsequent filtration of the supernatant (using 0.45, 1.0 or 5.0 μm membrane filters) were conducted to extract AOM from the algal cell suspensions. The AOM obtained from the three different growth phases (1 μm pre-filtered unless otherwise stated) were diluted to approximately the same concentration (5.0 ± 0.2 mg DOC/L) with tap water (1.9 ± 0.05 mg DOC/L) to prepare the feed water for MF tests.

2.2 Rig configuration

A 7-channel tubular ceramic ZrO_2-TiO_2 MF membrane with a nominal pore size of 0.1 μm (CeRAM ^{TM} INSIDE, TAMI Industries) was used. Filtration experiments were conducted using a laboratory-scale ceramic membrane system (Fig. 1). The rig can be operated in either dead-end or cross-flow mode by closing or opening the downstream valve. All filtration trials were carried out in dead-end mode at a constant pressure of 70 ± 1 kPa and operated at room temperature (22 ± 2 ^{o}C).

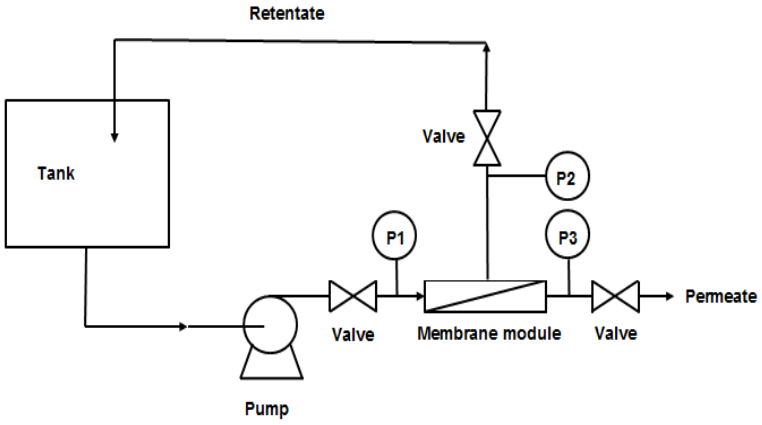

Fig. 1 Schematic diagram of the ceramic membrane filtration system

2.3 Microfiltration test

Prior to each filtration test, the clean water flux of the clean membrane (J_0) was obtained by filtering the tap water for 2 minutes. The pH of the AOM solutions was adjusted to 8.0 ± 0.2 using 1 M hydrochloric acid (HCl) or 1 M sodium hydroxide

(NaOH). In each MF run, the AOM solution was filtered for 90 minutes, and membrane permeate was sampled after 15, 30, 60 and 90 minutes filtration. After filtration of AOM solution, the clean water flux of the fouled membrane (J_a) was determined by filtering tap water for 2 minutes. The membrane was then backwashed using tap water at a transmembrane pressure of 70 kPa for 2 minutes, and the clean water flux of the backwashed membrane (J_b) was measured by filtering tap water for 2 minutes. Reversible fouling (RF), an indicator of the affinity of membrane foulant, in the MF of the AOM solutions was estimated using the following equation (Eq. (1)) (Hashino 2011).

$$RF = \frac{J_b - J_a}{J_0 - J_a} \times 100\% \quad (1)$$

The same membrane was used for all MF tests, and after each run the membrane was restored by Cleaning in Place (CIP) until the permeate flux reached 138-148 LMH. CIP was carried out through the following steps: 1) 0.1M NaOH solution (65 ^{o}C) for 30 mins; 2) 0.1M HNO_3 solution (65 ^{o}C) for 20 mins; 3) tap water (18 - 20 ^{o}C) for 2 mins. All filtration tests were run in duplicate. As the final flux of the duplicate tests typically agreed within 5% and the trend was found to be consistent between the duplicate tests, only one set of flux data was reported. Reversible fouling results were reported using average values with variations indicated.

2.4 Analytical methods

pH was measured with a pH meter (Mettler Toledo). DOC was determined using a Sievers 820 TOC analyser. UVA_{254} and OD_{684} were analysed by an UV/vis spectrophotometer (UV2, Unicam). Fluorescence excitation-emission matrix (EEM) spectra were obtained using a fluorescence spectrophotometer (LS 55, PerkinElmer) at an excitation and emission wavelength range of 200–550 nm. The concentration of calcium was measured with an atomic absorption spectrometer (AA240FS, Varian Australia). Apparent molecular weight distributions of the AOM from different phases of algal growth were determined using liquid chromatography with organic carbon detection (LC-OCD) at the Water Research Centre of the University of New South Wales, Sydney, Australia.

3. RESULTS AND DISCUSSIONS

3.1 Influence of AOM from different phases of M. aeruginosa growth on membrane fouling

3.1.1 Flux decline and reversibility of AOM fouling

Rapid flux decline was observed during the MF of the three solutions containing the AOM extracted at 10, 20 or 35 days of *M. aeruginosa* growth, with the majority of the flux decline occurring before the specific permeate volume reached 30 L/m^2 (Fig. 2). In the initial stage of filtration (< 30 L/m^2), the solution containing Day 35 AOM gave a

much quicker and greater flux reduction compared with Day 10 and 20 AOM solutions which had similar rate and extent of flux decline. The flux for the Day 35 AOM solution flatted after the initial stage of filtration, whereas Day 10 and 20 AOM solutions gave considerable further reductions in flux afterwards. At the end of the filtration, Day 20 AOM exhibited similar flux decline to Day 35 AOM, and was about 5% greater than Day 10 AOM. Control filtration tests with MLA solution (the content of the MLA in the MLA solution was the same as that found in the D10 AOM solution) and tap water showed the flux decline was relatively insignificant compared with the AOM solutions. The impact of MLA and the organic matter in the tap water on the membrane fouling was therefore negligible in this study.

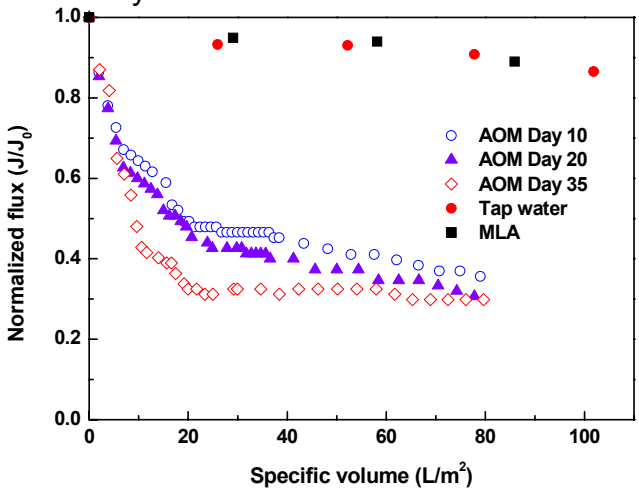

Fig. 2 Normalized flux as a function of specific volume for the MF of tap water, MLA solution and the solutions containing AOM from different phases of *M. aeruginosa* growth

The extent of reversible fouling by the AOM decreased with increased *M. aeruginosa* growth time, with 35% for Day 10, 17% for Day 20 and 10% for Day 35. Hence the AOM obtained from a later phase of algae growth had higher affinity for the ceramic MF membrane compared with the AOM from an earlier growth phase, and consequently led to more severe irreversible membrane fouling.

3.1.2 AOM rejection by the ceramic MF membrane

The DOC rejection was similar (31-35%) for the AOM at different phases of *M. aeruginosa* growth, and the DOC rejection for each individual AOM was fairly consistent (variation 2-4%) over the filtration period. A similar trend was observed for UVA rejection results (16-20%), however UVA rejection was markedly lower than DOC rejection. The higher DOC but lower UVA rejection indicated that the organic matter retained by the membrane contained less UV-absorbing organic materials. As suggested by Zheng et al. (2009), the retained organic matter would contain a large portion of biopolymer substances, such as proteins and polysaccharides.

3.1.3 Fluorescence EEM spectra of the AOM before and after MF

EEM spectra are widely used to characterise organic components in surface water and treated wastewater. According to Chen *et al.* (2003), EEM spectra can be divided

into 5 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 and region III (Ex/Em: 220-270 nm/380-550 nm) is associated with fulvic acid-like substances. Regions IV (Ex/Em: 270-440 nm/280-380 nm) and V (Ex/Em: 270-440 nm/380-550 nm) represent soluble microbial products (SMPs, e.g., proteins and polysaccharide-like materials) and humic acid-like materials, respectively. The AOM extracted from different phases of algae growth had markedly different EEM spectral features (Fig. 3(a), (b), (c)). The fluorophores increased during the growth phase. Noticeable reductions in fluorescence intensities at all regions were shown after MF, and more reductions were shown at Regions I, II and IV (Fig. 3(e), (f)) for Day 20 and 35 AOM. This suggested that more aromatic proteins, polysaccharide-like and fulvic-acid like materials were retained by the membrane, and they may play important roles in fouling the membrane.

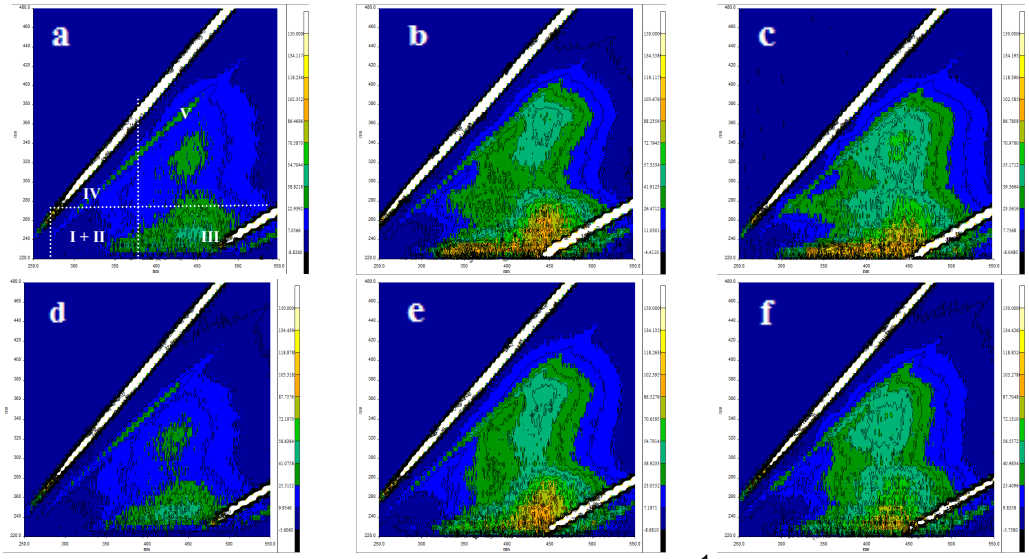

Fig. 3 EEM spectra of (a) Day 10 AOM (DOC 4.82 mg L^{-1}); (b) Day 20 AOM (DOC 5.01 mg L^{-1}); (c) Day 35 AOM (DOC 4.90 mg L^{-1}); (d) Day 10 AOM after MF (DOC 3.23 mg L^{-1}); (e) Day 20 AOM after MF (DOC 3.19 mg L^{-1}); (f) Day 35 AOM after MF (DOC 3.22 mg L^{-1})

3.2 Influence of AOM pre-filtration on fouling of ceramic membrane

The impact of AOM pre-filtration was studied by comparing the flux decline and reversible fouling for the feed solutions with 0.45, 1 and 5 μm pre-filtered AOM and non-pre-filtered AOM (with *M. aeruginosa* cells) (Fig. 4). The AOM after 5 μm pre-filtration gave significant less flux reduction during the whole period of the filtration compared with the other feed solutions. Around 70% algal cells were removed by 5 μm pre-filtration (data not shown), and the lower flux reduction for the 5 μm pre-filtered AOM indicated that the remaining particulates (including the smaller sized algal cells) formed the fouling layer with lower filtration resistance. The 0.45 μm and 1 μm filtered AOM caused a similar flux decline over the filtration period, which was likely due to the two pre-filtration membranes being relatively similar in pore size and hence their filtrates would have similar physico-chemical properties. They caused greater flux

decline in the initial stage of the filtration compared with the AOM solution with algal cells, and the majority of the flux decline was reached at about 20 L/m^2. This suggested the formation of a denser layer on the ceramic membrane for the 0.45 μm and 1 μm filtered AOM, leading to a rapid and great reduction in flux. However, the non-pre-filtered AOM produced a greater flux decline after 40 L/m^2, which indicated that larger sized particulates (> 5 μm, such as algal cells) played an important role in enhancing the flux decline at the later stage of the filtration.

The above results may imply that both dissolved AOM (< 0.45 μm) and the particulates in the AOM solutions can affect the filtration process. The dissolved AOM can cause much quicker and greater flux decline due to the resultant denser fouling layer, and the presence of particulates can alleviate the initial rapid flux decline due to the formation of a more porous layer of lower resistance. However, the particulates can build up on the membrane surface and make the fouling layer thicker as the filtration proceeds, and hence increase the filtration resistance, leading to greater further reduction in flux at the later stage (after 40 L/m^2) of filtration. In addition, the AOM covering the algal cells can cause linkages between the cells, leading to a more compact cake layer under the system pressure and hence further reduction in flux (Babel 2010).

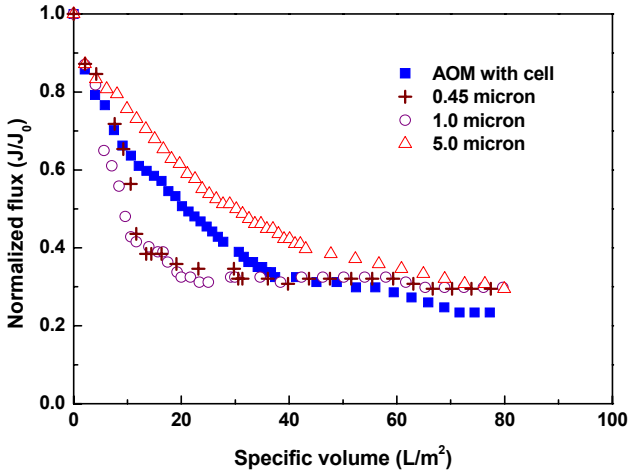

Fig. 4 Normalized flux vs. specific volume during MF of the solutions of: 1) AOM with cells; 2) 0.45 μm pre-filtered AOM; 3) 1.0 μm pre-filtered AOM; 4) 5.0 μm pre-filtered AOM.

It was observed that feed water with the 5 μm pre-filtered AOM gave the highest reversible fouling (around 21%). High reversible fouling was likely due to the loosely bonded “pre-layer” preventing the small organics from entering the membrane pores, which led to the reduced irreversible fouling. As a comparison, only 8-10% reversible fouling was obtained for the AOM pre-filtered by the 0.45 or 1 μm filters. The non-pre-filtered AOM solution (with cells) also produced lower reversible fouling (10%). This was probably due to the presence of the algal cell surface AOM (also termed bound EOM) which was reported to have higher potential of membrane irreversible fouling compared with the dissolved AOM (Qu 2012c).

3.3 Influence of calcium on AOM fouling

In order to get further insights into the interfacial characteristics of the AOM, calcium ($CaCl_2$) of different concentrations was added to the feed solutions containing the AOM from the stationary phase. Addition of calcium reduced the flux decline markedly (Fig. 5), with 2.5 mM of calcium giving slightly greater flux improvement compared with 1 and 5 mM which gave similar flux enhancement. At a higher calcium dosage (10 mM), the flux improvement was reduced initially (before 40 L/m^2), but the flux was then maintained over the later stage of the filtration. The reduction of flux decline by addition of calcium was most likely due to AOM-Ca^{2+} interaction. As noted by Qu (2012a), the addition of calcium increased the AOM molecular sizes due to complexation effect. The "enlarged" AOM could form a more porous pre-layer and result in a higher filtration flux. This also led to the increased reversible fouling at all calcium dosages (from 11% to 20-25%).

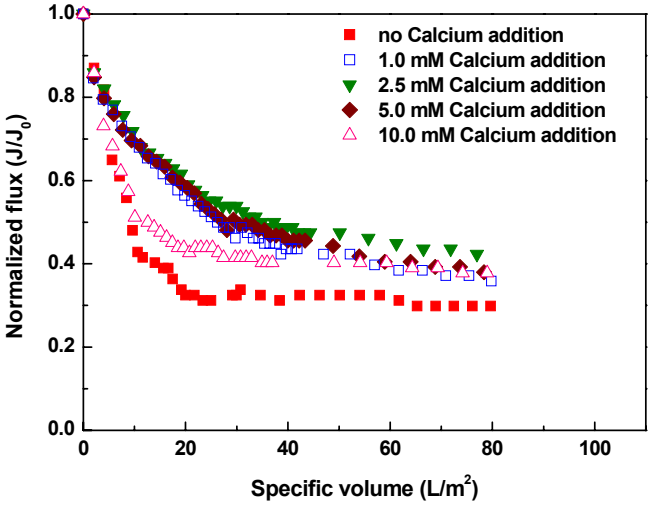

Fig. 5 Normalized flux vs. specific volume for the MF of AOM solutions with and without addition of calcium

4. CONCLUSIONS

The influences of the AOM extrated from different phases of *M. aeruginosa* growth, AOM pre-filtration and the presence of cacium ions on the fouling of a ceramic MF membrane were studied. AOM from different algal growth phases all casued rapid and great flux decline, but exhibited different fouling potentials, with fouling for Day 35 (stationary phase) > 20 > 10. The major components responsible for the fouling were identified as the soluble microbial products such as proteins and polysaccharides and humic substances including fulvic-acid like materials. At stationary phase, the 0.45 and 1 μm pre-filtered AOM caused more rapid flux decline compared with the 5 μm pre-filtered AOM. However, non pre-filtered AOM solution (with algal cells) produced the greatest fouling at the later stage of the filtration (specific permeate volume > 40 L/m^2), which was likely resulted from the increased filtration resistance due to the build up of

the cake layer. The addition of calcium to the AOM solutions led to reduced flux decline and increased reversible fouling due to the AOM-calcium interactions, where the AOM molecules were combined with calcium ions to form lager sized complexes and hence more porous foulant layer on the membrane surface.

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