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Fabrication of PES/F-MWCNT/LiCl Membrane and Separation of Nannochloropsis Sp

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ABSTRACT

Background: Nannochloropsis sp. is one of the promising candidate for biofuel production. The membrane application in separating the Nannochloropsis sp. is refering to microalgae harvesting in the conventional biofuel production. **Objective:** The purpose of this modification is to develop an efficient membrane for separating Nannochloropsis sp from water solution **Results:** It was found that the membrane morphology, pore size, hydrophlicity and permeation rate were influenced by the quantity of LiCl inside the membrane. Morover, larger membrane pore size and porosity have help in high separation rate of Nannochloropsis sp. despite of flux loss. **Conclusion:** As conclusion, all PES modified membranes were able to separate 100% of Nannochloropsis sp. from the water solution.

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INTRODUCTION

Nannochloropsis is a genus of unicellular microalgae and mainly compose of chlophyll a, and xanthopyl pigmnents. This microalgae is an excellence source for fatty acid, lipid, protein, carbohydrates and vitamins. Thus, it has been widely used in the human and aquaculture supplement products. Nannochloropsis sp. can be cultivated in an open land with variable temperature or in an indoor photobioreactor. The residence time of Nannochloropsis sp. in bioreactor plays an important role for the biomass production. The fact that the cells growth in short duration time will tend to prolong its cellular cycle and synthesized more biomass nutrients due to limiting sources (Rebolloso-Fuentes *et al*, 2001). Nannochloropsis sp. demonstrated relatively equal and higher productivity of both lipid and biomass (Daon *et al*. 2011). It consist of high lipid substance more than 40%wt. Hence, recent studies have reported that Nannochloropsis sp. is the promising candidate for biodiesel resource.

Generally, the production of biodiesel involved the extraction of triglycerides from fatty acid lipid, followed by the transesterification process. Maximal amount of fatty acid lipid can be achieved by growing the Nannochloropsis sp. in a conducive growth of environment. Similar to the biomass production, lipid production is influenced by the quantity of light and nitrogen the microalgae received. In appropriate light condition with nitrogen starvation, doubled increase in productivity can be achieved (Dipasmita *et al*., 2011 , Vooren *et al*., 2012). The conventional approach to obtain the fatty acid lipid and subsequently extracting the triglycerides needs the microalgae to be dewatered or harvest at first. Many methods were seen being used to separate microalgae from water and make it concentrated. Among methods that were commonly used for Nannochloropsis sp. separation are coagulation, flocculation and centrifugation. These methods have it pros and cons such as the centrifugation system can separate microalgae faster but yet it consumed energy.

The advantage of using membrane for microalgae recovery is it does not required extensive energy. It only needs appropriate molecular weight cut-off (MWCO) of a pressure-driven membrane to separate the microalgae from water. Membrane technology has also been used for Nannochloropsis sp. Among three different polymeric membranes (polysulfone, polyvinylidenefluoride, regenerated cellulose), 100 kDa and 30 kDa of regenerated cellulose membrane were found suitable for separating Nannochloropsis sp. This result was obtained by performing ultrafiltration and absorption test. At the beginning, the three types of membranes were intact with Nannochloropsis sp. cell culture for 20 minutes and results for water flux differences before and after contact with the microalgae were compared. Then, the membrane with better water flux which cellulose was continued to filter with Nannochloropsis sp. cell culture. The best filtration rate achieved was approximately 24 Lh-1m-1 (Giorno *et al*., 2013).

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Membrane technology is a rapidly emerging technology as it keeps developing to meet the needs for separation process. From a single main polymer, it has recently being incorporated with others hydrophilic polymer, inorganic salt, inorganic and nanoparticle materials known as additives. Membrane system is capable in separating microalgae but yet more work need to be done in order to improve its separation property. Thus, main aim of this paper is to modify the polyethersulfone (PES) polymer membrane by incorporating it with functionalized multiwall carbon nanotubes (F-MWCNT) nanoparticles and lithium chloride (LiCl). The modified membranes characteristic was studied and were tested for Nannochloropsis sp. separation. The amount of F-MWCNT was 1wt% which is the effective amount a membrane should have based on literature. Whilst, the amount of LiCl was varied from 1 - 4wt%.

1.0 Methodology:

1.1 Membrane Fabrication:

Materials to make the membrane are polyethersulfone (molecular weight = 58 kDa) from BASF, Germany, anyhydrous LiCl from Merck and functionalized MWCNT nanoparticles (length avg.= 12 micron, diameter avg.= 10 nm) obtained from China. The modified membranes were prepared from a homogenous dope solution where 18 wt% of PES, 1wt% of MWCNT and 1-4wt% of LiCl were dissolved in dimethyl acetamide (DMAC) solvent at 80^oC for 45 minutes. Membrane for control was made of PES with LiCl (4wt %) as the pore former agent (Idris *et al*, 2009). Then, the dope solution was placed inside an ultrasonic bath for complete mixing and bubbles removal. After that, the cool dope solution was poured onto a glass plate and casted with a casting knife and been immersed in distilled water to formed a flat sheet membrane. The membrane was washed with distilled water before being used for further investigation.

1.2 Nannochloropsis sp. Culture Preparation:

Nannochloropsis sp. that obtained from Borneo Marine Research institute (BMRI), Universiti Malaysia Sabah, Malaysia was cultured according to a standard method. It was cultivated in sterilized seawater containing Walne's medium. 500 ml of Nannochloropsis sp were then placed in 1000 mL flasks under the growing condition of 23 ± 0.5 ^oC, pH 8 ± 0.2 and light intensity of 100 $\mu molm^-2\ s^-1$.

1.3 Membrane Characteristic Analysis:

The membrane characteristic was compared between the control membrane and the modified membrane. Both membranes were characterized according to its morphology, membrane composition, average pore diameter, porosity and surface hydrophilicity. The membranes morphology were performed using field emission scanning electron microscopy (FESEM) to identify the membranes structure. The determination of membranes composition and functional group were carried out using fourier transform infrared (FTIR) and energy dispersive X-ray analysis (EDX). The membrane surface hydrophilicity were measured using a contact angle meter. The membranes average pore diameter and porosity were obtained from calculation as follow:-

The pore diameter was calculated using Guerout-Elford-Ferry equation:

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\mu\gamma Q}{\varepsilon \times A \times \Delta P}}$$

where μ is the water viscosity (8.9×10−4 Pa s), γ is the membrane thickness (m), Q is the water volume flow rate (m^3s^{-1}), A is the membrane effective area (m^2) and ΔP is the operational pressure.

The porosity (Ɛ) of the membrane:

$$\varepsilon = \frac{w_1 - w_2}{A \times l \times d_w}$$

where w_1 is the weight of wet membrane (g), w_2 is the weight of dry membrane (g), *l* is the membrane thickness (cm) and d_w is the water density (0.998 g/cm^3).

1.4 Membrane Performance Analysis:

PES/MWCNT/LiCl membranes performance were analyzed based on membrane water flux rate and membrane filtration rate of Nannochloropsis sp. Both analysis were carried out using a membrane filtration cell. The effect of LiCl on PES membranes were observed. The initial concentration of Nannochloropsis sp. solution before and after was recorded. Total weight of dry Nannochloropsis sp. accumulated on membrane surface was also taken. The water and filtration flux were calculated using following equation:

$$J_w = \frac{V}{A\Delta t}$$

where, V is the volume of permeated water (*l*), A the membrane area (m^2), and Δt the permeation time (h).

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2.0 Result:
2.1 Membrane Morphology:

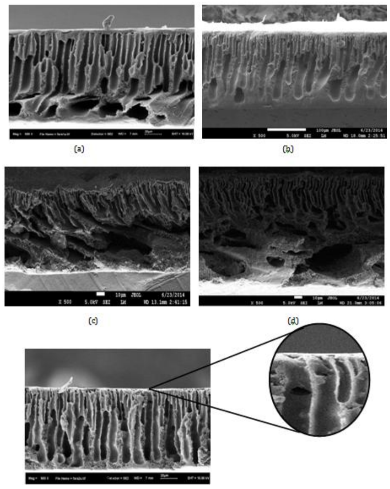

Fig. 1: FESEM cross-section images at 500x magnificence of a) PES/LiCl-4wt% b) PES/MWCNT/LiCl-1wt% c) PES/MWCNT/LiCl-2wt% d) PES/MWCNT/LiCl-3wt% e) PES/MWCNT/LiCl-4wt%.

The PES membrane structure analyzed by FESEM shows that all fabricated membranes possessed an asymmetric type and fingerlikes structure. However, there was a slight different at membranes upper layer and sub layer. PES membrane with high concentration of LiCl without F-MWCNT (a) established a dense skin layer and macrospores at the membrane's sub layer. By adding F-MWCNT, the skin layer of the PES membrane seems like to disappear and the fingerlike structures was connected from top to bottom layer of the membrane (e). The disappearance of membrane's skin layer and developing microvoids were observed when LiCl concentration in the membrane increased with the presence of F-MWCNT.

2.2 Membrane composition:

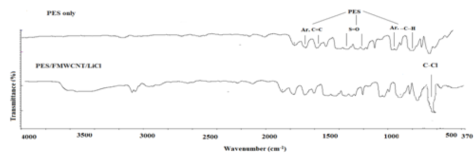

Fig. 2: FTIR spectrum of PES/MWCNT/ LiCl membrane.

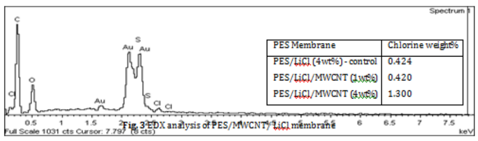

Fig. 3: EDX analysis of PES/MWCNT/ LiCl membrane.

Both FTIR and EDX analysis have confirmed the complete mixing of PES, MWCNT and LiCl in membrane solution. The FTIR spectrum result shows existence of C=C, S=O, C-H and C-Cl functional groups. Meanwhile, EDX analysis contain peaks corresponding to the elements that making up the composition of the membrane. The appearance of carbon, sulfur and oxygen have confirm the use of PES and F-MWCNT materials and the element of chlorine repersenting the use of LiCl. Moreover, the attachment of Cl^- molecule was more stable in PES membrane containing F-MWCNT nanoparticles. As depicted in figure 3, the PES membrane for control shows lesser Cl^- attachment from other membrane with F-MWCNT but having the same concentration of LiCl.

2.3 Membrane Properties:

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Table 1: Fabricated membranes characteristics.

Membrane thickness = 0.1mm Membrane effective area = 3.8 cm^2 Pressure = 3 bar				Contact angle (°)
PES Membrane	Pore diameter (μm)	Porosity	Water Flux rate (l/m^2h)	
PES/LiCl (control)	0.004	0.70	31.3	77.61
PES/MWCNT/LiCl-1wt%	0.028	0.63	94.0	64.27
PES/MWCNT/LiCl-2wt%	0.034	0.84	244.4	73.31
PES/MWCNT/LiCl-3wt%	0.036	0.91	313.3	74.66
PES/MWCNT/LiCl-4wt%	0.040	0.98	548.2	74.94

Table 1 shows the membrane characteristics that consist of membranes pore size, porosity, water flux rate and contact angle measurements. The mixture of PES with additives had produced an ultrafiltration type membrane ranged 0.02 – 0.04 μm. The PES membrane (control) without F-MWCNT have the smallest average pore size. Meanwhile, the modified PES with highest LiCl have the greater pore size. High in porosity was demonstrated by all modified PES membrane. The membrane with greater LiCl was extremely porous which almost 100% porosity. This indicated that the membrane contain larger membrane voids. Furthermore, the water permeation was tremendously increased for the membrane that contain MWCNT and higher LiCl as shown by flux rate measurement. In other hand, the PES control membrane had the obvious lowest water permeation. The contact angle measurements for the control and PES modified membrane depicts hydrophilicity effect in all membranes. As shown by the decrease in contact angle, all membranes that contain F-MWCNT nanoparticles were more hydrophilic compared to membrane without F-MWCNT. The hydrophilicity of the surface increased with decreased of LiCl concentration. As overall, presence of LiCl and MWCNT in PES membrane gives better effect on membrane characteristics.

2.4 Nannochloropsis sp. separation rate:
Graph:

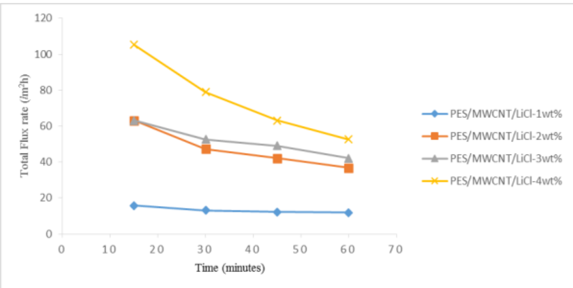

Fig. 4: Nannochloropsis sp. filtration flux rate on PES modified membrane.

Algae collection:

Table 2: Weight of dry Nannochloropsis sp after 1 hr filtration (membrane effective area=3.8 cm^2).

Feed absorption = 1.88 abs. at 400 nm wavelength Permeate absorption = 0 abs.	
Membranes	Dry weight of algae (mg)
PES/MWCNT/LiCl-1wt%	5.6
PES/MWCNT/LiCl-2wt%	5.9
PES/MWCNT/LiCl-3wt%	7.6
PES/MWCNT/LiCl-4wt%	10.3

Fully separation of nannochloropsis sp from water was achieved by all modified membranes despite of different in LiCl composition. Figure 5 shows an example of clear water of permeate from one of the fabricated membrane. This means that the mixture of PES with LiCl and F-MWCNT was able to formed a membrane that can separate microalgae. However, different in membrane composition have affected the separation rate. Membrane with highest LiCl composition gave high separation rate and flux loss. Meanwhile membrane with lowest LiCl composition gave low separation rate but the flux rate was almost constant over time. According to amount of algae collected in 1 hour (table 2), PES membrane with highest LiCl filtered more compare to other membranes.

Fig. 5: Picture of before and after filtration of Nannochloropsis sp. solution by the PES modified membranes.

3.0 Discussion:

3.1 Membrane fabrication and Characteristic:

The result achieved shows that LiCl concentration and MWCNT nanoparticles does play an important role in membrane characteristics. These characteristics were also believed to influence the membrane performance in Nannochloropsis sp. separation. In membrane morphology, the fingerlike structure was formed due to the presence of LiCl and MWCNT nanoparticles. LiCl is soluble in polar solvent such as water. Many reports have been made previously on LiCl function as the pore former agent in membrane fabrication (Song *et al*, 2014; Idris *et al*, 2010). LiCl is able to form membrane's pore since this chemical is easily to leach out during polymer precipitation inside the coagulation bath. MWCNT which is functionalized contain –OH bonds attached to its sidewall. This bond may create instability in polymer solution and induces the precipitation process. Therefore, adding these additives will greatly increase demixing of liquid-liquid or fasten the exchange rate of solvent/non-solvent. This mechanism of formation lead to porous, fingerlike structure and thin upper-layer. Thus, it is believed that no form of skin layer in membrane with 4% of LiCl was because of very rapid demixing rate.

The PES modified membrane composition analysis displayed elements and functional group that correspond to all material use in making up the membrane. Such as sulfur and S=O bond are due to the use of PES polymer. For LiCl , only Cl- ions were seen attached to the membrane molecule components, i.e C-Cl instead of Li+ ion. This may be explain by the study of ion hydration structure in lithium chloride by Yamaguchi *et al*, 2010. In this study, neutron diffraction with an isotopic substitution method was used to determine the bond distance, hydration number, and orientation correlation of water of hydration ion in an aqueous lithium chloride. The author stated that at ambient temperature, one lone pairs of water molecules will be moving towards Li+ ions forming Li-O and Li-H hydrogen bond. This was due to the strong electrostatic cation field of lithium. Thus, it is believed that Li+ ion had leave the membrane during the polymer precipitation in phase inversion process. In which Li+ ions was more attracted to water molecules from coagulation bath and leaving behind Cl- molecule. Furthermore, the role of F-MWCNT nanoparticles in polymer solution was confirmed as the anchoring agent between the PES and Cl- since more chlorine was still attached in membrane even after membrane precipitation in membrane with F-MWCNT.

The PES modified membrane performed tremendous water permeation. High water flux rate was achieved by PES membrane with 4% LiCl. The reason behind this achievement was related to the membrane structure, pore size and porosity. Invisible skin layer and longer fingerlike structure made the water flow faster through the membrane. Moreover, this membrane have larger pore size that allow water molecule to pass through it without difficulty. Obstacle for water flow only happened in membrane that have thick and less macrovoids structure. The membranes pore size and porosity increase with the increase in LiCl with F-MWCNT was due to the instability in polymer solution during phase inversion that triggers pores and voids formation. Furthermore, hydrophilicity factor seems did not affected much in water permeation. Althought PES with 4% LiCl has the highest value of contact angle, depicted low in hydrophilicity, the membrane still have the highest water permeation. No evidence so far related to Cl- ion with increase of hydrophobicity but as far as we concern in this study, the higher Cl- the higher the contact angle.

3.2Nannochloropsis sp separation by membrane:

Nannochloropsis sp. was separated from the PES modified membrane through an ultrafiltration. All membranes achieved 100% efficiency of Nannochloropsis sp. removal from water content. Filtration flux increased with increasing LiCl content of PES modified membrane. Generally, filtration flux would increase with the increase of membrane pressure. In this study, constant membrane pressure was applied for all membranes tested to study the effect of different composition of PES modified membrane on Nannochloropsis sp separation. Increasingly dropped off flux was observed for membrane with above 2% LiCl content and was believed due to the formation of fouling cake layer. Although PES with 1% LiCl shows better anti-fouling displays by its constant flux, the steady-state filtration flux of this membrane was not higher than those membrane with above 2% LiCl. Thus, it is believed that it must be due to lower pore size instead of fouling layer. As aforementioned, the membrane characteristic might influenced Nannochloropsis sp. separation rate. All membranes exhibit different flux rate, indicating that pore size and porosity are important for Nannochloropsis sp separation. Hydrophilic surfaces demonstrate no different in Nannochloropsis sp separation since the membrane with highest hydrophilicity produced lower flux rate. This suggest that physical characteristic study of the membrane plays important role in determination of Nannochloropsis sp. separation.

Conclusion:

Membrane composition is the main factor in determine the membrane characteristic and property. Regardless of the additives composition, the fabricated membrane with F-MWCNT and LiCl is a promising membrane for Nannochloropsis sp. separation. The combination of both additives have produced fast permeation and full microalgae separation without the use of excessive membrane pressure. This was due to the pore former and hydroxyl effect from LiCl and MWCNT nanoparticle that created the UF membrane with desirable pore size. In future work, we will make more analysis pertaining to the possible deposition layer on membrane surface to study the membrane fouling better.

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