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# Polysulfone Filtration Membranes with Polyvinilpirrolidone (PVP) Additive for Batik Wastewater Treatment

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## ABSTRACT

The development of the batik industry in Indonesia has not been followed by adequate wastewater processing. Most of the batik producers dispose of their wastewater directly into the surface water. In this study, an effort to treat batik waste using a membrane was conducted by evaluating the Polysulfone-based membrane and feed pressure on the membrane filtration process on the ability to remove the impurities such as chemical oxygen demand (COD), total dissolved solids (TSS), Color (Pt-CO), total dissolved solids (TDS), and conductivity. The polysulfone-based flat membrane was prepared using a composition of Polysulfone (PSf), polyvinylpyrrolidone (PVP), and N-methyl-2-pyrrolidone (NMP) as a solvent of 14.7, 0.3, and 85% (w/w), respectively. The membrane produced was characterized using SEM, FTIR, and contact angle measurement. The membrane filtration process was conducted by varying the feed pressure at around 4, 5, 6, and 7 bar. The experimental results showed that the lower the feed pressure, the higher the rejection of COD, color (Pt-Co), TDS, and conductivity. The highest rejection percentages at a pressure of 4 Bar for COD, color, TDS, and conductivity were 27.51, 28.06, and 24.29%, respectively. Meanwhile, the feed pressure did not significantly affect the permeated *p*H of the wastewater.

*Keywords*: Batik wastewater, membrane characterization, PSf, PVP, rejection

## 1.0 INTRODUCTION

Clean water is a vital necessity for the survival of life, so that various efforts are created to treat and purify water, especially those polluted by industries. One industry that produces wastewater in large amounts is the Batik Industry. Batik is a traditional cloth typical of Indonesia. The process of making Batik usually requires wax and dyes to make motifs and provide various colors to the Batik cloth [1]. The most waste produced in the Batik-making process is waste releasing wax in water with high temperatures [2]. The waste parameters produced by the Batik industry are COD, BOD, TSS, TDS, dyes, and metals [3]. Various conventional waste treatment methods are available such as activated sludge [4] and anaerobic biological [5] methods, but the methods have their respective drawbacks. To overcome the disadvantages of conventional wastewater treatment, an effective method is needed to be applied in water purification, one of which is the membrane filtration process. The membrane filtration process is often chosen for economic and environmental reasons. However, membranes' use has a drawback, namely, the time limit for use because there is the possibility of fouling the membrane [6]. This can be overcome by selecting the appropriate membrane material. Therefore, membrane

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preparation was conducted to modify the material to obtain a membrane structure with the appropriate morphology for the desired separation process in this study.

The membrane materials commonly used are polysulfone, polyvinylidene fluoride (PVDF), polyamide, and cellulose acetate. Cellulose acetate, polyamide, and polysulfone have a typical porosity of 80%, 82%, and 83%, respectively. Compared to PVDF and cellulose acetate, polysulfone is more resistant to alkaline solutions suitable for batik waste [7]. However, polysulfone membranes have antifouling ability and low membrane flux values due to their low hydrophilic properties [8]. Hydrophilic polymers' addition to the printing solution is often done to increase the membrane's permeability and antifouling ability. PVP is used due to its solubility in various solvents [9]. Research states that PVP has non-solvent properties that accelerate the de-mixing process and suppresses macro pore- forming properties that inhibit de-mixing [10]. In addition, it is important to have a suitable solvent for the polymer used. Solvents commonly used for polysulfone include n-methyl-2-pyrrolidone (NMP), n,n-dimethylacetamide (DMAc), and dimethylformamide (DMF) [11]. Based on the relative energy difference (RED) parameter developed by Hansen and Skaarup, NMP, DMAc, and DMF, each has RED values of 0.7, 0.9, and 1.0 for polysulfone RED <1 indicates a suitable solvent. With these polymers and the solubility increases as RED approaches zero [12]. Therefore, NMP was chosen in this study, as it has a high solubility with polysulfone. Another characteristic of NMP is that it is non-toxic and dissolves in water [13]. Water is used as a non-solvent because it is environmentally friendly and cheap [14]. The membrane preparation method applied depends on the membrane material selected. Asymmetric membranes can be created using various phase inversion techniques, such as solvent evaporation, precipitation from the vapor phase, precipitation via controlled evaporation, thermal precipitation, and immersion precipitation. The technique used in this study was immersion precipitation, which is the most commonly used technique because it allows the manufacture of various membrane morphologies [11]. This study examines the effect of feed pressure in the filtration process on the membrane performance, such as COD, TDS, conductivity, TSS, and color removal efficiencies.

## 2.0 MATERIALS AND METHODS

### 2.1 Materials

The materials used in the study, such as Polysulfone (PSf, UDEL P-1700 NT11) as a base polymer was provided from Solvay, USA. N-methyl-2 pyrrolidone (NMP) and Pt-CO color standard were purchased from Merck. Co. Polyvinyl pyrrolidone (PVP, Mw: 40000 g/mole) as an additive was provided from Sigma Aldrich, and COD digestion vials (Low range, pk/150, method 8000) provided from HACH, USA. The Batik waste was provided from Batik Industry in Tegal, Indonesia.

### 2.2 Membrane Preparation

The membrane was prepared by the phase inversion method. NMP was put into Erlenmeyer, then PSf and PVP were added slowly at 25 $^oC$ with stirring at a speed of 200 rpm. The composition of PSf, PVP, and NMP is 14.7, 0.3, and 85% (w/w), respectively. The %weight of PVP is 0.3% due to

PVP's large molecular weight used in this study. It is also proved that with a small percentage and large molecular weight, PVP has the ability to form pores in the PSf membrane. Stirring was continued by increasing the temperature to 60 °C and stirring speed of 300 rpm until the polymer was completely dissolved. The stirring speed was then increased to 500 rpm for 5 hours. The solution was allowed to stand at room temperature for 1 hour to remove any air bubbles. The dope solution is then poured and flattened on a glass plate and left to stand for 8 minutes. The layer formed along with the glass plate is then immersed in a coagulation bath filled with pure water for one night. The layers were immersed in 50% ethanol solution for 1 hour, then in 96% ethanol for 30 minutes. Finally, the membrane formed was dried at room temperature.

## 2.3 Membrane Characterization

Membrane characterization aims to determine the morphology, functional groups, and hydrophilicity of the membrane surface. The membrane surface morphology analysis was carried out using a scanning electron micrograph (ZEISS Ultra 60), where the sample was coated with Au and then observed at an excitation voltage of 15 kV. Functional group analysis was performed using attenuated total reflectance Fourier transform infrared (ATR-FTIR, Nicolet ™ iS50) with a NIR module and a wavenumber range of 600 - 4000 $cm^{-1}$. Meanwhile, to determine the membrane surface's hydrophilicity, a contact angle analysis was performed with three repetitions using deionized water drop, and the degree of water contact angle was measured using an angle meter.

## 2.4 Wastewater Pre-treatment

Pre-treatment is conducted on the wastewater prior to processing in the membrane filtration using the coagulation-flocculation method at *p*H 4 with 500 ppm of poly aluminum chloride (PAC) coagulant. After the coagulation process, the waste is filtered and neutralized to *p*H 7. The sediment that appears during the neutralization process was filtered again, and the filtrate was analyzed for COD, TDS, TSS, conductivity, and color (Pt-Co).

## 2.5 Membrane Performance Test in Batik Wastewater Treatment

The prepared membrane was then tested for its performance by the membrane filtration process in the Batik wastewater treatment. The membrane filtration processes were conducted at a pressure of 4 to 7 bar. The membrane's diameter, membrane-active area, and membrane thickness are 3.6 cm, 10.17 $cm^2$, and 55.5 µm, respectively. The pure water and batik wastewater fluxes were calculated by [15]:

$$J = \frac{V}{A.t} \tag{1}$$

Where $J$ is the flux value, $V$ is the permeate volume (mL), $A$ is the effective membrane area ($cm^2$), and $t$ is time (s). The rejections ($R$) of COD, TSS, TDS, color (Pt-Co), and conductivity were calculated by [16]:

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

$C_p$ and $C_f$ are the parameter concentrations in the permeate and the feed, respectively.

## 3.0 RESULTS AND DISCUSSION

The SEM characterization results are shown in Figure 1, where the membrane's pore size ranges from 0.57 to 1.72 µm. The addition of PVP in the membrane materials increases pores' formation on the outer surface, whereas due to its hydrophilic properties, PVP can migrate from one point to another. This migration helps pore formation and can cause two or more pores to coalesce to form a large pore. The addition of PVP to the dope solution causes an increase in the number of pores on the membrane surface due to more solvent and solute exchange space [17-19]. In this case, the thermodynamic influence on the addition of PVP is more dominant; thus, the demixing process increases and accelerates pores' formation in the membrane [20]

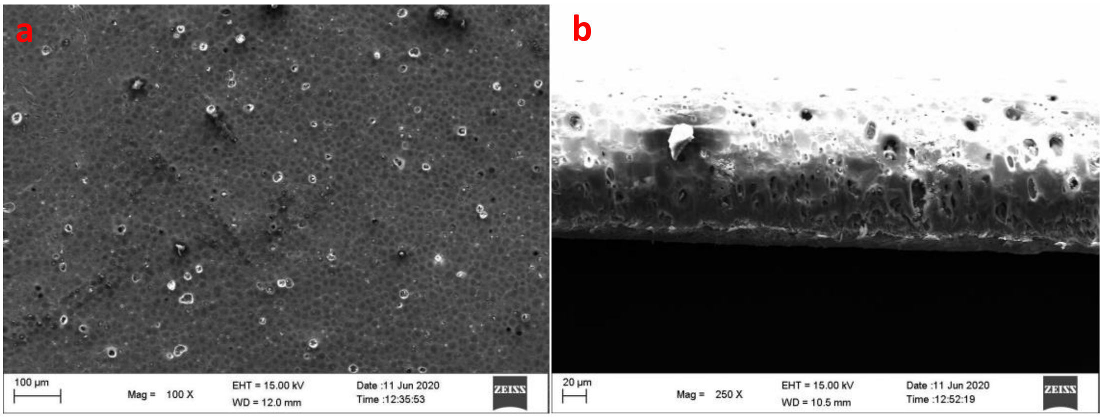

**Figure 1** SEM characterization results (a) Membrane surface with 100 times magnification (b) Cross-section of membrane with 250 times magnification

The result of the FTIR characterization is shown in Figure 2. The peaks at wavelengths of about 1681 $cm^{-1}$ and 1161 $cm^{-1}$ indicate carbonyl (C = O) and amine (C-N) groups, respectively. These groups' existence indicates that there is PVP trapped between the polysulfone films [11]. Basically, the polysulfone membrane surface has hydrophobic nature due to aromatic compounds' bonds [18]. However, the addition of PVP additives can reduce the hydrophobic properties of the polysulfone membrane surface. Base on the contact angle measurement as presented in Figure 3, the PSf/PVP membrane is hydrophilic due to PVP, which has a hydrophilic functional group, so that the addition of PVP to the dope solution increases the hydrophilic properties of the membrane [21].

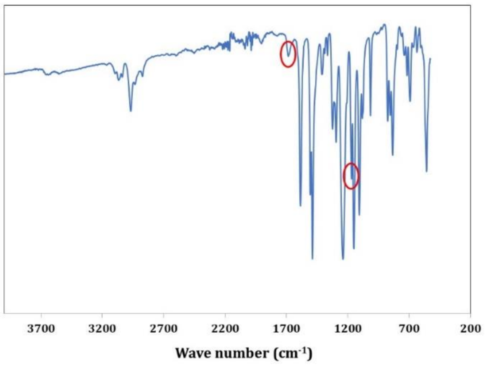

**Figure 2** FTIR characterization results of PSf/PVP membrane

Pretreatment of batik wastewater succeeded in reducing impurities in all parameters except TDS, as shown in

Table 1. The *p*H adjustment caused the increase in TDS after pretreatment, which caused salts' formation due to acid addition to the previously alkaline waste. The same phenomena also happened when setting the wastewater to *p*H 7; salt formation causes flocs, increasing TDS, TSS, conductivity, and color, respectively. The increase in conductivity also occurred due to changes in the *p*H of the pretreatment process. The *p*H adjustment was made by adding strong acids and strong bases, so that increased the conductivity. Table 1 shows that the wastewater pretreatment can drastically reduce COD, TSS, and color by 86.8, 95.6, and 95.2%, respectively.

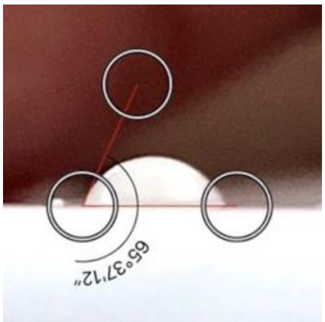

**Figure 3** Contact angle measurement of PSf/PVP membrane

**Table 1** The results of batik wastewater treatment process

| **Parameter** | **Initial wastewater** | **After coagulation-flocculation process** | ***p*H 7** | **After filtration** | **%Reduction for pre-treatment** |
|---|---|---|---|---|---|
| COD (mg/L) | 5100 | 1100 | 1215 | 674 | 86.8% |
| TDS (mg/L) | 2200 | 2250 | 2670 | 2590 | -17% |
| TSS (mg/L) | 700 | 325 | 362 | 3 | 99.5% |
| Conductivity (S/m) | 4.2 | 4.39 | 5.34 | 5.18 | -23.3% |
| Color (Pt-Co, mg/L) | 8500 | 378 | 405 | 405 | 95.2% |
| *p*H | 9.40 | 4.09 | 6.99 | 7.00 | |

The permeate flux of pure water and batik wastewater in the membrane filtration process is shown in Figure 4. The higher the pressure, the higher the permeate flux due to the increased driving force for water to penetrate the membrane pores [22]. Figure 4 shows that the presence of impurities in batik wastewater has reduced the water flux by about 80% on average.

Figure 5 shows the membrane rejection to COD, color, TSS, TDS, and conductivity, where the largest rejection was at a pressure of 4 bar. Figure 5 also shows the *p*H of the water produced in the membrane filtration process. The decrease in the COD rejection with the increase in feed pressure is caused by the more chemical substances present in the batik wastewater, which can penetrate the membrane pores into the permeate stream due to the increase in the driving force. The COD of water produced from the membrane filtration process at a feed pressure of up to 7 bar still not meets the National Environmental Quality standard, which is below 200 mg/L, while the lowest COD produced was 265 mg/L. As with COD, color rejection decreased with increasing feed pressure. At a pressure of 4 bar, the highest color content removal occurred according to the COD removal parameter due to the dye is also the cause of the high COD in the batik wastewater. The TSS was completely rejected in the membrane filtration process as the TSS in the wastewater was mostly removed in the pretreatment process, indicating that the membrane could resist the suspended solids not to penetrate the membrane pores [23]. The *p*H of the water produced in the membrane filtration process is relatively constant to the feed pressure because the membrane pores are still too large to filter out ions that affect *p*H.

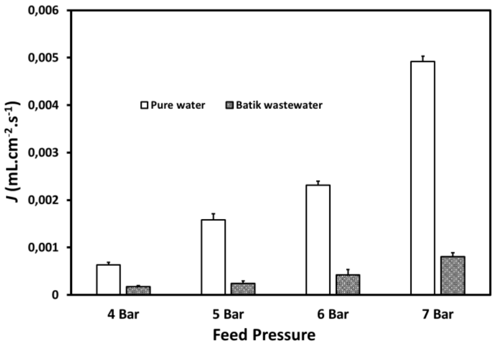

**Figure 4** Water flux for pure water and batik wastewater in membrane filtration process

Experimental results show that for all pressures, the TDS rejection and conductivity are extremely low. TDS has a direct relationship with conductivity as the TDS includes salts in wastewater that affect the conductivity. The filtration process through membranes other than Nanofiltration and reverse osmosis has a pore size that is too large to remove low molecular mass compounds and salts, so it cannot reduce the TDS and conductivity [24]. TDS rejection and conductivity by the membrane occurred because the membrane has PVP that is not completely dissolved during the demixing process and is left in its pores. PVP can bind and form colloid suspensions with salts such as sodium carbonate and sodium phosphate, often used during the batik coloring process. This results in retained TDS by interacting with PVP rather than across the membrane. The highest TDS and conductivity rejections were 24.3% at the feed pressure in the membrane filtration process of 4 bar, while the lowest TDS and conductivity rejections were 1.3 and 2.2%, respectively, at a feed pressure of 7 bar. The differences in Batik waste before and after the membrane filtration process can be seen in Figure 6.

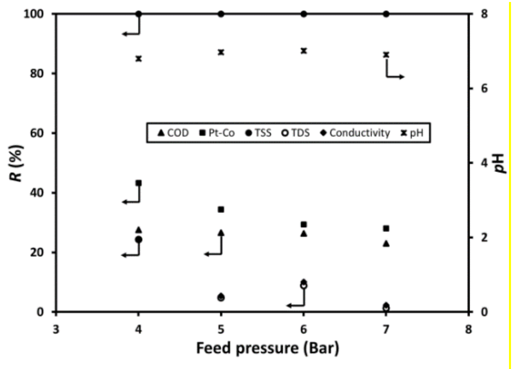

**Figure 5** Variation of COD, Pt-Co, TSS, TDS, and conductivity rejections and *p*H with pressure

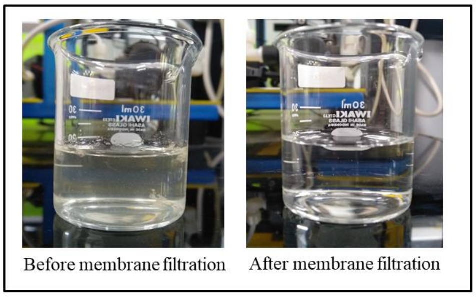
Before membrane filtration After membrane filtration

**Figure 6** Left: Batik waste before membrane filtration (after pre-treatment). Right: Batik waste after membrane filtration

## 4.0 CONCLUSION

Adding PVP to the dope solution in the membrane preparation process is to accelerate the demixing process due to the hydrophilic nature of PVP (thermodynamic effect) and increase the solution's viscosity (kinetic effect). The faster demixing causes pore formation and increases the hydrophilic properties of the membrane. In the membrane filtration process, the higher the pressure applied, the higher the driving force for mass transfer, and the more particles that can pass through the membrane pores, which increases the water flux but decreases the rejection of COD, color, TDS, and conductivity. Meanwhile, the feed pressure did not significantly affect the produce water's *p*H in the membrane filtration process.

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