

The effect of poly ethylene glycol additive on the characteristics and performance of cellulose acetate ultrafiltration membrane for removal of Cr(III) from aqueous solution

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Abstract. The effect of polyethylene glycol (PEG) additive on the characteristics and performance of the cellulose acetate ultrafiltration membrane to chromium metal removal has been studied using some variation of concentration in the casting solution. The concentration of cellulose acetate polymer was 17.5%, whereas the variations of PEG concentration were regulated at 0, 2.5, 5, 7.5 and 10% by weight. Dimethyl formamide (DMF) was used as a solvent. Pure water flux, membrane morphology test, functional group analysis, and molecular weight cut off (MWCO) were investigated to characterize of the prepared membranes. Membrane performance was tested against Cr(III) metal removal. The results confirmed that the pure water flux improved with the increasing of additive concentration. The maximum improvement occurred at membrane with modification using 7.5% PEG. At this PEG concentration, the pure water flux elevated from 49.5 L/m².h to 62.2 L/m².h. The addition of PEG successfully improved the membrane flux because the role PEG plays as a pore-forming agent. Membrane with addition of 7.5% PEG showcased rejection result for chromium metal of 31.89%. This value is lower than that of pure CA membrane which rejection value against Cr(III) metal amounted to 35.72%.

1. Introduction

The scarcity of clean water has become an extremely serious problem with the increasing of population. Approach such as degradation by advanced oxidation process, distillation, and filtration have been performed to address this issue. The membrane process has gained a particular attention as it can separate or eliminate bacteria, viruses and ions based on pore size and pressure differences as driving forces [1]. This process is used to remove particles, turbidities and microorganisms in water and wastewater [2]. This technology also produces high quality water, eliminates toxicity or recovers valuable components from the output of various industrial processes [3]. Hydrophilicity and pore structure of the membrane play an important role in membrane separation processes. For separation process, a membrane has to have a good porosity, as well as high permeability, hydrophilicity and resistance to impurities.



Phase inversion is one of many important processes used to fabricate asymmetric porous membranes such as microfiltration, ultrafiltration, reverse osmosis and support for composite membranes. In the process of membrane structure formation, besides thermodynamic process, kinetic process also plays an important role. The structure and properties of membranes made with phase inversion techniques are influenced by many factors. Additives are one of those that plays a role in enlarging or preventing macrovoid formation, increasing pore size and enhancing membrane hydrophilicity [4].

A considerable number of researchers has investigated the influence of additive types on morphology and membrane performance. Some researchers have studied the effects of natural additives on membrane performance. The hydrophilic structure was obtained by addition of additives such as glycerol, poly ethylene oxide, LiCl and ZnCl₂[5]. Polyvinylpyrrolidone (PVP) is the most commonly used additive for membrane modification [6-7]. Polyethylene glycol (PEG) has the same role as PVP in membrane formation, PEG acts as a macrovoid formation barrier and increases membrane hydrophilicity [4]. In addition, PEG additive can also improve membrane characteristic in term of pore size, flux and rejection to protein [8]. The addition of additives on the ultrafiltration polymer membrane made by phase inversion has been done by some researchers including Poly Ethylene Glycol [9], Aminated polysulfone [10], and Polyvinylpyrrolidone [11]. Intensive investigation on the effect of several molecular weight of PEG has been done to improve the performance of polyethersulfone membrane [5]. So far, the modification on cellulose acetate membrane by PEG as additive has been done only using one molecular weight of 600 Da [3].

In this study, cellulose acetate (CA) membrane was prepared using poly ethylene glycol PEG additive with molecular weight of 20000 Da. The aim was to investigate the best PEG loading in order to obtain an excellent modified membrane. The effect of additive concentration is reviewed on membrane characteristics and performance. The evaluated membrane characteristics include pure water flux, membrane morphology, and functional group analysis. Membrane performance was studied against chromium metal removal in solution samples.

2. Experimental

2.1 Materials

Cellulose Acetate obtained from Wako Chemical Japan with an average molecular weight of 30,000 g/mol was used as the main polymer in the casting solution, Dimethyl Formamide (DMF) purchased from Merck used as a solvent. Polyethylene Glycol (PEG Mw_20000 Da) obtained from Merck was used as an additive. The distilled water is used as a non-solvent. Chromium nitrate, Cr(NO₃)₃.9H₂O was used as a sample of artificial solution used for the solute rejection test.

2.2 Membrane Preparation

Celulosa Acetate flat sheet membrane was prepared by phase inversion technique. The CA Polymer of 17.5%, a certain amount of PEG additive (0, 2.5, 5, 7.5 and 10%) and the DMF solvent were stirred at room temperature. The solution was stirred until homogeneous. The solution was then allowed for 24 hours without stirring to remove air bubbles present in the casting solution. Afterwards, the membrane was casted on top of the glass plate using a casting knife. Furthermore, layer that are still stuck on the surface of the glass was dipped into a coagulation bath containing precipitant media in the form of pure water that serves as a non-solvent (precipitation process). This process was allowed until the membrane layer detached from the glass plate. Following that, the membranes underwent annealing process for 15 minutes at temperature of 70°C. After annealing, the membranes were ready for use. An illustration of the experimental conditions for the membrane composition is shown in Table 1.

2.3 Membrane Characterization

Pure water flux was investigated through filtration experiment using a set of dead-end ultrafiltration module as shown in Figure 1. The distillate water was flowed through a membrane that has been

compacted with Trans Membrane Pressure (TMP) in the pressure range of 1, 1.25, 1.5, 1.75 and 2 bar. The membrane surface area was 0.00152 m². After reaching a constant state, pure water flux was calculated using Equation 1.

$$J_w = \frac{Q}{A.t} \quad (1)$$

Where J_w represents pure water flux (Lm⁻²h⁻¹), Q is generated permeate (L), A is effective surface area of the membrane (m²) and t is permeation time (h).

Table 1. Composition of CA/PEG casting solution.

Membrane	CA (%W)	PEG (%W)	DMF (%)
M-1	17.5	0	82.75
M-2	17.5	2.5	80
M-3	17.5	5.0	77.5
M-4	17.5	7.5	75
M-5	17.5	10	72.5

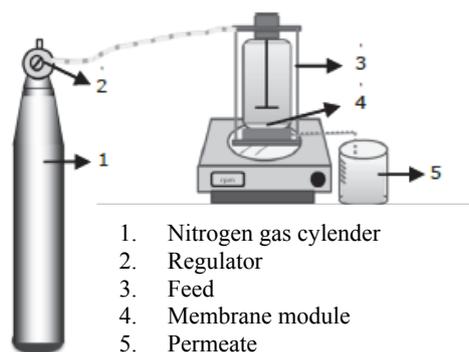


Figure 1. Ultrafiltration Equipment with Dead End Process

Membrane morphology was observed using Scanning Electron Microscopy (SEM). Observations were made on surface, and cross-sectional structure, which prepared by breaking the membrane with liquid nitrogen and then coated with gold. The compositions of M-1, M-3, M-4 and M-5 membranes were analyzed using ATR-FTIR spectrometer (UATR, Perkin Elmer) in the wavenumber range of 500-4000 cm⁻¹.

2.4. The removal of Cr(III)

Chromium-containing solution was prepared by dissolving Chromium nitric Cr(NO₃)₃.9H₂O in distillate water. A total of 200 mL solution containing Cr(III) metal with a concentration of 20 ppm was passed through the membrane at a pressure of 2 bar. The filtration experiment was conducted for 2 hours. The concentration of Cr(III) ion in permeate was analyzed by means of Atomic Absorption Spectroscopy (AAS). The percentage of rejection was calculated using Equation 2

$$\text{Rejection} = \frac{C_F - C_p}{C_F} \times 100\% \quad (2)$$

Where C_F and C_p are dextran concentrations in the sample (feed) and permeate

3. Results and Discussion

3.1. Pure Water Flux (J_w)

The pure water flux is directly related to the number and size of the pore on the membrane surface [4] and is an important characteristic for membranes when applied to the industry [8]. Pure water flux is also used to confirm membrane stability [4]. The effect of additive concentration on pure water flux is shown in Figure 2.

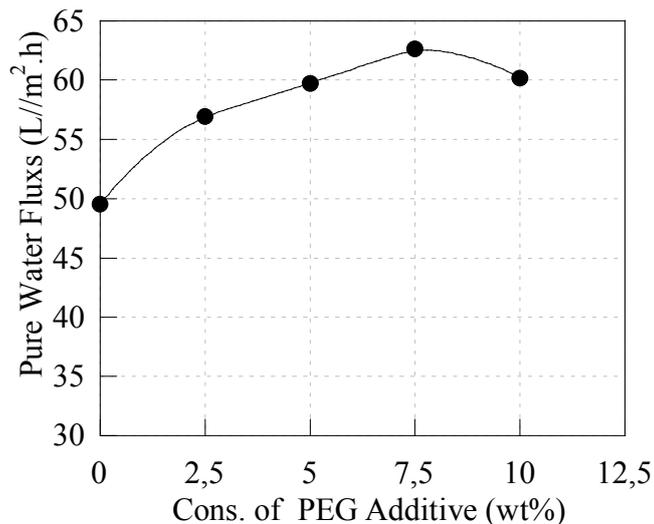


Figure 2. Effect of PEG Additive Concentration on Pure Water Flux

Figure 2 shows that the pure water flux is affected by the concentration of PEG additives added to the casting solution. M-1 membrane produces a pure water flux of 49.53 L/m².hour. The addition of 7.5% PEG increases the pure water flux up to 62.63 L/m².hour. PEG is a pore forming agent and its presence in the casting solution assists the formation of more pores on the membrane surface as it facilitates the formation of the nucleus after the casted film is immersed into the coagulation bath [3]. Increased loading of PEG declines the flux of pure water, this is because the possibility of PEG additives added to the casting solution is detached from the polymer solution and moves into the coagulation bath when casted film is immersed into a non-solvent [2]. Addition of PEG additive with concentration of 0-7.5% increase thermodynamic instability in casting film causing the occurrence of instantenious demixing. The addition of additives above the concentration makes the casting solution more viscous thus the diffusion rate of solvent and non-solvent exchange in the membrane formation process in the coagulation batch decreases resulting in the occurrence of delayed demixing event. This phenomenon caused the top-layer to become denser and suppress its pores.

3.2. Membrane Morphology

Scanning Electron Microscopy (SEM) was used to analyze the changes in modified membrane structure with variations performed on the casting solution. The membranes are code named as M-1, M-4 and M-5. The membrane with PEG concentration of 7.5% (M-4) gives a fairly good pore distribution on the membrane surface, so does cross sectional structure, the pore structure of membrane sublayer seen larger. If the PEG concentration is continuously increased and reaches 10% (M-5) the membrane surface structure looks almost identical to the membrane without the PEG additive (M-1).

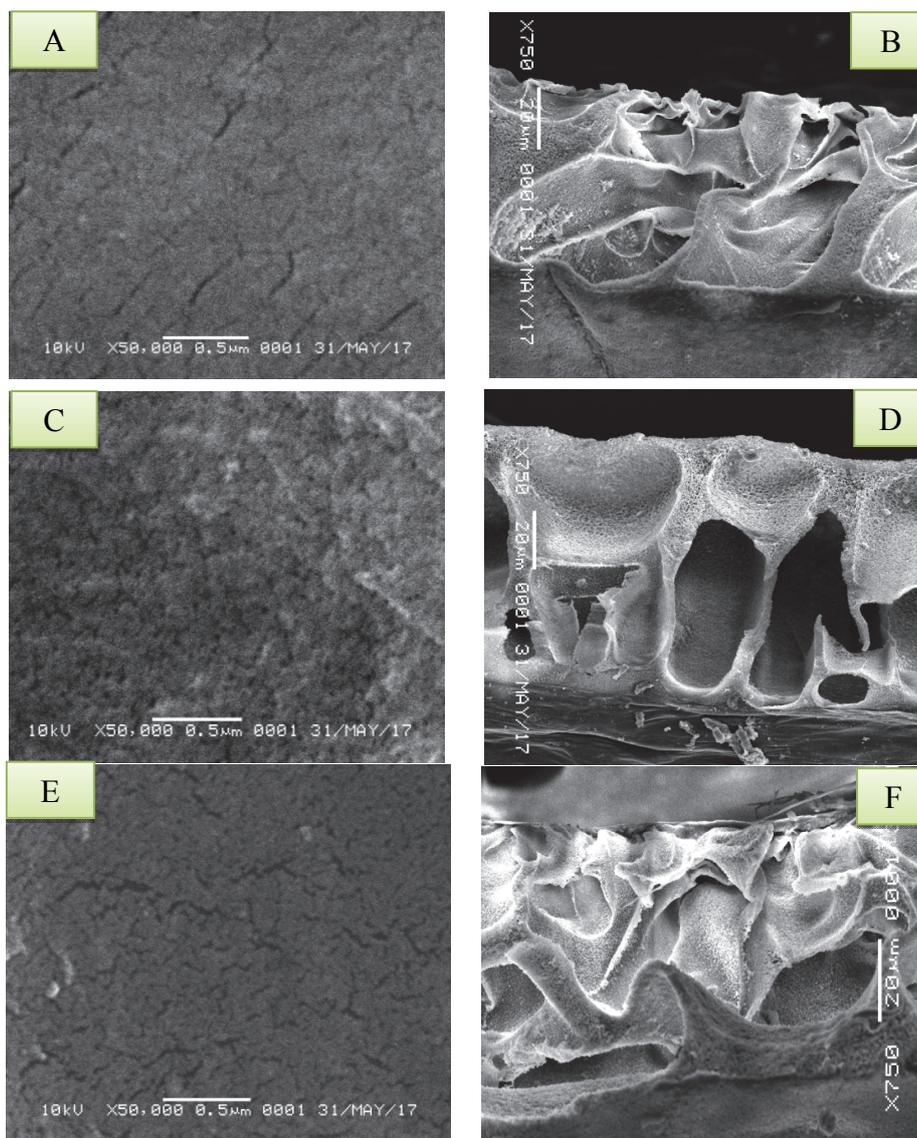


Figure 3. SEM images of CA membranes. (A) The surface of M-1, (B) The cross section of M-1 (C) The surface of M-4, (D) The cross section of M-4 (E), The surface of M-5, (F) The cross section of M-5

3.3. Functional Groups Analysis

Spectroscopy is a method used to identify the basic content of a polymer. Attenuated total reflectance infrared spectroscopy (ATR-FTIR) is the most commonly employed method for analysing functional groups of a polymer [12]. The analysis was conducted on pure CA membrane (M-1) and that with addition of 2.5% (M-2), 7.5% (M-4) and 10% (M-5) of PEG. FTIR analysis for pure and PEG-modified cellulose acetate membrane is shown in Fig. 4. The spectrum for all samples shows that the pure and modified membranes contain a hydroxyl group (O-H). The group is present at wavenumber of $3376\text{--}3377\text{ cm}^{-1}$. The alkane group (C-H) appears at wave number of 1374 cm^{-1} . The C-O group also appears at 1044.90 and 1233 cm^{-1} . The C=O group is seen at the wave number of 1641 cm^{-1} . For membranes with the addition of PEG the appearance of little peak at wave number of 619.33 cm^{-1} indicates the presence of O-H torsional vibrations.

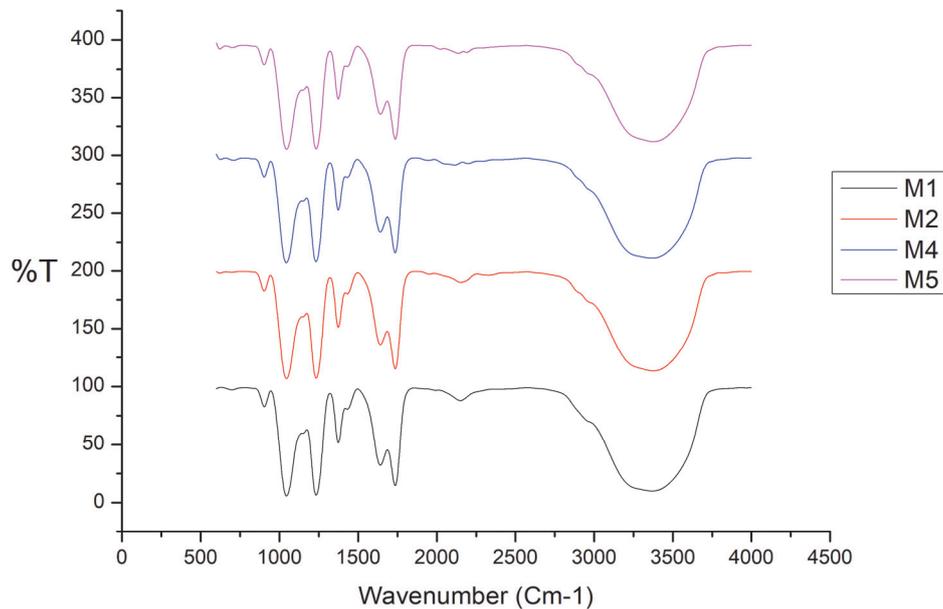


Figure 4. The spectrum of CA membranes with and without additive; M1 is unmodified CA membrane, M2, M4 and M5 are modified membranes with PEG concentration of 2,5%, 7,5%, and 10% respectively

3.4. Membrane Performance

Membrane performance was determined by measuring rejection of Cr(III) metal removal by passing a 100 ml metal sample through the prepared membrane. The membrane having the best permeability of pure water is a membrane with a 7.5% of additive concentration. The rejection of Cr(III) ion for each of fabricated membranes is shown in Figure 5.

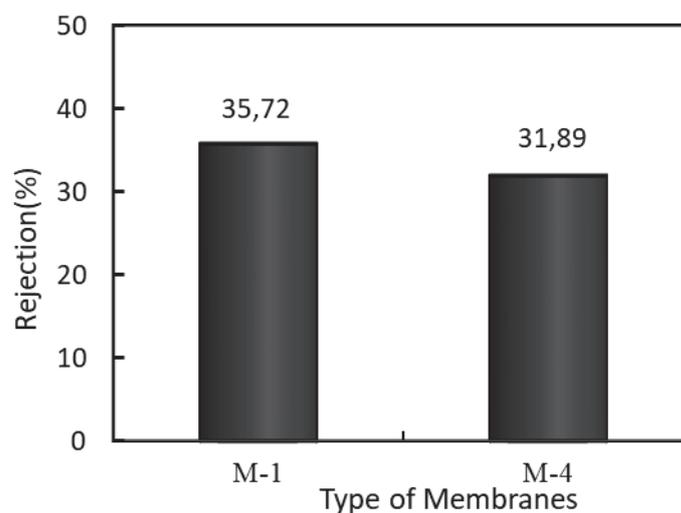


Figure 5. Cr(III) removal of pure CA membrane (M1) and that with 7,5 % PEG addition (M4)

From Figure 5 presents the removal performance of membrane without PEG additive (M1) and that with 7,5% PEG addition (M4). Only M4 is used for performance test as it showcased the best characteristic amongst all the other PEG-modified membranes. It can be observed that the Cr(III) metal removal for pure CA membrane (M-1) is 35.72% while the rejection for this metal in the

modified membrane (M-4) is 31.89%. In comparison to pure CA membrane (M-1), the rejection of Cr(III) metal on modified membrane is lower. The addition of PEG additive that acts as a pore-forming agent causes the membrane to pass the solute more easily. This leads to the decline of rejection. The residue of Cr(III) in the permeate is still beyond the permissible threshold. The removal using a membrane process can reduce 35.72% of Cr(III) metal in maximum.

4. Conclusions

Cellulose acetate membranes have been prepared by preparing a casting solution containing cellulose acetate as the main polymer and Dimethyl Formamide (DMF) as solvent. PEG with molecular weight of 20000 Da of varying concentration was used as an additive to enhance the characteristic and performance of the membrane. In general, it is confirmed that the presence of PEG in the membrane system did improve the characteristics such as morphology and pure water flux. This is because PEG plays a role as a pore-forming agent which facilitates the pore distribution of the membrane. In addition, PEG enhanced the hydrophilicity of the membrane as it is a hydrophilic material, which can be observed by the appearance of O-H functional group from the FTIR analysis result. However, the removal performance of the PEG-modified membranes declined with increasing concentration used.

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