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PREPARATION, CHARACTERIZATION AND USED OF POLYSULFONE MEMBRANES FOR THE TREATMENT OF WATER SOLUTIONS CONTAINING HUMIC ACIDS

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ABSTRACT

PREPARATION, CHARACTERIZATION AND USED OF POLYSULFONE MEMBRANES FOR THE TREATMENT OF WATER SOLUTIONS CONTAINING HUMIC ACIDS. Polysulfone (PSf) membranes were cast by phase inversion method using PSf as matrix, N,N-Dimethylacetamide (DMAc) as solvent and distilled water as coagulant. The microporous membrane has studied using Scanning Electron Microscope (SEM) and filtration techniques. The filtration experiments were performed on a flat sheet membrane using pure water and humic acids (HA) solution as feeds. The results show, the Pure Water Flux (PWF) and Product Flux (PF) values decrease with increasing thickness of the membranes. They are consistent with the SEM images that thicker membranes have smaller pore size and less in numbers. The Rejection coefficient (R) values show that the membranes are able to filter HA in the form of solution, with the performance dependent on the characteristics: thickness and microporous structure. They were increased with increase in the thickness of the membranes and with increase in the wavelength from 250-665 nm. It suggests that, the PSf membranes can be used to minimize the amount of Humic Acids from water process to improve the quality of treated to an acceptable quality level.

Key words : Polysulfone membrane, Phase inversion, Microfiltration, Humic acid

ABSRTAK

PEMBUATAN, KARAKTERISASI DAN APLIKASI MEMBRAN POLISULFON UNTUK MENYARING AIR TERCEMAR ASAM HUMAT. Membran Polisulfon (PSf) dibuat dengan metode inversi fase, menggunakan PSf sebagai matriks, *N,N-Dimethylacetamide* (*DMAc*) sebagai pelarut dan air suling sebagai koagulan. Struktur mikroporous membran telah diteliti dengan menggunakan *Scanning Electron Microscope* (*SEM*) dan teknik filtrasi. Teknik filtrasi dilakukan menggunakan membran datar, dengan air murni dan larutan Humic Acids (*HA*) sebagai umpan. Hasil penelitian memperlihatkan, nilai *Pure Water Flux* (*PWF*) dan *Product Flux* (*PF*) penyaringan menurun dengan bertambahnya ketebalan membran. Hasil ini konsisten dengan gambar *SEM* yang diperoleh, bahwa membran yang lebih tebal memiliki ukuran pori lebih kecil dan jumlah lebih sedikit. Nilai koefisien rejeksi (*R*) menunjukkan bahwa membran mampu menyaring HA dalam bentuk larutan, dengan kinerja bergantung pada karakteristik membran seperti ketebalan dan struktur *microporous*. Koefisien rejeksi meningkat dengan bertambahnya ketebalan membran dan dengan bertambahnya panjang gelombang dari 250 nm hingga 665 nm. Ini menunjukkan bahwa, membran PSf dapat digunakan sebagai alat untuk menurunkan kadar *Humic Acids* (*HA*) pada air tercemar *Humic Acids* (*HA*), yang akan diolah, sehingga dapat meningkatkan kualitasnya ke tingkat kualitas yang memenuhi standar.

Kata kunci : Membran polisulfon, Fase inversi, Mikrofiltrasi, Asam humat

INTRODUCTION

Aquatic humic acids (HA) are large organic molecules formed by microbiotic degradation of biopolymers and polymerization of small organic molecules that are derived from soil humus, terrestrial and aquatic plants. It's generally classified as natural organic pollutants, but they need to be removed from the aquatic medium. The presence of HA in a water supply is undesirable for several reasons as they raise the total organic pollution level, color intensity, distinct absorbing capacity and chemical activities. They strongly interact with toxic heavy metals, oxides and clay minerals to form water soluble or insoluble complexes and also interact with organic compounds such as alkenes, fatty acids and pesticides [1-6].

They lead to the formation of biodegradable organic compounds during ozonation and enhance growth of microorganisms within the water distribution systems. Besides these aspects, reaction between aquatic HA and halogen-based oxidants during water chlorination process can cause the formation of trihalomethanes (THM) with potential carcinogenic effects [7-8].

Humic acids have been reported having capability to induce cytotoxicity for many mammalian cells and induce growth retardation and apoptosis of fibroblasts It contains polycyclic aromatic hydrocarbons (PAH) which are toxic and many of them are known carcinogenic and mutagens. Their redox properties are shown to be capable of reducing iron (III) to iron (II) in aqueous conditions over a broad range of pH (4.0-9.0). They are capable to reduce and release iron from ferritin storage to promote lipid peroxidation, then disturb the redox balance and elicit oxidative stress within a biological system [9-11]. Also, HA have been implicated as a causal factor for goiter and bladder cancer [12].

In the past decade, there has been an increasing interest in the application of membrane processes to remove organic and inorganic water pollutants. However membranes have limitations. So, the quest for improvement of removal processes continues. According to the data reported, removal efficiency varies depending on the type of membrane, the structure, the chemical composition and the operation condition [7, 13-16].

Municipal wastewater is one of the most reliable sources of water since its volume varies little through the year. The reuse of such water requires treatment to an acceptable quality level that satisfies regulatory guidelines. Ghayani et al. reported that employed hollow fiber microfiltration (MF) system as a pretreatment for wastewater for reverse osmosis (RO) in the production of high-quality water [17]. UF membranes may also be employed to improve the quality of treated, potable water by removing suspended solids and colloids [18].

Based on those background above, the motivation of this work came from the endeavor to remove HA from aquatic environment using microfiltration (MF) method based on polysulfone (PSf) membrane. The capability of PSf membranes to address water solution treatment containing HA has been evaluated in terms of pure water flux (*PWF*), product flux (*PF*) and rejection coefficient (*R*).

EXPERIMENTAL METHOD

Humic Acids Solution

The extraction and characterization of HA have been reported in somewhere [19]. Humic acids solution, as water pollution model was prepared in distilled water (DW). Around 120 mg of dried HA was dissolved in 100 mL of 0.05N $NaHCO_{3-}$ and then diluted with DW to make a total volume of 10 L.

Membrane Preparation

Polysulfone (PSf) resin was purchased from Aldrich (18,224-3). The average molecular weight is 22,000. The solvent, N,N-dimethylacetamide (DMAc) was purchased from Kemphasol (K04640); the molecular weight is 87.12. A solution of PSf in DMAc was prepared by mixing PSf and solvent and stirring the mixture for 24-48 hours to get a clear solution (dope solution). Dope solution was cast using phase inversion technique [20]. The flat sheet formed membranes were cut into different forms and sizes and were dried before being used as a sample.

Membrane Characterizations

The thickness of membranes was measured using a digital micrometer screw gauge. The thickness obtained was 0.051 ± 0.0025 mm, 0.108 ± 0.0042 mm and 0.163 ± 0.0032 mm.

Scanning Electron Microscope

The surface structure of each membrane was characterized using SEM (SEM, JEOL JSM-6360A). Each membrane in square form and of area approximately 1 cm^2 was coated with gold under vacuum condition by auto fine coater machine (JEOL JFC-1600) to make the membrane conducting and then was examined with SEM.

Flux and Rejection

Dead-end filtration method was used to characterize the pure water flux (*PWF*) of the membranes. Membranes in the form of circles, each of diameter approximately 6 cm, were cut from the dried membranes. They were kept in distilled water (DW) for around 1 hour before being used as a filter.

For the application, the membranes have been exposed to water solution containing HA. The performance of PSf membranes were evaluated in terms of product flux (*PF*) and rejection coefficient (*R*).

Pure water flux and product flux were calculated using Equation (1), and the rejection coefficient (*R*) was calculated using Equation (2). For rejection studies, the following steps were followed. The 10 mL of feed and permeate solution were analyzed using UV-Vis spectroscopy. The curve at 250, 275, 365, 465 and 665 nm wavelengths, which are characterization of HA [1,19] have been standardized to find out the concentration of permeate and feed solution.

$$Flux(J) = \frac{V}{At} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$\text{Rejection}(R) = \left(1 - \frac{C_P}{C_f}\right) x100\% \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

Where :

V = Volume of the permeate (L)
A = Area of the membrane (m^2)
t = Time (h)
C_P = The solute concentration in the permeate(mg/mL)
C_f = The solute concentration in the feed (mg/mL)

RESULTS AND DISCUSSIONS

Scanning Electron Microscope Images

Figure 1 shows the surface structure of PSf membrane using SEM. It was observed that the pore size obtained was in the range 0.03-0.19 μm for the membrane with 0.051 mm thickness, 0.03-0.06 μm for the membrane with 0.108 mm thickness and 0.03-0.05 μm for the membrane with 0.163 mm thickness. The number of pores is more in the thinnest membrane.

SEM images (Figure 1) show that the thicker membranes have smaller pore size and less number of pores. This indicated that more PSf content is present in the thicker membranes, so the solidification becomes slower. Hence, the pore size obtained smaller, lesser in number and also the shrinkage of the membrane is observed. These results are consistent with the *PWF* obtained from each membrane, which decreased with increase in thickness (Figure 2).

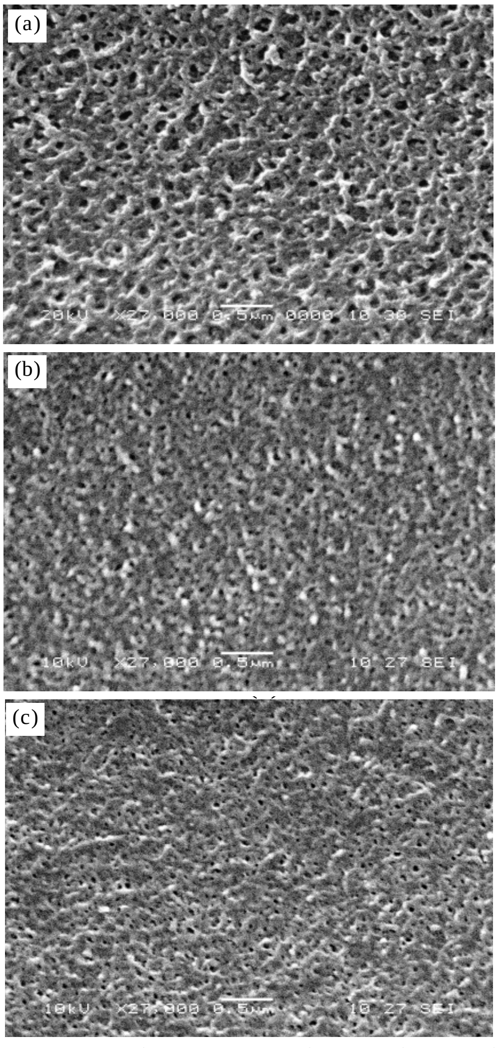

Figure 1. Surface structure of polysulfone (PSf) membranes using SEM: (a) 0.051 mm, (b) 0.108 mm and (c) 0.163 mm

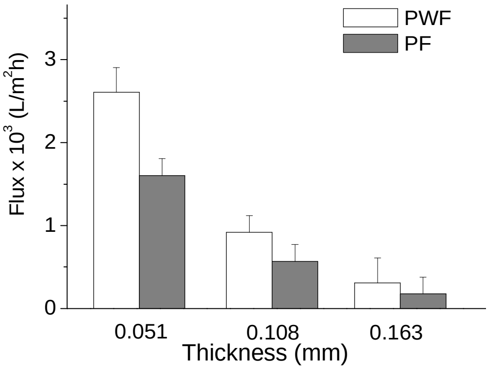

Figure 2. The pure water flux (PWF) and product flux (PF) of three different thicknesses (0.051 mm, 0.108 mm and 0.163 mm) of polysulfone (PSf) membranes

Microfiltration

Pure Water Flux and Product Flux

Figure 2 shows the pure water flux (*PWF*) and product flux (*PF*) of polysulfone (PSf) membranes of three different thicknesses. The *PWF* values show significant decrease with increasing thickness. The decrease was around 65% for membranes with 0.108 mm thickness and 88% for membranes with 0.163 mm thickness as compared with membranes with 0.051 mm thickness. A similar trend was observed for the product flux (*PF*) studies. The *PF* values of membranes decreased as increase in thickness of the membranes. The decrease was around 65% for membranes with 0.108 mm thickness and around 89% for membranes with 0.163 mm thickness as compared with membranes with 0.051 mm thickness.

Rejection Studies

Using Equation (2) and the rejection coefficient (*R*) of membranes has been calculated. The values obtained were shown in Table 1. The rejection coefficient increased as the thickness of the membranes increased. At 250 nm wavelength (*R*-250), the increase was in the range of 61% to 74%, for membranes with 0.108 and 0.163 mm thickness, respectively as compared to membranes with 0.051 mm thickness; similarly were observed at other wavelengths. Also, the rejection values were increased with increase in the wavelength from 250 to 665 nm. At membrane with the thickness of 0.051 mm, the increase was from 8.9% to 130.4%; similarly were observed for the two other membranes (0.108 mm and 0.163 mm).

Table 1. The rejection coefficient (R) values at 250, 275, 365, 465 and 665 nm wavelengths (characteristics wavelengths of HA) for each thickness of PSf membranes

Membranes thickness (mm)	*R* (%)				
	250 nm	275 nm	365 nm	465 nm	665 nm
0.051	8.9 ± 1.2	9.3 ± 1.2	18.9 ± 1	46.2 ± 2.6	130.9 ± 7
0.108	23.0 ± 3 (61%)	23.8 ± 3 (61%)	28.4 ± 3 (33%)	55.4 ± 4 (17%)	152.2 ± 5 (14%)
0.163	34.4 ± 2 (74%)	34.4 ± 3 (75%)	47.3 ± 2.3 (60%)	61.5 ± 3.2 (25%)	163.0 ± 10 (20%)

Note: ( ) is the increase of rejection (*R*) values of each thickness of PSf membranes compared with the thinnest membranes (0.051 mm).

From the rejection (*R*) values of PSf membranes, it can be seen that the performance of each membrane to filter HA varies for each wavelength which is characterization of HA i.e. 250, 275, 365, 465 and 665 nm as shown in Table 1. In general, the rejection values were increased with increase in the thickness of the membranes and were increased with increase in the wavelength from 250 to 665 nm. The highest rejection was found in the highest wavelength (665 nm). This was found in every PSf membranes. This suggests that the compounds with the higher molecular weight (absorbance at 665 nm) [14, 21-23] had been trapped more by the membranes than the compounds with lower molecular weight (absorbance at 465 nm and lower).

CONCLUSION

From the experimental data, the study has demonstrated that microporous PSf membranes prepared by phase inversion method are able to filter HA in the form of solution. The performance of the membranes was found to be dependent on their characteristics such as thickness and microporous structure. It suggests that, the PSf membranes can be used to remove or minimize the amount of HA in the water pollution from process water before filtration by complexation i.e. flocculation/coagulation will be done.

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