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Investigation of severe UF membrane fouling induced by three marine algal species

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ABSTRACT

Reducing membrane fouling caused by seawater algal bloom is a challenge for regions of the world where most of their freshwater is produced by seawater desalination. This study aims to compare ultrafiltration (UF) fouling potential of three ubiquitous marine algal species cultures (i.e., *Skeletonema costatum*-SKC, *Tetraselmis* sp.-TET, and *Hymenomonas* sp.-HYM) sampled at different phases of growth. Results showed that flux reduction and irreversible fouling were more severe during the decline phase as compared to the exponential phase, for all species. SKC and TET were responsible for substantial irreversible fouling but their impact was significantly lower than HYM. The development of a transparent gel layer surrounding the cell during the HYM growth and accumulating in water is certainly responsible for the more severe observed fouling. Chemical backwash with a standard chlorine solution did not recover any membrane permeability. For TET and HYM, the Hydraulically Irreversible Fouling Index (HIFI) was correlated to their biopolymer content but this correlation is specific for each species. Solution prefiltration through a 1.2 μm membrane proved that cells and particulate algal organic matter (p-AOM) considerably contribute to fouling, especially for HYM for which the HIFI was reduced by a factor of 82.3.

1. Introduction

Dual membrane system for seawater desalination treatment (i.e., low-pressure membrane followed by reverse osmosis) has been a worldwide research challenge since the last two decades (Huehmer, 2011). Its important development at full scale started during early 2000s and this combination of processes was quickly adopted as a promising technology (Busch et al., 2010). Energy saving and membrane maintenance under normal operation conditions were the major operational goals, however, algal bloom represents a major concern to this technology. For instance, in 2008, a *Cochlodinium polykrikoides* bloom in the Arabian Gulf led to the shutdown of several desalination plants (Berktay, 2011; Pankratz, 2008).

From an operational point of view, algal growth involves an increase of both suspended solid concentration and organic substances, which are responsible for severe membrane fouling (Caron et al., 2010). Even though the removal of algal cells is significantly higher with UF than with dissolved air flotation (DAF) and granular media filter (GMF), it may lead to algal cell lysis and therefore to the release of easily biodegradable organic matter, thus increasing the biofouling potential on seawater reverse osmosis membrane (Voutchkov, 2010).

In addition, the role of algal organic material in UF membrane fouling has been widely discussed in previous publications. However, these studies were mainly focused on freshwater algal culture with *Microcystis aeruginosa* as targeted phytoplankton (Qu et al., 2012a, 2012b; Yu et al., 2014; Zhang et al., 2013; Zhou et al., 2014). Qu et al. (2012b) showed that high-molecular weight extracellular organic matter exuded from *M. aeruginosa* highly contributes to UF membrane fouling. More recently, Zhou et al. (2014) confirmed that hydrophilic molecules caused higher flux decline while hydrophobic molecules are responsible for

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irreversible fouling. However, the impact of representative marine algal species on UF membrane performances has not been extensively studied (Castaing et al., 2010; Ladner et al., 2010; Villacorte et al., 2015b). Moreover, algal solutions used in previous studies were only harvested at a unique growth stage and the fouling evolution of an outside/in UF membrane system over an algal bloom was, to the best of our knowledge, never investigated (Villacorte et al., 2015c).

Another major question nowadays concerns the contribution of algal cells and large AOM structures in fouling reversibility. It has been suggested that cells fouled MF and UF membrane and a consequent reversible and irreversible fouling were observed by filtering a re-suspended cell solution (Ladner et al., 2010; Qu et al., 2012a). Nevertheless, a comparison between different marine algal cultures would allow us to conclude if bloom events of any algal species would reduce UF performances by a similar order of magnitude.

For the current study three ubiquitous marine algal species were selected. *Skeletonema costatum* is a diatom with a silicate wall forming colonies, *Tetraselmis* sp. is a green alga used in marine culture a with high lipid content, and *Hymenomonas* sp. is an algal species with a calcite wall. The occurrence of algal blooms for these three species has been widely studied by previous researchers (Álvarez-Salgado et al., 2005; Caroppo, 2000; Daoudi et al., 2012; Houdan et al., 2004; Shen et al., 2012). Ultrafiltration experiments were performed with outside/in hollow fiber membrane and algal solutions at constant colloidal Algal Organic Matter (c-AOM) content prepared from the dilution of cultures harvested over their exponential and decline growth phases. Complementary experiments investigated the impact of 1.2 μm (GFC, Millipore) prefiltration using cultures harvested during the decline phase.

2. Materials and methods

2.1. Algal cultures

Three ubiquitous marine algae provided by the Oceanological Observatory of Banyuls-sur-Mer were selected as model microorganisms: *S. costatum* – SKC (Diatom), *Tetraselmis* sp.- TET (Prasinophycea), and *Hymenomonas* sp.- HYM (Coccolithophycea). Their characteristics are presented in supporting information (Table S1). These species were separately cultivated in 10 L glass bottles filled with natural Red Sea water collected from the King Abdullah University of Science and Technology (KAUST) bay (Thuwal, Saudi Arabia). Raw seawater was filtered through a 0.45 μm cellulose acetate membrane filter, autoclaved at 121 °C for 20 min, and stored in the dark at 18 °C. Before algae incubation, F/2 medium (Guillard, 1975) was added to the filtered seawater. Algal cultures were exposed to a 12 h/12 h light/dark cycle, at a controlled room temperature of 18 °C. Aeration was provided to mix up the solution and to provide buffering of oxygen and CO_2. Two batches of cultures were prepared over the period of experiment showing some slight difference in quality (i.e., DOC and biopolymers content). SKC_1, TET_1, and HYM_1 refers to the first batch, while TET_2 and HYM_2 refers to the second batch.

2.2. Monitoring of cell growth by flow cytometry and Chlorophyll-a measurement

Cultures were sampled every 2 days to measure cell density and Chlorophyll a (Chl-a) concentration according to the method developed by Marie et al. (2001). Cell density was determined with a FACSVerse flow cytometer (Becton Dickinson, Belgium). 200 μL of sample were excited with a blue laser at 488 nm. The combination of the right-angle light scattering (SSC, related to cell size) and red emission fluorescence (i.e., 700–754 nm) was used to discriminate and enumerate the different populations. The standard deviation was calculated by analyzing the algal solution thrice.

Chl-a concentration was measured in vivo using a 10 AU field fluorometer (Turner Designs, USA). Calibration standards were prepared according to the EPA method 445.0.

2.3. Characterization of the algal organic matter

Algal Organic Matter (AOM) includes Extracellular Organic Matter (EOM) produced during the exponential phase (EP) of growth and Intracellular Organic Matter (IOM) released from cell lysis during the decline phase (DP) of growth. In this study, colloidal Algal Organic Matter (c-AOM) was defined as the fraction going through a 1.2 μm glass fiber membrane, while the fraction retained on the membrane was defined as particulate Algal Organic Matter (p-AOM). Flow cytometry was used to confirm the absence of algal cells in permeates. The Total Organic Carbon (TOC) concentration of c-AOM was measured with a TOC analyzer (TOC-V-CSH, Shimadzu, Japan) in which the sample was acidified by HCl and spurge during 4 min with high purity air before thermal catalytic oxidation. The carbon dioxide formed during the oxidation step was measured with an infrared detector.

Size exclusion chromatography equipped with an organic carbon detector (LC(SEC)-OCD, DOC-Labor, Germany) was used to separate and quantify the biopolymer fraction. Prior to analyses, all feed solutions were filtered through a 1.2 μm glass fiber membrane (GFC, Millipore) while permeates were not filtered. This analytical tool and conditions of use were thoroughly described by Huber et al. (2011).

2.4. Filtration set-up

Ultrafiltration experiments were conducted at room temperature (21 °C) with a fully automated device (OSMO HYDRA, Convergence, Netherland).

The filtration module consisted of 7 hydrophilized DOW PVDF UF hollow fibers of 24.5 ± 0.3 cm (OD: 1.3 mm, ID: 0.7 mm, active surface area: 70.0 ± 0.9 cm^2) operating in outside-in filtration mode. A new module (i.e., virgin hollow fibers) was used for each experiment. For membrane conditioning, MilliQ water was filtered through the membrane for 8 h until reaching a constant initial permeability of 456 ± 30 L m^{-2} h^{-1} bar^{-1}.

The sequence of filtration was divided in 10 cycles under a constant flux of 70 L m^2 h^{-1} for 30 min, followed by a backwash step using permeate water at 120 L m^2 h^{-1} for 2 min. A Chemically Enhanced Backwash (CEB) was implemented after the 10th cycle with a 350 mg L^{-1} NaOCl solution at 120 L m^2 h^{-1} for 3 min followed by a 5 min soaking. A following second filtration sequence was performed to assess the CEB efficiency.

The feed solution was prepared by dilution of pure algal culture harvested during the exponential (i.e., approximately 3–5 days before the beginning of the decline phase) or decline phase with synthetic seawater (Grasshoff et al., 1999). The harvested algal culture was used as produced or after prefiltration through a 1.2 μm glass fiber membrane (i.e., only colloidal organics present in solution). UF membrane fouling experiments were conducted by diluting the culture solution to DOC contents near 0.5 and 1.0 mg C L^{-1}. The feed water quality is presented in Table 1.

For all experiments, permeate was collected during the 5th cycle of the first sequence at least 10 min after the last backwash step and until the end of the cycle.