Enhancing Properties and Performance of Cellulose Acetate/Polyethylene Glycol (CA/PEG) Membrane with the addition of Titanium Dioxide (TiO₂) by Using Surface Coating Method

Siti Nurkhamidah*, Yeni Rahmawati, Ignatius Gunardi, Pitsyah Alifiyanti, Krisna Dinas Priambodo, Ryanda Luthfi Zaim, and Wahyuni Eka Muqni

Department of Chemical Engineering, Faculty of Industrial Technology, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya 60111, Indonesia

Abstract. In this study, cellulose acetate/polyethylene glycol (CA/PEG) membrane with composition 80/20 was prepared by phase inversion method. Titanium dioxide with different number has been added by using surface coating. Hydrophilicity, morphology, flux permeate and salt rejection of membranes has been studied. The hydrophilicity is determined by Fourier-Transformed Infrared (FTIR) spectra and contact angle analysis. Surface and fractured morphology are identified by using Scanning Electron Microscopy (SEM). The experiment results show that hydrophilicity of CA/PEG membrane increases with the addition and the increasing of TiO₂ contents. However, with further increasing of TiO₂, hydrophilicity of CPT membrane decreases. The optimum membrane is CA/PEG/TiO₂ 80/20/1,25 g/L solvent (CPT 3) with flux permeate of 111.82 L.m⁻².h⁻¹ and salt rejection of 48.30%.

1 INTRODUCTION

Water is essential for the survival of all forms of life on earth. On an average, a human being consumes about 2 L of water every day [1]. Water accounts for about 70% of the weight of a human body [2]. Today, access to clean water is becoming a difficult task in many regions of the world. According to the World Health Organization, 1.2 billion people lack access to sufficient amounts of clean fresh water and 2.6 billion lack adequate sanitation [3]. Poor sanitation combined with unhealthy water quality accounts for the largest single cause for disease and death in the world. About 75% part of the earth is covered with water and out of which 97% is saltier and only 3% is available for drinking, agriculture, domestic, and industrial consumption [4]. Fresh water is about 2.8% of the total water in the world, whereas among fresh water, only 0.6% is available for use while the rest is locked up in oceans as salt water, polar ice caps, glaciers, and underground reservoirs [5].

The need for fresh clean water is growing rapidly due to the world population growth that imposes larger demands of water supply for domestic use, agriculture, and industry. Another reason is deterioration of fresh water supplies: aquifers, the largest fresh water resource, are being contaminated constantly by industrial and agricultural activities, as well as by intrusions of seawater or saline water due to overuse. Rivers and lakes (surface water resources) are also in threat. Hence, there is a strong need to increase fresh water availability either by recycling waste water or by production of fresh water from seawater [6]. The need to increase fresh water supply and more extensive water treatment drove the advancement of new water technologies and the maturity of existing ones, in all fields of water: desalination and ion removal by reverse osmosis (RO), disinfection techniques by catalysts and by biological treatment, decontamination, new filtration techniques, and monitoring of water quality. Desalination is a general term for methods to remove salt from salty water to produce fresh water.

The common material used for membrane desalination is cellulose. Cellulose acetate/polyethylene glycol (CA/PEG) membrane has been observed by Ahmad et al. and the result shows that CA/PEG with composition 80/20 has the best performance in salt rejection and flux permeate [7]. The pore number and flux permeate of the cellulose membrane can be increased by the addition of PEG and it is hydrophilic material [8]. However, if flux permeates increase, salt rejection will be decrease. Adding materials to increase salt rejection should solve this problem.
In the previous study, nanomaterials such as silica [9], silicon dioxide (SiO₂) [10], zinc oxide (ZnO) [11], titanium dioxide (TiO₂) [12], alumina (Al₂O₃) [13], and carbon nanotube (CNT) [14] have been added to increase the membrane’s performance. For the addition of silica into CA/PEG membranes, the results show that hydrophilicity increases when the particle size of silica decrease [9]. The addition of TiO₂ into polyamide membrane has been study by Lee et al. resulting high and stable salt rejection [12]. In this study, CA/PEG membrane is modified with the addition of TiO₂ nanoparticles to increase its performance.

2 Materials and Methods

2.1 Materials

Cellulose acetate (CA, Mw 3000 Da, acetyl content 39%), polyethylene glycol-200 (PEG, Mw 200 Da) are purchased from Sigma Aldrich. Titanium dioxide (TiO₂) with particle size of ≤ 25 nm, surface area of 45 – 55 m²/g, and purity of 99.7% was purchased from Sigma Aldrich. Aceton was used as solvent and water as non-solvent.

2.2 Membrane Preparation

2 gram of CA and 0.5 gram of PEG were dissolved in 17 mL of acetone. This solution was heated at 130°C up to homogen. Then, solution was cast at room temperature and dip into water for 15 min. After immersion process in water, membrane was removed at room temperature from the mold resulting CA/PEG membrane. TiO₂ nanoparticles were self-assembled on the surface of prepared pore-filled membranes by dipping the membranes in the TiO₂ colloidal suspension of 0.05 wt.% TiO₂ distilled water. Before dip-coating of membrane, the TiO₂ suspension was sonicated about 15 min to avoid the agglomeration of nanoparticles in water. UV lights radiated the coated membranes with 160 W lamp for 15 min. TiO₂ colloidal suspension was varied by 0, 0.5, 0.75, 1, and 1.25 g/(L solvent) and named as CPA, CPT1, CPT2, CPT3, and CPT4, respectively.

2.3 Membrane Characterizations

CA/PEG/TiO₂ membrane is characterized for their hydrophilicity, surface and fractured morphology. The hydrophilicity is determined by Fourier-Transformed Infra-Red (FTIR) spectra and contact angle analysis. Surface and fractured morphology are identified by using Scanning Electron Microscopy (SEM).

2.4 Membrane Performance

The permeate flux (J) represents the amount of pure water collected per unit time and per unit area at variable pressures. It was calculated by: J = Q/t × A, where J is the permeate flux (mL/h.m²), Q is the amount of permeate(mL), t is the time and A is the area (m²). Percentage of salt rejection is the efficiency of membrane and its ability to remove contaminants and calculate by using this equation: R=(1-C_p/C_f) x 100%, where R is the percentage of salt rejection, C_p (in ppm) is the salt concentration of the permeate, C_f (in ppm) is the salt concentration in the feed water.

3 Results and Discussion

3.1 Fourier Transformed Infra Red (FTIR) Characterization

FTIR result shows the increasing of −OH group with the addition of TiO₂ and the increasing of it contents as shown by the increasing of area in the wavenumber of 3300 cm⁻¹ as shown in the Figure 1. The increasing of −OH group up to CPT 3 and decrease at CPT 4. This result shows that hydroxyl group increases up to the addition of TiO₂ is 1 g/L solvent. The increasing of hydroxyl group in TiO₂ is caused by photo catalysis process.

In the formation process of CA/PEG membrane with the addition of TiO₂, there is a step; that is: dipping
the membrane into TiO$_2$ solution. After that, the membrane was contacted with UV light for 15 minutes. Photo catalytic reaction occurs when the electrons are resulted due to the interaction between membrane and UV light. Those electrons interact with photon and resulting free photoelectrons and photoholes [16].

TiO$_2$ is semiconductor material and UV light caused the hole and electrons. Anion of super oxide radical is formed from the interaction between photo-generated electrons with oxygen from the environment. However, when photo-generated holes react with water, -OH radical is formed [15].

### 3.2 Contact Angle Analysis

Another method to identify hydrophilicity of the membrane is by measuring its contact angle. Figure 2 shows contact angle of membrane CA/PEG with the addition of TiO$_2$. With the addition of TiO$_2$, contact angle of membrane CPT decreases up to CPT 3 and increases at the CPT4. The decreasing of contact angle shows the hydrophilicity of membrane increases. Contact angle measurement and FTIR results are the same. Hydrophilicity of CA/PEG membrane increases with the increasing of TiO$_2$ contents and the maximum is at CPT3, with the addition of 1 g TiO2/L solvent. With further increasing of TiO$_2$ content, hydrophilicity of CA/PEG membrane decreases.

![Figure 2](image)

**Figure 2** Contact angle of CPT membrane

### 3.3 Scanning Electron Microscopy (SEM) Characterization

Morphology of the membrane on the top surface of cross section was observed by using SEM. Figure 3 shows SEM images show the Top surface and cross section of membrane (a) CPA, (b) CPT 1, (c) CPT 2, (d) CPT 3, (e) CPT 4. The pore size of CPT membrane is higher than that of CPC membrane. However, from the pore size both of them are microfiltration membrane because the pore size is in the range 100 nm – 10.000 nm [17].

![Figure 3](image)

**Figure 3** SEM images show the Top surface and cross section of membrane (a) CPA, (b) CPT 1, (c) CPT 2, (d) CPT 3, (e) CPT 4

### 3.4 Salt rejection and Flux Permeate

Performance of the membrane for desalination process was observed from salt rejection and flux permeate of the membranes. Figure 4 shows the increasing of salt rejection with the increasing of TiO$_2$ contents and achieved maximum at CPT3 and decreases with further increasing of TiO$_2$ content (CPT4). Salt rejection of CPT3 is 48.302% which is higher than that of CPA, 34.053%. Compared to the previous result, salt rejection of CA/PEG membrane with the addition of TiO$_2$ is higher than that with the addition of silica. Salt rejection of CA/PEG with the addition of silica is 36.88% [9].

Figure 5 shows the increasing of flux permeate of CPT membrane. The result shows that flux permeate increases with the increasing of TiO$_2$ content and decreases with further decreasing of TiO$_2$ content. This phenomenon is in agreement with the pore size of CPT membrane as can be seen from SEM images. CPT3 has the maximum flux permeate (111,819 L.m$^{-2}$h$^{-1}$) because it has the biggest pore size.
4 Conclusions

Hydrophilicity of CA/PEG membrane increases with the addition and the increasing of TiO_2 contents as can be seen from FTIR results and contact angle measurements. However, with further increasing of TiO_2, hydrophilicity of CPT membrane decreases. The optimum membrane is membrane with the composition of CA/PEG/TiO_2 80/20/1.25 g/L solvent (CPT 3) with flux permeate of 111.82 L.m^{-2}h^{-1} and salt rejection of 48.30%.

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