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Pilot scale dewatering of *Chlorella sorokiniana* and *Dunaliella tertiolecta* by sedimentation followed by dynamic filtration

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ABSTRACT

The present work focuses on the application of pH-induced sedimentation combined with dynamic filtration for microalgae culture concentration at pilot scale. Concentrations were performed on cultures of two microalgae species: *Dunaliella tertiolecta* and *Chlorella sorokiniana*. The objective of the combined process was to reduce microalgae dewatering costs. It is true that sedimentation reduces operation costs considerably, but the results of membrane filtration offer a total rejection and high final concentrations, at even a cheaper cost than centrifugation. When using the two technologies in series, high concentration factors with values up to 207.4 for *Dunaliella tertiolecta* and 245.3 for *Chlorella sorokiniana* were achieved. The final concentration of *Dunaliella tertiolecta* was 184.58 g L^{-1} with 81.5% of water content in the sludge. The concentrations obtained were high enough to dispense with further operations for the sludge to be ready for a cell disruption step using steam explosion. Analytic techniques used were dry weight and optical density. For the filtration, experiments were performed using both commercially available and self-prepared membranes, manufactured from Acrylonitrile Butadiene Styrene: a novel polymer in membrane technology, selected to reduce costs. Each of them could perform in a similar way to commercial membranes in a pilot scale high-shear stress membrane module.

1. Introduction

Microalgae are the scope of wide research studies concerning the culture and the final composition, harvesting techniques as well as biorefinery [1]. Being a source of lipids, proteins and carbohydrates microalgae can be processed into food supplements, fodder, colorants, enzymes, biofuels and pharmaceuticals [2–4]. In the general production process, they are primarily cultivated either in an open pond or in a closed photobioreactor (PBR), reaching a biomass concentration between 0.02 and 0.5 wt% [5]. However, for most of the applications, microalgae need to be harvested after cultivation. From the culture medium, the biomass can be concentrated to 15–22% in a single step or in a sequence of concentration steps, before further treatment via drying, extraction or other downstream processing steps [6]. Nevertheless, as the costs of this single step as high as 20–30% of the total cost of microalgal biomass production, harvesting optimization is strongly recommended [7].

The cheapest and most conventional method available is flocculation/sedimentation, which allows to discard at least 90% of the liquid for further processing. This technique is commonly being used at wastewater treatment plants for sludge treatment. Sedimentation enables liquid or solid particles to separate from suspensions with different densities, producing effluents of mostly clear liquid. In order to decrease the sedimentation time, the aeration of microalgae cultures can be stopped, which causes the cells to flocculate on their own. This technique, called auto-flocculation, occurs as a result of the precipitation of carbonate salts with algal cells at higher pH, arising from algae's photosynthetic CO_2 consumption [8]. Moreover, auto-flocculation can be improved by adding NaOH to achieve optimal pH values [9,10]. In many cases the average dry solids concentration of microalgal biomass to be achieved is around 0.5–3%. However, if the density difference is small, the process can result in being slow and ineffective [11,12].

A quick dewatering of algae using centrifugation can be obtained with 84% removal efficiency (0.2 g L^{-1} algal culture at a flow of 379 L min^{-1} and under a rotational velocity of 3000 rpm) although, at the same time, it is high energy demanding. To harvest algae cultures with the same technique from 0.04% to 4% dry weight costs 1.3 kW h m^{-3} of pond water. To increase the efficiency of the drying

Abbreviations: ABS, acrylonitrile butadiene styrene; CA, contact angle; DMA, *N,N*-dimethylacetamid; MF, microfiltration; MWCO, molecular weight cut-off; NMP, 1-methyl-2-pyrrolidinone; OD, optical density; ODCF, optical density concentration factor; PAN, polyacrylonitrile; PBR, photobioreactor; PE, polyethersulfone; SEM, scanning electron microscope; TCF, total concentration factor; UF, ultrafiltration; VCF, volumetric concentration factor; VSEP, vibratory shear enhanced process

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process, the algal biomass concentration has to be increased to at least 20% dry weight in the dewatering stage. The energy demand for increasing the microalgae culture concentration to 22% of dry biomass via centrifugation is of 8 kWh m^{-3} [13,14]. This could be applicable in processes to obtain high-value products, whereas for other applications, e.g. a biodiesel production process, this would be too expensive.

Other techniques such as membrane filtration, which is capable of consuming as little as 0.25 kWh m^{-3} at 70% harvest efficiency, appears to be more suitable for this purpose [13,14]. However, as biological feeds are a mixture of organic matter of different size and shape, they are usually difficult to filter because the cake is very compressible. Also, the surface charge of the cells may result in concentration polarization phenomena, affecting the interaction between the membrane surface and the biomass [15]. The filtration ability depends also on the cell viability and the harvesting time [16]. The fouling issue is the main disadvantage when working with the conventional cross-flow filtration and can result in up to 99% permeability reduction [17–19]. Vibratory shear enhanced process (VSEP) also called dynamic filtration can overcome this issue by increasing the turbulence and raising the shear stress over the membrane surface [20,21]. Moreover, in the case of dynamic filtration it was proved that in spite of the permeability decrement, when the initial biomass concentration increases, an asymptotic behavior occurs. Therefore, the filtration performance may continue to be satisfactory with sludge concentration increment [22]. For the purpose of microalgae dewatering, membrane micro/ultrafiltration (MF/UF) can be applied by using ceramic as well as polymeric membranes. However, as the cost of the overall process is the key parameter, polymeric materials are much more suitable as their price is considerably lower compared to the ceramic ones [17].

In order to reach the highest concentration of microalgae with the lowest dewatering cost, two techniques should be combined resulting in an effective and economic harvesting process [23]. The more efficient and cheaper the methods chosen are, the lower the final cost of the process will be. The main hypothesis of the work is that the combination of sedimentation and dynamic membrane filtration reduces the harvesting cost. This work describes the combination of pH-induced sedimentation of two different microalgae species, *Dunaliella tertiolecta*, and *Chlorella sorokiniana*, with dynamic membrane filtration. Novel cheap polymeric membrane material was compared with commercially available ones and tested for the dewatering of microalgae *Dunaliella tertiolecta* with both conventional and dynamic filtration setups.

2. Materials and methods

2.1. Materials

2.1.1. Microalgae biomass

Sedimentation and filtration experiments were performed with the green microalgae *Chlorella sorokiniana* (strain CCAP 211/8k) and *Dunaliella tertiolecta* (strain CCAP19/6B).

Cultures of *Dunaliella tertiolecta* for experiments designed to compare the performance of commercial membranes and self-made membranes in cross flow and dynamic filtration were grown in 5 L flasks. Culture medium consisted of 4 L natural seawater (37‰) enriched with $NaNO_3$ (4.4 mM), $Na_2HPO_4.2H_2O$ (0.04 mM) and the same micronutrient concentrations as in Guillard's f/2 medium described in Andersen (2005). The cultures were aerated with air enriched with 0.5% CO_2 and illuminated with OSRAM L30 W/865 Lumilux, Cold Daylight fluorescents giving an irradiance at the flask surface of 200 μmol photon $m^{-2} s^{-1}$ in a L: D cycle of 16:8.

The cultures of *Chlorella sorokiniana* and *Dunaliella tertiolecta* used in the sedimentation experiment and the culture of *Dunaliella tertiolecta* used in the experiment for the determination of the maximum concentration attained by VSEP were grown in column photobioreactors (50 cm diam., 300 L or 150 L for the maximum concentration experiment). They were aerated with air and illuminated with Philips MASTER TLD 58 W/865 fluorescents giving an irradiance at the photobioreactor surface of 300 μmol photon $m^{-2} s^{-1}$ in a L: D cycle of 16:8. *Chlorella sorokiniana* was grown in tap water enriched with $NaNO_3$ (2 mM) Na2HPO_4.2H_2O (3 μM) and the micronutrients of BBM (Andersen 2005) at 1/8 strength. *Dunaliella tertiolecta* was cultured in artificial seawater prepared with tap water and 37 g·L^{-1} of Aquaforest Reef Salt® enriched with $NaNO_3$ (2 mM), $Na_2HPO_4.2H_2O$ (3 μM) and the same micronutrient concentrations as in Guillard's f/2 medium. In the cultures prepared with tap water, phosphate was daily fed-batch to increase 3 μM the concentration in the medium, in order to avoid precipitation, presumably operated by magnesium and calcium ions. Temperature during culture was 20 ± 2 °C.

Table 1
Commercial polymeric ultrafiltration membranes used for the dewatering of microalgae.

Membrane commercial names	Producer	Supplier	Material	MWCO
PE5	Sepro	Nanostone	Polyethersulfone	5000 Da
PAN50	Sepro	New logic	Polyacrylonitrile	50,000 Da

2.1.2. Membranes

Experiments were performed with both commercially available polymeric membranes and synthesized ones. The filtration area was 0.0139 m^2 for conventional cross-flow filtration module and 0.0446 m^2 for dynamic filtration module. The properties of the commercial membranes are listed in Table 1.

DMA (*N*,*N*-Dimethylacetamide, ≥99.5%) was purchased from Sigma-Aldrich. ABS copolymer Novodur P2H-AT NR, kindly provided by Styrolution, was employed with a density of 1.05 g cm^{-3}, processing temperature between 230 and 260 °C and tensile stress at yield of 44 MPa. DMA was used as a solvent to dissolve the polymer for the synthesis of non-commercial membranes.

2.2. Methods

2.2.1. Membrane synthesis

Polymeric membrane synthesis was performed via phase inversion precipitation with a polymer concentration of 30 wt% and water used as a non-solvent in a coagulation bath.

The polymer and the solvent were mixed and stirred for 72 h to obtain homogenous polymeric solution. Afterwards, the solution was left for at least 24 h to remove all the bubbles from the bulk. The solution was deposited onto a glass plate using a casting knife with adjustable thickness gap regulated by an incorporated micrometer [24]. The casting knife gap was adjusted to 300 μm and set in motion by an automatic film applicator with a constant traverse speed of 50 mm/s (BYK – Gardner Automatic Film Applicator). The immersion of casted polymeric solution into a coagulation bath caused a phase inversion precipitation, which resulted in the formation of a thin film. The temperature of the coagulation bath was fixed to 50 °C, ± 5 °C, to produce a membrane applicable for use with dynamic filtration module.

2.2.2. Sedimentation combined with dynamic filtration

In order to determine the optimum pH value for sedimentation in 300 L photobioreactors, a preliminary study of sedimentation experiments was performed with both microalgae species in 2 L graduated cylinders. 2 M NaOH solution was added into the cylinders and mixed with a magnetic stirrer until flocculation occurred. Once the formation of aggregates was observed the stirring was stopped and the suspension was allowed to settle. pH was constantly monitored during those experiments.

1200 L of *Dunaliella tertiolecta* and 900 L of *Chlorella sorokiniana* cultures were treated with pH induced sedimentation by adding 2 M