Separation of 17β-Estradiol Hormone Using Newly Fabricated Nanofiltration Membrane

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Abstract. Hormones producing organs in animals and humans released naturally occurring chemical messages into their blood stream. The steroidal hormones which is 17β-estradiol produced by animals as well as humans are frequently being eliminate into the environment in their active forms. Recently, as the demand of chickens is increasing, the released of hormone also increased hence endangered the environment. Thus, the concentration of hormones in river need to be determined and poultry wastewater required appropriate treatment. In this study, a newly formulation nanofiltration membrane was fabricated to treat hormones from the poultry wastewater. The polymer polysulfone (PSF) are blend into solvent N-N, dimethylacetamide and polyvinylpyrolidone (PVP) as additive to enhance the hydrophilicity and fouling resistance of nanofiltration membrane. The Sulfonated polysulfone (PSF) was mixed at varying concentrations of polyvinylpyrolidone (PVP) from 1 to 5 %. In this study, major finding was the suitable range of polymer (PSF/PVP) that able to separate 17β-estradiol from poultry wastewater effectively. The result of the study justify that, as the concentration of PSF/PVP increased, the rejection of solute increased while the permeate flux decreased. The nanofiltration membrane able to reject approximately 95% of 17β-estradiol (E2) from the poultry wastewater with the concentration of 17β-estradiol retained is 0.5 ng/L. This was obtained from the optimum concentration of PSF/PVP in the nanofiltration membrane which is 3 %. However, the permeate flux decreased as the concentration of PSF/PVP increased. The evaluations were in order to analyze performances of newly fabricated nanofiltration membrane on the flux rate, estrogens and salt rejection. Therefore, nanofiltration membrane can exhibit the alternative method to enhance the wastewater treatment in terms of hormones separation for poultry industry.

1. Introduction
Rivers act as water resources in various country including Malaysia. However, the river water are exposed to numerous pollutants. Normal detected pollutants were focused on physical, chemical and biological characteristics includes Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Dissolved Oxygen (DO) and Suspended Solids (SS). Other than these pollutants, there are pollutants that can caused cancer and human fertility [1]. These pollutants are hormones excreted from human and animal waste. The sources of steroidal estrogens hormones are originated from natural hormones excreted by animals and humans, active pharmaceutical constituent, waste lagoon, and...
commercial swine [1, 2, 3]. These hormones had entered the natural watercourse and cause vitellogenesis where even at low concentration of 1.0 ng/L it able to develop egg yolk in male fishes. The 17β - estradiol (E2) is the most ample hormones found in poultry wastewater with concentration ranging from 14 to 533 ng/g [1, 3].

Currently, conventional treatment methods are being used to treat poultry wastewater includes aeration, slow sand filtration, and adsorption [3, 4]. However, these conventional wastewater treatments are unable to significantly remove organics that are very small such as the steroidal hormones. The treatments conducted still allow the remaining hormones to contaminate the natural watercourses [3, 4]. Hence, further research need to be conducted to develop treatments for hormones removal to the acceptable limit 0 to 50 ng/L as stated in the World Health Organization (WHO) standard. Membranes separation shows potential and are well known for its extensive application in removal of the steroidal hormones [5, 6]. Membrane materials are vital in membrane fabrication due to its selectivity and permeability. Polysulfone (PSF) are widespread for its broadly application in the nanofiltration membrane as a material in various industrial fields due to its high mechanical strength, chemical stability resistance to compaction and heat, and the ability to implement in an extensive range of pH values [2]. However, the hydrophobic characteristics of a Polysulfone (PSF) membrane may results in the deposition and adsorption of solute on the surface of membrane, which subsequently may causes irreversible fouling that significantly and reduces the membrane permeability throughout the wastewater treatment [4, 5]. Therefore, to improve the efficiency of membrane, Polysulfone (PSF) is blend with polyvinylpyrolidone (PVP) as hydrophilic additive because of the unique of the physicochemical properties to perform as a hydrophilic properties.

2. Experimental Method

2.1. Sampling of Wastewater

The poultry wastewater was taken from Kuala Garing, Rawang Selangor. The initial and final concentration of 17β-estradiol in wastewater were determined using a gas chromatograph (GC-MS) equipped with a split/splitless injector, auto sampler and a 5973-N mass spectrometric detector (Agilent Technologies). The VF-1 ms (Varian), 30m×0.32 mm fused silica capillary column with a thickness of 0.25μm and smeared with a 100% dimethylpolysiloxane in a stationary phase were used to separate the analytes [3]. The temperature was programmed at 70 °C, hold 1 min, to a final temperature of 300 °C and then hold for 2 min. The carrier gas used is Helium at a flow rate of 1.2 mLmin⁻¹ [3]. Injection volume was 1 L and temperature was fixed at 250 °C with a 2 min of splitless time. The MS was operated in electron impact ionization (EI) mode (70 eV). The expected limit of detection by GC-MS for 17β–estradiol is range from 1.0 ng/L to 5.0 ng/L.

2.2. Fabrication of Flat Sheet Membrane

Flat sheet membrane consists of a base support polysulfone integrated with additive polyvinylpyrolidone (PVP) has been mixed in solvent N-N, dimethylacetamide. The PSF/PVP dope solution was placed on a glass plate and cast onto a thin layer by using a glass rod. The flat sheet membrane produced from this process was immersed in coagulation bath full with distilled water under room temperature. The flat sheet membrane was air-dried under room temperature (25°C) for one day. After that, membranes then were cut into round shape at desired diameters to put in a cell for performance testing.

2.3. Characterization of Flat Sheet Membrane

The characterization for several formulations of flat sheet membrane had been conducted by Fourier Transform Infrared, scanning electron microscopic and contact angle analysis. The sessile technics as shown in Figure 1 were used to determine the contact angle of various formulation of membrane. The air dried sample of synthesized membrane was placed in an environmental chamber mounted to the contact angle goniometer. The equilibrium value was taken based on the average value between the left and right side. For the contact angle measurement, 4uL of de-ionized water was tipped onto the membrane surface by micro syringe. After 3s, the value of the water contact angle was recorded.
Triplicate values of contact angle were determined at different positions on the surface of membrane and the averaged values was calculated.

![Contact angle measurement by sessile technic](image)

**Figure 1.** Contact angle measurement by sessile technic

The efficiency of newly fabricated nanofiltration membrane was accessed based on pure water permeation fluxes (PWP) and solute rejection rates (SR) [4]. The concentration of solute which is the feed and permeate were determined by UV Spectrophotometer for salt rejection and gas chromatograph (GC-MS) for 17β-estradiol (E2) rejection.

3. **Results and Discussions**

3.1. **Flat Sheet Membrane Characteristics**

Figure 2 shows the FTIR spectra for membranes from PSF/PVP from various concentrations. The peaks at 1244 cm\(^{-1}\) is refer to C-O-C. While the value of 1488 cm\(^{-1}\) is correspond as CH\(_3\)-C-CH\(_3\) [6]. The presence of various concentration of PSF/PVP as presented stretching of O-H at the broad band of 3200-3500 cm\(^{-1}\). As the concentration of PSF/PVP increased, the intensity of the band also increases. The peak at 1100 cm\(^{-1}\) is a sign to the C-O stretching vibration of additive PVP. The same trend is observed for different PSF/PVP concentration particularly on the intensity of band range 3200 – 3500 cm\(^{-1}\). The significant different was the band at 1100 cm\(^{-1}\), which was more intense and broader as the PSF/PVP concentration increase. This occurrence is due to a cross- linking reaction that resulted in a formation. Furthermore, the subsequent analysis on surface morphology could give an indication on the effect of various PSF/PVP concentrations.

Hydrophilicity is one of the vital properties of membrane surface, hence water contact angle measurement is an appropriate method to determine the hydrophilicity as well as wetting characteristics of membrane [5]. In this study, the separation is dealing with foulant of estrogen, hence, high hydrophilicity of membrane’s surface is desirable. Various PSF/PVP concentration of membranes showed increased in a hydrophilicity, which indicated through lower contact angle value as shown in Table 1. This is due to membranes with addition of PVP as additive able to increase the hydrophilicity unlike polysulfone, which is hydrophobic [4, 7]. The highest hydrophilicity occur for membrane with the incorporations of PSF/PVP 3% due to cross linking reaction that led to exhaustion of hydroxyl group compared to 1 % PVP that are with highest contact angle. This results indicated that the addition of PVP contributes towards improving the hydrophilicity of membrane surface with lower contact angle.
Figure 2. FTIR spectra of membrane at different PSF/PVP Concentrations

Table 1. Contact angle for membrane from various formulation

| Membrane         | Contact angle (°) |
|------------------|-------------------|
| 1% of PSF/PVP    | 75.00             |
| 2% of PSF/PVP    | 50.20             |
| 3% of PSF/PVP    | 47.00             |
| 4% of PSF/PVP    | 53.80             |
| 5% of PSF/PVP    | 52.00             |

Based on Table 2 the SEM image of membrane surface for different PSF/PVP concentrations range from 1 to 5% shows finger like structure of membrane for cross section area. The SEM image of cross-section area also show irregular spacer and more condensed pores as the PSF/PVP concentrations increased. Thus, the decreasing of membrane pore size on thin layer surface and irregular finger like structure of membrane sub layer may results in decreasing of flux with increasing of salt rejection.
Table 2. The morphology of Membrane at different PSF/PVP Concentrations

| Membrane | Scanning Electron Microscopy | Surface | Cross-section |
|----------|------------------------------|---------|---------------|
| 1% of PSF/PVP | ![Image of 1% of PSF/PVP Surface](image1) | ![Image of 1% of PSF/PVP Cross-section](image2) |
| 2% of PSF/PVP | ![Image of 2% of PSF/PVP Surface](image3) | ![Image of 2% of PSF/PVP Cross-section](image4) |
| 3% of PSF/PVP | ![Image of 3% of PSF/PVP Surface](image5) | ![Image of 3% of PSF/PVP Cross-section](image6) |
| 4% of PSF/PVP | ![Image of 4% of PSF/PVP Surface](image7) | ![Image of 4% of PSF/PVP Cross-section](image8) |
| 5% of PSF/PVP | ![Image of 5% of PSF/PVP Surface](image9) | ![Image of 5% of PSF/PVP Cross-section](image10) |

3.2. Performance of Flat Sheet Membrane

Figure 3 shows pure water flux and salt rejection at different PSF/PVP concentrations. The results show that pure water flux decreases at PSF/PVP concentration of 4%. Similar trend was reported where the value of flux decreased when the concentrations increases due to low permeability of membrane was produce at high concentrations [4, 8]. This improved coordination initiating the polymer molecular to compact to each other. Thus, the dense layer thickness increased with the increasing in the PSF/PVP concentrations. On contrary, the salt rejection increased as the PSF/PVP concentration increased up to 3% due the low pore formation on thin surface layer and compact sublayer of membrane. Based on experimental results, the highest salt rejection was 56.8 % at 3% concentration of PSF/PVP. The salt rejection performance be subject to the tighter dense arrangement structure and lower free volume spacer that formed during dry phase inversion at the outer surface of the membrane [9]. Figure 3 concluded that 3% concentration of PSF/PVP as the best formulation for membrane fabrication since it shows optimum flux and salt rejection.
Based on Figure 4, an increasing trend in the percentage rejection of estrogens was observed by increasing the PSF/PVP concentration. The increasing trend was attributed to the denser pore morphology of membrane surface [4, 8]. By comparing between different PSF/PVP concentration, 3% showed a sharp increasing in the of percentage estrogens rejected as compared to 4% and 5% concentrations. Furthermore, at 3% PSF/PVP concentrations, membrane formulation causes excellent rejection of the estrogens (90-100%). The active layer features, such as pore radius and internal surface area, were found to affect the total mass retained and therefore permeates through the membrane [10].

**Figure 3. Performance of Membrane in terms of salt rejection and pure water flux**

**Figure 4. Estrogen Rejection at different PSF/PVP concentrations**

**4. Conclusions**

In summary, the increasing concentration of PSF/PVP in the membrane formulation lead to increasing of estrogen rejection and optimum flux. By increasing concentrations form 1% to 5% of PVP in a dope formulation, enhancement in rejection of estrogen can be observed. The additive PVP that was added to
the membrane formulation has an excellent outcome on the estrogen rejection. Nevertheless, it can be concluded that the fabricated PSF/PVP membrane will provide a pathway for future water and wastewater treatment related to hormonal contaminants and also can be used for application of purification process.

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