Combination of microalgae cultivation with membrane processes for the treatment of municipal wastewater

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ABSTRACT

The treatment of wastewater by microalgae cultivation has attracted more and more attention. However, the way to harvest microalgae cells from the wastewater and the treatment of the large quantity of residual solution have become critical issues. In this work, a new approach for the treatment of municipal wastewater is presented. The combination of flocculation for removing mainly microalgae and thereafter membrane filtration for chemical oxygen demand (COD) and conductivity reduction of the residual solution after flocculation is discussed. The COD concentration of the wastewater decreased from 260 to 84 mg/L after flocculation by chitosan. Five ultrafiltration (UF) membranes and two nanofiltration (NF) membranes were used for filtration to find a suitable membrane for COD and conductivity reduction. Among the five UF membranes, GR82PE showed the best performance, whose permeate flux and COD retention at 4 bar were 189.66 L/(m²·h) and 43.03%, respectively. NF membranes showed higher COD and conductivity retentions than UF membranes. The COD retention of Desal5-DK reached 98.3% at 20 bar. Lastly, the flux recovery after the filtration test of each membrane is also discussed.

Key words | filtration, flocculation, microalgae, wastewater treatment

INTRODUCTION

The increasing amount of waste originating from human activities causes many negative impacts on the environment, especially on the water quality. Recently, considerable attention has been focused on the utilization and reclamation of wastewater as freshwater resources are becoming increasingly scarce. Microalgae, as a potential source for many products like proteins, food additives, biodiesel and other valuable chemicals, have been investigated for many years. Compared to the traditional resources like maize, sugar-cane, soybean and oilseed rape, microalgae have a relative high lipid oil and protein content and areal productivity (Chisti 2007; Mata et al. 2010; Halim et al. 2011). Municipal wastewater, which is rich in nutrients like carbon, nitrogen and some minerals, has the potential for use as a resource for microalgae cultivation (Hammouda et al. 1995; Hoffmann 1998). This will reduce a large part of microalgae production cost. Coupling the microalgae cultivation with wastewater treatment is a prospective and economical method for producing high density microagal biomass. This method was first proposed by Oswald (1988). In the past decades, some research has been done on the cultivation of algae in the secondary wastewater to remove the nitrogen and phosphorus in order to avoid eutrophication (Mallick 2002; Li et al. 2011; Ahmad et al. 2012). Relatively higher algal biomass and lipid content of microalgae, which were cultivated in the wastewater, were obtained than in the normal medium (Attasat et al. 2012; Zuka et al. 2012).

One of the major and practical limitations of using this algal treatment system in the real production process is harvesting or separation of microalgal cells from the treated water. Numerous efforts have been made on developing a suitable technology for harvesting the microalgae. Flocculation is becoming one of the most promising methods due to the easy operation and energy-saving (Lavoie & de la Noüe 1987). However, a new problem arises – what to do with the large quantity of residual solution after flocculation, which may still not meet the direct discharge standard. Most research tried to solve this problem by using non-toxic flocculants to harvest the algal cells in order to reuse the medium after flocculation (Wu et al. 2012). In this work, the combination of
flocculation with membrane filtration was used for trying to solve this problem. This method had been widely used in drinking water treatment. Pre-coagulation/flocculation in combination with both ultrafiltration (UF) and membrane filtration (MF) is an effective hygienic barrier against the MS2 virus for drinking water treatment (Fiksdal & Leiknes 2006). The aim of this work is to demonstrate the possibility of using UF or nanofiltration (NF) membrane to treat the residual solution for direct discharge after harvesting the algal cells by flocculation. Seven commercial membranes including five UF membranes and two NF membranes were used for membrane filtration in this work. The influences of operating pressure on the quality of the treated water and flux recovery after filtration are discussed.

MATERIALS AND METHODS

Algae solution

The algae solution used in this work was provided by Green Center Algae Innovation Center, Lolland, Denmark. The microalgae were Scenedesmus sp. which were cultivated in the municipal wastewater without adding other nutrients and harvested in the late logarithmic growth phase, which usually takes 10–15 days to reach. The details of microalgae cultivation in the wastewater will be published elsewhere. The wastewater was taken from the grit-chamber of the Søllested, Denmark, municipal treatment plant.

Membrane

Seven commercial membranes (Alfa Laval, Nakskov, Denmark, and GE) were used in this work as presented in Table 1: five UF membranes (ETNA01PP, GR95PP, GR82PE, RC70PP and UFX10PP) and two NF membranes (Desal-5 DK and Alfa Laval-NF). The membrane materials, molecular weight cut off (MWCO) and the recommended range of operating conditions obtained from manufacturers are shown in Table 1.

Flocculation and prefiltration of the algae solution

The flocculant used in this work was chitosan, which was purchased from Sigma-Aldrich, Denmark. The dosage of chitosan was calculated according to the previous research (Chen et al. 2015). Chitosan (0.04 g/L) was added into the algae solution (10 L) while the solution was mixed rapidly (800 rpm). Then the solution was agitated at 250 rpm for 3 min. The supernatant was collected after 20 min of sedimentation and filtered through Whatman No. 1001-185 filter paper (pore size of 11 μm) on a Buchner funnel with slight suction as the prefiltration step. The filtrate was used for UF or NF filtration experiments.

Membrane filtration experiment

The filtration experiments were carried out in a plate-and-frame membrane module (DSS LabStak M20, Alfa Laval, Nakskov, Denmark), which is a cross-flow membrane filtration system. The schematic diagram of this system is shown in Figure 1. The membrane sheets were stacked
and compressed together with spacer plates in a vertical frame in the membrane module. The system was operated under recirculating flow. The flow rate of the feed solution was 480 L/h during the experiments. The diameter of each membrane sample was 20 cm, and the effective area during the filtration was 0.0174 m² for each piece of membrane. Four pieces of each membrane were used in the experiments. The influences of different operating pressures were investigated in this work. The pressure was controlled by the pressure gauge and calculated by the average pressure of the inlet and outlet pressure. The temperature was controlled by the temperature control system. The permeate samples were taken by cylinders for flux calculation.

Before the filtration test, membranes needed to be cleaned by 0.5 wt% Ecolab Ultrasil-10 solution for 30 min at 50 °C and 2 bar to remove the residual chemicals and then flushed with deionized water at 20 °C for at least 10 min. Thereafter, the pure water flux was measured at 20 °C after recirculation for 30 min. Then the solution (8 L) after flocculation and prefiltration was added into the feed tank, and the feed solution began to recirculate at 20 °C. The operating pressure of UF and NF filtration investigated in this work were 2, 4, 6 bar and 10, 15, 20 bar respectively. The permeate flux was measured after every 30 min recirculation until the flux was stable, and the total filtration time was typically 4–5 hours until stable flux was reached. The flux was measured two times to obtain an average value. After the filtration of solution, the pure water flux of each membrane was measured before and after the chemical cleaning of membranes. The chemical cleaning (i.e. 0.5 wt% Ecolab Ultrasil-10 solution for 30 min at 50 °C and 2 bar) after the filtration was the same as for the beginning of the experiment.

**Analytical methods**

The pH was measured by a pH meter (pH M83 Autocal pH meter, Copenhagen, Denmark). The optical density (OD) of algae was measured by a UV-spectrophotometer (Hach Lange DR5000) at a wavelength of 665 nm. The conductivity was measured by a Radiometer CDM92 conductivity meter. Chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were determined with cuvette tests (LCK 414 (5–60 mg COD/L), LCK 314 (15–150 mg COD/L) and LCK 555 (4–1,650 mg BOD₅/L)) on a spectrophotometer (Hach Lange DR 2800). Total nitrogen (TN) was obtained using the cuvette test LCK 138 (1–16 mg N/L) with the same spectrometer. The observed COD and conductivity retentions of each membrane were obtained by the following equation:

$$R(\%) = \left(1 - \frac{C_R}{C_p}\right) \times 100$$

where $C_p$ and $C_R$ are permeate and retentate concentration, respectively. The flux recovery rate is defined as the ratio of the pure water flux after cleaning by 0.5% Ultrasil-10 solution (after the filtration of wastewater) to the initial pure water flux.

**RESULTS AND DISCUSSION**

**Flocculation and prefiltration**

The characteristics of the solution at different experimental steps are shown in Table 2. The possibility of reducing the
concentration of COD and BOD in the wastewater by algae cultivation had been proved by many researchers (Mallick 2002; Wang et al. 2010). As shown in Table 2, the COD, BOD₅ and TN value of the solution after microalgae cultivation were reduced to 260, 10 and 12.4 mg/L, respectively. Previous research has shown that flocculation is an economical and efficient way to harvest microalgae cells from the medium (Schlesinger et al. 2012). Chitosan is one of the suitable flocculants which could obtain high flocculation efficiency and be non-poisonous to cell viability. The COD concentration decreased from 260 to 84 mg/L after flocculation. The reduction of COD value after flocculation by chitosan is probably due to the transformation of the organics in the solution into the flocs that were settled down with the algae cells. However, the solution after flocculation was still unable to be discharged directly, as it could not meet the first class discharge standard of Integrated Wastewater Discharge Standard (GB 8798-1996). Therefore, a subsequent treatment by membrane processes was necessary for further reduction in COD and BOD after flocculation. In order to avoid the membrane fouling caused by the residual flocs in the supernatant, prefiltration by filter paper was done. As can be seen in Table 2, the BOD₅ and TN values had achieved the discharged standard and had no big differences after prefiltration. Only COD had a small reduction after prefiltration. The slight decrease of the COD was due to the residual insoluble organics in the supernatant being removed by the filter paper. The conductivity measurement allowed the estimation of the residual ions concentration in the solution. The subsequent experiments focused on the reduction of COD and conductivity by different membranes.

Ultrafiltration

Five UF membranes, all of which are tight UF membranes whose pore size is smaller than 10 nm, were investigated under three different operating pressures in this work. The selection of these membranes was due to their small pore size and the aim for major COD reduction after the UF step. The effects on permeate fluxes, and COD and conductivity retentions of them are shown in Figure 2. As a general rule, the fluxes of these five UF membranes increased with the increment of the operating pressure. GR82PE, RC70PP and UFX10PP had higher fluxes of more than 150 L/(m²·h) at 4 bar, whereas GR95PP only showed 13.18 L/(m²·h). This flux difference may reflect the different characteristics of membranes, such as porosity, molecular weight cut off, and pore size distribution. UFX10PP and RC70PP possessing the same MWCO achieved different permeate fluxes and COD and conductivity retentions due to their different materials. GR82PE and GR95PP possessing different MWCO, 5,000 and 2,000 Da respectively, which were made by the same polymer, showed a big difference between their fluxes. Theoretically, the UF membrane could only separate the particles and high molecular weight molecules from the solution, which means that the conductivity retention should be zero. However, the results showed the conductivity retention of ETNA01PP and GR95PP increased when the operating pressure increased, since the fouling tendency becomes larger at higher pressure, and the fouling layer could reduce the ions concentration (conductivity) in the solution. As shown in Figures 2(b) and 2(c), the COD and conductivity retention of GR95PP was the highest one among these membranes. GR95PP is a hydrophilic membrane which was easier to be fouled than a hydrophilic membrane like RC70PP. It is likely that this membrane experienced severe fouling during the filtration, and the fouling layer on the membrane surface could help the membrane reject the ions and salts in the solution. Therefore, GR95PP could achieve higher conductivity retention than the other four UF membranes. Having MWCO of 1000, ETNA01 did not show the best COD and conductivity reduction, which is attributed to its hydrophilic membrane surface (Wei et al. 2006).

Among these five membranes, GR82PE shows the best performance, with COD and conductivity retentions being relatively higher with higher permeate flux than the other membranes. Since the energy consumption will increase with the increment of operating pressure, finding a suitable operating pressure is very important. As is shown in Figure 2, the increment of COD and conductivity retentions from 2 to 4 bar was higher than from 4 to 6 bar. Therefore, the suitable operating pressure of this membrane was 4 bar. Furthermore, the UF process is typically operated under pressure of less than 10 bar. Therefore, choosing 4 bar is quite reasonable for UF. Generally speaking, UF membrane can reject part of the organics and decrease a little bit the conductivity in the solution. After UF, the COD value was already lower than the discharge standard; however, the ion concentration (conductivity) in the solution was still high.

Nanofiltration

A NF membrane possesses intermediate properties between a porous membrane and a dense (non-porous) membrane. The mechanism of separating by NF membranes was not only molecular sieving effects but also electrostatic effects and the pore size of membranes (Bowen et al. 1997).
As the NF membrane has higher membrane resistance, higher operating pressure was needed than for the UF membrane to overcome the osmotic pressure. The effects of different pressure on several parameters of two NF membranes (Desal5-DK and Alfa Laval-NF) were investigated in this work and the results are shown in Figure 3. The permeate flux, as expected, increased with the increment of operating pressure. When the operating pressure increased from 10 to 15 bar, the increment of permeate flux of these two membranes was bigger than it was from 15 to 20 bar, especially for Alfa Laval-NF. The permeate flux of Alfa Laval-NF was higher than Desal5-DK at each operating pressure. The permeate flux at 15 bar was 284.14 L/(m²·h) (Desal5-DK) and 382.07 L/(m²·h) (Alfa Laval-NF). However, the COD and conductivity retentions of Desal5-DK membrane were higher. The COD retention of Desal5-DK and Alfa Laval-NF at 15 bar were 96.23 and 93.02%, respectively. Both of them could reach a higher COD retention than the UF membranes, which means most of the organic matters in the solution were rejected by NF membranes. In general, the higher the operating pressure, the higher will be the flux and conductivity and COD retentions. However, as can be seen in Figure 3(c), the conductivity retention of the two membranes only had a slight change at different operating pressures. The reason for this phenomenon could be explained the separation mechanism of the NF membrane. Compared with a reverse osmosis membrane, the structure of the NF membrane is more open. That means the NF membrane could obtain high retention of divalent ions (like Ca²⁺, Mg²⁺, SO₄²⁻, and CO₃²⁻) whereas retention of the monovalent ions (such as Na⁺, K⁺, Cl⁻, and NO₃⁻) was very low (Balan nec et al. 2005). Most divalent ions and a minor part of monovalent ions had been rejected by membranes when the operating pressure was 10 bar and the rest of the monovalent ions will not be rejected with the increasing pressure. Therefore, the change of operating pressure has no obvious effect on the conductivity retention. The operating pressure for the treatment of the solution by Desal5-DK and

![Figure 2](https://iwaponline.com/wst/article-pdf/68/11/2374/471625/2374.pdf)
Alfa Laval-NF should be 15 bar, because the results in Figure 3 only showed a small difference between 15 and 20 bar. It would reduce the energy consumption by choosing lower operating pressure.

Flux recovery

Membrane fouling is the biggest obstacle to utilizing the membrane filtration in the industrial production. Comparing the pure water flux before and after treating the wastewater is a common way to estimate the extent of membrane fouling and its recovery ability. The pure water flux of each membrane at different stages is shown in Figure 4. For UF membranes, the flux recovery rates of GR95PP and UFX10PP were relatively low, which were only 59.58 and 55.38% respectively, and GR82PE obtained the highest rate (96%). The composition of solution after algae cultivation could be complicated as it may contain some substrates and metabolism substances released by algal cells. Part of them will settle down with the flocs after flocculation and some small and dissolvable substances may still exist in the solution, which would cause the membrane fouling. Normally, membrane fouling is mainly caused by the organic fouling, biofouling, inorganic fouling and particulate (Moreno et al. 2013). In this study, almost all the algal cells and microbes had been eliminated before the membrane filtration. Thus the possibility of biofouling, which is the most severe and difficult to be removed among those fouling mechanisms, was very low (Goosen et al. 2005). The organic fouling is easier to be removed by chemical cleaning. However, as the membrane material of GR95PP and UFX10PP are hydrophobic ones that were easier to be fouled, the fouling layer on membrane surface was formed as early as the beginning of the experiment. That layer was compressed when the operating pressure increased, and part of the contaminants came into the membrane pore structure and blocked some pores, which made it more difficult to be cleaned by chemicals.

The change of pure water flux of Desal5-DK and Alfa Laval-NF is shown in the Figure 4(b). The flux just had a slight reduction after the experiment, especially Desal5-DK. However, both of these two membranes were not
recovered after cleaned by Ultrasil-10 and the flux was even lower after the chemical cleaning. The results indicated that the membrane fouling caused by this solution may be irreversible or cannot be cleaned by this kind of chemical. The fouling mechanisms are probably quite different for different membranes due to the different membrane materials, membrane characteristics and the composition of the feed solution. Different cleaning agents could solve different fouling problems. Inorganic fouling caused by metal ions could be removed by citric acid by chelation. Organic fouling could be cleaned by alkaline solutions, such as NaOH and Ultrasil-10, hydrolysis and solubilization. High concentration of NaClO could destroy the gel structure formed by algal cells and bacteria (Liang et al. 2008).

CONCLUSION

A new strategy for the treatment of municipal wastewater was suggested and demonstrated in this work. Microalgae cultivation can significantly reduce COD and BOD in the wastewater. Microalgae can be effectively harvested by flocculation. The subsequent membrane processes using either UF or NF will ensure that the wastewater can be discharged. The membrane processes were investigated in detail in this work. Five UF membranes and two NF membranes were investigated to reduce COD and ion concentration after algae harvesting by flocculation. Compared with the results for different UF membranes, GR82PE could achieve relatively high COD and conductivity retentions with high permeate flux. Although GR95PP had the highest COD and conductivity retentions, it is not suitable for industry processes due to its low permeate flux and flux recovery. However, the UF membrane could reject only part of the organic matters in the solution. The conductivity value was still high. NF membranes not only reject almost all organic matters but also can achieve relatively high conductivity retention. Most metal ions like Ca$^{2+}$ and Mg$^{2+}$ which may contaminate the water resource were removed by NF membranes. The rejection of Alfa Laval-NF was a little bit lower than Desal5-DK, whereas its flux was much higher. Therefore, Alfa Laval-NF is more suitable for applying in the industrial production. Further investigation is still needed to address how to improve or keep the retentions when the characteristics of feed solution change.

Microalgae cultivation was conducted in pilot scale, and flocculation and the membrane process were performed in lab scale. However, further investigations are needed at large scale for final commercialization of this technology.

ACKNOWLEDGEMENTS

This work was financed by National Natural Science Foundation of China (Grant No. 20976140). The authors wish to acknowledge Alfa Laval Nakskov A/S for the support of the work and would like to thank Jørgen Enggaard Boelsmand at Green Center Algae Innovation Center, Lolland, Denmark, for providing algae suspensions and helpful discussions.
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First received 13 March 2013; accepted in revised form 12 August 2013. Available online 22 October 2013