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Microalgae dewatering based on forward osmosis employing proton exchange membrane

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HIGHLIGHTS

- Electrically-facilitated forward osmosis was established for microalgae dewatering.
- Proton exchange membrane was employed for the suggested forward osmosis module.
- Dewatering flux and final biomass concentration was significantly increased.
- Chlorophyll was successfully removed from the dewatered biomass.
- Both microalgae dewatering and chlorophyll removal were achieved simultaneously.

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ABSTRACT

In this study, electrically-facilitated forward osmosis (FO) employing proton exchange membrane (PEM) was established for the purpose of microalgae dewatering. An increase in water flux was observed when an external voltage was applied to the FO equipped with the PEM; as expected, the trend became more dramatic with both concentration of draw solution and applied voltage raised. With this FO used for microalgae dewatering, 247% of increase in flux and 86% in final biomass concentration were observed. In addition to the effect on flux improvement, the electrically-facilitated FO exhibited the ability to remove chlorophyll from the dewatered biomass, down to 0.021 ± 0015 mg/g cell. All these suggest that the newly suggested electrically-facilitated FO, one particularly employed PEM, can indeed offer a workable way of dewatering of microalgae; it appeared to be so because it can also remove the ever-problematic chlorophyll from extracted lipids in a simultaneous fashion.

1. Introduction

Microalgae are thought of as a truly renewable feedstock for biodiesel production due to their high productivity without infringing on food crops, superb ability to assimilate carbon dioxide, and potential of treating wastewater via nutrients uptake (Black et al., 2013; Kim et al., 2016a, 2017; Larronde-Larretche and Jin, 2017; Park et al., 2014; Seo et al., 2016, 2015). The much awaited commercial success of the microalgae-derived biodiesel, which is far from close, needs technological maturation of each of the following four basic steps: microalgae cultivation, harvesting/dewatering, lipid extraction, and biodiesel conversion (Li et al., 2008). Separating and concentrating microalgae cells from the culture medium serves as one of the technical and economical bottlenecks to large-scale microalgae production (Bhave et al., 2012; Cai et al., 2013) as microalgae cells have density similar to water and final biomass concentration is exceedingly low.

Forward osmosis (FO), as being a relatively new membrane separation process, has many advantages in algae harvesting such as low energy consumption, limited fouling and superb cleaning efficiency, and excellent recovery of unbroken algae cells (Larronde-Larretche and Jin, 2016). Dilution of draw solution, which requires energy for regeneration, and high level of reverse salt flux, which may induce complicated interactions with algal biomass, are two critical issues to be dealt with to exploit its full potential (Larronde-Larretche and Jin, 2016; Nguyen et al., 2016). Most of recent researches thus have focused on types of draw solution and algal species to investigate biofouling behavior and improve dewatering efficiency (Bucs et al., 2016; Honda et al., 2015; Larronde-Larretche and Jin, 2017, 2016; Nguyen et al., 2016). None

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has not yet explored any possibility to take advantage of back-diffused salts in algal solution.

Chlorophylls, because of being hydrophobic, are not removed through the lipid extraction step, greatly deteriorating the quality of final fuels and even fuel conversion efficiency (Ghasemi Naghdi et al., 2016; Li et al., 2016). An additional step, which adds a burden to the entire process, needs be included to eliminate them.

In this study, therefore, a new way of dewatering microalgae was developed on the basis of the electrically-facilitated FO equipped with proton exchange membrane as a FO membrane. The back diffusion of salts, which was even further worsened by the applied electric field, was made use of in a way that became beneficial.

2. Materials and methods

2.1. Membrane preparation

TFC from Aquaporin Inside™ was used as a commercial FO membrane for comparison, and was immersed in deionized water overnight before use. All FO experiments with the TFC membrane were done in active-layer-facing-feed-solution (AL-FS) mode. Nafion® N117 and N211 (DuPont Co. Ltd.), widely known as proton exchange membrane (PEM), were also used as FO membranes. The membrane was pretreated before use (Kim et al., 2014). Briefly, it was cleansed in 3 wt% H_2O_2 (34.5 wt%, Samchun Chemicals) for 1 h at 80 °C and preserved in de-ionized water for 2 h at 80 °C. To ensure proton conductivity, it was then treated in 0.5 M H_2SO_4 (95.0% purity, Samchun Chemicals) for 1 h in 80 °C and rinsed several times in de-ionized water.

2.2. Microalgae preparation

A locally isolated freshwater species of microalgae (*Chlorella* sp. KR-1), obtained from the Korea Institute of Energy Research (KIER), was cultivated in a nutrient medium containing the following ingredients: KNO_3, 5 mM; KH_2PO_4, 5.44 mM; Na_2HPO_4, 1.83 mM; $MgSO_4{\cdot}7H_2O$, 0.20 mM; $CaCl_2$, 0.12 mM; FeNaEDTA, 0.03 mM; $ZnSO_4{\cdot}7H_2O$, 0.01 mM; $MnCl_2{\cdot}4H_2O$, 0.07 mM; $CuSO_4$, 0.07 mM; $Al_2(SO_4)_3{\cdot}18H_2O$, 0.01 mM. The microalgae were then cultivated in a Pyrex bubble-column reactor in 30 °C and 10% (v/v) CO_2 in air was supplied at a rate of 2.5 L/min. After 7 days, microalgal cells were harvested by centrifugation (4000 rpm, 10 min) and lyophilized.

2.3. Forward osmosis experimental setup

All FO experiments were conducted using a custom-fabricated cross-flow FO system (Fig. 1) at room temperature. Each Teflon chamber for draw and feed solutions had an effective inner volume of 6.4 mL (W, 4 mm; D, 40 mm; H, 40 mm). The effective surface area of the membrane was 40 × 40 mm^2. Each of the draw and feed solutions was prepared outside the module and circulated at 60 mL/min of flow rate from separate reservoirs by a peristaltic pump. Weight of the draw solution was monitored and recorded every 10 min to calculate flux. To monitor the water flux, 300 mL of de-ionized water was used as feed solution and 500 mL of 0.5, 1, 2, 5 M NaCl (99.0% purity, Samchun Chemicals) was used as draw solution. For a dewatering experiment with the FO system, 50 mL of microalgal solution with the concentration of 50 g/L and 200 mL of 2 M NaCl were used for feed and draw solutions, respectively. Experiments were conducted in triplicate.

To generate an electric field across the membrane, a platinum plate with the reaction area of 40 × 40 mm^2 was used as an electrode and placed at the end of each chamber. A programmable DC power supply (HD-3005D, FinePower) was connected to provide constant voltage to the module and monitor the current. An electrode placed in the draw solution was fixed as a cathode, a negative electrode, and an electrode placed in the feed solution was determined as an anode, a positive electrode. Electrical conductivity (EC) and pH of the feed solution were measured every 5 min using a multi-parameter meter (HQ40d, HACH).

2.4. Lipid extraction

A slightly modified Folch method was used for lipid extraction (Folch et al., 1957). A portion of dewatered cells after the FO process was transferred to a 250-mL Erlenmeyer flask with a screw-cap and a mixture of chloroform (99.0% purity, Junsei Chemicals) and methanol (99.5% purity, Samchun Chemicals) (2:1, v/v) was added. The injected weight of dewatered microalgal solution after FO was 5 wt% of the chloroform-methanol mixture. As a control, one gram of untreated dried cell was immersed in 20 mL of de-ionized water and 20 mL of chloroform-methanol mixture was added in the flask with a screw-cap. The mixture in each flask was then stirred at 1000 rpm for 24 h at room temperature, and then the chloroform layer was separated by 3000 rpm centrifugation for 5 min. Lipid extraction yield was determined by reference to the weight of the recovered lipids from the chloroform layer. All experiments were conducted in triplicate.

2.5. Chlorophyll content

After the FO process, chlorophyll content was measured using the modified acetone method (Seo et al., 2015; Stavreva-veselinovska et al., 2010). A 300 μL of cell suspension from a feed solution was added to an acetone-water mixture (8 mL, 90% v/v acetone, 99.5% purity, Sigma Aldrich) and treated for 24 h in a refrigerator (4 °C) after vigorous mixing. Absorbance of the supernatant after centrifugation was analyzed at wavelengths 650 and 665 nm by a UV–VIS spectrophotometer (ADR 5000, HACH). From the absorbance values, the chlorophyll content was calculated. Experiments were conducted in triplicate. The extracted lipids underwent transesterification using a method described by Lee and Han (2015). Nitrogen contents in the extracted lipids and fatty acid methyl esters (FAMEs) after transesterification were analyzed to verify the removal of chlorophyll using an elemental analyzer (FLASH 2000 series, Thermo Scientific). All experiments were conducted in triplicate.

3. Results and discussion

3.1. Effect of external voltage on FO system with PEM

Fig. 2 depicts the effect of external voltage when PEM was used as a FO membrane of the FO system. N117 which has the membrane thickness of 183 μm was used, and 300 mL of de-ionized water and 500 mL of 5 M NaCl were applied as feed and draw solutions, respectively. When 20 V of external voltage was suddenly applied between both electrodes placed in each chamber of the module, a dramatic increase in water flux took place, implying that the electric field indeed caused water flux to increase (Fig. 2).

3.2. Water flux comparison of PEM and TFC

Average water flux of the FO system with N211 (membrane thickness: 25.4 μm) during 1 h operation was compared with that of the system with TFC (Fig. 3a). To this end, 8 V of external voltage was applied across the N211 membrane and an increase in water flux monitored. As expected, the more the concentration of draw