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Understanding the fouling of a ceramic microfiltration membrane caused by algal organic matter released from *Microcystis aeruginosa*

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ABSTRACT

Algal organic matter (AOM) released from *Microcystis aeruginosa* has high potential to cause fouling of water treatment membranes. The role of AOM components in the fouling of a commercial tubular ceramic microfiltration (MF) membrane (ZrO_2–TiO_2, 0.1 μm) was investigated. The organic matter extracted from the three operationally-defined fouling layers (i.e., outer, middle and inner layer detached from the membrane using cross-flow flush, backwash and chemical cleaning, respectively) was characterised to gain an understanding of the fouling mechanism. The majority of the flux decline in the MF of the AOM solution was attributed to the large amount of organic matter (51% of total DOC of feed, primarily very high molecular weight (MW) hydrophobic molecules) deposited on the ceramic membrane surface to form a thick and dense outer layer. The middle layer contained a very small amount of organics (3%), mainly very high MW hydrophilic molecules, and contributed very little to the flux decline. The inner layer (22% of total DOC), which was responsible for the hydraulically irreversible fouling, was dominated by the high and low MW hydrophilic compounds. These molecules reached the membrane inner pores due to their hydrophilic nature, leading to pore restriction by adsorptive fouling.

1. Introduction

Low pressure ceramic membranes are gaining increasing popularity for water and wastewater treatment due to their many inherent advantages over conventional polymeric membranes such as higher mechanical and chemical stability, and higher hydrophilicity [1]. However, membrane fouling by aquatic organic matter remains a critical factor limiting the efficiency of the low pressure ceramic membrane water treatment systems including microfiltration (MF) and ultrafiltration (UF) [2]. The fouling can result in a marked reduction in product water flux and a significant increase in transmembrane pressure, leading to increased operating and management costs [3]. Organic fouling of membranes is generally related to the formation of a gel/cake layer by colloidal/particulate organic matter on the membrane surface, and/or adsorption of dissolved organics within the membrane pore structure [4]. The fouling process can be influenced by various factors including the characteristics of the organics in feed water, membrane properties, solution environment and operating conditions [5].

Blooms of cyanobacteria (also referred to as blue-green algae) in fresh water and treated wastewater are a nuisance to the water industry, since the blooms can not only degrade the water quality but also negatively impact water treatment processes due to the presence of the algal organic matter (AOM) in the influent [6]. A number of studies have shown that the AOM can cause severe fouling of polymeric MF/UF membranes, leading to significant reduction of membrane permeability [7–11]. Very limited information has been published on the effect of AOM on ceramic membranes, which are significantly different from polymeric membranes in terms of physical, chemical and mechanical properties. Recently, Zhang et al. [12] demonstrated that the AOM released from *Microcystis aeruginosa*, a major bloom-forming cyanobacterium, reduced the flux of a ceramic MF membrane markedly at an AOM concentration of 3 mg L^{-1} of dissolved organic carbon (DOC). The fouling potential of the AOM was found to increase with increasing culture age, and it was concluded that the high molecular weight biopolymers/soluble microbial product-like substances (which include proteins and polysaccharides) in the AOM were a major cause of the fouling. However, there is still a lack of more detailed information about the contribution of AOM components to the fouling of low pressure ceramic membranes, which is critical to the development of strategies to mitigate their fouling when treating AOM-contaminated water.

A 3-step membrane cleaning approach for identifying the preferential deposition of organics on membranes has been used in some recent studies of the organic fouling of low pressure polymeric membranes in which the operationally defined fouling

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layers were sequentially detached from the fouled membranes by increasing the severity of the cleaning process [13–15]. The aim of the present work was to clarify the role of the components in the AOM released from *M. aeruginosa* in the fouling of a commercial ceramic MF membrane by using a modified 3-step membrane cleaning approach. The fouling layers were characterised using mass balances based on the DOC, protein and carbohydrate content of the MF feed, permeate and the foulant residing in each of the fouling layers. 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 organic matter fractionation by resin adsorption chromatography were also employed to gain further information on the AOM fouling mechanism.

2. Materials and methods

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 [16] under humidified aeration. A 16/8 h light/dark cycle was used to simulate natural light conditions. Algal cultures were harvested at the 35th day of growth (stationary phase). Centrifugation ($3270 \times g$ for 30 min) of the algal cell suspensions and subsequent filtration (1 μm membranes) of the supernatant were conducted to extract the soluble AOM. In order to avoid the interference due to the presence of other types of organic matter (e.g., natural organic matter in tap water), the AOM feed solutions were prepared by diluting the extracted AOM to 8 mg DOC/L with deionised water (DOC ~0.09 mg/L). In order to simulate the natural water matrix at the cyanobacterial bloom conditions, the pH of the feed solution was adjusted to 8.0 ± 0.2 using 1 M HCl or 1 M NaOH, and ionic strength to 9×10^{-4} M using NaCl prior to each run.

2.2. Microfiltration test

Filtration trials were carried out using a laboratory setup with a commercially available 7-channel tubular ceramic MF membrane (nominal pore size 0.1 μm, CeRAM™, TAMI Industries). The major specifications of the membrane can be found in the Supplementary Information (Table 1S). The surface layer of the ceramic membrane is made of ZrO_2 and the support layer is made of TiO_2. The membrane surface was considered as hydrophilic since ZrO_2-based membranes usually have a contact angle less than 20° due to the presence of surface hydroxyl groups [17], and would be negatively charged under the experimental conditions (i.e., at pH 8) [1]. The rig can be operated in either dead-end or cross-flow mode by closing or opening a downstream valve. More details about the filtration rig are available from elsewhere [12]. All filtration experiments were conducted for 90 min at room temperature (22 ± 2 °C) and at a constant transmembrane pressure (TMP) of 70 ± 1 kPa. The MF tests were carried out using inside-out and dead-end mode. The water flux for a virgin membrane under the above conditions was ~240 LMH. Prior to each MF test, the membrane was thoroughly cleaned by 0.05 M NaOH solution for 30 min and followed by 0.05 M HNO_3 for 20 min until the clean water flux reached 220 ± 10 LMH.

2.3. Detachment of membrane foulant

A modified 3-step cleaning protocol based on the approach reported by Henderson et al. [14] was employed to dissect the fouling layer, and hence to determine the preferential attachment of AOM components to the ceramic MF membrane. The three cleaning steps were firstly, a cross-flow flush with deionised water to detach the *outer* foulant layer and secondly, a dead-end backwash with deionised water (i.e., filtration of deionised water in outside-in mode) to release the foulant layer termed the *middle* layer. The third step was to detach the *inner* layer with cross-flow chemical cleaning. During the cross-flow flush, the hydraulic forces remove the organics mainly deposited on the membrane surface as a result of the strong hydraulic force on membrane surface. These foulants are considered to be weakly attached to the membrane. For the backwash, as the hydraulic force of the reverse flow inside the membrane pores is applied, the organics detached in this step are mainly those trapped in the membrane pores and some residual organics on the membrane surface, which cannot be removed by cross-flow flush. These organics are regarded as attached to/trapped in the membrane pores but are hydraulically removable. Since chemical cleaning can completely recover the flux of the membrane, the foulants removed by this step represent those strongly attached to the membrane since they are hydraulically non-removable. Upon removing each fouling layer, a clean water flux was measured to determine the filtration resistance associated with the fouling.

The details of the cleaning protocol are given below:

(1) After filtration of the AOM solution, the feedwater was replaced with deionised water which was filtered for 2 min to obtain the clean water flux of the fouled membrane (J_a).
(2) The membrane was flushed using deionised water for 5 min. The flush cleaning was carried out at a cross-flow velocity of 2.5 m/s and TMP of 40 kPa. The flushed membrane was then used to filter deionised water for 2 min to obtain the clean water flux (J_b).
(3) The membrane was backwashed with deionised water for 2 min at the TMP of 70 kPa. The backwash cleaning was conducted in outside-in and dead-end mode. The backwashed membrane was then used to filter with deionised water for 2 min to measure the clean water flux (J_c).
(4) Chemical cleaning was carried out using 0.05 M sodium hydroxide solution for 30 min in a cross-flow and inside-out mode and at the TMP of 40 kPa. The chemical cleaning solution was then replaced with 0.05 M HNO_3 solution for further cleaning for 20 min. This was to remove some precipitates formed during alkaline chemical cleaning. The clean water flux of the chemically cleaned membrane (J_d) was measured.

All the cleaning steps were carried out in place and the cleaning wastes were sampled for further chemical analyses. Filtration resistance (R) was determined using the following equations:

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

$$R_{Total} = R_{outer} + R_{middle} + R_{inner} + R_{membrane} \quad (2)$$

where ΔP is the transmembrane pressure; J stands for the flux and μ is the water viscosity at 22 °C (0.955×10^{-3} Pa s); R_{inner} represents the resistance of inner layer, R_{middle} denotes the resistance of middle layer, R_{outer} is associated with the resistance of outer layer and $R_{membrane}$ is the clean membrane resistance. The R values can be calculated by Eqs. (1) and (2) using the J values (J_a, J_b, J_c and J_d) determined using the cleaning protocol.

2.4. Analytical methods

DOC was determined using a Sievers 820 TOC analyser. UVA_{254} was measured using a UV/vis spectrophotometer (UV2, Unicam).