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MF/UF rejection and fouling potential of algal organic matter from bloom-forming marine and freshwater algae

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HIGHLIGHTS

- Membrane fouling during algal blooms linked to algal organic matter (AOM).
- Membrane fouling potential of AOM varied with algal species.
- MF/UF mainly rejected the biopolymer fraction of AOM.
- Tight UF (10 kDa) removed up to 97% of algal-derived biopolymers.
- Cake filtration with compression is the dominant AOM fouling mechanism.

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ABSTRACT

Pretreatment with microfiltration (MF) or ultrafiltration (UF) membranes has been proposed for seawater reverse osmosis (SWRO) plants to address operational issues associated with algal blooms. Here, we investigated the MF/UF rejection and fouling potential of algal organic matter (AOM) released by common species of bloom-forming marine (*Alexandrium tamarense* and *Chaetoceros affinis*) and freshwater (*Microcystis* sp.) algae. Batch culture monitoring of the three algal species illustrated varying growth pattern, cell concentration, AOM released and membrane fouling potential. The high membrane fouling potential of the cultures can be directly associated ($R^2 > 0.85$) with AOM such as transparent exopolymer particle (TEP) while no apparent relationship with algal cell concentration was observed. The AOM comprised mainly biopolymers (e.g., polysaccharides and proteins) and low molecular weight organic compounds (e.g., humic-like substances). The former were largely rejected by MF/UF membranes while the latter were poorly rejected. MF (0.4 μm and 0.1 μm pore size) rejected 14%–56% of biopolymers while conventional UF (100 kDa) and tight UF (10 kDa) rejected up to 83% and 97%, respectively. The retention of AOM resulted in a rapid increase in trans-membrane pressure (ΔP) over time, characterised by pore blocking followed by cake filtration with enhanced compression as illustrated by an exponential progression of ΔP.

1. Introduction

Algal blooms are increasingly being reported as a major cause of operational problems in seawater reverse osmosis (SWRO) desalination plants [10,38,48]. The adverse effect of algal blooms on SWRO started to gain more attention during the severe "red tide" bloom in the Gulf of Oman between 2008 and 2009. The bloom forced several SWRO plants in the region to reduce or shutdown operations due to clogging of conventional pre-treatment systems (i.e., granular media filters) and/or due to unacceptable RO feed water quality (high fouling potential) which triggers concerns of irreversible fouling problems in RO membranes downstream [4,34,40]. Although conventional pre-treatment systems are often effective in removing algae, a substantial fraction of the algal-derived organic material (AOM) can still pass through the pre-treatment systems [2,17] which can then potentially cause fouling in the downstream RO system.

The failure of conventional pre-treatment to provide sufficient and acceptable feedwater quality for SWRO during severe algal blooms has shifted the focus of the desalination industry to the application of low pressure membranes such as microfiltration (MF) and ultrafiltration

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(UF) as the main pre-treatment technology for SWRO [22,55]. Considering their nominal pore sizes (from 5 μm down to 5 nm), MF/UF membranes is expected to remove not only algae but also a significant fraction of AOM [11,46]. However, it has been demonstrated that MF/UF membrane systems may also suffer from fouling during algal blooms [25,27,39,44,45]. Most of these studies have suggested that the accumulation of AOM is the main cause of membrane fouling rather than the algae themselves.

During algal blooms, various forms and differing concentrations of AOM might be present in the water such as polysaccharides, proteins, lipids, nucleic acids and other dissolved organic substances [7,14,16,32]. A major fraction of AOM, known as transparent exopolymer particles (TEP), is highly sticky and usually involved in the formation of mucilaginous aggregates such as marine snow and sea foam [1,36]. Recently, this fraction of AOM has been associated with biological fouling in RO systems [3,5,51,52] and organic fouling in MF/UF systems [6,15,24,53]. Although a number studies has been conducted to characterise AOM from bloom-forming species of algae [12,18,19,54], their composition, size distribution and membrane fouling propensity are still largely unknown. Moreover, AOM, especially in seawater, have not been sufficiently studied in terms of their removal by MF/UF membranes.

The objective of this study is to investigate the MF/UF membrane retention and fouling potential of AOM from three species of bloom-forming algae in marine and freshwater sources by applying various characterisation techniques and the modified fouling index.

2. Materials and methods

Selected algal species were grown in batch cultures to represent an algal bloom situation in freshwater and seawater. The algal organic matter (AOM) produced by the three species was extracted and a series of analyses was performed to measure their fouling potential and their rejection by MF/UF membranes.

2.1. Algal cultures

Three strains of bloom-forming algal species were selected for this study, namely: *Alexandrium tamarense* (CCAP 1119/32) *Chaetoceros affinis* (CCAP 1010/27) and *Microcystis* sp. (CCAP 1450/13). *A. tamarense* and *C. affinis* were inoculated in sterilised synthetic seawater spiked with nutrients and trace elements based on the L1 and f/2 + Si aqueous medium, respectively. The artificial seawater (ASW) was prepared to resemble the typical inorganic ion composition of the North Sea (TDS 34 g/L, pH 8 ± 0.2). *Microcystis* sp. was grown in sterilised BG-11 medium for freshwater algae. The composition of the prepared media and the protocol of culturing the three algal species were described by Villacorte et al. [50].

The average algal cell concentration in batch cultures was monitored by sampling every 2–4 days and counting the cells using Thoma chamber glass slides and a light microscope (Olympus BX51). Additional samples were collected for TEP (see Section 2.3) and modified fouling index (MFI-UF) measurements (see Section 2.7) on selected days during the exponential and stationary-death phases.

2.2. AOM extraction and dialysis treatment

Two sets of algal culture samples (0.5 l each) were collected during the exponential and stationary-death phases from the three batch cultures of algae. To extract AOM from the culture, the samples were filtered through polycarbonate filters (Nuclepore PC membranes, Whatman) with <0.2 bar of vacuum. Polycarbonate membranes with different pore sizes were used depending on the lower size range of the algal cells: 10 μm for *A. tamarense*, 5 μm for *C. affinis* and 1 μm for *Microcystis*. The filtered solutions were analysed using LC-OCD (see Section 2.4). Larger AOM which may have been retained by the filters and AOM bound to algal cells were not included in the subsequent analysis.

To remove dissolved components present in the culture medium and isolate particulate/colloidal AOM, dialysis treatment was performed for selected AOM samples collected during the stationary/death phases. The samples were dialysed using 3.5 kDa RC membrane sacks (Spectra/Por 3, SpectrumLabs) and ultra-pure water (Milli-Q, Millipore) as the draw solution. The draw solution was continuously stirred (using a magnetic stirrer) and replenished 1 to 2 times per day. Each dialysis treatment lasted for 4–6 days to remove most of the dissolved salts and low molecular weight organics. After dialysis, the AOM samples inside the membrane sacks were freeze dried and then analysed using FTIR spectroscopy (see Section 2.5).

2.3. TEP measurement

The concentrations of acidic polysaccharides produced by algae as TEP (>0.4 μm) and TEP precursors (<0.4 μm) were measured following the methods described by Passow and Alldredge [37] and Villacorte et al. [49], respectively. TEP were measured after retention on 0.4 μm polycarbonate membrane. TEP and TEP precursors combined were measured after retention on 10 kDa regenerated cellulose membrane. The retained TEP (and precursors) were semi-quantitatively measured based on staining with Alcian blue and spectrophotometric techniques. The absorbance results were then calibrated using Xanthan Gum standard to express concentrations in mg Xanthan equivalent per liter (mg X_{eq}/L).

2.4. Liquid chromatography-organic carbon detection (LC-OCD)

AOM samples extracted from algal cultures were analysed by DOC-Labor (Karlsruhe, Germany) using liquid chromatography-organic carbon detection (LC-OCD). The relative responses of organic carbon, ultraviolet and organic nitrogen at different retention times were measured with an online organic carbon detector (OCD), UV detector (UVD) and organic nitrogen detector (OND). Organic carbon concentrations of biopolymers, humic substances, building blocks, low molecular weight (LMW) acids, and neutrals were determined based on the chromatographic peaks and their retention times according to the method described by Huber et al. [20]. A more detailed description of these organic fractions is summarised in Table 1. Since AOM usually contains large macromolecules (e.g., TEP), LC-OCD analyses were performed without the 0.45 μm pre-filtration of samples. The theoretical maximum chromatographable size without sample pre-filtration is 2 μm, which is based on the pore size of the sinter filters of the column used [21].

To estimate the molecular weight distribution of the biopolymer fraction of AOM, selected samples were analysed using high resolution LC-OCD. This modified technique follows a similar principle as described by Huber et al. [20] but using two columns in series (HW65S and HW50S) instead of one (HW50S was used for single column analyses), doubling the mobile phase retention time and the resolution of the chromatogram. Molecular weight fractionations were defined based on calibration with pullulan (PSS, Germany), a polysaccharide with molecular weight between 0.3 and 700 kDa [21].

Table 1
Descriptions of organic matter fractions measured by LC-OCD [20].

Organic fraction	Typical size (Da)	Typical composition
Biopolymers	>20,000	Polysaccharides, proteins, amino sugars, polypeptides
Humic subst.	~1000	Humic and fulvic acids
Building blocks	300–500	Weathering and oxidation products of humics
LMW Neutrals	<350	Mono-oligosaccharides, alcohols, aldehydes, ketones, amino acids
LMW acids	<350	All monoprotic organic acids