

## Fast and efficient separation of seawater algae using a low-fouling micro/nano-composite membrane

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### ABSTRACT

High suspended solid loadings due to harmful algal bloom (HAB) pose serious threat to the operation of membrane based desalination plants. Clogging of algal biomass could lead to irreversible damage of the filtration units and eventually disrupting the sustainability of water supply. In this study, we demonstrated a fast and efficient method for separating algae from seawater using a low-fouling micro/nano-composite membrane. The composite membrane was made of a nanoporous nanofiber selective layer on top of a microporous microfiber support layer. The optimized nanoporous selective layer of this composite membrane can effectively separate seawater algae with high efficiency (average 99%) and high flux ( $3 \times 10^{-5} \text{ m}^3/\text{m}^2\cdot\text{s}$ ) under low operation pressure. More importantly, the membrane exhibits excellent anti-fouling property by maintaining constant water flux and algae rejection rate after a simple backwashing without chemical usage. This superior antifouling property attributes to the underwater superoleophobicity of the composite membrane. These combined merits of fastness, effectiveness and fouling resistance render this membrane-based separation method with greater potential for industrial application.

### 1. Introduction

Occurrence of harmful algal bloom (HAB) in seawater and freshwater has been widely reported in these recent years [1–4]. HAB severely affects the operation of many industries related to coastal tourism, fishing, water supplies and etc. Apart from inflicting massive economic losses, HAB poses serious threats to the sustainability of potable water supply. It is considered as the most disruptive water related contaminants that could significantly alter the physical, chemical and biological characteristics of water bodies [5–8].

Many water scarce countries rely on membrane based desalination plants as their primary source for safe and sustainable drinking water supply. Continuous and uninterrupted operation of desalination plants during algal bloom is very challenging. Operation of a desalination plant can be easily disturbed during bloom periods due to additional solid loadings, fluctuation of pH, increase in chemical demand (e.g. chlorine, coagulant and etc.) and etc. Rapid clogging of pre-filtration units due to excessive biomass loadings and possibilities of algal toxin carry over in the permeate are the primary concerns of desalination plant operators during algal bloom [5,9,10]. It has been reported that

seawater desalination plants in the Gulf of Oman and Arabian Gulf were shut down or reduced operation due to extensive fouling of the granular media filtration units during the bloom periods in 2008–2009 [11,12]. There are several ways that can be adopted to minimize fouling in the pre-treatment units during algal bloom. Retrofitting of additional equipment such as dissolved air flotation (DAF) unit prior to media filtration process has proven to be successful in several desalination plants [11]. Despite being effective in handling high solid loadings during bloom, DAF is an energy intensive process [13]. Another possible alternative to minimize particulate fouling is by using antifouling low-pressure membranes. Some membranes have been developed with lower fouling tendency, due to its hydrophilic nature that minimizes deposition of algae on its surface [14,15]. However, these membranes still suffer from low permeation flux and irreversible fouling issues. Therefore, it is still in high demand to develop a novel membrane-based separation technique with combined merits of high permeation flux, algae removal rate and fouling resistance.

In this study, we demonstrated a fast and efficient technique for separating algae from seawater using a low-fouling micro/nano-composite membrane. The proposed membrane was developed by

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depositing ultra-long superhydrophilic sodium titanate nanofiber on a cellulose substrate. The membrane deposition formula was optimized to specially suit for algae removal. The fluxes and rejection properties of the micro/nano-composite membrane were investigated with real seawater algae. Various characterization tools such as optical microscope, SEM, contact angle and AFM were used to observe the algal fouling behaviors on the surface of the membrane. A simple and environmental-friendly backwash practice was applied to investigate the long-term reusability of this membrane. Given the low cost and facile fabrication of this new membrane, this study aims to establish a new approach for low-fouling and economically-viable separation of seawater algae.

## 2. Materials and methods

A vacuum filtration device (Nalgene 300-4050, Rochester, NY, USA) with an effective membrane area of  $11.3 \text{ cm}^2$  was used to evaluate the performance of the micro/nano-composite membranes. The separation process was driven under vacuum with a pressure differential of 10 kPa at which the corresponding flux was obtained. Algae rejection rate were calculated by measuring chlorophyll intensity of each cell using BD Accuri C6 flow cytometer (Ann Arbor, Michigan, USA). Dual threshold triggers on FL3 (Excitation: 488; Emission: 670 LP) and FL4 (Ex: 640; Em:  $675 \pm 12.5 \text{ nm}$ ) were set just above background noise. For each run, a sample of  $50 \mu\text{L}$  were injected at the medium fluidic settings ( $35 \mu\text{L}/\text{min}$ ; core size  $16 \mu\text{m}$ ) to obtain the corresponding cell counts. The dead end filtration studies were conducted over a period of 6 min per cycle at a fixed pressure difference of 10 kPa. 1 min of backwash is performed at end of each cycle using deionized (DI) water at a similar pressure difference by reversing the membrane position on the filtration cell. Flux of the membrane was calculated by measuring the permeate volume at a fixed filtration time:

$$J = \frac{V}{A \times t} \quad (1)$$

where  $J$  represents flux ( $\text{m}^3/(\text{m}^2 \cdot \text{s})$ ),  $V$  is volume of permeate ( $\text{m}^3$ ),  $A$  is the effective membrane area ( $\text{m}^2$ ) and  $t$  is the filtration time (s). Algae rejection rate of the membrane is calculated as following:

$$RR = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

where  $RR$  represents rejection rate (%),  $C_p$  and  $C_f$  denote the chlorophyll cell counts in the permeate and feed solution respectively. Total resistance,  $R_{Total}$  is another important parameter that was used to compare the performance of cellulose and composite membranes. It is calculated as below:

$$R_{Total} = \frac{\Delta P}{\mu \times J} \quad (3)$$

where  $R_{Total}$  represents total membrane resistance ( $\text{m}^{-1}$ ),  $\Delta P$  is the pressure drop across the membrane (Pa),  $\mu$  is permeate viscosity (Pa.s) and  $J$  is the flux ( $\text{m}^3/(\text{m}^2 \cdot \text{s})$ ).

## 3. Results and discussions

The feed solution used in this study was collected from local seashore and spiked with phosphate, nitrate, potassium, and micro-nutrients to simulate a naturally occurring bloom. A high algae count was obtained (average of  $430 \pm 12 \text{ cells}/\mu\text{L}$ ) after a period of three weeks and this feed concentration was used for all the performance studies. Algae size distribution in seawater was measured using Jorin-Visual Process Analyser (ViPA B HiFlo). In Fig. 1, the resulting statistical plots display a narrow distribution of algae particle size mainly ranging from 1 to  $19 \mu\text{m}$  in size. The mean diameter of algae was approximately  $3.7 \mu\text{m}$  with a  $d_{90}$  of  $5 \mu\text{m}$ .

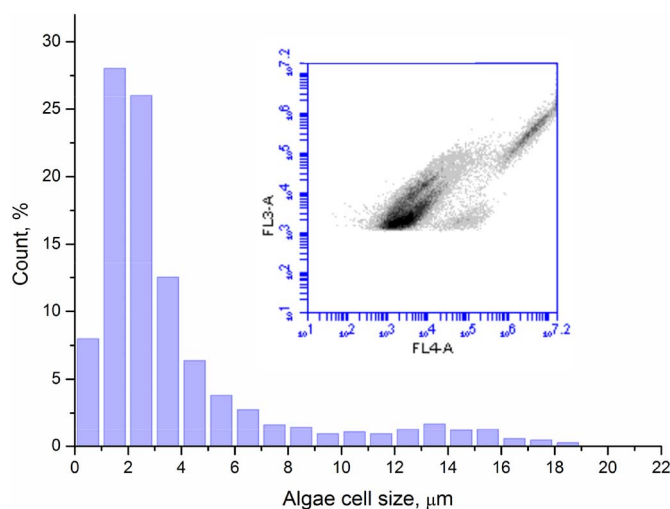


Fig. 1. Particle size distribution of algae in the feed seawater. Insert is the fluorescence intensity plot of flow cytometer that represents algae cell counts.

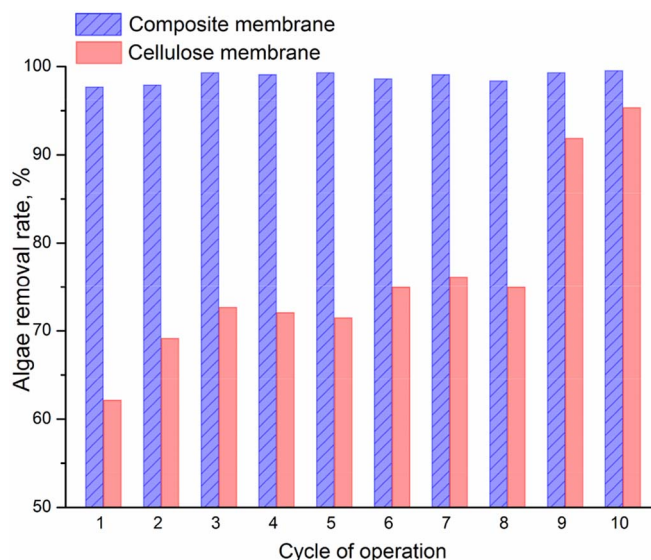


Fig. 2. Algae removal rate using low-fouling micro/nano-composite and cellulose membranes for a period of ten cycles of filtration and membrane backwash.

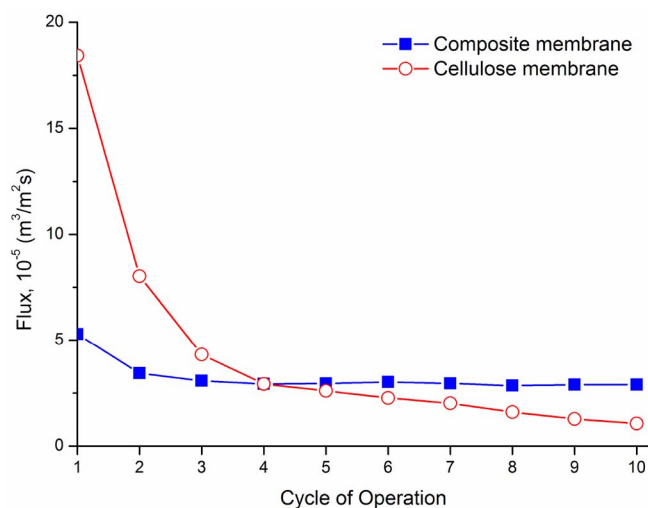


Fig. 3. Flux profile of low-fouling micro/nano-composite membrane and cellulose membrane for a period of ten cycles of algae filtration and membrane backwash.

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