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ORIGINAL ARTICLE

Effect of Cetyle Trimethyl Ammonium Bromide (CTAB) Surfactant on Nanofiltration Membrane for Dye Removal

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Abstract

Nanofiltration membranes technology commonly used for wastewater treatment especially wastewater containing charged and/or uncharged species. Commonly, textile wastewater possesses high chemical oxygen demand (COD) and non-biodegradable compounds such as pigments and dyes which lead to environmental hazard and serious health problem. Therefore, the objective of this study was to investigate the effects of hydrophilic surfactant on the preparation and performance of Active Nanofiltration (ANF) membrane. The polymeric ANF membranes were prepared via dry/wet phase inversion technique by immersion precipitation process. The Cetyletrimethylammonium bromide (CTAB) as cationic surfactant was added in casting solution at concentrations from 0 to 2.5 wt%. The synthesized membrane performance was evaluated in terms of pure water permeation (PWP) and dye rejection. The experimental data showed that the membrane demonstrated good increment of PWP ranging from 0.27 to 10.28 L/m^{2}h at applied pressure from 100 to 500kPa, respectively. Meanwhile, the ANF membranes achieved high removal of Methyl Blue and Reactive Black 5 dye up to 99.5% and 91.6%, respectively.

Keywords: Polymeric membrane; phase inversion; surfactant; nanofiltration; dye removal.

Introduction

East coast of Malaysia has become a tourist attraction and has been known as the nation's biggest textile industry producer. Producing a lot of clothes every year, this textile industry also produces abundant wastewater contain synthetic dyestuff. According to applications, dyes can be classified as acid (16%), disperse dyes (18%), direct dyes (16%), and reactive dyes (13%). One class of dye may be used for different applications (Tehrani-Bagha and Holmberg, 2013). Besides, many dyes are difficult to be decolorized and decomposed biologically due to their complex structure and synthetic origin. A typical textile industry generates many types of wastewater effluent with different quality and magnitude especially printing and dying process (Chakraborty et al., 2003). The discharged of synthetic dyes to the main stream are usually toxic, non-bio-degradable and contribute significantly to environmental pollution and serious health hazard. Thus, many researchers try to find an effective and economical way of dyes wastewater treatment for protecting the environment and to meet the stringent government law.

Hence, the most promising technology for effluent treatment of dyes wastewater has been proven through membrane separation processes. By reducing water consumption and minimizing effluent discharge, membrane separation process can recover reusable water from the permeate stream (Kim and Lee, 2006). Besides, nanofiltration membrane has several advantages that give it used in large scale industrial applications due to low operating pressures, high fluxes and high retentions of multivalent salts, low investment and operation costs (Baker, 2004). According to Akbari et al., (2002), the results have affirmed that nanofiltration membrane was the suitable separation process to be employed for the treatment of textile wastewater and generally showed an acceptable rejection. The addition of new materials such as surfactant is one of the effective techniques to produce membranes with high performance in separation process.

Several studies have revealed that the used of surfactant produced the uniform pore distribution, suppressed macrovoids, better performance and morphology. The differences on morphological structure will lead to the different performances of the membrane. It has been investigated that addition of surfactant will enhance the permeation flux of nanofiltration membrane and give high performance on the separation process of the nanofiltration membrane. Moreover, different types of surfactants will give different morphological structure on the membrane. For example, if Span-80 surfactant is added to the polymer solution, it will supress the macrovoids of the membranes. This will lead to the high performance of the membrane itself. Another example is, if Tween-80 is added on the small amount, it will increase the formation of macrovoids and finger-like in the sub-layer of the membranes (Amirilargani et al., 2009).

In phase process, there are four principals method which are; (i) immersion precipitation; (ii) vapour-induced phase separation; (iii) thermally-induces phase separation and (iv) dry-casting (Altinkaya and Ozbas, 2004). For preparing a variety asymmetric membrane, phase inversion is a well-known processed. In this study, membranes were prepared via dry/wet phase inversion technique by immersion precipitation process. A homogenous polymer solution consisting of polymer, solvent additive and surfactantare cast on a glass plate, and immersed in a coagulation bath. Liquid-liquid phase has been introduced in this process from the diffusive exchange of solvent and non-solvent where the formation of a polymer-rich and a polymer-poor phase in the casting solution lowers the Gibbs free energy of mixing. From this solidification of the phase-separated solutions, it will give a porous, asymmetric structure. As well as kinetics of the phase separation process, the morphology and performance of membranes depends strongly on the thermodynamics. Because of instantaneous phase separation, systems exhibiting high mutual affinity of solvent with non-solvent will give finger-like structures (Kim et al., 2001).

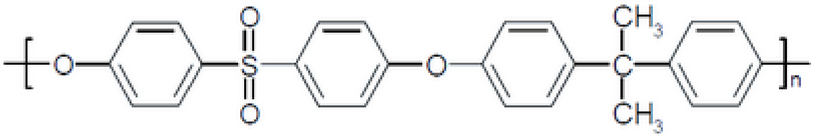
Hence, the aim of this study is to investigate the effect of surfactant on nanofiltration membrane based on dyes removal. The synthetic dyes were used in order to evaluate the dyes removal on the membrane by using UV-Vis Spectrophotometer.

Materials and Methods

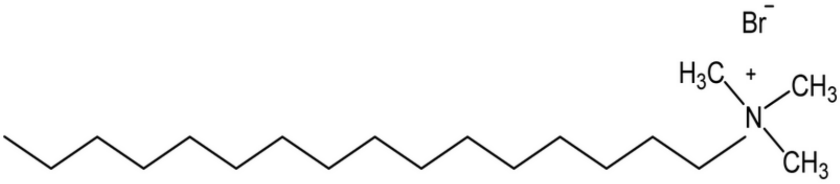
Materials

Polysulfone (Psf) (Udel A-300) supplied from SOLVAY was used as a polymeric material in this study. N-Methyl-2-Pyrrolidone (NMP) with analytical purity of 99.5 % was purchased from Merck as solvent. Distilled water was used as non-solvent agent in preparation dope. Cetyltrimethylamonium bromide (CTAB) with molecular weight 364.5 g/mol from Calbiochem was used as surfactant. The structure of these polymer and surfactant is shown in Figure 1.

Ethanol and n-hexane both which were used in the coagulation were purchased from Merck. Reactive Black 5 (RB 5) was purchased from Sigma-Aldrich and Methyl Blue (MB) from Merck were used as synthetic dyes.



Polysulfone (PSF)



Cetyletrimethylamonium bromide (CTAB)

Figure 1. PSF and CTAB molecules structure.

Formulation of Polymer Solution

Generally, a polymer solution formulation consisted of polymer, solvent and non-solvent but sometime polymeric additive was added which can be known as multi component casting formulation. The formulations of multi component dope are summarized in Table 1.

Table 1. Multi component dope formulations.

Membranes	Materials (wt %)			
	PSF	**NMP**	**H_2O**	**CTAB**
NFC1	18	76.6	5.4	0.0
NFC2	18	76.1	5.4	0.5
NFC3	18	75.6	5.4	1.0
NFC4	18	75.1	5.4	1.5
NFC5	18	74.6	5.4	2.0
NFC6	18	74.1	5.4	2.5

In making polymer solution, polymer was first dried for at least 24 hours in a vacuum oven at a temperature of about 100±2 °C in order to remove all absorbed water vapour. The existence of water in the polymer solution will influence the quality of a polymer solution. Firstly, the solvent and water was poured into the round bottom flask until the temperature increase to 50-60 °C. When temperature has reached 50 °C, polymer was added gradually until the entire polymer is dissolved before an additive was added. The solution was being stirred for 1 hour before surfactant was added into the polymer solution.

Membrane Fabrication and Casting

In this study, asymmetric nanofiltration membrane was fabricated at room temperature (30±2 °C). CTAB surfactant was added in NMP to a concentration of 0-2.5 wt%. Polysulfone was dissolved in the solvent mixture to form a casting solution at room temperature. The degassed casting solution was cast on a glass plate by casting knife at casting time of 10 s. The peeled off membrane was stored in water for 24 hours, and then immersed in ethanol for 24 hours. As the final stage, the membranes were soaked in n-hexane for 2-3 hours before dried at room temperature at least 24 hours to remove residual organic compounds. The use of the liquid exchange treatment is to prevent changes in the structure and properties of membranes caused by large capillary forces during drying. This is especially important when non-volatile solvents are being dried afterwards, water will be removed first and the solvent left behind may damage the membrane structure.

Membrane Performanceand Analysis

The membrane performance was analysed in term of pure water permeation, flux and percentages of dyes removal. The pure water permeation test was carried out at different pressures: 100-500 kPa. Figure 2 shows the nanofiltration set up. The pure water permeation was determined using distilled water. The permeation flux was calculated by (1):

$$Jw = \frac{Qp}{A} \tag{1}$$

Where Jw is the permeate flux (L/m^2.h), $Qp$is the permeate flow rate per hour and A is active surface area of membrane (m^2). Meanwhile, the dyes removal efficiency was evaluated by using UV-Vis Spectrophotometer. An absorbance value at 663 nm and 597 nm were used to measure dye concentrations for Methyl Blue, (MB) and Reactive Black 5, (BRB5), respectively. The dyes removal was expressed as in (2):

$$R\% = \left(1 - \frac{Cp}{Cf}\right) \times 100 \tag{2}$$

Where Cp is the concentration solute in permeate and Cf is the concentration of solute in feed. All the experimental works were carried out with three times of replications.

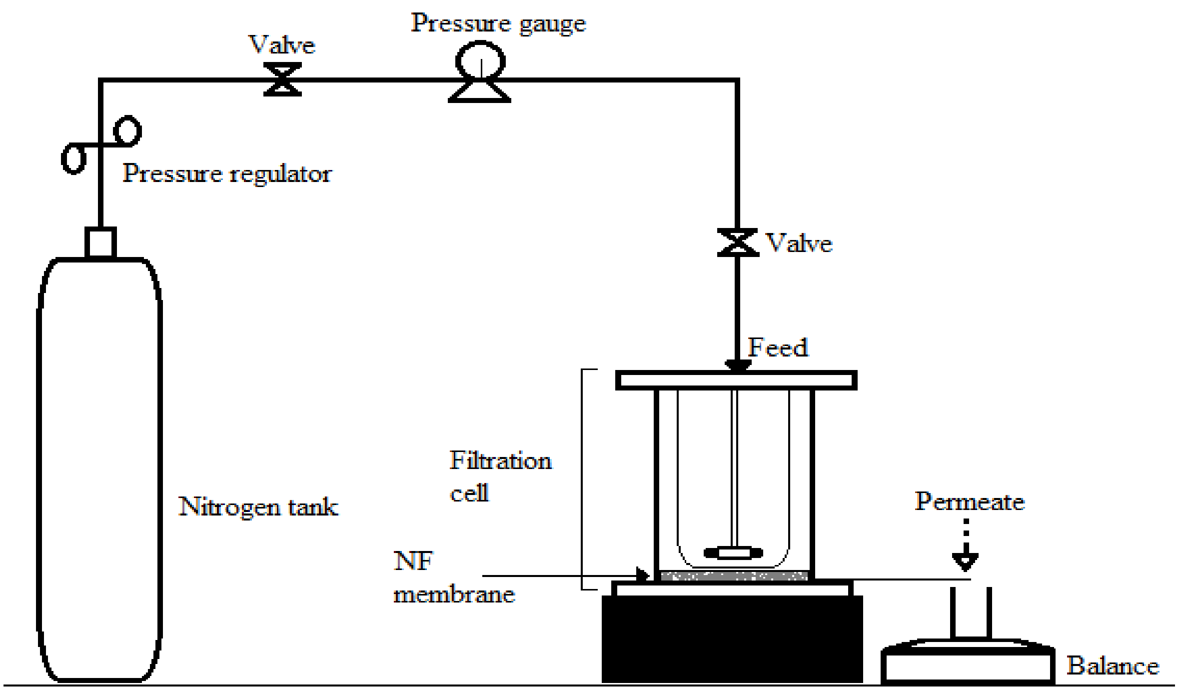


Figure 2. Nanofiltration set up.

Results and Discussion

Pure Water Permeation (PWP)

The PWP of ANF membrane was determined by measuring distilled water flux at different operating pressure (100-500 kPa). As shown in Figure 3, the pure water fluxes of the NFC1-NFC6 membranes increase with increasing pressure. The NFC1-NFC6 achieved water flux of about 0.269 L/m^{2}h, 1.357 L/m^{2}h, 0.404 L/m^{2}h, 0.692 L/m^{2}h, 1.384 L/m^{2}h and 0.791 L/m^{2}h, respectively. Meanwhile the highest PWP increased up to 10.277 L/m^{2}h. As can be seen, the presence of CTAB in casting solution (NFC2-NFC6) increases permeation flux compared to NFC1. Besides, additive CTAB acts as pore forming agent that enhanced porosity of the membrane structure. Not only that, CTAB also improved hydrophilicity of the membranes, eventually increased the permeation of membranes (NFC2-NFC6).

The experimental data showed that, good performance of PWP was achieved by NFC5 membrane about 1.384 L/m^{2}h up to 10.277 L/m^{2}h. It might due to the optimum amount of additive CTAB in the polymeric membrane that would improve the properties of the membranes pore. In addition, higher amount of additive could be suppressed the pore of membranes which decrease the performances of filtration. The values of permeate flux also were increased due to the influences of osmotic pressure on the membrane surface and mechanical compaction at higher operating pressure. According to the solution-diffusion model, flux was proportional to the net pressure differential across the membrane (Saedi et al., 2012).

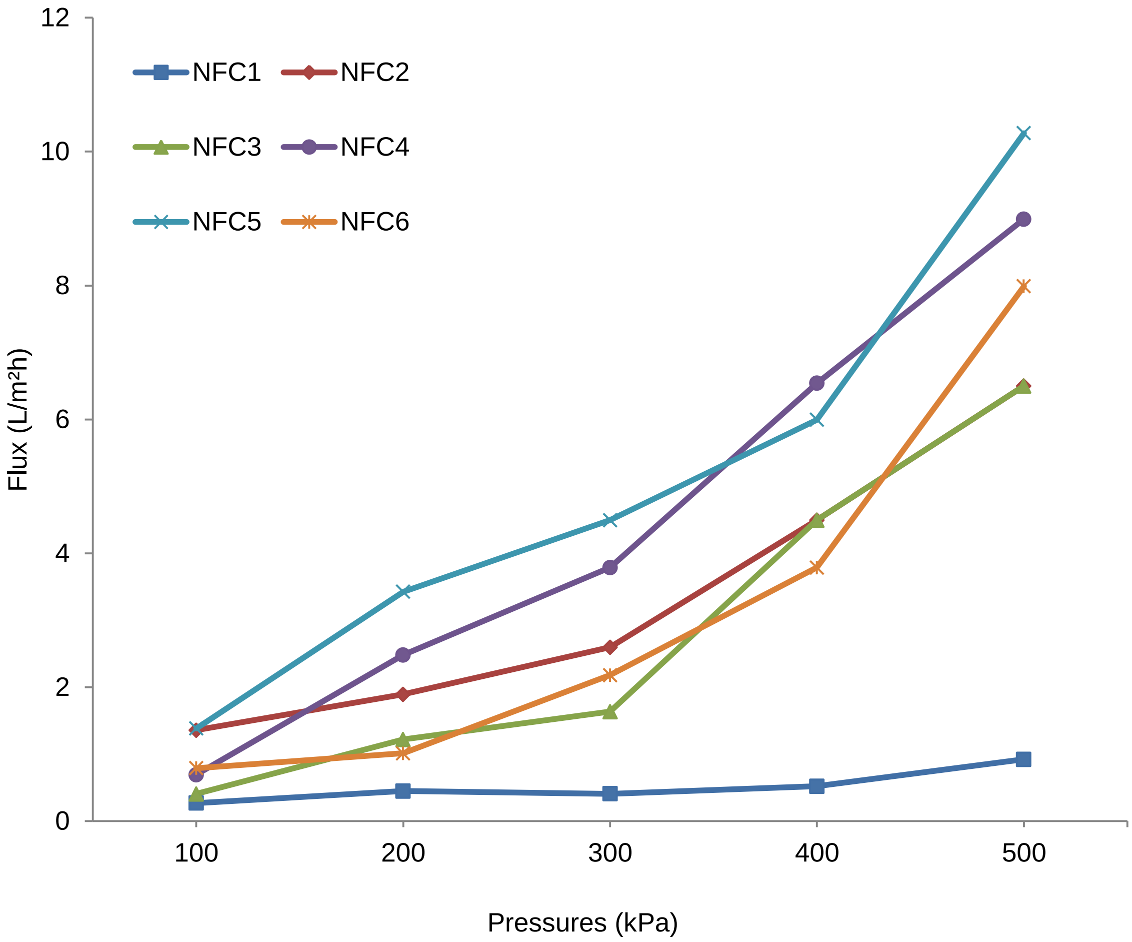


Figure 3. PWP of nanofiltration membrane at different pressure.

Dyes Flux

The data in Figure 4 shows the variation of flux values of Reactive Black 5 and Methyl Blue dye. Membrane without surfactant (NFC1) showed lowest dye flux about 0.73 L/m^2h and 0.38 L/m^2h of Methyl Blue dye and Reactive Black 5 dye, respectively. Meanwhile, highest Methyl Blue dye flux was achieved by NFC6 membrane (with 2.5 wt% of CTAB) about 3.33 L/m^2h and 8.55 L/m^2h for Reactive Black 5, respectively. It showed that CTAB improved the pore and the structure of NF-CTAB membranes.

During the permeation of dye solutions, the adsorption of dye molecules at the membrane surface and inside the pores contributes to the reduction of dyes flow through the membrane pores and led towards the alteration of the dye fluxes (Aouni et al., 2012).The decreasing of permeation fluxes also due to the effect of concentration polarization that retained the solutes on the membrane surface and formed the accumulation of particles on the surface of the membrane (Petrinić et al., 2007).

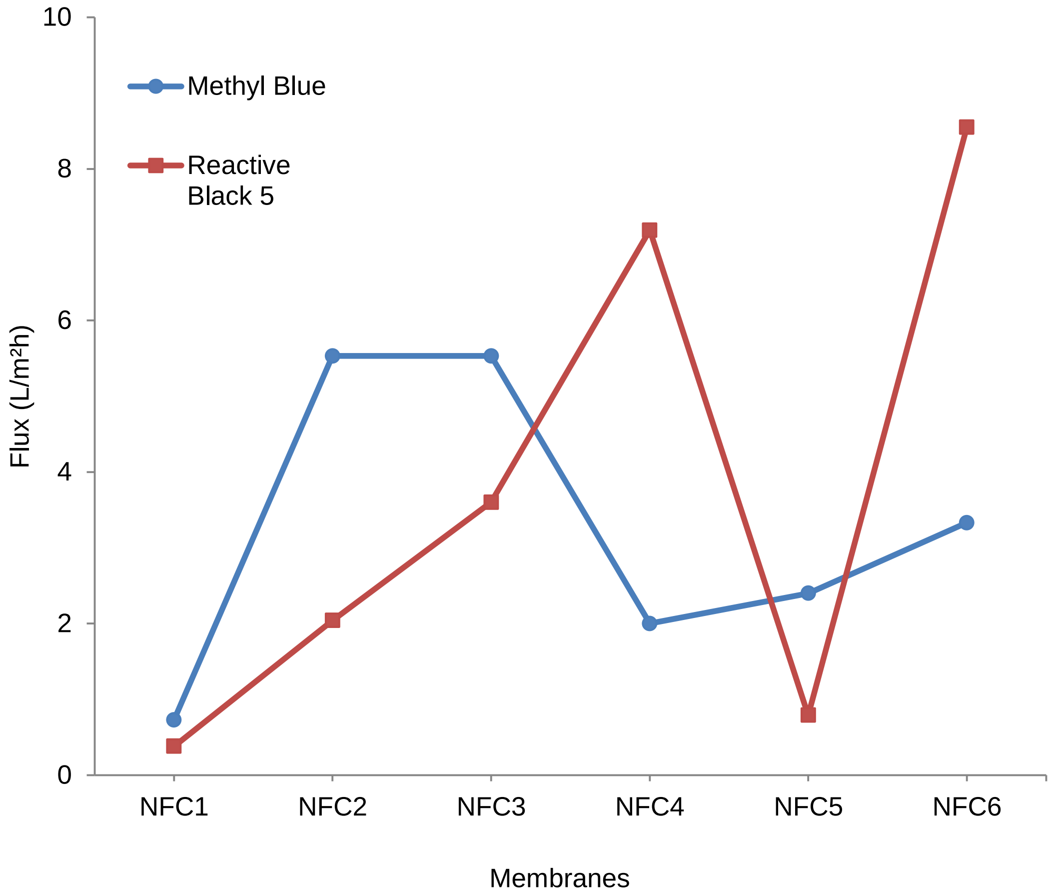


Figure 4. Dyes flux with different concentration of CTAB.

Dyes Removal

Figure 5 illustrates the variation of dye removal (R %) at different concentration of CTAB surfactant. In general, the dye removal is corresponding to the CTAB concentration. Results showed when CTAB concentration increased from 0.0 to 1.0 wt% (NFC1-NFC3), the Methyl Blue dye removal of ANF membrane increased from 96.6 % to 99.5 %. However, when CTAB concentration increase from 1.5 to 2.5 wt %, the dye removal decreased from 99.5% to 58.9 %. Akbari et al., (2002) in their studies have discovered that concentration play an important aspects in nanofiltration membrane.

Meanwhile, Reactive Black 5 dye showed moderate result ranging from 89.7% to 50%. The highest dye removal was achieved by NFC5 of about 91.6%. The electrostatic repulsive interaction between dye and membrane surface promotes the dye removal and decreases concentration polarization and dye adsorption on the membrane surface (Mikulášek and Cuhorka, 2012). The experimental data revealed that the concentration of feed solution also played an important role in determining the performance of membrane separation using dyes solution.

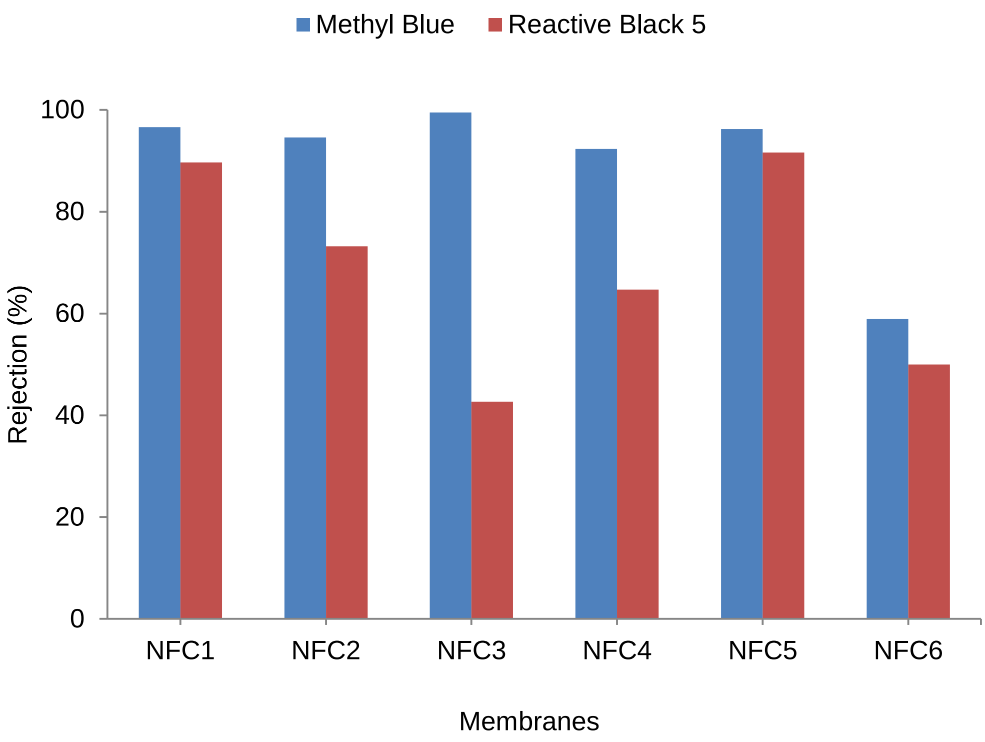


Figure 5. Dyes removal of NF membrane with concentration of CTAB.

Conclusion

From this study, the addition of surfactant (CTAB) into casting solution was found to improve the membrane performance. In terms of water permeation, dye flux and removal, the fabricated membrane showed to have good separation performance. CTAB surfactant contributed a significant effect on the dyes removal of the membranes. The increased of CTAB concentration the better membranes was produced. Therefore, the addition of CTAB is significantly promoted the better performance as well as the promising additives for membrane making and modification agents.

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