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Research paper

# Application of ABS membranes in dynamic filtration for *Chlorella sorokiniana* dewatering

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ABSTRACT

This work focuses on the use of dynamic membrane filtration with cheap membranes manufactured from acrylonitrile butadiene styrene polymer for dewatering of *Chlorella sorokiniana* microalgae strain.

Dynamic filtration based on vibration was used at pilot scale and compared to conventional cross-flow filtration to demonstrate how fouling can be greatly minimized. Experiments were carried-out with different types of commercial membranes from different pore sizes and materials such as polyethersulfone or polyacrylonitrile.

ABS membranes were produced, characterized (scanning electron microscopy, contact angle and porosity measurements) and tested with conventional and dynamic filtration. Composition of acrylonitrile butadiene styrene polymeric solution as well as conditions of membrane preparation were examined in order to obtain a useable membrane for microalgae filtration. Acrylonitrile butadiene styrene membranes offered promising results in terms of permeability when applied to both filtration techniques for *Chlorella sorokiniana* dewatering. The influence of different concentrations of microalgae culture as a feed for dynamic membrane filtration was examined. To confirm total microalgae rejection the optical density of feed, permeate and retentate was studied in all experiments.

Acrylonitrile butadiene styrene material is order of magnitudes cheaper than conventional membrane materials. Combined with dynamic filtration, both may turn membrane filtration into a preferred technology for microalgae dewatering.



## 1. Introduction

Finding an alternative for nonrenewable energy sources became the objective of extensive studies. Because of its advantages over conventional fuels, its sustainability, biodegradability and suitability to use in existing diesel engines, biodiesel seems to be a proper substitute for petroleum diesel [1,2]. Microalgae with their unicellular structure can efficiently turn solar into chemical energy. Due to their ability to capture carbon dioxide, fast growth rate and high content of lipids, carbohydrates and proteins are considered as a competitive material for various industrial purposes [3,4]. They are being commonly used in the production of nutraceuticals, pharmaceuticals, cosmetics, fine chemicals and to provide fuel [5,6]. Although the idea of using microalgae as a feedstock for biofuel production has been proposed in the 50s, in recent years they became a highly considered alternative for fossil fuels. However, costs of the overall process need to be decreased.

In comparison with plant crops, microalgae have higher biomass productivity and lower cost per yield [7]. They have a very short harvesting time and require much less land area for cultivation than terrestrial plants. Moreover, they are capable of growing in more radical conditions, from fresh water up to extremely saline water. The cultivation of microalgae in sea water, which is inapplicable in agriculture, reduces the demand of fresh water consumption [8]. Regardless of the numerous advantages of using microalgae as a staple for biofuel production, the overall process still needs to be improved in order to reduce the production costs in the industrial scale [9]. Since a high volume of microalgae is processed and implies a considerable cost, dewatering becomes a critical step to be optimized. Techniques commonly used for harvesting are flocculation/sedimentation [10], flotation [11], centrifugation [12] and filtration. The flocculation/sedimentation process refers to the aggregation of microalgae in a suspension to form masses that subsequently can settle. Even if flocculation reduces the need of energy

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**List of abbreviations**

| | |
|---|---|
| ABS | acrylonitrile butadiene styrene |
| CA | contact angle |
| DMA | N,N-dimethylacetamid |
| IPA | isopropanol |
| MF | microfiltration |
| MWCO | molecular weight cut-off |
| NMP | 1-methyl-2-pyrrolidinone |
| OD | optical density |
| PAN | polyacrylonitrile |
| PES | polyethersulfone |
| SEM | scanning electron microscope |
| UF | ultrafiltration |
| VSEP | vibratory shear enhanced process |

intensive separation mechanisms, the concentration obtained is low (<10% of solids content) [13] and needs further concentration using other methods, like centrifugation. Even though centrifugation is more effective, the shear forces can disrupt microalgae cells and it is high energy demanding, which results in substantial operational costs. For those reasons, filtration is a promising technique [14,15]. Microalgae cell size allows for the application of membrane micro/ultrafiltration (MF/UF) for the dewatering purpose. The list of benefits in using membranes includes no chemical additives, simplicity in operation and low energy consumption [16]. For the dewatering purpose, both polymeric and ceramic membranes can be used. Although ceramic membranes offer good performances in terms of flow and reproducibility, they are much more expensive than polymeric ones [17]. Recent studies showed that membranes produced from cheap polymers, such as ABS, are promising materials which could be applied in the dewatering step for microalgae biorefining [18]. Therefore, when using those cheaper membranes, a significant reduction in the costs of the overall process can be obtained.

The main disadvantage in microalgae MF/UF is fouling [17]. Filtration of biological feeds results in additional difficulties due to the compressibility of the mass formed. Another factor that has a significant influence on the membrane performance is the increase in the feed concentration. In conventional cross-flow filtration, cake formation over the membrane surface and pore-blocking can result in up to 99% permeability reduction. Previous studies showed that fouling issues can be minimized by using dynamic filtration, which increases turbulence and raises shear stress over the membrane surface [19]. There are several types of commercially available dynamic filtration systems, like rotating cylindrical membranes, rotating disk systems and vibrating systems [20]. Vibratory shear enhanced process (VSEP) was already successfully applied for the purification of drinking water, skim milk ultrafiltration, pervaporation as well as for baker's yeast microfiltration [21]. It was also found to be a proper technique for microalgae dewatering [22,23]. However, so far only commercial membranes have been used in the microalgae filtration experiments with VSEP.

When compared to other polymers, ABS is up to three orders of magnitude cheaper. Depending on the market, PES costs vary between 432 $ kg$^{-1}$ (GoodFellow) and 480 $ kg$^{-1}$ (Sigma Aldrich), PAN 375 $ kg$^{-1}$ (GoodFellow) and 1850 $ kg$^{-1}$ (Sigma Aldrich), and ABS price is only 2.4 $ kg$^{-1}$ (Plasticker) [18]. ABS polymers are highly resistant, have good thermal stability and durability [24]. Due to their properties and low price, they are being commonly used in packaging industry, for toy production as well as for 3D printing [25–27]. Although this material is so ubiquitous in everyday life, it is not so common in membrane industry. Some research with ABS membranes can be found in gas permeation studies [28–30]. Preliminary studies with filtration of *Phaeodactylum tricornutum* were performed for ABS synthesized membranes, however only conventional cross-flow technique was used for this purpose [18].

The main aspect considered in this work was to combine vibrating filtration method with new cheap membrane materials for the dewatering of microalgae. *Chlorella sorokiniana* was used in dewatering with both conventional and dynamic filtration modules.

## 2. Materials and methods

### 2.1. Microalgae biomass

Experiments were carried out with the freshwater microalgae *Chlorella sorokiniana* Shihira & R.W.Krauss (strain CCAP 211/8K), a 2–5 μm spherical to ellipsoidal freshwater green unicellular alga. Dynamic filtration was performed with 300 L cultures whereas cross flow filtration was conducted with material from either 300 L cultures or 4 L cultures. Cultures were illuminated (16:8 light: dark cycle) with cool daylight fluorescents and kept at 24 ± 2.5 °C. Four litre cultures were grown in five litre flasks (18 cm in diameter) with BBM3N3S medium [31] and aerated with air with 0.5% $CO_2$. They were illuminated with OSRAM L30W/865 fluorescents, which gave irradiance on the flask's surface of 200 μmol photon m$^{-2}$ s$^{-1}$ : 300 L cultures were grown in column photobioreactors (50 cm diam.) with tap water enriched with the following nutrients (in g m$^{-3}$): $NaNO_3$ (500), $K_2HPO_4.3H_2O$ (21), $KH_2PO_4$ (37.5), $Na_2EDTA$ (16.7), $FeCl_3$. $6H_2O$ (4.84), $ZnSO_4 \cdot 7H_2O$ (0.485), $MnCl_2 \cdot 4H_2O$ (0.887), $Na_2MoO_4.2H_2O$ (0.025), $CuSO_4 \cdot 5H_2O$ (0.043) and $CoCl_2 \cdot 6H_2O$ (0.014). Cultures were aerated with air and illuminated with Philips MASTER TLD 58W/865 giving irradiance on the photobioreactor surface of 300 μmol photon m$^{-2}$ s$^{-1}$.

For the tests with concentrated microalgae biomass, retentate obtained from the vibratory dewatering of original culture was collected and used as a feed for further experiments.

### 2.2. Membranes

Experiments were performed with commercially available polymeric membranes and synthesized ones. The filtration area was 139 cm$^2$ for conventional cross-flow filtration module and 446 cm$^2$ for dynamic filtration module. In order to ensure total microalgae rejection, the main criterion for membrane selection was the molecular weight cut-off (MWCO), chosen according to *Chlorella sorokiniana* cell size. Commercial membranes PES5 (polyethersulfone, MWCO 7000 Da), PAN50 (polyacrylonitrile, 50,000 Da) and PES20 (polyethersulfone, 200,000 Da) produced by Sepro were purchased from New Logic (United States).

For the synthesis of non-commercial membranes N,N-Dimethylacetamid, DMA (≥99.5%, CAS 127-19-5), 2-Propanol, IPA (≥99.8%) and 1-Methyl-2-pyrrolidinone, NMP (anhydrous, 99.5%, CAS 872-50-4) were purchased from Sigma-Aldrich (Spain). Acetone, for synthesis (BP, USP) was purchased from LABKEM (Spain). ABS copolymer Novodur P2H-AT NR, kindly delivered by Styrolution (Spain), was employed with a density of 1050 kg m$^{-3}$, processing temperature between 230 and 260 °C and tensile stress at yield of 44 MPa.

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