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Performance Evaluation of Locally Fabricated Asymmetric Nanofiltration Membrane for Batik Industry Effluent

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Abstract: Batik wastewater contains high concentration of pollutants such as high colour, carcinogenic dyes and toxic heavy metals. Due to low cost operation required as well as high selectivity achieved, separation using membrane technology has becoming promising alternatives to treat coloured wastewater. In this study, locally fabricated asymmetric membrane coded as NF23 was prepared from locally made aromatic polyethersulphone (PES) polymer with 23% of concentration, using N-*Methyl-2-Pyrrolidone* (NMP) and water (H₂O) as solvent and non solvent, respectively. This membrane was prepared using dry-wet phase inversion process; with casting speed of 10 seconds (over 300 mm length) and 50°C coagulation bath temperature with permeability coefficient of 3.64 l/m².h.bar. The membrane was found to be best operated at pH 7.4. The rejection of heavy metals elements such as Mn, Cd and Cu were more than 90%, meanwhile the COD rejection was of about 80%. The molecular weight cut off (MWCO) for NF23 which was obtained from Polyethylene glycol (PEG) permeation experiment was approximately 3000 Da. In spite of the high MWCO, the self-made membranes showed similar or even higher rejections when filtrating dyes and other pollutants from Batik industry effluent, combination with high permeate fluxes.

Key words: Pollutants • Asymmetric • Polyethersulphone • Optimum conditions

INTRODUCTION

Environmental quality recognized as an essential part of our quality of life. Accordingly, we need to undertake great efforts in order to improve the water quality of lakes and rivers. Colored wastewaters contain dyes are mainly from dye factories and textile, pulp and paper and leather industries. The evidence from scientific studies proves that those effluents comprise of hazardous and toxic compounds, which are known carcinogens and probably carcinogens. Textile industries are major water consumers and contribute to the considerable pollution [1].

The rapidly growing textile industries in Malaysia especially in the East Cost of Peninsular Malaysia and Sarawak have contributed positively into government economic. However, the color of the textile effluent is unacceptable under Malaysia environmental regulation besides other parameters such as COD, BOD and total iron and so on [2]. The wastewater from dyeing and rinse in a textile industries are often rich in color, containing residuals of reactive dyes and organic pollutants such as

salt and surfactant and needs proper treatment before releasing into the environment [3].

As been reported by Jiang, colour is the most notorious characteristics of dye wastewater and has a strong negative impact on aquatic environment [4]. Because of dyes can absorb sunlight, plants in the water stream may destroy and the aquatic ecosystem can be seriously affected. The carcinogenic and mutagenic effects of the dyes, heavy metals and other pollutants in textile wastewater have been reported in the [5-7].

Various physico-chemical processes, such as coagulation[8], flotation [9], chemical oxidation [10] and biodegradation like use of activated sludge are conventional treatment processes to remove color and improve water quality. However, the waste compounds contained is very complex and usually present high salinity. Color removal by conventional treatment methods (e.g. ozonation, bleaching, hydrogen peroxide/UV, chemical and electrochemical techniques) was found to be inadequate because most textile dyes have complex aromatic molecular structures that resist

degradation [8]. So far, however, only membrane filtration can solve these problems while also upgrading dye house effluents [12].

Membrane technology is presently an established part of several industrial processes and is a relatively new technology, which can be found in all industrial areas. A membrane is a thin barrier capable of perm-selective mass transport. Advantages of membrane filtration among others are low energy consumption, the separation can be carried out continuously, up-scalling is relatively simple and membrane technology can be used for almost any kind of separation. There are many categories of membrane exists and its classification based on particle's size range; which can be rejecting and driving force. A functional available membranes for liquid separation includes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and dialysis (D). NF is a relatively young description for filtration processes using membranes with a pore size ranging from 1 to 10 nm [1]. It has flux or permeability range from 1.4-12 l/m².h.bar as been reported by Mulder [14] and Baker [15]. This membrane is able to retain a molecules in size range 0.001 µm and particles with molecular weight more than 200 Da in a combination of sieving and sorption diffusion mechanisms [11].

NF membranes separation already has significant industrial applications in the separation of dyes and salts [16] and treatment of wastewater [17]. The practical breakthrough in membrane development is to treat the water which contaminated by batik effluents. In NF, a higher rejection of dyes and other low-molecular-weight organic compounds (200-1000 MW) is achievable [18]. The performance of NF membranes has improved by either changing the chemical composition of the membrane or modifying the membrane surface [19]. The aim of this paper is to evaluate the optimum operating conditions for self-made asymmetric NF membrane to remove dye and other organic pollutants from aqueous solution. This paper will study the optimum conditions in removal color, heavy metals, dyes, COD and pH using synthetic solution.

MATERIALS AND METHODS

Materials: Polyether sulfone (PES Radel A 300) as a membrane material was obtained from Amoco. Reagent grade N-methyl-pyrrolidone (NMP> 98%) was used as solvent and H_2O as non-solvent. Dyes used in this works are Reactive Black 5 (RB5), Reactive Orange 16 (RO16),

Acid Yellow 17 (AY17) and Methyl Orange (MO), supplied by Sigma-Aldrich. Polyethylene Glycol with molecular weight of 200 (PEG200) to PEG3000 were used for MWCO determination. Heavy metals compounds such as Mn(NO₃)₂, Cd(NO₃)₂ and Cu(NO₃)₂ for NF experiments were obtained from MERCK. The pH is adjusted using 0.1M NaOH or 0.1M HCl.

Membranes Preparation: PES was used in this formulation base on the studies that have been done before by some researchers. A specified quantity of PES (23%) was dissolved at 60°C in NMP and de-ionized water (H₂O) until it became homogenous (ternary system). The dope solutions were pouring on glass plates with 150 µm thickness for casting (10s) and were immersed immediately into the coagulation bath (water) at temperature 50°C. This step called dry-wet phase inversion process. After complete coagulation, the membrane was transferred into pure water bath and kept in the water for 1 day to remove residual solvent before transferred into the ethanol solution (post treatment) and dried at room temperature before it ready to use. This asymmetric membrane then coded as NF23 with pure water permeability 3.6434 1/m2.h.bar, having a negatively charged skin layer (0.4 mm) with 1.471 nm of pore radius. The membrane's properties could be obtained using Steric-Hindrance-Pore (SHP) model and Teorell-Meyer-Sievers (TMS) model using salt permeation data. The detailed procedure was explained in references [23, 29, 30].

Permeation Experiment: The performance of the synthesized membrane was studied using a dead end filtration module (SterlitechTM HP4750, USA). The stirred permeation cell was pressurized by nitrogen. To minimize concentration polarization, the feed solution is continuously stirred with magnetic stirrer. Pure water permeation (PWP) was determined with de-ionized water at a constant pressure ($\Delta P=10$ bar) in the room temperature using membranes with an area of 14.6 cm² and diameter was 49 mm. Feed and permeate concentration of the dye, salt and PEG were measured using UV-Vis Spectrophotometer (Thermo Spectronic, USA; model GENESYS 2), CON 510 Bench Conductivity meter (EUTECH MEASUREMENTS) and Shimadzu Total Organic Carbon (TOC) analyzer, respectively while heavy metals were measured using HACH DR/2400 Spectrophotometer. The wavelengths of dyes were 592 nm for RB5, 493 nm for RO16, 390 nm for AY17 and 465 nm for MO.

RESULTS AND DISCUSSION

Effect of pH on Dye Rejection: In order to evaluate the behavior of NF23 for rejection of dye at different pH in wastewater, the filtration of RB5 (anionic dye) was performed and the effect of pH was investigated. Increase or decrease the pH of solution will contribute significant effect on ion rejection in charged membrane where the charge of membrane is also changed [20]. Buffer pH has a direct effect on surface charged of the membrane where only specific value of pH produced suitable conditions to obtain excellent performance [21]. Therefore, this part of study was done to determine the appropriate pH in removing dye and colour at optimum pressure. Figure 1 and 2 show rejection and flux of RB5 at different pH from 3 to 11. As been studied by some researcher, they found that isoelectric point (IP) is approximately pH 4.2 where the membrane charge is near zero [12, 20]. Below this value, membrane is positively charged and above it, the membrane is negatively charged. This finding also been supported by Xu and Lebrun [21] and NF23 also gives the same result where at pH 4 to 8, RB5 rejection increased as pH increased.

This shows that NF23 is in negatively charged. At pH 7.4 the membrane is still negatively charged but as isoelectric point is approached, the repulsion between solution and membrane become less strong due to lower concentration of SO²⁻⁴ [12]. Therefore the permeate flux become higher as can be seen in Fig. 1 (b). From the experiment, it has been verified that for rejection of RB5 until 92.8%, the pH value fixed at 7.4 remain efficient.

Rejection of Color in Dyes: Colored solution with different concentration had been prepared using different type of dyes. Platinum/Cobalt (Pt/Co) Scale (or also known as Apha-Hazen Scale) was commonly used in describing the pollution levels in wastewater. It is specific to the color yellow and is based on dilutions of a 500 ppm platinum cobalt solution. The color range of concentrations from 400 to 1200 Pt/Co has been chosen, based on the previous study on characterization of actual Batik wastewater effluent. For all concentrations, the rejection of color are high which exceeded 90% for $\Delta P=10$ bar. The results presented in Fig. 2 shows higher rejection of color is 93%, obtained at 800 PtCo.

However, flux for color rejection decreased from concentration 800 PtCo which had been reported by Machenbach, where flux decline is caused by colloidal fouling layer of dyes [13]. This situations been affected by accumulated of dyes solute on membrane surface

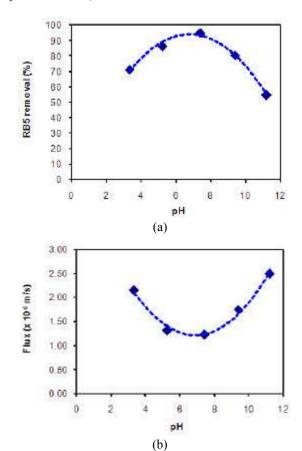


Fig. 1: (a) RB5 rejection versus pH and (b) Flux versus pH using NF23 at $\Delta P=10$ bar

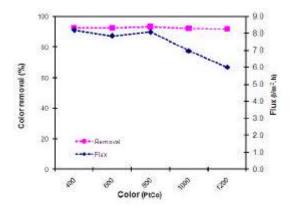


Fig. 2: Color (*PtCo*) rejection using NF23 at different concentrations

which act as additional barrier to increase color rejection but at the same time, lower the permeation.

Heavy Metals Filtration: The next section goes on to investigate the heavy metals rejection as been studied by

some researchers [22-27]. The rejection of different type of solutions contained Mn(NO₃)₂, Cd(NO₃)₂ and Cu(NO₃)₂ have been tested to investigate the performance of NF23 in rejection toxic metals from aqueous solutions. All metals were prepared in different concentrations, which are higher or equal to the standard concentration of discharge (Environmental Quality (sewage & industrial effluent) Regulations, 1979). Calculations of salts rejection were been performed using the *Spiegler-Kedem* equations. Table 1 shows the rejection rates of different heavy metals compounds at 10 bar operated pressure.

As can be seen from the table, all metals had given more than 90% rejection except for Mn at 0.5 mg/l concentration, whereby only 84% rejection achieved. However, concentration after permeate is still under standard concentration and safe to discharge into the river. This findings is also been reported by Saffaj *et al.* [22]. As the metals radius are lower than the estimated pore radius (1.471 nm), they still cannot enter into the pores because of they are partially been retained by surface forces. Thus, the rejection of cations metals are strongly depending on Ion Valence, Hydration Energy and Diffusivity of ions.

Ion Valence: As been reported in the literatures [24, 25], rejection of salts are enhanced with increasing valency of the anion to increase electrostatic repulsion by the negatively membrane.

However, an experiment in this study was been done to compare the rejection of salts when the same anion is associated with different cations. It was found that, for same anion and valence number of cations (at 0.4 mg/l salts concentration), the rejection of Cu²⁺ is much higher than the rejection of Cd²⁺ and Mn²⁺, which is 97.0%, 95.5% and 92.2% respectively. This observation might relate to hydration energy or diffusivity and had discussed below.

Hydration Energy (kJ mol l⁻¹**):** Hydration energy considered as a force, which is necessary to extract the solute from the solvent and push it into the pores. The higher hydration energy of the solutes, the higher it would require an energy to extract and push it into the pores [25]. As can be seen from table above, molecular weight (MW) of Cd²⁺ is higher than Cu². However, Cu²⁺ has higher hydration energy (2105 kJ mol l⁻¹) than Cd²⁺ (1815 kJ mol l⁻¹) and it observed that cations rejection increase with increasing cation hydration energy [24-26]. As hydration energy for Mn²⁺ (1841 kJ mol l⁻¹) is higher than Cd²⁺ (1815 kJ mol l⁻¹), it has lower rejection than Cd²⁺. It could be explain; because of little differences between

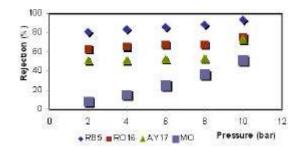


Fig. 3: NF23 membrane performances with different dyes (RB5, RO16, AY17 and MO)

both values, diffusivity effect will take place where it has strong influence than hydration energy for both cations.

Diffusivity (m²/s): The order of diffusion coefficient inversely reflected in the rejection sequence, as been reported by Labbez *et al.* [27], the diffusion coefficient for KCl is much higher than for NaCl, Na₂SO₄ and MgSO₄, a high diffusion contribution can be expected resulting in a lower rejection. In this study, the diffusion coefficient for Cd²⁺ (1.0290×10⁻⁹ m²/s) is lower than for Mn²⁺ (1.4079×10⁻⁹ m²/s) and causes a higher rejection for Cd²⁺.

Dyes Filtration: The results in Fig. 3 shows different dye rejection and this membrane showed an acceptable performance, which are 93.1% rejection for RB5, 75.16% rejection for RO16, 73.15% rejection for AY17 and 52.2% rejection for MO. All three-dye rejections are lower due to smaller size compared to RB5. Solute radius, r_s for RB5, RO16, AY17 and MO are 0.667 nm, 0.5425 nm, 0.516 nm and 0.4107 nm respectively according to the equation; d = 0.065 (MW) $^{0.438}$, where d is diameter (nm) and MW is molecular weight (g/mol) [29]. The difference in solute diffusivity, D_s could be a factor affecting their rejections. The diffusion coefficient for RB5, RO16, AY17 and MO are 4.11×10^{-10} m²/s, 4.88×10^{-10} m²/s, 5.13×10^{-10} m²/s and 6.44×10⁻¹⁰ m²/s respectively. These values are applicable in free solution and were been obtained using Stokes-Einstein equation.

The dye diffusivity in a membrane is generally different due to hindrance and electrostatic interactions between the mobile ions (dye) and the fixed charges (negative) of the membrane[28]. The difference in diffusion coefficient suggests that MO diffuse faster than RB5 in dilute solution.

Rejection of COD at Different Concentration: COD filtration with different concentrations (300 to 1500 mg/l) were done to see NF23 efficiency in rejection COD.

Table 1: Different type of metals rejection, $\Delta P = 10$ bar

				Rejection (%) at Different Concentration (mg/l)				
	Hydration energy							
Salt	(kJ mol l ⁻¹)	MW (g/mol)	Diffusivity (m ² /s)	0.2	0.3	0.4	0.5	0.6
Mn(NO ₃) ₂	1841	54.94	1.4079×10 ⁻⁹	-	95.6	92.2	85.2	-
$Cd(NO_3)_2$	1815	112.40	1.0290×10^{-9}	96.9	96.8	95.5	-	-
$Cu(NO_3)_2$	2105	63.54	1.3048×10^{-9}	97.1	-	97.0	-	91.6

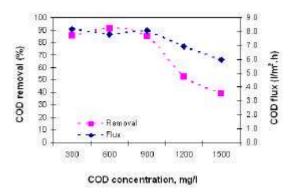


Fig. 4: COD rejection and flux using NF23 (d) at different concentration

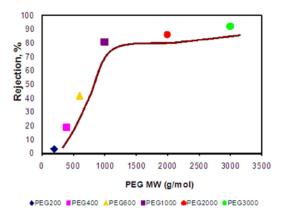


Fig. 5: Molecular weight cutoff curve for NF23(d) performed at 10 bar

Carbon sources from glucose (850 mg/l as COD), acetic acid (150 mg/l as COD) and EDTA (500 mg/l as COD) were dissolved with DI water as 1500 mg/l stock solution. The solution diluted with appropriate volume of DI water to obtain needed concentration of COD [31]. As been shown in Fig. 4, COD permeates for concentration 300 and 600 mg/l are less than 50 mg/l (below the standard of 50 mg/l) which are 86 and 91% of rejection respectively. However, rejection and flux decreased as concentration of COD increased due to fouling on membrane surface. It has been stated that this membrane is able to remove COD for concentration below than 600 mg/l.

MWCO Determination: Figure 5 shows the percent rejection of various PEG's by NF23. The rejection characteristics of NF membranes are typically had expressed in terms of a nominal molecular weight cutoff (MWCO). The MWCO defined as the molecular weight of the species for which the rejection by membrane is greater than or equal to 90 percent [7]. This analysis provides information concerning the rejection of solutes as a function of size, since the molecules are uncharged and assumed to be spherical in nature [32]. As the molecular weight of PEG increases, the rejection also increases, which is to be expected [23]. In this study, membrane NF23 gives 91.88% of rejection results in a MWCO to be approximately 3000 Da.

CONCLUSION

In Batik making process, the wastewaters are often rich in colour and organic pollutants which need proper treatment before discharging into environment. The performances of asymmetric membranes made by phase inversion technique were studied. NF23 had shown a high selectivity property, whereby the rejection of heavy metals and color were more than 90% rejections. The rejection evolution for the different species can be interpreted by taking into account the physical properties or electrical interactions between the ions and membrane charged. The pH value has a direct effect on surface charged and the highest rejection of ion (RB5) obtains at neutral pH around 6 to 8 (7.4). In conclusion, this membrane can be improved in the future for removing color and polluting metallic species especially in effluent produced by Batik industry. This preliminary finding should find interesting application for the treatment of liquid effluents in local industries.

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