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# Performance of Polysulfone/PANI Membrane for Humic Acid Separation

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The effect of polymer mixed matrix membrane was investigated by mixing Polyaniline (PANI) in Polysulfone (PSf) membrane for humic acid separation. The purpose addition of PANI in PSf was to improve the membrane hydrophilicity and increase membrane permeability The membrane preparation was undergo phase inversion method at high concentration of PANI (0-15 wt.%). The characterization and performance of the membrane were evaluated in respect to membrane hydrophilicity, pure water flux and rejection properties against humic acid. The result showed that by blending PANI in PSf membrane, the contact angle decreased up to 17 %. This result indicate that addition of PANI improve surface hydrophilicity of membrane. Meanwhile, the addition of PANI increased membrane permeability up to 84 %. The rejection properties also improved up to 25 %. According to the membrane hydrophilicity and the performance against humic substance, PANI has a strong potential to be used as an additive in membrane fabrication.

## 1. Introduction

Humic acid is one of many substances which are available in river water. It is generally displays macromolecular characteristics from a subclass of humic substances. It contains both hydrophobic and hydrophilic moieties and numerous substance capacities, for example, carboxylic, phenolic, carbonyl, and hydroxyl gatherings associated with the aliphatic or fragrant carbons in the macromolecules. Yunos et al. (2013a) reported that the properties of humic substances are depending on the sources of humic acid which is degradation product from plants, creature residue and microorganism's activities. The presence of humic acid in water will discolour the water to brown or black.

Nowadays, membranes can be used for many different types of water filtration applications. It acts as a physical barrier that permits certain compounds to pass through (Harun et al., 2013a). It is depending upon their physical and chemical properties. It regularly comprises of a porous support layer with a dainty thick layer on top that forms the actual membrane (Saini, 2014). According to Yunos et al. (2013b), membrane process only need a low space and its separation process will not change the water phase. Membranes are used on large scale industrial effluents and recover valuable constituents, to concentrate, purify, or fractionate macromolecular mixtures in the food and drug industries, and to separate gases and vapors in petrochemical processes. They are also key components in energy conversion and storage system, in chemical reactors, in artificial organs, an in drug delivery devices.

It is strongly agreed that water treatment using membrane filtration is one of the best method in order to reduce carbon footprint in our surrounding. Furthermore, Mehrparvar et al. (2014) reported that the ultrafiltration (UF) method is commonly used by researcher because it can removed all humic substances and some viruses. UF is the separation process of very small particles and dissolve molecules from liquids. The important factor for

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separation is molecular size. Moreover, the permeability of a filter medium will be affected by the chemical, molecular or electrostatic properties of the sample in all filtration applications (Kumar et al., 2015). Jamalludin et al. (2013) also reported that However, high concentration of inorganic additives will lead to increase surface roughness and reduce water permeability due to pore blockage.

In recent decades, there are a lot of researches on improving membrane surface to improve membrane hydrophilicity. The membrane surface modifications utilizing grafting, plasma, and blending technique with hydrophilic polymer or nanoparticle were produced with excellent result. Among those techniques, polymer blend is less complicate method to improve membrane separation. The design of polymer blends constitutes an interesting alternative to improve membrane hydrophilicity. According to Jaymand (2013), it is reported that the cost of membrane blending is quite reasonable and it is free from time-consuming procedures.

In this study, PSf membrane surface will be improved by blending hydrophilic PANI in PSf dope solution. PSf need to be modified to reduce membrane fouling with the hydrophilicity properties of PANI (Harun et al., 2013b). However, there are limit number of studies that investigate the behaviour of PANI in PSf membrane. Thus, the influence of PANI concentration in PSf membrane were investigated in respects to its chemical properties, permeability and rejection against humic acid.

## 2. Details Experimental

### 2.1 Materials and Procedures

In this study, Polysulfone (PSf) has been used as the base polymer in the membrane casting solution and N-methyl-2-pyrrolidone (NMP) acts as the solvent. Polyaniline (PANI) has been chosen as an additive and Polyethylene glycol (PEG) act as pore former agent. The concentrations of PANI used are as follows: 0 wt. %, 5 wt. %, 10 wt. % and 15 wt. %. The flat sheet membranes were prepared via phase inversion method. The solution was poured on a glass plate and the casting process occurs on the glass plate using a casting steel knife. In order to get wet thin films on average 0.10 μm to 0.14 μm thickness, the membrane was exposed to air for 30 s, and immersed in a coagulation bath of distilled water for a few seconds. All of the membranes were prepared under environmental humidity of 60 % at room temperature of 25 °C.

### 2.2. Membrane Evaluation

The performance of PANI membrane was conducted by using three different tests on the samples. At this stage, the sample of membrane went through each test and the performance of it was clearly seen after the result came out. Each test has shown variety of different features at each sample. Below are some general explanations about the test for this membrane evaluation.

The characteristics of hydrophilic and hydrophobic of membrane were investigated by using contact angle measurement. This test was conducted using VCA Optima contact angle machine. The measurement of contact angle as a primary data, which indicated the degree of wetting when the solid and liquid interact is call as a wet ability studies. Small contact angle which is less than 90 is in a hydrophilic property while more than 90 degree is in the hydrophobic properties. The membrane was cut into 5 cm x 2 cm. 2 μL of water were injected onto the membrane surface to measure the degree of contact angle. After the water drop to the tip of the needle, the position of the moving plate was adjusted to fit with the scale in the screen monitor. Image was captured and the measurement of angle was recorded. This testing had been repeated for 5 times to minimize the experimental error. Average values were calculated to take the result.

The water permeability test of the membrane was measured by using UF/NF Membrane Permeation Testing Unit. The test was conducted to examine permeation flux and rejection. The sample will be cut into disk-like shapes and then will be placed in the glass between two rubber rings. The distilled water were use during pure water flux testing while the rejection test were conduct using humic acid. This permeation test has been done with constant hydrostatic pressure. At the beginning of the testing, the pressure used is about 0.3 MPa until the flow of distilled water in a steady state condition. Then, slowly drop the pressure to 0.1 MPa to determine the value of pure water flux and rejection process. Record the result in every 10 minutes. The permeation water flux was calculated using the Eq(1) and to calculate the rejection flux, the formula used as in Eq(2):

$$\mathrm{PWF} = \frac{Q}{A \times \Delta T} \quad (1)$$

Where PWF is the permeation water flux, ($Lm^{-2}h^{-1}$), Q is the permeate volume (L), A is membrane areas ($m^2$) and Δt is the time interval (s).

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

Where $C_p$ and $C_f$ are retentive of permeate and feed.

## 3. Results and Discussion

### 3.1 Contact Angle Analysis

Figure 1 shows the result of contact angle result for the four membrane samples with different content of PANI. The result shows that contact angle of membrane is reduced as concentration PANI increases. This is due to the presence of PANI that enhances the hydrophilicity of the PSf membrane. This result is in line with Razali et al. (2014) where the hydrophilicity increases with the addition of PANI. Yunos et. al. (2014) also reported that the mechanisms and causes of fouling that strongly depend on the membrane surface characteristic which is the hydrophilicity, charge and roughness that have been well reported.

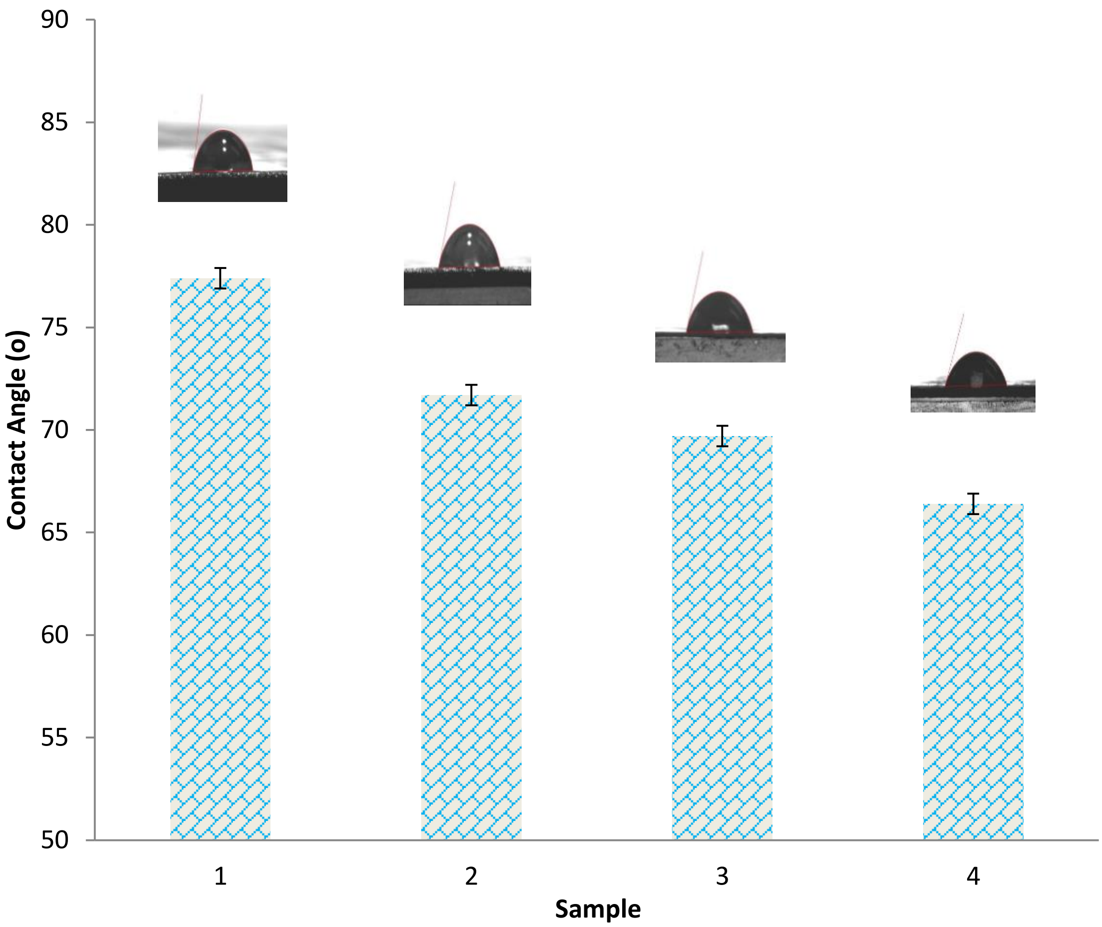


*Figure 1: Contact Angle result*

### 3.2 Water Permeability Analysis

Figure 2 demonstrates the increment of membrane permeability properties with addition of PANI from 5 to 10 g (sample 2 and 3). This increment of membrane permeability is led by the improvement of hydrophillicity on membrane with addition of PANI which was discussed in previous section.

The hydrophilicity membrane increases with addition of PANI gradually reduces surface tension between water and membrane. This reduction increases absorption rate of water molecule on membrane. This result is in line with Zhu et al. (2015) where the increased membrane roughness with the presence of PANI will increase membrane surface area which allowed more way for water molecule to permeate trough membrane. According to Fan et al. (2008), PS/PANI nanofibers blended membranes had higher influence on pure water flux result. The increased of porosity allowed more water to be transported inside the membrane. The result is in line with where blended membranes had better hydrophilicity, thus increase water permeability.

However, addition of PANI at 15 g (sample 4) reduced water permeability. This result might be due to pore blocking of membrane surface due to the presence of PANI. Although the hydrophilicity and membrane roughness increases, membrane pore blocking limited the number of channel for water to be transported in a membrane. Hence, it reduces membrane permeability. Costa et al. (2005) also reported that in the more permeable membranes was fabricated, the convection fluxes overcome in several orders of magnitude. Thus, the back diffusion fluxes and this together with the decrease of membrane/humic solutes interactions results in humic acid deposition and leads to flux decline.

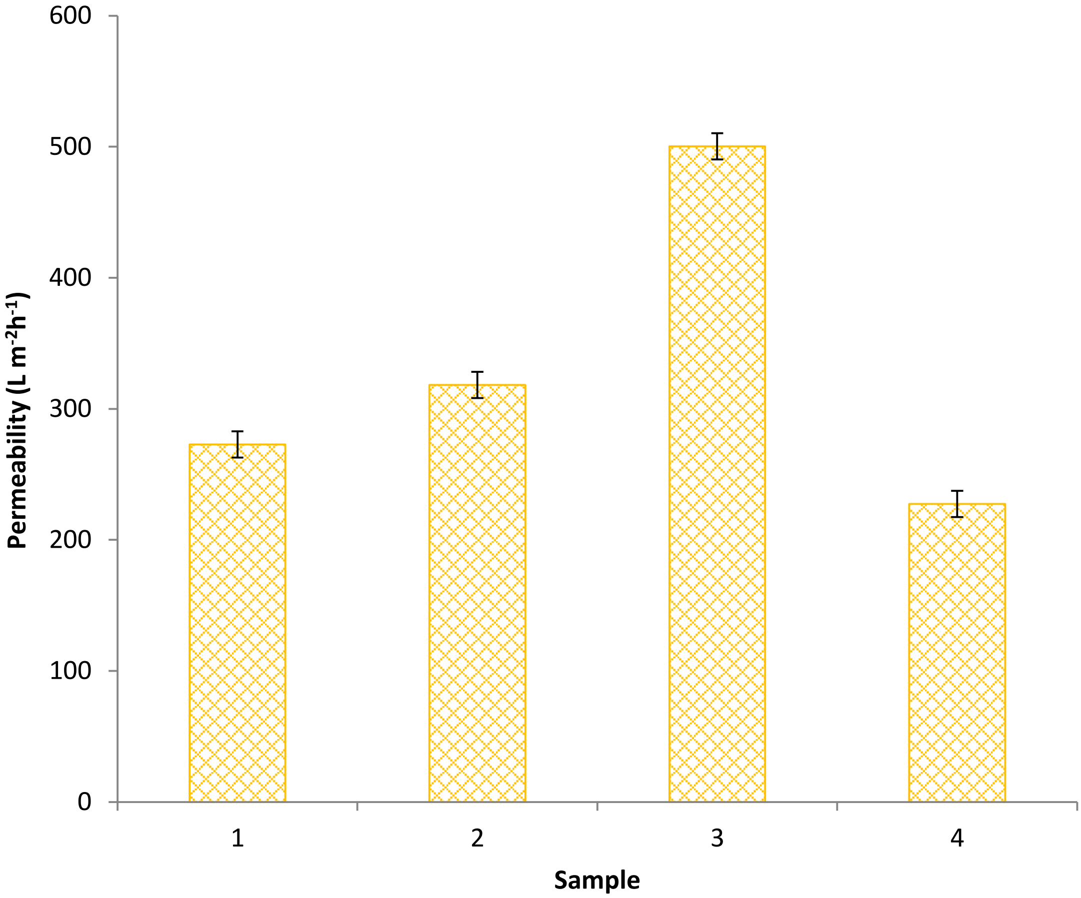


*Figure 2: Water Permeation Result*

### 3.3 Rejection Analysis

The rejection test was carried out using 100 mg/L humic acid as a waste water to be filtered by membrane. The influence of PANI concentration in PSf membrane is shown in Figure 3. As shown in the figure, membrane rejection increases up to 25 % at 15 g PANI in PSf membrane as compared to pristine PSf membrane. This result shows that the porosity of the membrane was reduced as increasing the amount of PANI. This result is in line with Shohur et al. (2013) which the membrane with smallest mean pore size will provide better rejection properties. Apart from that, the flux decline, rejections, flux recovery ratio, and anti-fouling properties of the membranes were significantly enhanced by the membrane modification after blending with PANI (Tokala et. al., 2015).

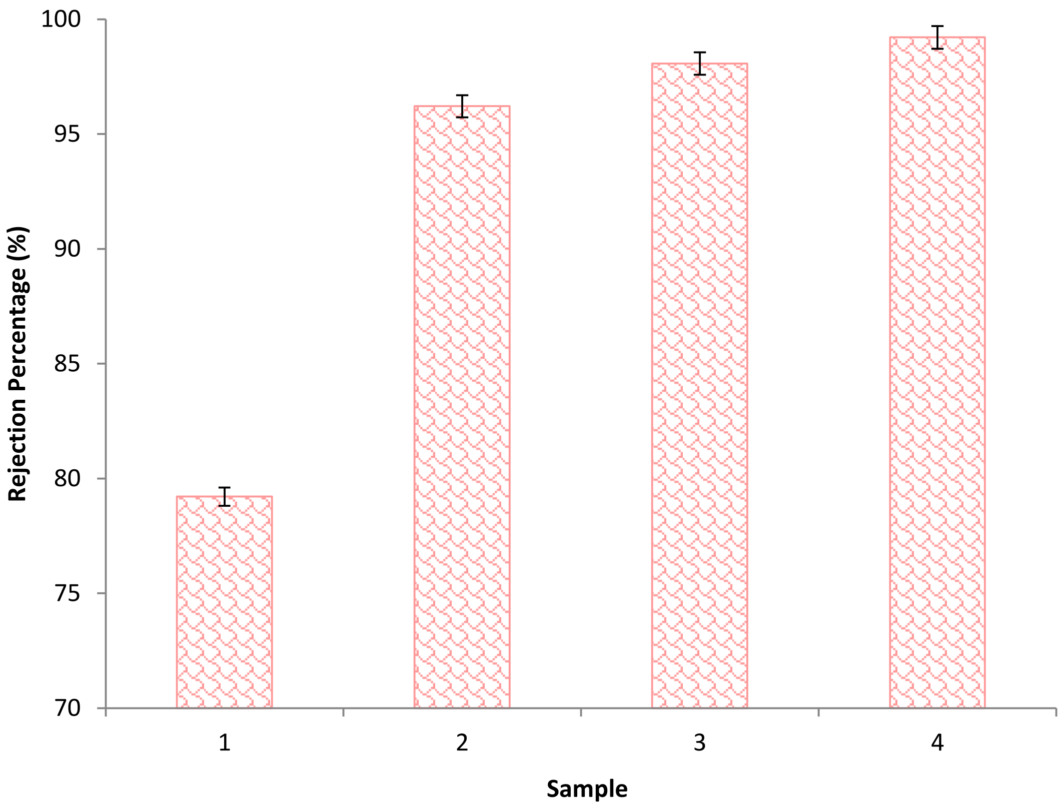


*Figure 3: Rejection test result*

## 4. Conclusions

In this study, the fabrication of PSf membranes containing different concentration of Polyaniline (PANI) was successfully prepared through polymer blending method. Difference concentration of PANI does affect the membrane performance and characteristics. The membrane hydrophilicity had been observed via contact angle measurement. It is found that membrane contact angle reduced significantly with PANI addition. The performance test was evaluated by permeability and rejection test. The result showed that PANI concentration had highly influenced the membrane properties and performance. Membrane permeability and rejection was increased by 84 % and 25 %. Statistical data allow a better and more precise evaluation of the permeation data obtained. From this study, the result strongly suggested that PANI is suitable to be an additive in membrane modification process for water treatment application.

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