Preparation of Polyvinyl Chloride/ZnO Composite Ultrafiltration Membrane for Peat Water Treatment

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Abstract. In this research, composite polyvinyl chloride ultrafiltration (PVC-UF) membrane was used for peat water treatment. The UF membrane was prepared by mixing polyvinyl chloride (PVC), polyethylene glycol (PEG400), ZnO, acetone, and N-dimethylacetamide (DMAC). The concentration of PVC was varied from 10 to 14 wt.%, while the PEG400 was varied from 0 to 15 wt.%. The concentration of acetone and ZnO was fixed at four (4) wt.% and two (2) wt.%, respectively. Immersion precipitation method was used to form the membrane structure. The experimental results showed that higher humic substance rejection (>50%) was achieved when 12 wt.% PVC and 10% wt.% PEG was added into the polymer solution. The permeate flux of the membrane was above 100 L/m²-h. Higher rejection of humic substances was obtained at an operating pressure of 30 psig.

Keywords: peat water, ultrafiltration, humic substance, clean water.

1. Introduction

Since the availability of clean water is scarce, peat water has been considered as an alternative water source for the people who live in the peatland areas. However, the peat water cannot be consumed directly due to the dissolved organic content, particularly humic substances, which give brownish-yellow color to the water[1, 2]. Pressure driven membranes have been widely used in water treatment field to produce clean water, such as reverse osmosis (RO)[3], nanofiltration (NF)[4], ultrafiltration (UF)[5], and microfiltration (MF)[6]. The RO membrane rejects the humic substances and other natural organic matter by almost 99 – 100% to produce drinking water[7]. Nevertheless, this technology is limited by the high operating pressure required, which has an impact on operating costs. Ultrafiltration (UF) membrane becomes a choice but needs to be modified to increase the selectivity.

The UF membranes are mostly prepared from a polymeric material, such as polysulfone (PSf)[8], polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), and polyvinyl chloride (PVC). Among these polymers, PVC becomes a good alternative due to its high chemical resistance and low cost[9]. Several studies have been conducted on the modification of the PVC membranes. Bilad et al.[10] modified PVC membrane by blending the polymer with silica. The modified PVC membrane had a critical flux of 18 Lm²-h⁻¹ and suffered from severe irreversible fouling compared to the commercial PVDF UF membrane. Demirel et al.[11] added 1 (one) wt.% of Fe₂O₃ nanoparticles into the PVC solution. They obtained a PVC membrane with water flux of 782 Lm²-h⁻¹ and sodium alginate rejection of 91.9% as well as suitable antifouling property. It has been reported that the addition of nanoparticles into the polymer solution inhibited the formation of macrovoids in the membrane structure and improved the mechanical strength of the membrane [12]. Some antibacterial particles,
such as silver[13], carbon nanotubes[14], and ZnO[15], have also been used in UF membrane modification to reduce biofouling formation on the membrane surface.

Besides inorganic fillers, the hydrophilic polymers, such as polyethylene glycol (PEG)[16] and polyvinylpyrrolidone (PVP)[17], are frequently used as pore former to enhance the membrane porosity. Mei et al.[18] compared 3 (three) types of additives, i.e., PEG1000, PVP (Mw 40000), and sucrose, on the PVC membrane performances. They found that the presence of additives enhanced the viscosity of the polymer solution, in the sequence of additives: PVP>PEG>sucrose. Besides, the presence of additives reduced the thermodynamic stability of the solution when the membrane is immersed in water. As a result, higher membrane porosity was formed. The addition of sucrose tended to generate a sponge-like pore structure, while the PVP and PEG produced finger-like pore structure. Rabiee et al.[19] prepared PVC membrane by adding PEG6000 and ZnO with 1-Methyl 2-pyrrolidone (NMP) as the solvent. The addition of 4 wt.% of PEG6000 and 3 wt.% of ZnO resulted in PVC membrane with a flux recovery ratio of 90% and rejection of BSA of 97%. ZnO addition in the PVC solution led to more porous membrane.

In this research, the PVC membrane was prepared by blending polymer with PEG400 and ZnO into N-dimethylacetamide (DMAc) as a solvent. A low concentration of acetone was added into the solution to improve the membrane selectivity. The influence of polymer concentration (PVC and PEG400) on permeate flux and humic substance rejection was investigated.

2. Materials and Methods

2.1. Materials

PVC resin (FJ-60 type) was supplied by PT. Asahimas Chemical (Cilegon, Indonesia), while N-dimethylacetamide (DMAc), with the purity of 99.9%, by Shanghai JingsanJingwei Chemical CO., Ltd. The PEG400, acetone, and ZnO nanoparticles were provided by local suppliers. Demineralized water was used as a coagulant. The peat water was obtained from Pekanbaru River-Riau, Indonesia, with a pH of 3.

2.2. PVC Membrane preparation

The flat-sheet UF-PVC membrane was prepared by blending PVC resin (10 to 14 wt.%) with PEG400 (0 - 15 wt.%), acetone (4 wt.%), ZnO-NPs (2 wt.%) in DMAc. The membrane solution was stirred in a closed tank until homogenous and then left until all the bubbles disappeared from the solution. The homogenous membrane solution was cast on flat glass with a membrane thickness of 150 µm. The membrane film was immediately immersed in a coagulation bath for 24 hours.

2.3. Analysis of Membrane Morphology by Scanning Electron Microscope

The morphology of UF-PVC membrane was analyzed by Scanning Electron Microscope (SEM, JSM-6510LV low vacuum SEM equipped with a super conical lens) with 500x magnification. The membrane samples were immersed in liquid nitrogen to preserve the pore structure and then cut using a metal clamp. Prior to imaging, the analyzed part of sample was coated with a thin layer of gold.

2.4. Measurement of UF-PVC Peat Water Flux and Humic substances Rejection

The experimental procedure refers to our previous work, as shown in Figure 1 [20]. The flat-sheet UF-PVC membrane was placed in a circular module with a membrane area of 45 cm². Prior to use, the UF membrane was rinsed with demineralized water for 15 minutes at 15 Psig. The ultrafiltration process was conducted for 2 (two) hours. The permeate flux was measured every 20 minutes and then calculated using the following equation:

$$J_{w1} = \frac{V}{A \times \Delta t}$$  

(1)

where $J_{w1}$ is peat water flux at the beginning of ultrafiltration process (Lm⁻²h⁻¹), $V$ is the volume of permeate (m³), $A$ is the membrane area (m²), and $t$ is the operating time (min). The peat water flux after $t$ time of ultrafiltration denotes as $J_t$. 


The humic substances rejection (R,%) was measured after 2 (two) hour of peat water ultrafiltration and calculated by the following equation:

\[ R(\%) = \left[ 1 - \frac{C_p}{C_f} \right] \times 100\% \]  

\( C_p \) is the concentration of humic substances in the feed solution, while \( C_f \) is the concentration of humic in permeate side. The concentration of humicsubstances was analyzed by UV-Vis spectrophotometer with a wavelength of 254 nm [2].

![Figure 1](image1.png)  
**Figure 1.** Experimental set-up of UF-PVC membrane system

3. Result and Discussions

3.1. Morphology of Flat-sheet UF-PVC Membrane  
The morphologies of PVC UF membranes are shown in Figure 2. The PVC-UF membrane had some macrovoids at the bottom of the membrane layer (Figure 2A). The macrovoids were eliminated by the addition of PEG400. The presence of PEG400 in the polymer solution enhanced the solution viscosity that hindered the growth of membrane pore. As a result, narrower finger-like structure has formed.

![Figure 2](image2.png)  
**Figure 2.** SEM of PVC-UF membrane structures at fixed concentration of PVC(12 wt.%), acetone (4 wt.%), and various concentration of PEG400: (A) 0% wt.%, (B) 5 wt.%, (C) 10 wt.%, and (D) 15 wt.% (magnification 500x)

3.2. The influence of PEG400 concentration on permeate flux and humic substances rejection  
Figure 3 presents the influence of PEG400 on peat water flux and humic substances rejection. the concentrations of PVC, ZnO, and acetone werefixed at 12, 2, and 4 wt.%, respectively. It shows that the addition of PEG400 in the membrane solution increased the peat water flux. The addition of PEG400 by 15 wt.% in the PVC solution produced UF membrane with a peat water flux of 207 Lm⁻²h⁻¹ at the beginning of the filtration process. It was almost 10 times higher than the absence of PEG400. The presence of PEG400 in the membrane structure improved the interaction between membrane and water, which resulted in the formation of greater membrane porosity and permeate flux. However, higher porosity in the membrane structure, particularly in the skin layer, resulted in lower rejection of humic substances. Humic substance rejection was achieved above 50% when 10 wt.% of PEG400 was added into the polymer solution.
3.3. The influence of PVC concentration on permeate flux and humic substance rejection

The influence of PVC concentration on peat water flux of the UF-PVC membranes is shown in Figure 4. It has been reported that the polymer concentration influenced the viscosity of solution [21]. The increase of polymer viscosity with the raise polymer concentration inhibited the growth of membrane pore. As shown in Figure 4, the lower polymer concentration (10 wt.% of PVC) resulted in higher permeate flux. After 2 hours of ultrafiltration, the peat water flux was decreased from 296 Lm⁻²h⁻¹ to 88 Lm⁻²h⁻¹ (or by 70%). When the PVC concentration was raised to 14 wt.%, the peat water flux was dropped significantly (7 Lm⁻²h⁻¹). The higher concentration of PVC enhanced the viscosity of membrane solution, which results in the formation of smaller membrane pores. Consequently, the permeation flux became smaller but showed a stable flux for two hours of ultrafiltration. The formation of tight surface structure at high concentration of PVC minimized irreversible fouling in the membrane structure. The fouling of contaminants on the membrane surface can be more easily swept by crossflow stream. Therefore, a stable flux was resulted during the ultrafiltration. The decrease in flux was inversely proportional to the rejection of humicsubstances. The increase of humic substances rejection was obtained when the concentration of PVC was enhanced.

3.4. The influence of operating pressure on permeate flux and humic substance rejection

Figure 5 shows the influence of operating pressure on peat water flux and humic substances rejection. The UF membranes were prepared by blending 12 wt.% of PVC, 10 wt.% of PEG400, 2 wt.% of ZnO, and 4 wt.% of acetone. The UF membrane performances were investigated at different operating pressures, i.e., 10, 15, and 30 psig. The normalized flux is the ratio of peat water flux at a specific operating time (J_t) during the fouling experiment to the initial peat water flux (J_0). It shows that the highest flux reduction occurred when the UF membrane system was operated at 10 and 15 psig compared to 30 psig. It was suggested that fouling on the membrane surface was properly swept by
crossflow stream at higher operating pressure and form a thin fouling layer on the membrane surface. The fouling layer acted as a secondary layer on the membrane surface, which increased the rejection of humic substances.

![Figure 5](image-url)

**Figure 5.** The influence of PEG400 concentration on (A) peat water flux and (B) humic rejection

4. Conclusions

The PVC membrane is prepared by blending the polymer with PEG400, ZnO, and acetone in DMAC as a solvent. The addition of PEG400 in the polymer solution reduces the formation of macrovoids in the membrane structure and forms narrower finger-like structure. The addition of PEG400 by 15 wt.% in the PVC solution produces UF membrane with a water flux of 207 Lm⁻²h⁻¹, which is almost 10 times higher than the absence of PEG400. Humic substance rejection is achieved above 50% when 10 wt.% of PEG400 is added into the polymer solution. Further increase of PEG400 concentration to 15 wt.%, the humic substance rejection is decreased to 35%. PVC concentration also influences the membrane performance. Lower PVC concentration (10 wt.%) produces a permeate flux of 296 Lm⁻²h⁻¹. When the PVC concentration is raised to 14 wt.%, the peat water flux is significantly decreased to 7 Lm⁻²h⁻¹. A suitable flux and rejection are achieved at PVC concentration of 12%. In addition, higher rejection of humic substances is obtained at an operating pressure of 30 psig compared to 10 and 15 psig. The compact fouling formed on the membrane surface acts as a second layer, which improves the humic substances rejection.

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