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Influence of the characteristics of soluble algal organic matter released from *Microcystis aeruginosa* on the fouling of a ceramic microfiltration membrane

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ABSTRACT

The influence of the characteristics of soluble algal organic matter (AOM) on the fouling of a 7-channel tubular ceramic microfiltration membrane (ZrO_2–TiO_2, 0.1 μm) was investigated at lab scale. The AOM (3 mg DOC/L) extracted from a *Microcystis aeruginosa* culture at three phases of growth (10, 20 and 35 days) all caused severe flux decline, and its fouling potential increased with increasing growth time. Size exclusion chromatography, fluorescence excitation–emission matrix spectra and organic matter fractionation showed that the high MW biopolymers were the major component determining the severity of the AOM fouling of the ceramic membrane. For the AOM at stationary phase (35 days), 0.45 and 1 μm pre-filtration gave greater flux decline and hydraulically irreversible fouling than 5 μm pre-filtration due to the denser foulant layer formed and greater amounts of small organic molecules entering membrane pores. However, the non-pre-filtered AOM (with algal cells) caused the greatest flux decline which was likely due to the presence of the high fouling potential cell surface organic matter. The addition of calcium to the feed solutions led to a marked improvement in flux and reduction in membrane irreversible fouling due to the lower fouling potential of the AOM-calcium complexes formed.

1. Introduction

Low pressure membrane processes such as microfiltration (MF) and ultrafiltration (UF) are being widely used for the purification of drinking water and wastewater treatment due to their high cost-effectiveness [1]. 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 conventional polymeric membranes, such as higher selectivity, higher mechanical and chemical stability, and higher hydrophilicity [2]. However, membrane fouling remains a major drawback for most of the membrane-mediated water treatment processes, since it can lead to substantial losses of product water flux over time and the consequent great reduction in the efficiency of the treatment systems [3].

Blooms of cyanobacteria (also termed blue green algae) such as *Microcystis aeruginosa* in increasingly eutrophic aquatic systems have become a serious environmental issue worldwide. The blooms in natural surface water and treated wastewater can result in a large amount of soluble algal organic matter (AOM) entering downstream water treatment systems [4]. The algal organic compounds are commonly dominated by hydrophobic proteins and hydrophilic polysaccharides which have been widely regarded as responsible for the significant fouling issues in membrane filtration processes [5]. 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 flux of polymeric MF/UF membranes [6–8]. Some efforts have been made since to characterise the AOM fouling of the polymeric MF/UF membranes, with a view to understanding the fouling mechanisms. Qu et al. [9] investigated the influence of the interfacial characteristics of AOM extracted from *M. aeruginosa* including surface charge, molecular size and hydrophilicity on the fouling of UF polymeric membranes. They also studied the impact of the AOM and algal cells on membrane fouling, and reported that the AOM caused greater flux decline than algal cells due to greater pore plugging and less porous cake layer formed by the AOM [10]. It was found in a further study by the research group that the dissolved AOM could cause greater flux decline but less irreversible membrane fouling compared with cell surface AOM. They suggested that this was because the cell surface AOM contained more large and hydrophobic molecules, which could result in the foulant layer being more porous but having a higher affinity to the membrane surface than dissolved AOM [11]. In another study, Huang et al. [12] observed that different AOM compositions due to different nutrient conditions had different impacts on the fouling of the polymeric MF membranes. The high fouling potential of AOM was attributed to

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the high molecular weight polysaccharide-like and proteinaceous substances.

Although great attention has been drawn to the application of ceramic membranes in water and wastewater treatment, the information regarding AOM fouling of these membranes is very limited 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 the effective design and operation of the processes. As such, the aim of this study was to investigate the impact of the characteristics of soluble AOM on the fouling of a commercially available ceramic MF membrane at lab scale. The influence of the AOM from different phases of *M. aeruginosa* growth, feed solution pre-filtration, and the presence of calcium ions on the fouling was investigated. Advanced organic matter 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 employed to gain a better insight into the characteristics of the organic compounds involved.

2. Experimental

2.1. Cultivation of algae, 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 at 22 °C using MLA medium [13] under humidified aeration. A 16/8 h light/dark cycle was used to simulate natural light conditions. According to several reports, the algae have high absorbance at 684 nm [14–16]. Optical density (OD) of the algal cell suspension was therefore used to measure algal cell concentration. The correlation between OD_{684} and cell count ($5\times10^3-5\times10^6$ cells mL^{-1}) was verified as indicated by their strong linear relationship ($R^2>0.99$) (data not shown).

Algal cultures were harvested at the 10th (early exponential phase), 20th (late exponential phase) and 35th day (stationary phase) of growth. Centrifugation ($3270\times g$ for 30 min) of the algal cell suspensions and the subsequent filtration of the supernatant (using 1 μm membranes unless otherwise stated) were conducted to extract the dissolved extracellular AOM [8,9]. In the preparation of the MF feed solutions, the extracted AOM was diluted to approximately the same dissolved organic carbon (DOC) concentration (5.0 ± 0.2 mg/L) with tap water (1.9 ± 0.05 mg DOC/L). The pH of the MF feed solution was adjusted to 8.0 ± 0.2 using 1 M HCl or 1 M NaOH prior to each filtration run.

2.2. Ceramic membrane filtration rig

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. The active layer of this membrane is made of a mixture of ZrO_2 and TiO_2, and the support layer is made of TiO_2. These materials give the membrane a highly hydrophilic nature which can reduce the fouling potential to some extent. According to the manufacturer, the membrane can be operated at high temperature (up to 350 °C) and is insensitive to bases and acids. A schematic diagram of the lab-scale ceramic membrane system is presented in Fig. 1. The rig can be operated in either dead-end or cross-flow mode by closing or opening the downstream valve (Valve 3). All filtration runs were carried out in inside-out and dead-end modes at a constant transmembrane pressure (TMP) of 70 ± 1 kPa and under room temperature (22 ± 2 °C). Membrane backwashing was carried out by filtering tap water in outside-in operation mode (i.e., closing Valves 1 and 4, opening Valves 2 and 3) at the same TMP as the filtration runs.

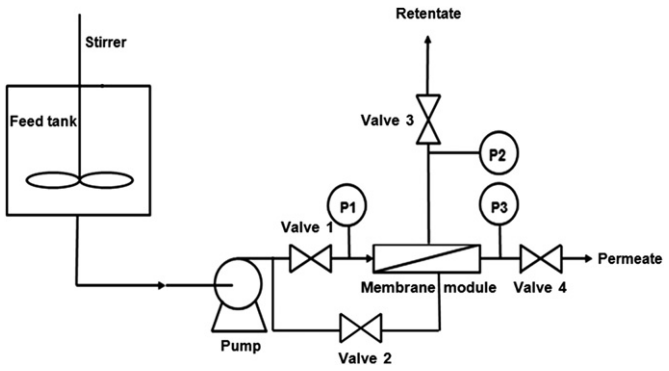

Fig. 1. Schematic diagram of the ceramic membrane filtration system, P1, P2, P3 are manometers.

2.3. Microfiltration test

Prior to each MF run, the clean water flux of the clean membrane (J_0) was obtained by filtering tap water for 2 min. The AOM solution was then filtered for 90 min under the defined conditions. Membrane permeate flow rate was recorded continuously, and the permeate was sampled after 15, 30, 60 and 90 min filtration for chemical analyses. After AOM solution filtration, the clean water flux of the fouled membrane (J_a) was determined by filtering tap water for 2 min. The membrane was then backwashed for 2 min, and the clean water flux of the backwashed membrane (J_b) was measured by filtering tap water for 2 min. Reversible flux (*RF*), an indicator of the affinity of foulant for the membrane, was estimated using the following equation (Eq. (1)) [17]. The series resistances including reversible (R_r) and irreversible filtration resistance (R_i) were also calculated using the method described elsewhere [18].

$$RF=\frac{J_b-J_a}{J_0-J_a}\times100\% \quad (1)$$

The same membrane was used for all MF runs, 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) 0.1 M NaOH solution (65 °C) for 30 min; (2) 0.1 M HNO_3 solution (65 °C) for 20 min; (3) tap water (18–20 °C) for 2 min. 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 runs, only one set of flux data was reported. Reversible fouling results were reported using average values.

2.4. Analytical methods

DOC was determined using a Sievers 820 TOC analyser. UVA_{254} and OD_{684} were measured using a UV/vis spectrophotometer (UV2, Unicam). The pH was measured using a Hach Sension 156 pH meter. The concentration of calcium was measured with an atomic absorption spectrometer (AA240FS, Varian). 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