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Experimental studies and statistical analysis of membrane fouling behavior and performance in microfiltration of microalgae by a gas sparging assisted process

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HIGHLIGHTS

- Fouling and transmission studies of microalgae (*Chlorella* sp. suspension).
- A quadratic model was developed to predict the permeate flux by RSM.
- EPS transmission was studied in different TMPs, CFVs, and flow regimes.
- Higher gas velocity resulted in higher shear stress and therefore more EPS release.
- Slug flow resulted in higher flux enhancement in lower microalgae concentrations.

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ABSTRACT

Response surface methodology (RSM) and central composite design (CCD) were applied for modeling and optimization of cross-flow microfiltration of *Chlorella* sp. suspension. The effects of operating conditions, namely transmembrane pressure (TMP), feed flow rate (Q_f) and optical density of feed suspension (OD_f), on the permeate flux and their interactions were determined. Analysis of variance (ANOVA) was performed to test the significance of response surface model. The effect of gas sparging technique and different gas–liquid two phase flow regimes on the permeate flux was also investigated. Maximum flux enhancement was 61% and 15% for *Chlorella* sp. with optical densities of 1.0 and 3.0, respectively. These results indicated that gas sparging technique was more efficient in low concentration microalgae microfiltration in which up to 60% enhancement was achieved in slug flow pattern. Additionally, variations in the transmission of exopolysaccharides (EPS) and its effects on the fouling phenomenon were evaluated.

1. Introduction

Microalgae are invaluable biological resources that have a wide range of applications. They can be used in: (i) pharmaceutical, dermocosmetics, aquaculture, food and feed industries (Spolaore et al., 2006), (ii) environmental applications (Harun et al., 2010), and more recently (iii) bio-fuel production (Christenson and Sims, 2011). Due to the dilute nature of microalgal cultures, their similar density to water and the small size of the cells (3–30 μm in diameter), algal biomass separation from cultivation broth has still remained challenging. Therefore, finding an economical and efficient harvesting technique is an important factor for consideration in order to make microalgae a commercially viable source for production of valuable products (Molina Grima et al., 2003; Christenson and Sims, 2011).

Selection of appropriate harvesting method is dependent on both microalgae properties (density of culture medium, cell size, etc.) and desired product quality (acceptable level of moisture, etc.) (Richmond, 2004); a suitable method may involve one or more solid–liquid separation steps and contribute 20–30% of the total biomass production cost (Molina Grima et al., 2003). Microalgae biomass can be harvested by different techniques like centrifugation, flocculation, filtration, flotation, electrophoresis, gravity sedimentation, and membrane technology (Richmond, 2004; Harun et al., 2010; Christenson and Sims, 2011).

Between the mentioned methods, membrane filtration forms a very promising technology for algal harvesting due to its high efficiency, mild operating conditions with no need for chemical additives, reliability and safety (Rossi et al., 2008; Bhave et al., 2012). Furthermore, this process offers the advantages of almost

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complete retention of biomass (Bilad et al., 2012), and potential disinfection via removal of protozoa and viruses (Zhang et al., 2010).

However, a well-known drawback of filtration is the permeate flux decrease owing to the membrane fouling; which becomes more complex with mixed feeds, such as microalgae broth, where the biomass is in the presence of extracellular organic matter (EOM) (Rossi et al., 2008; Babel and Takizawa, 2010; Ladner et al., 2010; Discart et al., 2013). The removal of algae by micro- and ultra-filtration (MF and UF) has been reported, though not extensively. Rossi et al. (2004, 2005) studied the harvesting of *Arthrospira platensis* both with organic and inorganic membranes where UF membranes showed better performance than MF ones. Besides, they found polyacrylonitrile (organic, 40 kDa) and ATZ (inorganic, 50 kDa) membranes as the most suitable, since fouling phenomena and internal pore clogging were minimum.

On the other hand, understanding the mechanism of fouling and developing antifouling strategies are critically important for sustainable biomass concentration by filtration. The benefits of dynamic filtration method compared with traditional crossflow filtration have also been evaluated (Ríos et al., 2012) where 2–3 times higher fluxes have been achieved. Several studies (Teixeira and Rosa, 2003; Dong et al., 2006; Zhang et al., 2012) have focused on the influence of pH on membrane fouling and found that the low pH can accelerate this phenomenon.

One concern that has been lightly addressed in microalgae filtration studies is the release of EOMs (exopolysaccharides (EPS), proteins, lipids, humic substances, etc.) due to high shear stress which is known to generate severe fouling. Babel and Takizawa (2010) found that excretion of EOM could significantly increase the specific cake resistance. Morineau-Thomas et al. (2002) observed the same results, when harvesting two species of algae (*Chlorella* sp. and *Porphyridium purpureum*) by ultrafiltration. They showed that these extracellular materials can create linkage between the cells and induce more compact deposit eventually leading to less flux. Besides, Ladner et al. (2010) reported that high fraction of the fouling is actually caused by the cell-derived material rather than the cells themselves. Moreover, some studies have pointed out that the permeate flux depends greatly on hydrodynamic conditions such as crossflow velocity (CFV) and transmembrane pressure (TMP) (Rossi et al., 2008; Ladner et al., 2010; Ahmad et al., 2012).

Although separation of algae by MF and UF has been documented in the literatures, there has not been a great deal of work focusing on the effect of operating conditions on crossflow microfiltration. Moreover, the EPS release and the fouling problem has remained still challenging. Furthermore, to the best of the authors' knowledge, almost all of the previous published researches on this topic have adopted the conventional experimentation methods in which one parameter is varied maintaining the others constant. These methods have some disadvantages (involving too many time-consuming experimental runs, ignoring the effects of interactions between the considered factors, leading to low efficiency in process optimization) that can be avoided by applying the response surface methodology (RSM). The RSM includes statistical design of experiments, developing a mathematical model for prediction of the out-put responses, checking the adequacy of the developed model, and optimization of experimental conditions based on the valid model.

Therefore, the objective of this study was applying microfiltration for harvesting of *Chlorella* sp. and evaluating the effects of operating conditions on the permeate flux, EPS exertion, and the fouling problem. To do this, RSM tool was used for the experimental design, modeling, and optimization of the process. Besides, gas sparging technique was introduced to establish different gas/liquid two phase flow regimes to minimize the fouling problem. In this gas sparging assisted microfiltration of microalgae, the effects of different patterns on the membrane performance were examined and the effects of gas flow rate, concentration of biomass, and EPS content were thoroughly discussed.

2. RSM theory

RSM is a mathematical-statistical method that can be used for studying the effect of different levels of operational factors and their interactions. The objectives of RSM are: (1) finding an approximating function for predicting future response, and (2) optimization of the response based on the factors investigated. In developing the response surface model, the input variables (x_i, $i = 1, 2, \ldots n$), must be scaled to coded levels between -1 and +1 (Xiangli et al., 2008), where -1 corresponds to the minimum and +1 suit to the maximum value of the variable. The most popular RSM design is the central composite design (CCD) which is composed of:

- Factorial points (full or fractional): the possible combinations of two levels (high, +1 and low, -1 levels) of the factors.
- Axial points or "star" points: The axial points have all of the factors set to coded level 0 – the midpoint of each factor range – except one factor, which has the value +/$-$Alpha.
- Center points: where all levels set to 0 (the center). Center points are usually replicated to provide a good estimate of experimental error variance.

According to the CCD, a full quadratic approximation can be used for developing a response surface models of second-order, which is written in general form as:

$$\hat{Y} = \beta_0 + \sum_{i=1}^{n}\beta_i x_i + \sum_{i=1}^{n}\beta_{ii}x_i^2 + \sum_{i<j}^{n}\beta_{ij}x_i x_j + \xi \quad (1)$$

where $\hat{Y}$ is the predicted response, β_0, β_i, β_{ii} and β_{ij} are the regression coefficients, which can be computed by means of Multiple Linear Regression (MLR) method or the ordinary least squares (OLS) method (details are described elsewhere (Montgomery, 2001a,b; Myers and Montgomery, 2002)), x_i refers to the coded values of the input variables, ξ is the statistical error, and n is the total number of designed variables.

3. Methods

3.1. Microalgae cultivation

Pure culture of the unicellular green microalgae, *Chlorella* sp., was obtained from Iranian Fisheries Organization, and cultivated under laboratory conditions. The microalgae were grown in Rudic culture medium which is composed of 0.36 g/L KNO_3, 0.02 g/L KH_2PO_4, 0.065 g/L Na_2HPO_4, 35 g/L NaCl, 0.047 g/L $CaCl_2$, 0.01 g/L $MgSO_4{\cdot}7H_2O$ and 1.0 ml trace elements (TE). TE (mg/L): $ZnSO_4{\cdot}7H_2O$, 0.1; $MnSO_4{\cdot}H_2O$, 1.5; $CuSO_4{\cdot}5H_2O$, 0.08; H_3BO_3, 0.3; $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 0.3; $FeCl_3{\cdot}6H_2O$, 17; $Co(NO_3)_2{\cdot}H_2O$, 0.2; EDTA, 7.5. The photobioreactor (PBR) was a 4-L PET vessel continuously illuminated with an external light source (Incandescent lamp), and aerated by sterile air. The cultures were grown at ambient temperature (22–26 °C) and the light intensity was in the range of 1–2 klx as measured by a digital light meter (TES-1334A) at the surface of the reactor.

The cultured microalgae were taken at three different concentrations (as a function of cultivation time), with optical densities of 1.00, 2.00 and 3.00 (±0.08), and used for microfiltration tests. Table 1 shows the characteristics of feed suspensions used in the filtration experiments.