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Dewatering of *Chlorella pyrenoidosa* using diatomite dynamic membrane: Filtration performance, membrane fouling and cake behavior

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ABSTRACT

The diatomite dynamic membrane (DDM) was utilized to dewater *Chlorella pyrenoidosa* of 2 g dry weight/L under continuous-flow mode, whose ultimate algae concentration ranged from 43 g to 22 g dry weight/L of different culture time. The stable flux of DDM could reach 30 L/m^2 h over a 24 h operation time without backwash. Influences of extracellular organic matters (EOM) on filtration behavior and membrane fouling were studied. The DDM was divided into three sub-layers, the slime layer, the algae layer and the diatomite layer from the outside to the inside of the cake layer based on components and morphologies. It was found that EOM caused membrane fouling by accumulating in the slime and algae layers. The DDM intercepted polysaccharides, protein-like substances, humic-like substances and some low-MW organics. Proteins were indicated the major membrane foulants with increased protein/polysaccharide ratio from the slime layer to the diatomite layer as culture time increased. This method could be applied to subsequent treatment of microalgae coupling technology of wastewater treatment or microalgae harvesting for producing biofuel.

1. Introduction

Microalgae has drawn growing worldwide attention due to their influence on water quality and their potential in various fields such as depollution, therapeutics, dermocosmetics bioenergy, and the food and feed industries. There has been increasing interest in coupling microalgae feeding with wastewater treatment [1,2]. Also, algal biomass has been recognized as a promising alternative source of raw material for biofuel production [3]. The combination of wastewater treatment with algae and algal biofuel production has received widespread attention [4,5]. A major drawback in boosting the full-scale application involves microalgae is the lack of an efficient and economical method to dewater algal biomass [6]. Dewatering microalgal biomass is challenging because microalgae are small in size (3–30 μm) and have a low concentration (0.5–2 g/L) in water [3]. An optimal dewater method of algae for biofuel production should be species independent, use minimal chemicals and energy, and preferentially release intracellular materials for collection if possible [7]. Recent techniques for microalgae dewatering include centrifugation, flocculation, sedimentation, coagulation, flotation, and filtration [8], although most of these techniques are labor-intensive, energy-consuming and environmentally unfriendly [9]. It has been estimated that 90% of the cost algal biomass production may come from harvesting and dewatering [10], especially from energy consumption.

Membrane filtration is strictly a physical-absolute separative technique widely used for algae dewatering whose quality performance depends simply on membrane pore size and thus can achieve complete removal of algae [11]. However, the main obstacle for further incorporation of membrane processes is membrane fouling, which leads to increased resistance and energy feed, as well as a decreased membrane lifespan. The fouling results from algae is quite complex and is due to changing cell size, morphology and primarily the extracellular organic matter (EOM) [12]. It has been proved that algae cells themselves only play a small role in membrane fouling compared to EOM [11]. EOM released by cyanobacterial cells is mainly composed of oligosaccharides, polysaccharides, proteins, humic-like substances and amino acids [13]. Among these polysaccharides and proteins are responsible for significant fouling, especially when they exist as organic colloids [14]. The excretion of EOM depends on algal type, growth phase and growth conditions [15]. EOM causes membrane fouling by either increasing the quantity or changing the characteristics of its composition [11]. Therefore, looking for a suitable substitute

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technology which should be both energy economized and fouling-resistant is vital for boosting microalgae utilization.

The nowadays widely applied traditional membrane technology owns the merits of high retention efficiency of most of suspended solids and complete bacteria flocs, high mixed liquor suspended solids (MLSS) and solid retention time (SRT) [16], and excellent effluent quality. Whereas, there are many defects such as severe membrane fouling, high energy consumption and high membrane costs [17–19]. Many endeavors have been made to solve or alleviate these drawbacks, e.g., finding new membrane materials [20], improving operation conditions, and using gravity in the case of submerged MBR to reduce energy consumption [21], among which the dynamic membrane system represents a promising technology. Dynamic membrane is formed on the underlying primary filter surface when a feed solution containing fine particles is filtered [22]. Compared to traditional membrane system, dynamic membranes have advantages such as better antifouling properties [23,24], cheap support and coating materials [25,26], high permeate flux, and low energy consumption [27,28]. There have been a large amount of researches applying dynamic membranes to physical retention, including chemical compounds [29], macromolecular solutions [30] and sodium solutions [31], as well as wastewater treatment [25,32,33], which exhibited excellent solid–liquid separation capacity.

To evaluate the possibility and practicality of using a dynamic membrane system to concentrate microalgae, a DDM system was set up to dewater *Chlorella pyrenoidosa* biomass in this research. Furthermore, since EOM is the primary substance causes severe membrane fouling and EOM concentration varies during the life-cycle of microalgae, the applied microalgae were selected based on staged culture time to analysis the influences of EOM on operation conditions and dynamic membrane fouling. The structure and constituents of the cake layer were analyzed in details to discuss fouling mechanisms.

2. Materials and methods

2.1. Algae culture and EOM extraction

C. pyrenoidosa (green algae, Collection No. FACHB-9) was obtained from the Institute of Hydrobiology at the Chinese Academy of Sciences in China. Axenic cultures were carried out in batch mode with 20 mL (2 g dry weight/L) algae broth which was in log phase inoculated in 1 L of autoclaved SE medium in 2.5 L conical flasks. The culture was then placed in a light incubator at 30 °C and a 14 h light/10 h dark cycle with illumination of 5000 lx (GZX-300BS-III, CIMO Medical Instrument, Shanghai, China).

For EOM extraction, the algae broth and specimens of cake layers were firstly diluted with a 0.6% NaCl solution (to maintain the osmotic equilibrium and prevent the cell lysis) to 2 g/L, and then were centrifuged at 4000 rpm at 4 °C for 15 min using a high speed versatile refrigerated centrifuge (CT15RT, Shanghai, China). The supernatant was filtered through a 0.45 μm filter to remove the residual cells, and stored in a dark 4 °C refrigerator before use [34].

2.2. Experimental procedure

The schematic diagram of the dewatering process of *C. pyrenoidosa* is illustrated in Fig. 1. The feed tank with the total effective volume of 1.5 L was placed on a magnetic stirrer to mix the broth continuously. The dynamic membrane module had a 0.01 m^2 filtration area and used a stainless steel mesh with an equivalent aperture of 75 μm as the support layer with good mechanical properties for manufacture and sufficient support capacity for dynamic membrane according to the previous research results [28,35,36]. The module was fixed in the middle of the feed tank. Air, at the sparing rate of 4 m^3/m^2 h, was injected through a porous media at the bottom of the membrane module to induce a cross-flow near the dynamic membrane surfaces and to provide CO_2 for microalgae. The cross-flow condition generated a turbulence to minimize the deposition of biomass at both the bottom of the tank and the surfaces of cake layers [37]. Compared to other dynamic membrane systems for wastewater treatment, the aeration rate for microalgae separation by DDM in this research was relatively low to keep the turbulence from destroying the structure of cake layers [38]. The filtrate was withdrawn using a low capacity peristaltic pump (BT100-LJ, Kejian, China). The flux was automatically recorded using an electronic balance (UW6200H, Shimadzu, Japan) connected to a computer. A mercury manometer was fixed between the module and the pump to measure the TMP.

The experimental cycle for the DDM consisted of the precoating stage, the filtration stage and the backwash stage. In the precoating stage, the diatomite (2 g/L mixed liquor) was driven by a 1.0 m water head drop and formed a 2.0 ± 0.2 mm dynamic membrane on the support mesh. The stage lasted for approximately 15 min and was stopped when the turbidity of permeate was below 0.2 NTU. In the filtration stage, *C. pyrenoidosa* (2 g dry weight/L), at different culture time (2, 4, 6, 8, 10 days), was constantly filtered through the DDM for 24 h. Algae growth during the filtration process was ignored in this study. Batches of *C. pyrenoidosa* were cultured under the same conditions, meaning under the same inoculating concentration, culture medium, temperature and illumination. Therefore, discrepancies of culture time would mainly reveal the variation of EOM concentration and characteristics. The TMP and flux were recorded, and feed, broth, permeate and cake layer samples were collected. When the filtration stage was stopped, 15 min of air-water backwash was conducted and the DDM was precoated again to restore the membrane permeability. After backwash, the module could be entirely cleaned and the filtration performance was fully recovered without visible flux declination caused by irreversible fouling.

2.3. Analytical methods

After the filtration stage, the whole module was carefully taken out of the feed tank. The outer layer of the cake layer, which was mostly viscous semifluid, was gently scraped off using a slide. The rest of the cake layer was removed from the module and sliced into a series of small pieces (1 cm × 1 cm) under an electron microscope using a surgical blade. With a clear interface, the algae layer and the diatomite layer could be easily separated. Samples of the three layers were diluted with a 0.6% NaCl solution and stored at 1 °C.

The absorbance measurement (UV-1101 UV/visible Spectrophotometer, China) was used to quantify the concentration of *C. pyrenoidosa* at a wavelength of 680 nm. The concentration of polysaccharides was measured using the phenol-sulphuric method [39]. Protein content was determined by the modified Lowry method [40]. Glucose and bovine serum albumin (BSA) were used for calibration.

CLSM (Olympus FV1000) was applied to observe the EOM of the cake layers. Two different probes were collectively applied: Concanavalin A, Alexa Flour 633 conjugate (5 mg/L, Invitrogen) to target the polysaccharides with α-Man, α-Glu (polysaccharide) and SYPRO orange (Invitrogen) to target all of the proteins. The filtrates of EOM samples were fractionated using a GFC analyzer, which consisted of a TSK G4000SW type gel column (TOSOH Corporation, Japan), a liquid chromatography spectrometer (LC-10ATVP, SHIMADZU, Japan), and a refractive index detector (RID-10A). Polyethylene glycols (PEGs) were used as standards for calibration.