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Microalgal dewatering using a polyamide thin film composite forward osmosis membrane and fouling mitigation

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ABSTRACT

In this study, the dewatering of *Scenedesmus acuminatus* suspensions using a polyamide thin film composite (TFC) forward osmosis (FO) membrane with enhanced surface shearing was investigated. The influence of the draw solution (DS) concentration and microalgal properties were studied, and a fouling mitigation method using mechanical shearing was developed. *S. acuminatus* suspension dewatering by the same FO membrane was repeated 8 times to test the membrane's recoverability and durability. The results showed that the membrane flux and the concentration of magnesium chloride DS presented a non-linear relationship. In addition, membrane flux did not increase once the DS concentration increased to 2 mol L^{-1}, when serious fouling occurred. However, the membrane flux was significantly improved by mechanical shearing across the membrane surface. At shear rate of 4 (1000 rpm), a 2 mol L^{-1} $MgCl_2$ solution resulted in an average flux as high as 25.9 L m^{-2} h^{-1} during the dewatering of a 1.0 g L^{-1} microalgal suspension. Microalgal cells and algogenic organic matter (AOM) were tested to determine the membrane fouling mechanism. The results showed that the microalgal cells and AOM resulted in 15.4% and 9.4% water flux loss in 1 h, respectively, whereas the combination of microalgal cells and AOM resulted in 24.7% water flux loss. After dewatering for 8 h, microalgal suspensions were concentrated 20 times, and the average membrane flux was 23.3 L m^{-2} h^{-1}. In addition, most of the membrane fouling was reversible by simple hydraulic flushing; the pure water flux remained more than 97% of original pure water flux after 8 repeated dewatering processes, which demonstrated the potential application of FO in microalgal dewatering.

1. Introduction

Although microalgal biofuel promising, issues related to the high cost of production must be solved. Biomass harvesting and dewatering of culture media have been reported to account for 20–30% of the total operating cost [1]. Conventional harvesting and dewatering methods include centrifugation, flocculation, sedimentation, flotation and any combination of these methods. However, these methods are either prohibitively energy intensive, or could damage microalgal cells, and negatively affect biomass quality [1].To solve these problems, pressure-driven membrane filtration processes that offer higher separation efficiency, easy operation and little or no need for chemical addition represent alternative techniques for microalgal harvesting. For example, Zhang concentrated the microalgal suspension 150 times to obtain a final cell concentration of 155 g L^{-1} [2]. However, microfiltration and ultrafiltration membrane processes are highly susceptible to fouling, which is irreversible [3] and results in additional time and energy consumption to recover membrane permeability.

The forward osmosis (FO) membrane filtration process is an emerging and promising alternative for microalgal dewatering. The FO process is driven by the osmotic pressure difference across the membrane and selectively allows for the passage of water but rejects solute molecules or ions [4]. Compared with pressure-driven microfiltration and ultrafiltration, FO demonstrates unparalleled advantages of lower energy consumption, superior separation efficiency, potentially lower fouling tendencies and greater recovery of intact microalgal cells because of free of hydraulic pressure [5]. It should be noticed that draw solution recovery could be the main energy contributor for FO process. From the cost point of view, the advantage of lower energy consumption of FO dewatering can only be achieved if the cost of draw solution

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recovery is dramatically reduced. The subsequent utilization of draw solution for culture media preparation provides us a unique way to avoid the costly draw solution recovery using traditional reverse osmosis process [6].

Despite the low fouling tendency, the FO dewatering performance may still be adversely impacted by membrane fouling, which results in a lower water flux and algae recovery efficiency, shorter membrane lifespan and higher operating costs [7]. Several studies have been conducted to address these challenges. Honda studied the effects of membrane orientation on fouling characteristics and found that the active-layer-facing-feed-solution mode was preferable for the concentration of microalgae because of its stability and better flux recovery [8]. Zou demonstrated that the use of a feed side spacer was beneficial for enhancing the initial flux as well as reducing the tendency of membrane fouling [9]. Xiao suggested that the overall order of the significance of experimental factors on membrane performance was: membrane orientation > solution temperature > different ions > pH > organic concentration > types of draw solutions [10].

Understanding the flux variation and the fouling of the FO membrane is critical for the development of an efficient FO microalgal dewatering process. However, most studies to date have been conducted with low concentrations of microalgal suspensions (i.e., less than $1.0\,g\,L^{-1}$). During the microalgal dewatering process, the cell concentration can increased to $20.0\,g\,L^{-1}$; however, the role of the microalgal suspension's dependent characteristics, such as the effects of changes in the microalgal cell and organic matter concentrations for membrane flux, is poorly understood.

The fluxes observed for most FO membranes are relatively low [11], and the membrane flux observed in microalgal FO dewatering studies is even lower. An initial water flux of $8.42\,L\,m^{-2}\,h^{-1}$ and 15% flux reduction was found for FO dewatering using *S. obliquus* [7]. With the development of FO technology, a new generation of membranes that offer higher permeation fluxes were released, and thin film composite (TFC) membranes have been shown to improve water permeability and salt rejection [12,13]. Until now, few studies have evaluated the performance of TFC-FO membranes on microalgal dewatering.

For the purpose of development of efficient and low cost dewatering techniques, which could be transferred into the production of microalgal based biofuel, in this study the performance of a novel polyamide TFC-FO membrane was tested for the dewatering of the microalgal *Scenedesmus acuminatus*. The specific aims are to: (1) identify the major water flux restrictive factors responsible for FO membrane fouling during microalgal harvesting, such as the draw solution concentrations and microalgal characteristics; (2) develop anti-fouling strategies to maintain membrane flux; and (3) evaluate the durability of the TFC membrane and flux recoverability after multiple microalgal dewatering processes.

2. Materials and methods

2.1. Microalgal cultivation and feed solution preparation

S. acuminatus was used as the model microalgal species in this study because it is widely used for biodiesel production owing to its rapid growth and robustness under extreme conditions. Microalgae strain GT-2 was originally isolated from Microalgae Biotechnology Center located in Hebei Province, China. *S. acuminatus* was cultured in 15-L panel photobioreactors using modified BG-11 medium [14]. The initial NO_3^--N concentration was modified to $30.88\,mg\,L^{-1}$. The culturing temperature was maintained at $23 \pm 0.5\,°C$, and was mixed by $0.4\,L\,min^{-1}$ continuous bubbling of air with 1% CO_2. Fluorescent lighting (Philips, Shanghai, China) was continuously provided with an intensity of $120 \pm 10\,\mu mol$ photons $m^{-2}\,s^{-1}$. The pH of the culture was controlled between 6.8 and 7.2 automatically using a pH monitor coupled with a pneumatic valve in the CO_2 supply line, which was switched off when pH was lower than 6.8, and switched on when pH was higher than 7.2. Residual nutrients in the seed culture were removed using centrifugation and the settled biomass was then re-suspended in modified BG-11 media. The inoculum dry weight was $0.2\,g\,L^{-1}$.

Four types of solutions were used as the feed solutions (FS), including: 1) deionized water (DI) (Milli-Q® Integral, Millipore, USA); 2) algogenic organic matter (AOM) solution; 3) microalgal cells re-suspended in DI water; and 4) microalgal cell re-suspended in AOM. The microalgal AOM solution preparation contained two steps. First, the microalgal suspension was centrifuged at $6000 \times g$ at 15 °C for 10 min (Avanti J-26S XPI, Beckman, USA). The supernatant was then filtrated through a mixed cellulose ether membrane with a 0.45 μm pore size (Shanghai, China). The microalgal cells after centrifugation were stored and then diluted with DI water or AOM solution.

2.2. Forward osmosis membrane

A commercially available polyamide TFC-FO membrane (FOMEM-0513, Porifera, USA), was used in this study. After receiving the membranes, the FO membrane samples were sealed and stored at indoor temperature $20 \pm 5\,°C$. The mean water permeability (A) is $11.7 \times 10^{-12}\,m^3\,s^{-1}\,m^{-2}\,Pa^{-1}$, the mean salt rejection (R) is 90.3%, the mean salt permeability (B) is $0.398 \times 10^{-6}\,m^3\,s^{-1}\,m^{-2}$, and the mean mass structure parameter (S) is $267 \times 10^{-6}\,m$ [15]. According to the manufacturer, the maximum operating parameters were 1.24 MPa and 70 °C, and the pH tolerance ranged from 2 to 11. A water flux of $33 \pm 2\,L\,m^{-2}\,h^{-1}$ could be obtained with pure water at a rate of $0.23\,L\,min^{-1}$ as the FS and $1.0\,mol\,L^{-1}$ NaCl as the draw solution at 25 °C. Membrane salt rejection can be as high as $99.6 \pm 0.15\%$. The contact angle of the membrane was measured as 98.5° (JC200DM, Powereach, China).

The DS used in this study was prepared by dissolving an appropriate amount of analytical grade magnesium chloride heptahydrate ($MgCl_2 \cdot 7H_2O$; China Chemical Reagent Company, China) in DI water. $MgCl_2$ was reported to provide the highest osmotic pressure among the frequently used DS reagents [4]. Mg^{2+} and Cl^- are inherent components in the culture media and do not introduce extrinsic ions into a concentrated biomass; thus, adverse effects on subsequent biofuel production should be minimal.

2.3. Experimental setup and protocols for the dewatering process

The schematic diagram of a bench-scale cross-flow FO setup (Flux-o-meter system, Porifera, USA) is shown in Fig. 1. During each

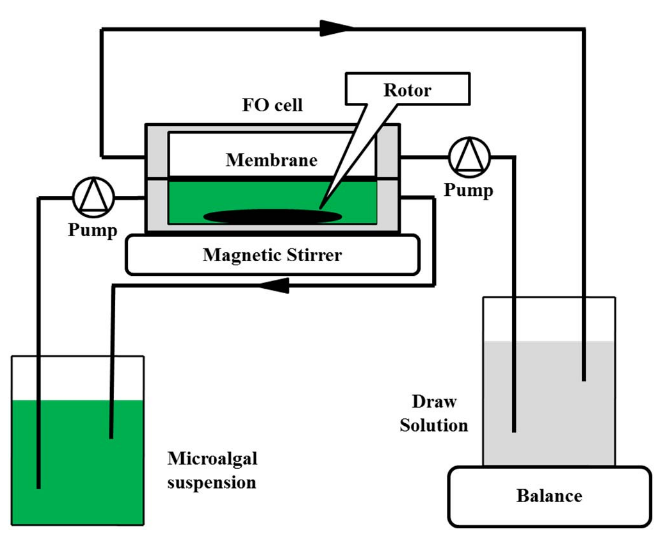

Fig. 1. Schematic drawing of the forward osmosis (FO) microalgal dewatering system.