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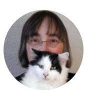

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Membrane-Based Energy Efficient Dewatering of Microalgae in Biofuels Production and Recovery of Value Added Co-Products

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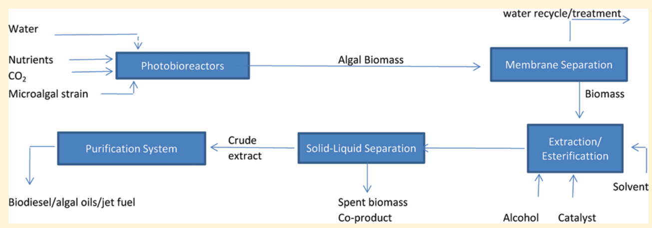
Supporting Information

ABSTRACT: The objective of this paper is to describe the use of membranes for energy efficient biomass harvesting and dewatering. The dewatering of *Nannochloropsis* sp. was evaluated with polymeric hollow fiber and tubular inorganic membranes to demonstrate the capabilities of a membrane-based system to achieve microalgal biomass of >150 g/L (dry wt.) and ~99% volume reduction through dewatering. The particle free filtrate containing the growth media is suitable for recycle and reuse. For cost-effective processing, hollow fiber membranes can be utilized to recover 90−95% media for recycle. Tubular membranes can provide additional media and water recovery to achieve target final concentrations. Based on the operating conditions used in this study and taking into scale-up considerations, an integrated hollow fiber-tubular membrane system can process microalgal biomass with at least 80% lower energy requirement compared to traditional processes. Backpulsing was found to be an effective flux maintenance strategy to minimize flux decline at high biomass concentration. An effective chemical cleaning protocol was developed for regeneration of fouled membranes.



INTRODUCTION

This work focuses on the evaluation of membrane-based energy efficient integrated separation processes and systems for the production of biofuels using domestic renewable alternatives to petroleum-based transportation fuels such as microalgal biomass.[1−4] Biofuels derived from renewable sources must have comparable fuel properties, and the potential to meet the global demand for transport fuels and are carbon neutral, a critical necessity for our long-term environmental and economic sustainability.[5]

Membrane-based separations are very attractive as these offer several advantages over traditional separation technologies including high reliability and direct scalability along with superior chemical, mechanical and thermal properties.[6] It is believed that biofuels from algal or cellulosic feedstocks can be more cost-effective through the generation of value added coproducts. Membrane-based dewatering offers the potential to concentrate biomass to recover valuable coproducts such as protein and for more efficient downstream processing to produce algal oils, biodiesel, or jet fuels.

There is considerable interest in the use of microalgae for biodiesel and other products due to their ability to sequester lipids.[7−9] Although microalgae-derived biodiesel has the potential to meet the demand with lower raw material costs, the current total production cost of biodiesel from microalgae is substantially higher than petrodiesel or oil crops,[7−13] primarily due to inefficiencies in cultivation, processing, and high energy requirements. Dewatering of algal biomass has been identified as a major bottleneck to cost-effective algal-based fuels production. However, current research is heavily focused on improved cultivation and plant cell wall modification to overcome recalcitrance to increase the yield of biofuels. Research effort to improve the efficiency of cell harvesting and dewatering is lacking which will impact the commercialization of algal biofuels. Current separation technologies such as sedimentation, centrifugation, dissolved air and/or froth flotation, rotary vacuum filter, and filter press are inefficient, cannot be reliably scaled-up, and suffer from high operating costs. Furthermore, many of these processing options do not produce filtrate suitable for recycle, a critical requirement to minimize freshwater usage and recovery of value added coproducts.

Microalgal-based biofuels production processes require removal of >99% water as the initial feed biomass is very dilute with typical cell densities in the range of 0.03−0.1 wt.% (0.3−1 g/L dry wt.). This is true of biomass grown using both open (raceway ponds) and closed (photobioreactors) systems.[14] Microalgal dewatering is a major challenge due to small particle size of algal cells (3−30 μm) and negligible density difference compared to water, which prevents cell aggregation and settling. Improvements in solid−liquid separation and pretreatment steps to reduce processing costs are critical to large scale commercialization. The dominant cell harvesting

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technology relies on centrifugation and/or flocculation-flotation. These are very energy intensive and can potentially create difficult to separate fine emulsions created by lipid release due to cell rupture resulting in yield loss and additional processing costs.[8] Membrane separations are more energy efficient and can concentrate biomass to high levels (often without pretreatment) with exceptional reliability under variable feed conditions and direct scalability adding further flexibility for expansion.[6,15−19]

There are a large variety of microalgal strains that could be used for conversion to biofuels. However, there are probably only a few microalgal strains that we believe are more promising candidates for large-scale mass production such as *Nannochloropsis*, *Schizochytrium*, and *Chlorella*.[20] Membrane-based systems can provide energy efficient and reliable process to dewater biomass with minimal yield loss. Despite these advantages, there have been very few comprehensive studies[8,21−23] to demonstrate the potential of membrane systems for cost-effective dewatering, an essential requirement for scale-up of an algae-based biofuels plant.

Uduman et al.[21] have reviewed the various technologies for dewatering algae and have highlighted the advantages and disadvantages for processes that can achieve high biomass concentration suitable for downstream processing. These options include flocculation, centrifugation and cross-flow (also known as tangential flow) filtration. Recently Zhang et al.[22] have described crossflow filtration performance of hollow fiber ultrafiltration membranes (polyvinyl chloride, 50 kD molecular weight cutoff) for the harvesting and dewatering of green microalga, *Scenedesmus quadricauda* and reported final calculated cell densities of up to 155 g/L. Although UF membranes can be used for algal concentration, there is no advantage in using a small pore size membrane as algae size is typically >1 μm. We have demonstrated that a membrane with pore of 0.1−0.8 μm can retain algae. It is preferable to use a membrane with <0.5 μm to ensure minimal pore fouling. This also ensures the effectiveness of backpulsing which is critical to maintain higher flux by controlling the biomass layer on the membrane surface, especially at high biomass concentration (>20 g/L). Although polymeric hollow fibers are suitable for algal harvesting and dewatering, they suffer from low flux at high biomass concentration and could pose difficulties in the regeneration of fouled membranes. This is one of the major reasons we believe a hybrid integrated dewatering system where polymeric hollow fibers are used in combination with tubular membranes to achieve optimal system performance. In this work, we describe the performance of such a system utilizing polyvinylidene fluoride (PVDF) hollow fiber modules and tubular inorganic membranes.

■ EXPERIMENTAL SECTION

Algae Cultivation. As discussed earlier, our goal was to utilize those cultures that are suitable for mass production with a high growth rate and are robust enough to survive not only varying light intensities, but also in the presence of some level of contamination. We believe *Nannochloropsis* cultures meet these criteria as they are known to adapt to varying degrees of salinities and to stress by increasing lipid production.[24,25] Doan and Obbard[25] have described *Nannochloropsis* sp. as marine picopleustonic algae with an average cell size of 3−4 μm. We used *Nannochloropsis oculata* LB2164 from UTEX collection.[20] The seed stock cultures were inoculated and grown at room temperature (22−26 °C), with agitation at 140 rpm, and with constant illumination at 300 lx from fluorescent daylight bulbs. Cultivation at larger scale was carried out in seawater media modified by replacing of $NaNO_3$ with an equimolar solution of $(NH_4)_2SO_4$ in an array of 20 × 1 gallon bottles, illuminated at 400−600 lx (lumen/m^2). Our protocol for continuous cultivation of up to 80 L of *Nannochloropsis* cultures made it possible to achieve algal biomass concentrations of up to 2 g/Liter. The pH of the harvested biomass was in the range of 7.5−8 for the majority of harvested microalgae in seawater media. The oil content of biomass was not measured as the focus of this work was on energy efficient dewatering of microalgae.

Crossflow Filtration. Hollow fiber membranes composed of polyvinylidene fluoride (PVDF) with 0.1 and 0.2 μm pore size (Pall Corp. NY) were evaluated in the crossflow configuration. The hollow fiber module (30 cm long) with 0.1 μm membrane (USP143) had an i.d. of 1.4 mm, whereas the module with 0.2 μm membrane had an i.d. of 2.6 mm (UMP 153). The 0.1 μm module had 140 hollow fibers with a membrane area of 0.12 m^2. The 0.2 μm module had 50 hollow fibers with a membrane area of 0.08 m^2.

Several inorganic membranes with pore diameters ranging from 0.1 to 1 μm were also evaluated which included Pall Exekia ceramic tubes and ORNL fabricated membranes with alumina, zirconia and silica layers on porous ceramic and metal supports, respectively. Ceramic membrane tubes had an inside diameter (i.d.) of 7 mm and outside diameter (o.d.) of 10 mm with a membrane area of 55 cm^2. ORNL porous metal supported tubular composite membrane had an i.d. of 10 mm and membrane area of 70 cm^2. Surface modified membranes to increase hydrophobicity (fluorocarbon and silica) were also evaluated for dewatering of *Nannochloropsis* culture.

A schematic of the crossflow filtration system with hollow fiber and tubular membrane module evaluated in this research can be found in the Supporting Information (SI). The system was equipped with a backpulse device to minimize fouling and flux decline as the biomass was progressively concentrated to achieve the desired final concentration. Crossflow was provided by a centrifugal recirculating pump. The system was designed to accommodate a hollow fiber, a tubular ceramic and porous metal supported ORNL membrane module in parallel. This allowed a direct comparison of filtration performance and was utilized in some biomass concentration runs where final volumetric concentration of >75× was achieved. The feed temperature was maintained within the desired range with the help of a recirculating bath. Backpulse operation, crossflow velocity, temperature, pressures and flow rates were controlled and monitored with automated valves and recorded with a data logger with a computer interface.

■ RESULTS AND DISCUSSION

In this research we have evaluated a number of membrane and process parameters to develop a set of membrane and operating conditions for the most energy efficient dewatering of algal biomass. The experimental error in each measured value was typically ±1%.

Algal Cultivation. Harvesting algae under the most optimal conditions includes not only selection of strain and nutrients but also light intensity. In this work, we have studied algal growth under varying light intensities (400 to 1200 lx) which would simulate low to moderate light conditions. We observed that culture growth rate at 400 lx (lumen/m^2) light intensity was adequate to achieve the desired algal growth rate and was

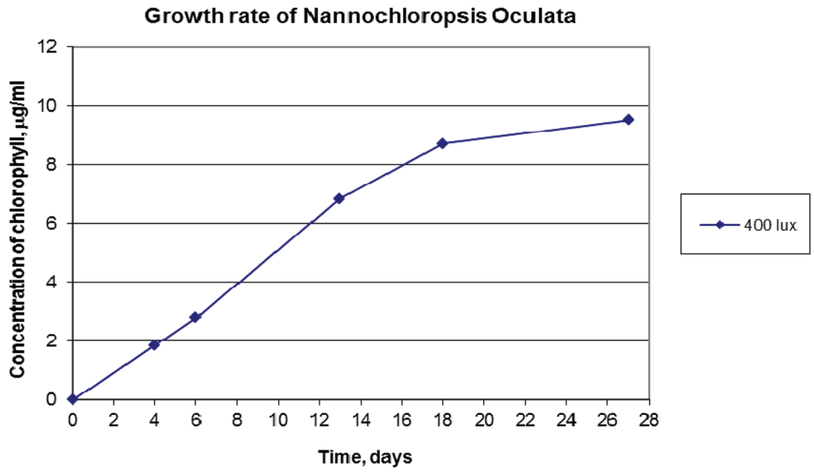

Figure 1. Harvesting of *Nannochloropsis oculata* microalgal cultures.

therefore used in this work. The authors did not aim at the optimization of the illumination at the lab scale cultures as those provide a poor model for mass cultivation where cell densities are different, and shading is a strong factor. The growth rate over time is shown in Figure 1. The temperature was maintained in the range of 22−26 °C. This is a desirable feature of *Nannochloropsis* indicating algae can grow all year round in low to moderate light intensity.

Another important aspect of algal growth is the time it takes to double the concentration (measured in biomass wt. in g/L). Figure 1 shows the duration required to reach the desired biomass concentration of up to 2 g/L dry wt. was about 27 days. The measured chlorophyll concentration ranged from 4 to 6 μg/mL for algal biomass cultivated over 10−14 days and 9.5 μg/mL in about 27 days (~4 weeks). Assessment of growth rates at laboratory scale is commonly done by measuring chlorophyll which is a method of choice recommended in the literature.[20] This demonstrates the suitability of *Nannochloropsis* to reach cell densities sufficient for more economically favorable large scale harvesting for industrial production of biofuels or coproducts.

Permeate Flux and Concentration Polarization. Permeate flow through microfiltration membranes can be described by the Hagen−Poiseuille law and/or Kozeny-Karman equation. These models assume the pores to be close-packed spheres with uniform pore size distribution, negligible fouling and concentration polarization.[18,19] In this work, permeate flux is expressed as LMH (liter/h-m^2).

$$J = \varepsilon r_p \Delta_{tm}/[8\mu t_m]$$

where, J = permeate flux; ε = membrane porosity r_p = membrane pore radius; Δ_{tm} = transmembrane pressure μ = liquid viscosity; t_m = membrane thickness

In most practical applications, the presence of concentration polarization and/or fouling cannot be eliminated. Flux is often limited by the formation of immobile cake or deposits on the membrane surface.

Permeate flux can also be expressed as,

$$J = \mathrm{P}_m[\Delta_{tm}/\mu]$$

where P_m is the membrane permeability coefficient $P_m = J/\Delta_{tm}$, at a given temperature and fluid viscosity

$$J = [\Delta_{tm}/R_t]$$

Total resistance to flow (R_t) is a contribution due to a number of individual resistances such as membrane resistance (R_m), resistance due to adsorbed material (R_a) and concentration polarization and/or gel layer (R_g). Effective membrane permeability is a measure of total resistance to flow. In this work, permeability is expressed as LMHB (liter/h-m^2-bar).

$$R_t = \mu/P_m$$

The effect of various operating parameters on flux is presented both in terms of permeate flux and effective membrane permeability. At high biomass cell densities, permeate flux was largely impacted by resistance due to concentration polarization.

Membrane Pore Diameter. The selection of optimal pore diameter for algal biomass separation was studied over a range of initial biomass concentrations (0.3−2 g/L) and operating conditions such as crossflow velocity and transmembrane pressure. *Nannochloropsis* cell size was in the range of 2−6 μm.Typically membranes with pore diameter an order of magnitude smaller than the smallest feed particle may be expected to retain all particles and prevent any internal pore fouling.

Hollow fiber (HF) and tubular membranes with pore diameters in the range of 0.05−1 μm were evaluated. Experiments were performed with hollow fiber module with 0.1 and 0.2 μm membranes with inside fiber diameter of 1.4 and 2.6 mm, respectively. at a crossflow velocity of 0.3−0.9 m/s and transmembrane pressure of about 15 psi. Inorganic tubular membranes were also evaluated which included Pall Exekia composite membranes on ceramic supports with pore diameters ranging from 0.05 to 0.8 μm. Porous metal supported tubular membranes fabricated at the Oak Ridge National Laboratory (ORNL) with pore size ranging from 0.2 to 1.2 μm were also evaluated. It was observed that membranes with pore diameter >0.5 μm produced a slightly turbid permeate. On the other hand, 0.1−0.5 μm membranes produced clear permeate with high average flux compared to larger pore diameter membranes. It was observed that 0.1 μm membrane showed the highest average flux with negligible pore fouling over the entire range of biomass concentrations. Based on these results, 0.1 μm membranes were primarily utilized to determine the performance characteristics of membrane-based dewatering of *Nannochloropsis* cultures harvested in-house up to prepare 60−80 L batch volume for dewatering experiments.

Membrane Surface Characteristics. Microalgae surfaces are hydrophilic with many having relatively high intracellular lipid content.[25] Algal lysis could occur due to mechanical stress from pumping action and crossflow, which may release macromolecules (polysaccharides) and lipids. *Nannochloropsis* cultures have robust cell wall which resists cell rupture under crossflow conditions. We evaluated hydrophobic PVDF membranes and surface modified tubular ceramic membranes. The tubular inorganic membranes were coated with fluorocarbon materials and silica (tetraethyl ortho silane) to render the surface and internal pore surfaces hydrophobic. Surface-enhanced hydrophobic membranes did not show a substantial flux (≤10%) increase compared to untreated ceramic membranes. Therefore, the ease of membrane regeneration may indicate weak adsorption of algae on the membrane surface. Membrane surface charge may have some benefits to minimize strong attachment of microalgae to the membrane surface but is not rate controlling as the biomass was concentrated to achieve high volumetric concentration factor (VCF). Concentration polarization and cake resistance were major factors limiting flux.

Feed Pretreatment. There are several pretreatment strategies described in the literature[21,23] to increase the filtration rates such as addition of a coagulant and/or chemicals to alter the surface charge on microalgae to promote flocculation and ease of filtration. Most flotation processes require the addition of a coagulant, whereas filter aid is required for pressure filtration systems for algae dewatering. Typical organic coagulants contain a high molecular weight cationic polymer and inorganic flocculants are based on iron and aluminum compounds. Although membrane-based biomass dewatering does not require addition of coagulants to produce clear permeate suitable for recycle, there may be a small added benefit with increased filtration rates due to enhanced coagulation of small sized (3−6 μm) microalgal cells. This may be especially valuable in downstream processing of concentrate prior to cell lysing and extraction of algal lipids. However, where potential contamination with high molecular weight polymers and/or metal based coagulants is undesirable the addition of a coagulant must be avoided.

We evaluated the effect of coagulant addition on flux using a variety of coagulants including polyaluminum chloride (PAC), ferric chloride, sodium alginate, polyacrylate ester and quaternary amines. The most effective coagulants for *Nannochloropsis* cultures were ferric chloride and PAC and were selected for further evaluation. The efficacy of coagulant dosing was determined from settling rates with a jar test under controlled stirring conditions. The results are shown in Table 1. It was observed that coagulants with a strong cationic charge such as $FeCl_3$ and PAC increased flux due to particle agglomeration resulting from charge neutralization of negatively charged algae particles. However, it should be noted that the effectiveness of a coagulant used for concentrating microalgae is adversely impacted in high salinity feed cultures. This is due to shrinkage in polyelectrolytic flocculant polymer at high ionic strengths.[23] As can be seen from Table 1, the filtration rates with the addition of 20−50 ppm ferric chloride were about 15−25% higher compared to without the addition of a coagulant. Filtration rates with a combined dosing of ferric chloride and PAC were lower compared to ferric chloride without PAC. This may indicate ferric chloride may be a more effective coagulant for algae. It should, however, be noted that although the use of coagulants can provide a beneficial effect on filtration rate, these materials were not essential to maximize flux.

Table 1. Effect of Coagulant Addition on Flux (0.1 μm Tubular Membrane, 23−29 °C)

biomass conc, g/L	coagulant dosing	TMP psi	flux LMH	permeability LMHB
2.0		10.0	240	348
2.0	20 ppm $FeCl_3$	10.0	283	411
2.0	50 ppm $FeCl_3$	15.0	458	442
2.0	50 ppm $FeCl_3$ + 50 ppm PAC	15.0	349	337

Crossflow Velocity and Transmembrane Pressure. The effect of crossflow velocity and transmembrane pressure (TMP) was evaluated to determine the minimum feed rate to provide the maximum impact on flux. When using a centrifugal pump to provide the crossflow, it is often difficult to achieve an independent control of crossflow velocity and TMP. However, every effort was made to maintain the crossflow velocity as close to the desired value as possible while varying the TMP. For bench-scale testing with hollow fiber modules, the feed rate was varied from 3 to 12 L/min which provided a crossflow velocity of 0.25 to about 0.95 m/s. The TMP was varied from 10 to 20 psi at crossflow velocity of about 0.5 m/s. For the tubular membrane module, the crossflow velocity was varied from 1 to 4 m/s. At the crossflow velocity of 2 m/s, the TMP was varied 5−30 psi. The system was also configured to connect modules in parallel with each module operating within the desired of crossflow velocity. This allowed a more direct comparison of membrane performance under similar conditions (biomass concentration, temperature and pressure).

Membrane performance as a function of crossflow velocity was evaluated for hollow fiber and tubular membranes. The results are summarized in Tables 2 for the PVDF hollow fiber membrane and in Table 3 and Figure 2 for the tubular ceramic membrane. These tests were performed in the batch recirculation mode, under a range of biomass concentrations. This is necessary to better understand the impact of crossflow velocity on flux over the entire run as biomass is progressively concentrated. For the 0.1 μm hollow fiber module, it can be seen from Table 2 that at the TMP of about 20 psi, there was minimal impact on flux (before or after backpulse) when the

Table 2. Effect of Operating Variables on Flux (0.1 μm Hollow Fiber Membrane, 24−30 °C)

biomass VCF	crossflow vel. m/s	backpulse before/after	TMP psi	flux LMH	permeability LMHB
1.0	0.28	after	2.3	119	751
1.2	0.51	before	10.3	237	333
1.2	0.50	after	9.3	467	726
1.3	0.50	before	15.8	230	211
1.3	0.50	after	13.7	526	558
1.4	0.53	before	20.3	248	177
1.4	0.53	after	17.2	684	576
1.8	0.74	before	20.0	245	178
1.8	0.74	after	18.5	644	505
2.1	0.93	before	25.6	250	141
2.1	0.93	after	23.2	723	453
15.0	0.74	after	15.2	70	67
20.0	0.70	after	16.0	50	45
75.0	0.70	after	16.5	35	31

Table 3. Effect of Operating Variables on Flux (0.1 μm Tubular Ceramic Membrane, 25−30 °C)

biomass VCF	crossflow vel. m/s	backpulse before/after	TMP psi	flux LMH	permeability LMHB
1.0	2.0	before	6.0	239	576
1.0	2.0	after	5.1	319	909
1.0	2.1	after	8.9	329	534
1.0	2.1	after	15.4	173	162
1.0	2.1	after	20.9	198	138
1.1	2.1	before	30.4	176	84
1.1	2.1	after	30.0	211	102
20.0	3.2	after	27.3	181	96
20.0	3.7	after	25.2	213	115
20.0	4.1	after	16.7	233	202
24.0	4.1	after	15.5	184	154
29.0	4.1	after	15.3	178	169
41.0	4.0	after	19.6	188	139
40.0	4.0	before	19.9	148	108
70.0	2.2	after	27.2	86	46
75.0	4.1	after	28.5	105	54
80.0	1.4	after	29.6	64	32
92.0	1.1	after	26.1	52	29

crossflow velocity was varied from 0.5 to 0.93 m/s . Likewise, at the crossflow velocity of 0.5 m/s the flux was relatively constant when TMP was varied from 10 to 20 psi. This suggests that there is fouling and concentration polarization occurring even at low volumetric concentration factor (VCF). The impact of biomass concentration on flux is more severe at high VCF. However, given that the flux values are still relatively high, hollow fiber membranes may be well suited at biomass concentration up to 15−20×. Table 3 shows for the ceramic tubular membrane at high biomass concentration (75×) there was a more substantial influence of crossflow velocity on flux due to the beneficial impact of higher shear rate in reducing cake layer thickness. With an initial feed algal concentration of 2 g/L dry wt., 75× represents algae concentration of about 150 g/L. These results are shown in Figure 2 for the 0.1 μm tubular membrane at a VCF of 75× (98.7% volume reduction). At 75×, tubular membrane flux is 3 times higher than hollow fiber membrane. This demonstrates that the tubular membrane geometry is well suited to achieve high dewatering efficiency despite the increased energy consumption at higher cross-flow velocity.

Flux Maintenance With Periodic Backpulsing. Fouling minimization is essential to control the flux decline as the biomass is progressively concentrated to achieve economical dewatering rate. There are several techniques that are utilized to remove foulants from membrane such as backpulsing, backflushing and backwashing. These are distinguished by the speed and force utilized to remove solids on the membrane filter. Backpulsing is an in situ method for removing deposits on the membrane by periodically reversing the transmembrane pressure.[15] This is well suited for more robust tubular membranes which can handle high reverse pressure (>10 bar) compared to polymeric hollow fiber membrane module where the operating pressure is limited to about 3 bar.

Backpulsing was successfully utilized in minimizing flux decline over a wide range of algal concentration for tubular membranes. For hollow fiber membranes, backpulsing had limited beneficial impact at high biomass concentrations. Figure 3 shows the effect of backpulse on flux for hollow fiber and tubular membrane. It can be seen that for hollow fiber modules, a substantial increase in flux (>25%) was observed right after backpulse at the beginning of the run. Over time, although the effect of backpulse was somewhat diminished, it was helpful to minimize flux decline at high VCF. On the other hand, for the

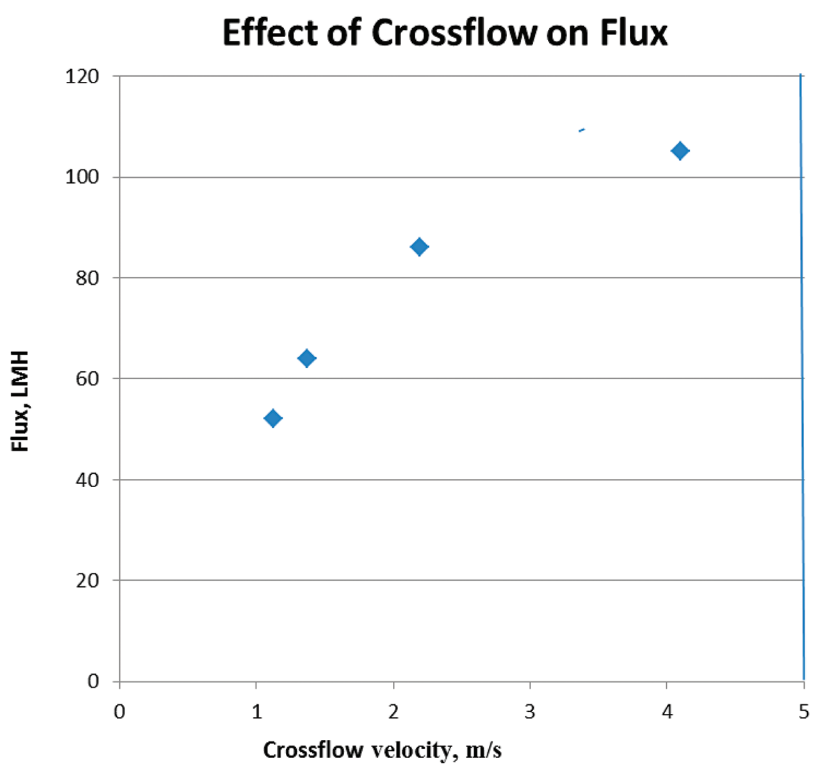

Figure 2. Effect of crossflow velocity on flux (0.1 μm Pall tubular membrane, VCF 75×).

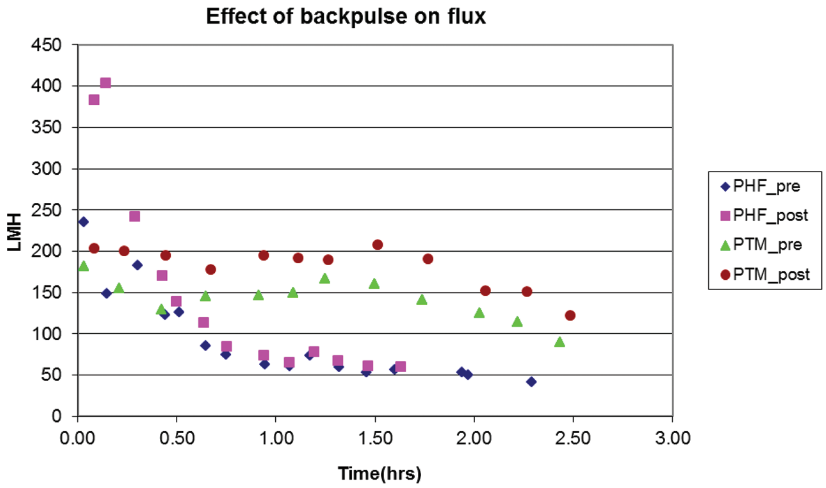

Figure 3. Effect of backpulsing on flux (hollow fiber and tubular inorganic membrane).

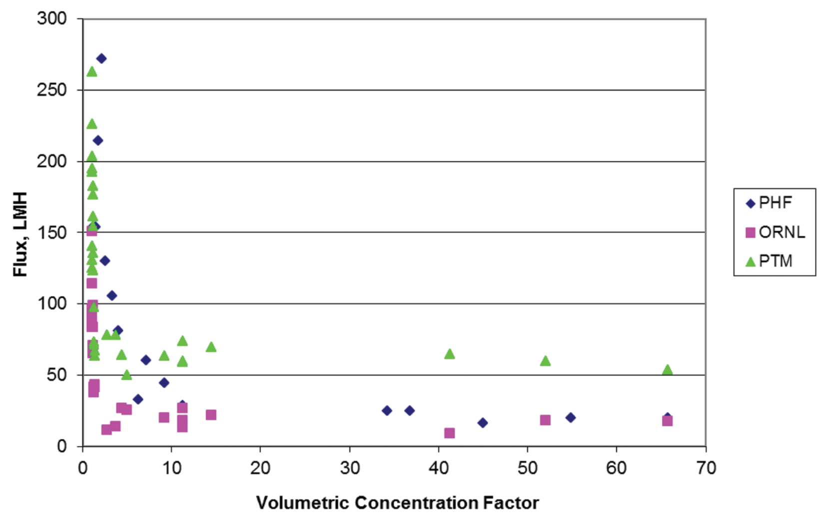

Figure 4. Flux versus volumetric concentration factor.

tubular membrane, flux value after backpulse was 15–30% higher compared to just before backpulse was deployed. Thus, backpulsing was more effective with inorganic membranes maintaining relatively high flux at high VCF (75×).

Membrane Regeneration. Regeneration of fouled membranes is a critical aspect for process viability and to ensure a long operating life of membrane modules for algal biomass dewatering. Fouled membranes were regenerated using dilute (<1 wt.%) caustic solution. The addition of a small concentration of sodium hypochlorite (100–500 ppm) along with enzymatic cleaners (e.g., Tergzyme) was found to be very beneficial for efficient regeneration of fouled membranes. Hollow fiber membranes were regenerated at 30–40 °C and tubular inorganic membranes at temperatures up to 70 °C. Clean water permeability recovery was >95% of initial value indicating the membranes were sufficiently clean for reuse. This demonstrated that membrane-based dewatering system can provide a long membrane life and thus lower the total operating costs and improve process reliability.

Biomass Concentration. To test the impact of high concentrations of biomass on filtration, the *Nannochloropsis* sp. was harvested to concentrations ranging from from 0.2 g/L up to about 2 g/L dry wt. for dewatering experiments. Cell density was analyzed gravimetrically as concentration measurements based on chlorophyll content were not reliable at high algae concentration. It was found that periodic backpulsing was critical to minimize fouling and to maintain high average flux. The beneficial effect of backpulsing was most pronounced with inorganic membranes due to their ability to withstand high pressure (~100 psi) versus hollow fiber modules (~40 psi).

Figure 4 shows the flux versus biomass concentration in the retentate. Initial algal cell density was about 2 g/L dry wt. The feed was concentrated without the addition of a coagulant. In this experiment, the PVDF hollow fiber (PHF), porous metal supported tubular membrane (ORNL) and Pall tubular ceramic membrane (PTM) were operated in parallel. Although this reduced the crossflow velocity in the tubular modules, it provided a good basis to compare hollow fiber dewatering rate with tubular membranes under otherwise uniform conditions. It can be seen from Figure 4 that although hollow fiber membranes show comparable flux at dilute biomass concentration, flux declines substantially at higher concentration (~VCF of 10×) largely due to concentration polarization and less effective backpulse at higher solids concentration. On the other hand, 0.1 μm Pall tubular membrane showed relatively high flux (>50 LMH) at high VCF with periodic backpulsing. Flux with ORNL fabricated 0.1 μm ZrO_2 membrane was lower than Pall 0.1 μm ZrO_2 membrane, primarily due to lower water

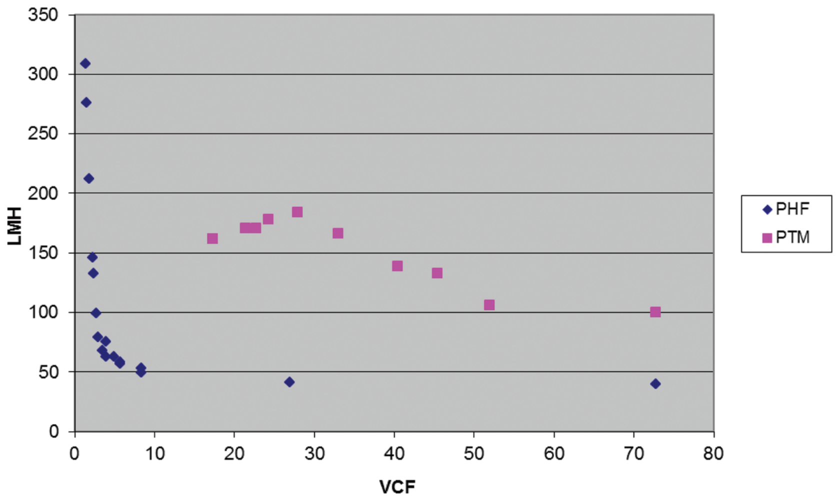

Figure 5. Dewatering of microalgal biomass with hollow fiber and tubular membrane system.

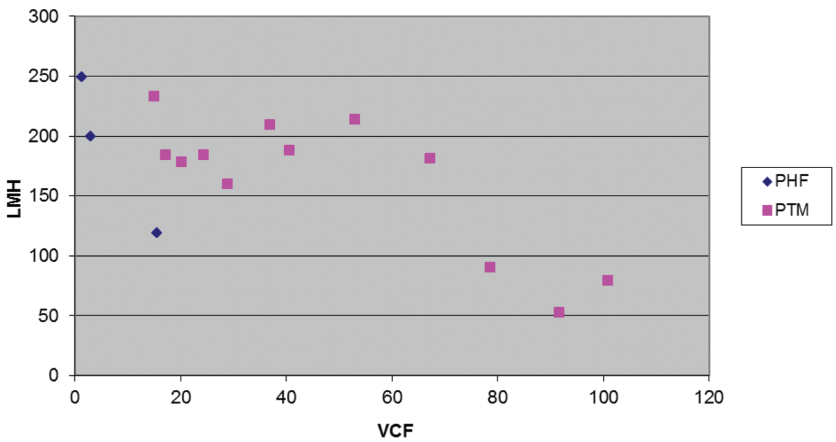

Figure 6. Dewatering with an integrated hollow fiber and tubular membrane system.

permeability and some pore fouling. As a result, Pall tubular membranes were selected for further evaluations in an integrated hollow fiber and tubular membrane system for algal biomass dewatering.

Figure 5 shows the performance data on the dewatering of *Nannochloropsis* sp. cultures with a PVDF hollow fiber membrane (PHF) to achieve at least 90% growth media recovery and tubular ceramic membrane (PTM) to increase the recovery to about 99%. The modules were connected in parallel. The harvested cultures were dewatered without the addition of a coagulant. It can be seen that the 0.1 μm tubular membrane showed more than 3-fold higher flux compared to 0.1 μm hollow fiber at VCF up to 20−30× and more than 2-fold higher at high VCF of 75× (~98.7% media recovery). Figure 6 shows the dewatering performance with hollow fiber module up to a VCF of 15× (~93% media recovery). This was followed by (second stage) dewatering the concentrate with a tubular membrane to achieve ~99% media recovery. With an initial feed concentration of 1.5−2 g/L (dry wt.) dewatered biomass concentration of >150 g/L can be achieved. Since hollow fiber membranes recover the bulk (90−95%) of the media, the size requirement for tubular membrane modules is substantially reduced. This is an important consideration as typically the capital cost (and energy consumption) of tubular modules is somewhat higher than hollow fiber modules. Thus an integrated hollow fiber and tubular membrane system (operating in stages) can provide a more cost and energy efficient dewatering option for large scale algal biomass dewatering for downstream processing in the production of biofuels or valuable coproducts.

Energy Efficiency. Membrane-based dewatering was evaluated in terms of energy consumption compared to more traditional biomass concentration and dewatering devices such as centrifuge, pressure filtration, dissolved air and/or froth flotation. Energy consumption per cubic meter of dewatered biomass can vary widely from 8 kWh for centrifugation, 10−20 kWh for flotation processes, 1 kWh for pressure filtration using depth media.[19] Pressure filtration is unsuitable for large scale processing as low microalgal concentration can result in inefficient capture and severe filter blockage occurs at high concentrations. Compared to these conventional processes, under the conditions described in this work (crossflow velocity <1 m/s for hollow fiber and 2−4 m/s tubular geometry at 15−30 psi), the energy consumption with an integrated algal dewatering system is estimated at 0.3−0.7 kWh/m^3. Hollow fiber modules recover 90−95% media for recycle with tubular modules achieving the final desired recovery (~99%). This represents a substantial reduction (80−95%) in energy requirement over traditional processes of centrifugation and froth filtration while producing algae and particle free clean filtrate (containing the culture media) suitable for recycle and reuse. It should be noted that hollow fiber based membrane systems consume substantially less energy due to the high packing density (up to 1000 m^2/m^3) compared to flat sheet geometry (plate and frame or cassette). This can also help reduce the space requirements of a membrane-based system compared to traditional processes for dewatering.

A hybrid integrated membrane-based system utilizing hollow fiber membranes to remove 90−95% water and tubular membranes to increase water recovery to >99% can provide a stable, reliable, efficient and cost-effective dewatering option for large-scale processing of microalgal biomass for the production of biofuels.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crossflow Filtration System. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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