

# Modification of PVC Membrane for Humic Substance Removal in Peat Water

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**Abstract.** Ultrafiltration (UF) membrane was prepared by blending polyvinyl chloride (PVC) with ZnO nanoparticle (ZnO-Np) and acetone as additives, and then used to treat peat water. The influence of PVC and ZnO-Np concentration on membrane morphology and humic substance rejection were studied. The experimental results showed that the increase of PVC and ZnO-Np concentration in the membrane solution enlarged the pore size of the UF membrane. Agglomeration of particles was found when 2 wt.% of ZnO-Np was added into the membrane solution. The addition of 10 wt.% of PVC concentration and 1 wt.% of ZnO-Np resulted in peat water flux above  $100 \text{ Lm}^{-2}\text{h}^{-1}$  and average humic substance removal of 61%. When the concentration of PVC and ZnO-Np was increased to 12 and 2 %wt, the humic substance rejection was decreased to 40%. More irreversible fouling occurred in the UF-PVC membrane that prepared by low PVC and high ZnO-NP concentration, which is indicated by the low value of the FRR.

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

## 1. Introduction

PVC-based ultrafiltration (UF-PVC) membrane has been increasingly used in the water treatment field due to its high chemical and mechanical stability, high resistance to temperature, and microbial corrosion with a low of material cost [1, 2]. Several studies have been conducted to modify UF-PVC membranes [3, 4]. Most of the UF membrane was modified by adding additives to improve the permeability as well as antifouling [5-8]. The additives commonly used in PVC membrane modification are hydrophilic polymers (such as polyethylene glycol/PEG, polyvinyl pyrrolidone/PVP, Pluronic) [9], surfactants (such as Tween agent) [10], and inorganic nanoparticles (such as  $\text{TiO}_2$ , zeolite, graphene, silver/Ag, ZnO) [11-14].

The pore structure of PVC membranes for water treatment is mostly asymmetric, which prepared by immersion precipitation method [15]. The additives are introduced to the polymer solution and stirred until homogenous, then fabricated into a flat-sheet or hollow-fiber membrane. The flat-sheet membrane is prepared by casting method, while the hollow-fiber membrane is prepared by spinning method [16]. The casted polymer film or the polymer spinning dope is immersed in a coagulant (non-solvent) bath, which induces solvent exchange between the polymer solution and the non-solvent until the polymer is solidified [17].

Some operating parameters should be considered in membrane preparation by immersion precipitation, such as polymer concentration, type of solvent and coagulant, as well as type and



concentration of additives [18]. Ariono et al. [19] studied the effect of polysulfone (PSf) concentration on the morphology of flat-sheet UF membrane. The higher concentration of polymer concentration enhanced the viscosity of the solution, which contributed to kinetic hindrance against the phase separation and membrane pore growth. As a result, the membrane permeability is decreased, while the membrane selectivity is increased.

Aryanti et al. [20, 21] prepared a tight skin UF membrane by adding a low concentration of acetone to the PSf/PEG400 solution. They found that the tight structure of the UF membrane improved the membrane selectivity to humic substance up to 80% during the peat water treatment. Acetone is a weak solvent, which can be easily separated and evaporated from the membrane solution. The rapid loss of acetone results in higher polymer concentration in the skin layer of the membrane and then forms a tight structure. Aryanti et al. [8] studied the influence of polymer ratio (PSf/PEG400) and polymer/solvent on the performance of PSf-UF membrane during the peat water treatment. They found that the increase of ratio PSf/PEG400 from 1:1 to 1:2.5 improved the membrane hydrophilicity, where the pure water flux was increased up to 200 times. A stable flux is achieved when the ratio PSf/PEG400 was 1:2, which resulted in 84% rejection of humic substances.

In this paper, the UF membrane was prepared by blending PVC with PEG400 and acetone as additives. In addition, ZnO nanoparticle (ZnO-NPs) was added to the membrane solution to improve membrane permeability due to its hydrophilic characteristics. The influence of PVC and ZnO concentration on the resulted UF membrane performance was investigated.

## 2. Experimental Methods

### 2.1. Materials

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

### 2.2. Preparation of Flat-sheet UF-PVC Membrane

The flat-sheet UF-PVC membrane was prepared by blending various concentrations of PVC (10 and 12 wt.%) with PEG400 (20 wt.%), acetone (4 wt.%), ZnO-NPs (1 - 2 wt.%), and 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  $\mu\text{m}$ . The membrane film was immediately immersed in coagulation bath for 24 hours. The composition of UF-PVC membrane is shown in Table 1.

Table 1. Composition of UF-PVC membrane

Membrane Code	PVC (wt.%)	ZnO (wt.%)	PEG400 (wt.%)	Acetone (wt.%)
PVC 10-1	10	1		
PVC 10-2	10	2		
PVC 12-1	12	1	20	4
PVC 12-2	12	2		

### 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. To view the cross-section of the resulted membrane, the membrane sample was 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 Membrane Water Flux and Humic substances Rejection

The experimental procedure refers to our previous work, as shown in Figure 1 [8, 21]. The flat-sheet UF-PVC membrane was placed in a circular module with a membrane area of 45 cm<sup>2</sup>. The UF membrane system was operated at crossflow mode at a different transmembrane pressure (10 and 15, and 30 Psig). Prior to use, the UF membrane was rinsed with demineralized water for 15 minutes at 15 Psig. The permeate flux was measured every 20 minutes during 2 (two) hours of ultrafiltration, using the following equation:

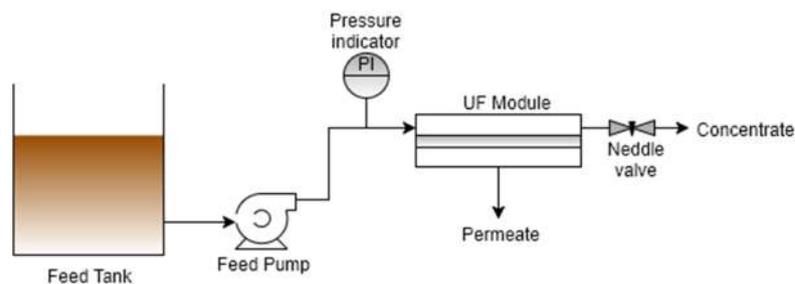
$$J_{w1} = V / (A \times \Delta t) \quad (1)$$

where  $J_{w1}$  is peat water flux at the beginning of ultrafiltration process (Lm<sup>-2</sup>h<sup>-1</sup>),  $V$  is the volume of permeate (m<sup>3</sup>),  $A$  is the membrane area (m<sup>2</sup>), 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:

$$R (\%) = \left[ 1 - C_p / C_f \right] \times 100\% \quad (2)$$

$C_p$  is the concentration of humic substances in the feed solution, while  $C_f$  is the concentration of humic in permeate side. The concentration of humic was analyzed by UV-Vis spectrophotometer with a wavelength of 254 nm [8].



**Figure 1.** Experimental set-up of UF-PVC membrane system

#### 2.5. Calculation of Flux Recovery Ratio (FRR)

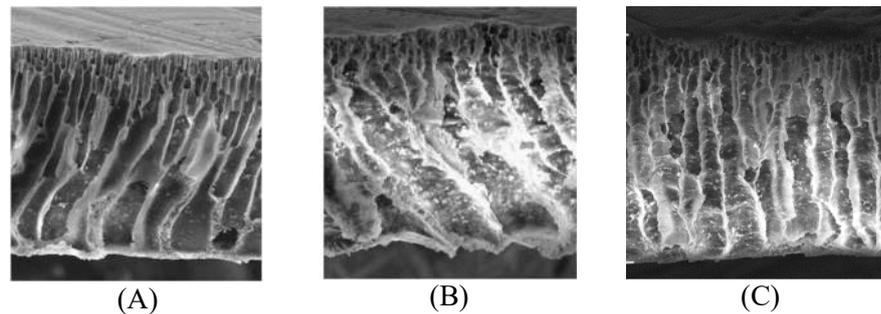
After 2 hours of ultrafiltration, the flat-sheet UF-PVC membrane was cleaned by flushing method for 30 minutes. The permeate flux of the cleaned membrane was measured and denoted as  $J_{w2}$ . The flux recovery ratio (FRR) was calculated by Eq. (3), as follows:

$$FRR (\%) = \left[ J_{w2} / J_{w1} \right] \times 100\% \quad (3)$$

### 3. Result and Discussions

#### 3.1. Morphology of Flat-sheet UF-PVC Membrane.

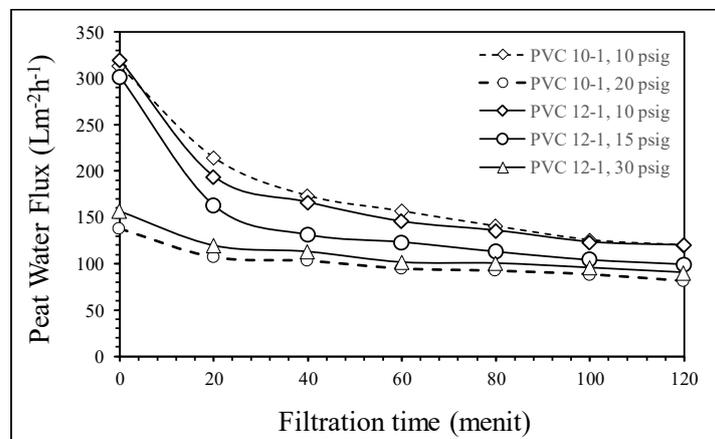
The morphologies of resulted UF-PVC membranes are presented in Figure 2. All the UF-PVC membranes have finger-like pore structure, consisting of a dense top layer and a porous sublayer. It shows that the increase of ZnO-NPs concentration from 1 to 2 wt.% enhanced the membrane pore size. Meanwhile, the pore size was reduced when the PVC concentration was increased from 10 to 12 wt.%. The presence of ZnO-NPs in the membrane structure improved the water diffusion into the membrane solution and formed a larger membrane pore size in the membrane structure. The increase of polymer concentration raised the viscosity of membrane solution, which inhibited the pore growth of the membrane pore. Therefore, a narrower finger-like structure has resulted. Agglomeration of particles was found when 2 wt.% of ZnO-Np was added into the membrane solution. The ZnO-Np concentration of 1 wt.% resulted in a preferable pore structure compared to other UF membranes



**Figure 2.** The SEM of UF-PVC membranes: (A) PVC 10-1, (B) PVC 10-2, and (C) PVC 12-2

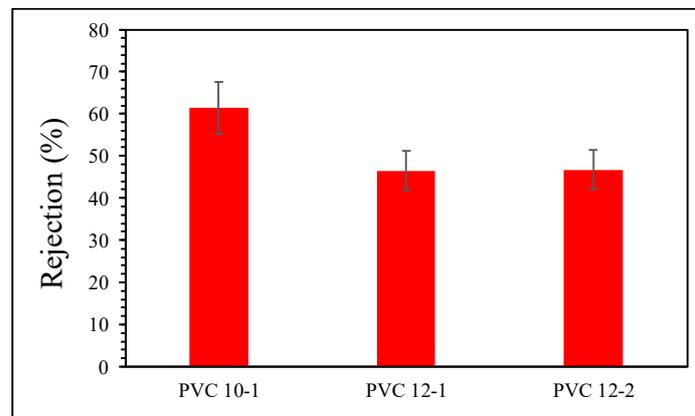
### 3.2. Profile of Peat Water Flux of UF-PVC Membrane and Humic Substances Rejection

Figure 3 shows the profile of peat water flux during 120 minutes of ultrafiltration. The permeate flux was declined during 2 hours of peat water ultrafiltration. The accumulation of solutes on the membrane surface reduced the effective pore of the membrane, and consequently, the amount of water through the membrane was decreased. The increase of operating (transmembrane) pressure raised the amount of solute accumulated on the membrane surface, which reduced the permeate flux. Besides operating pressure, the concentration of polymer also affected the permeate flux. The low viscosity of solution due to low concentration of polymer produced larger membrane pore size, which was susceptible to internal fouling. With a particle diameter less than 200 Da, the humic substance was easy to penetrate the membrane pore. The increase of operating pressure the humic substance may block the membrane pore, and therefore, lower permeate flux has resulted. The overall UF-PVC membrane provided permeate flux above  $100 \text{ Lm}^{-2}\text{h}^{-1}$  during 2 hours of ultrafiltration process. A stable permeate flux resulted when 10 wt.% of PVC and 1 wt.% of ZnO-NPs were used in the membrane solution.



**Figure 3.** The profile of peat water flux during 120 minutes of ultrafiltration

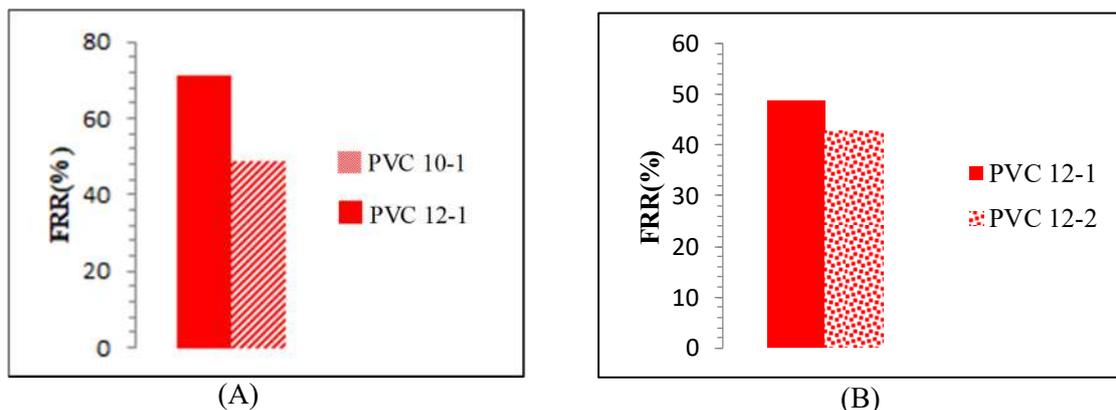
Figure 4 shows the influence of PVC and ZnO-NPs concentration on humic substances rejection. The highest rejection of humic substances (61%) was achieved at 10 wt.% of PVC and 1 wt.% of ZnO-NPs. It can be attributed to the fouling formation in the UF-PVC structure that reduced the effective pore of the membrane. Consequently, the rejection of humic substances was increased. When the ZnO-NPs concentration was raised from 1 to 2 wt.% in the 12 wt.% of PVC solution, the rejection of humic substances was slightly decreased from 48 to 45%. The slight increase of membrane pore size with the increase of ZnO-NPs increased the mass transfer of the solute through the membrane. Therefore, concentration of solutes in the permeate side of membrane PVC 12-2 was higher than the membrane PVC 12-1.



**Figure 4.** The influence of PVC and ZnO-NPs concentration of humic substances rejection

### 3.3. The Influence of PVC and ZnO concentration on Flux Recovery Ration (FRR)

The influence of PVC and ZnO-NPs concentration of FRR is presented in Figure 4. The FRR analysis was conducted to determine the cleaning efficiency of the membrane by flushing method. It shows that lower PVC concentration (10 wt.%) in membrane solution resulted in lower FRR (50%). The increase of PVC concentration to 12 wt.% enhanced the FRR value to 70%. It means that UF-PVC membranes prepared by blending a low concentration of PVC (below 12 wt.%) were more susceptible to irreversible fouling, which can not be cleaned by a simple method. The same result was found when the concentration ZnO-NPs was raised from 1 to 2 wt.%, where the FRR value was decreased from 48% to 43%. The UF membrane prepared by blending PVC with 2 wt.% of ZnO generated larger membrane pore compared to the 1 wt.% of ZnO. The humic substances can be easily penetrated to the membrane pore and formed irreversible fouling. Another method is needed to remove the irreversible fouling, such as backwash by clean water or chemicals.



**Figure 5.** The influence of (A) PVC and (B) ZnO concentration on flux recovery ratio

## 4. Conclusions

Ultrafiltration (UF) membrane has been successfully prepared by blending PVC, PEG400, ZnO-NPs, and acetone in DMAc as a solvent, and then use to treat peat water. The influence of PVC and ZnO-Np concentration on morphology of the resulted membrane and humic substance rejection are studied. The increase of PVC and ZnO-Np concentration in the membrane solution enhances the UF-PVC membrane pore size. Agglomeration of ZnO-NPs particles is found inside the membrane pore when 2 wt.% of ZnO-Np is added into the membrane solution. The ZnO-Np concentration of 1 wt.% results in a preferable pore structure compared to other UF membranes. The addition of 10 wt.% of PVC concentration and 1 wt.% of ZnO-Np results in peat water flux above  $100 \text{ Lm}^{-2}\text{h}^{-1}$  and average humic

substance removal of 61%. When the concentration of PVC and ZnO-Np is increased to 12 and 2 %wt, the humic substance rejection is decreased to 45%. Higher irreversible fouling occurs in UF-PVC membrane that prepared by low PVC and high ZnO-NP concentration, which is indicated by the low value of the FRR.

## References

- [1] Aryanti P. T. P., Yustiana R., Purnama R. E. D.. & Wenten I. G. (2015). Performance and characterization of PEG400 modified PVC ultrafiltration membrane. *Membrane Water Treatment*, **6**, 379-92
- [2] Zheng K., Zhou S.. & Zhou X. (2018). A low-cost and high-performance thin-film composite forward osmosis membrane based on an SPSU/PVC substrate. *Scientific reports*, **8**, 10022
- [3] Khakpour S., Jafarzadeh Y.. & Yegani R. (2019). Incorporation of graphene oxide/nanodiamond nanocomposite into PVC ultrafiltration membranes. *Chemical Engineering Research and Design*, **152**, 60-70
- [4] Sabzi Dizajikan B., Asadollahi M., Musavi S. A.. & Bastani D. (2018). Preparation of poly (vinyl chloride)(PVC) ultrafiltration membranes from PVC/additive/solvent and application of UF membranes as substrate for fabrication of reverse osmosis membranes. *Journal of applied polymer science*, **135**, 46267
- [5] Ariono D., Aryanti P. T. P., Hakim A. N., Subagjo S.. & Wenten I. G. (2017). Determination of thermodynamic properties of polysulfone/PEG membrane solutions based on Flory-Huggins model. *AIP Conference Proceedings*, **1840**, 090008
- [6] Ariono D., Wardani A. K., Widodo S., Aryanti P. T. P.. & Wenten I. G. (2018). Fouling mechanism in ultrafiltration of vegetable oil. *Materials Research Express*, **5**, 034009
- [7] Ariono D., Aryanti P. T. P., Wardani A. K.. & Wenten I. G. (2018). *Membrane Water Treatment*, **9** (5), 353-361
- [8] Aryanti P. T. P., Noviyani A. M., Kurnia M. F., Rahayu D. A.. & Nisa A. Z. (2018). Modified Polysulfone Ultrafiltration Membrane for Humic Acid Removal During Peat Water Treatment. *IOP Conference Series: Materials Science and Engineering*, **288**, 012118
- [9] Liu B., Chen C., Zhang W., Crittenden J.. & Chen Y. (2012). Low-cost antifouling PVC ultrafiltration membrane fabrication with Pluronic F 127: Effect of additives on properties and performance. *Desalination*, **307**, 26-33
- [10] Rabiee H., Shahabadi S. M. S., Mokhtare A., Rabiei H.. & Alvandifar N. (2016). Enhancement in permeation and antifouling properties of PVC ultrafiltration membranes with addition of hydrophilic surfactant additives: Tween-20 and Tween-80. *Journal of Environmental Chemical Engineering*, **4**, 4050-61
- [11] Badri A.. & Pouladsaz P. (2011). Highly selective and sensitive thiocyanate PVC membrane electrodes based on modified Zeolite ZSM-5. *International Journal of Electrochemical Science*, **6**, 3178-95
- [12] Behboudi A., Jafarzadeh Y.. & Yegani R. (2016). Preparation and characterization of TiO<sub>2</sub> embedded PVC ultrafiltration membranes. *Chemical Engineering Research and Design*, **114**, 96-107
- [13] Rabiee H., Farahani M. H. D. A.. & Vatanpour V. (2014). Preparation and characterization of emulsion poly (vinyl chloride)(EPVC)/TiO<sub>2</sub> nanocomposite ultrafiltration membrane. *Journal of Membrane Science*, **472**, 185-93
- [14] Zhao Y., Lu J., Liu X., Wang Y., Lin J., Peng N., Li J.. & Zhao F. (2016). Performance enhancement of polyvinyl chloride ultrafiltration membrane modified with graphene oxide. *Journal of Colloid and Interface Science*, **480**, 1-8
- [15] Almeida S. A. A., Amorim L. R., Heitor A. H., Montenegro M. C. B. S. M., Barbosa J., Sá L. C.. & Sales M. G. F. (2011). Rapid automated method for on-site determination of sulfadiazine in fish farming: A stainless steel veterinary syringe coated with a selective

- membrane of PVC serving as a potentiometric detector in a flow-injection-analysis system. *Analytical and Bioanalytical Chemistry*, **401**, 3355-65
- [16] Baker R. W. (2012). *Membrane Technology and Applications*: John Wiley & Sons.
- [17] Wang C., Quan X., Liao M., Li L.. & Zhou J. (2017). Computer simulations on the channel membrane formation by nonsolvent induced phase separation. *Macromolecular Theory and Simulations*, **26**, 1700027
- [18] Mulder J. (1996). *Basic principles of membrane technology*. University of Twente, Enschede: Springer Netherland).
- [19] Ariono D., Aryanti P. T. P., Subagjo S.. & Wenten I. G. (2017). The effect of polymer concentration on flux stability of polysulfone membrane. *AIP Conference Proceedings*, **1788**, 030048
- [20] Aryanti P. T. P., Khoiruddin. & Wenten I. G. (2013). Influence of Additives on Polysulfone-Based Ultrafiltration Membrane Performance during Peat Water Filtration. *Journal of Water Sustainability*, **3**, 85-96
- [21] Aryanti P. T. P., Subagjo S., Ariono D.. & Wenten I. G. (2015). Fouling and Rejection Characteristic of Humic Substances in Polysulfone Ultrafiltration Membrane. *Journal of Membrane Science and Research*, **1**, 41-5