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INTEGRATION OF POLYETHERSULFONE AND HYDROXYAPATITE NANOFILTRATION MEMBRANE FOR VANILLIC ACID SEPARATION

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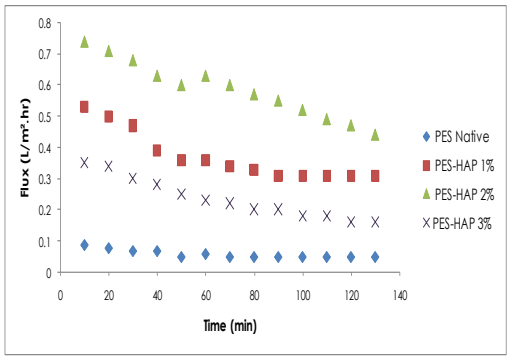
Graphical abstract



Abstract

In this work, the integration of polyethersulfone and hydroxyapatite was studied for vanillic acid separation. The polyethersulfone membranes were modified with hydroxyapatite via in-situ approach in order to enhance the performance of the membrane. The membranes were further characterized concerning permeability, morphology, membrane structural details, porosity and contact angle. The addition of hydroxyapatite in mixed matrix membrane increased the permeation rate from 19.05 L/m2.hr up to 95.76 L/m2.hr due to the increasing of hydrophilicity. The membrane permeability coefficients lie in the range of 1.909 – 10.05 L/m2.hr.bar which were nanofiltration range. The performances of the membrane exhibited higher rejection which showed the vanillic acid rejection up to 69.88% for modified membrane.

Keywords: Hydroxyapatite, polyethersulfone, vanillic acid, phenolic compounds, lignocellulosic biomass

1.0 INTRODUCTION

In Malaysia, oil palm industry generates the largest portion of lignocellulosic waste in the country [2]. Utilization of lignocellulosic waste and recovery value added material will reduce the environmental impact without sacrifying the nutrient recycling process. Phenolic compounds are wide and heterogenous group that are made up of two main groups; hydrobenzoic and hydrocinnamic acid. The interest of phenolic compounds lie on their special function and purpose as antioxidant properties. Hydrobenzoic acids include; gallic, p-hydrobenzoic, protocatechuic, vanillic acid and syringic acids. Hydrocinnamic acids are aromatic compounds which include; caffeic, ferulic, and p-coumaric being the most common. Vanillic acid is one of the phenolic compounds that could be found in plant extracts and abundantly available in lignocellulosic biomass such as empty fruit bunch (EFB) and oil palm frond (OPF). Vanillic acid is one of the most important metabolites in nature that has high functional value added byproducts, which can be used as the precursor for the production of vanilla as well as other important industrial derivatives, such as 5 – nitrovanillic acid and 5 – aminovanillic acid, for antibacterial applications [1].

Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] is a bioceramic whichcomposed of calcium and phosphorus which hydrogen is eliminated at increasing temperature [14]. Its properties include biocompatibility and bioactivity, high stability whether in oxidizing or reducing conditions, chemical stability, high removal capacity, and low water solubility [3][15]. The ion exchange property and adsorption affinity lead to the possesion of high stability and low water affinity that they can behave as both cation exchange media [15].

Membrane separation has emerged as the objective of the current research to perform the fabricated polyethersulfone nanofiltration membrane integrated with hydroxyapatite forming mixed matrix membrane. The HAP will be self – assembled with PES membrane via in- situ approach with varies loading capacity. The addition of hydroxyapatite forming mixed matrix membrane is believed to reduce the irreversible fouling on the surface of membrane by increasing the hydrophilicity of the membrane. The prepared membranes will be characterized using Scanning Electron Microscopy (SEM), contact angle, pure water permeation (PWP) and NaCl Rejection for identifying the membrane structural details via Steric Hindrace Pore (SHP) Model and other kind of approaches. Finally, the prepared membranes will be used for the vanillic acid separation in order to compare the performance of modified and unmodified membranes. The concentration of vanillic acid was quantified using Follin Ciocaltue reagent method.

2.0 METHODOLOGY

2.1 Materials

The chemicals used included; Polyethersulfone was purchased from AMTEC, University Technology Malaysia; Folin – Ciocaltue reagent (Merck,Germany); vanillic acid (Mw = 168g/mol), sodium carbonate, polyvinylpyrolidone, N – Methyl – 2 – pyrolidone was used as solvent (Sigma Aldrich, USA). All the chemicals were obtained from commercial sources and were of analytical grade. Hydroxyapatite was synthesized by wet chemical precipitation method.

2.2 Membrane Preparation

The nanofiltration membranes were prepared by phase inversion techniques. The 100g dope solution was prepared by using PES (19%), N – Methyl - 2 – pyrolidone (74%) and water (7%). The dope formulations for ternary dope solutions were depicted in Table 1. There were 4 types of membranes which include; 1) native PES membrane, 2) PES – HAP 1wt% membrane, 3) PES – HAP 2wt% membrane, and 4) PES – HAP 3wt% membrane. Membrane modification was conducted by adding respective amount of HAP via in – situ approach. 1wt% of polyvinylpyrolidone was added into dope solution as pore – former of the membrane.

Table 1 Ternary composition of dope solutions

Chemicals	Dope 1 (g)	Dope 2 (g)	Dope 3 (g)	Dope 4 (g)
PES	19.0	19.0	19.0	19.0
NMP	74.0	74.0	74.0	74.0
Water	6.0	5.0	4.0	3.0
PVP	1.0	1.0	1.0	1.0
HAP	0.0	1.0	2.0	3.0

The asymmetric flat sheet membranes were prepared by using dry/wet phase inversion techniques using semi – electrically controlled casting machine with 200µm casting knife gap set on the glass plate. The polymer was poured onto a glass plate and spread by using the casting machine. The glass plate with the thin film of composite membrane was then immersed into water bath overnight to produce flat sheet membrane. The membranes were washed further with distilled water to remove excess residual solvents before undergo characterizations process.

2.3 Membrane Characterization

2.3.1 Scanning Electron Microscopy (SEM)

The membrane morphology was characterized by using scanning electron microscopy (SEM) (Model JSM 6380LA) to reveal the cross sectional morphologies of all the fabricated membrane. All the membranes were dried in room temperature overnight and fractured by liquid nitrogen freeze – dried followed by sputtering with a thin gold layer (JFC 1600 Auto Fine Coater). The cross sections of the membranes were viewed under SEM with the x500 magnification applied.

2.3.2 Pure Water Permeation (PWP)

Sterlitech Dead End Permeation Cell, Model P/N HP4750 from Sterlitech Inc. with capacity of 300 ml was used for this experiment. PWP was conducted at different operating pressure ranging from 2 – 10 bars with an effective area of membrane 0.00146m^2. 250ml of distilled water was filled in dead end permeation cell for PWP test. Pure water flux was calculated as follows:

$$Jw = \frac{Q}{A\Delta T} \quad (1)$$

Where, J_w = pure water flux (L/m^2.hr), Q = volume of permeate solution collected (L), A = the effective area of membrane (m^2), T = time (hr)

2.3.3 Wettability

Contact angle was measured by using Contact angle Analyzer in order to characterize the wetting behavior. It was done at Universiti Malaysia Pahang. Every membrane was tested with 10 different points. The average of measured values was taken as membrane's contact angle.

2.3.4 Membrane Porosity

The porosity of the asymmetric membranes was estimated by using the following equation (2).

$$\varepsilon = \frac{wo - wi}{\rho w A H} X\ 100\% \quad (2)$$

Where, ε is the membrane porosity of the membrane (%), w_o and w_i are the weight of dry (g) and wet (g) membrane respectively. ρ_w is water density (g/cm³) while H is the membrane thickness. Porosity was calculated 3 times and the average value was reported. The dry membrane was dried in vacuum oven overnight at 50 °C and weighted.

2.3.5 Structural Parameter Details of the Developed Membrane via Theoretical Approach

Membranes were subjected to permeation test for 0.01 M sodium chloride (NaCl). The experimental data was used to estimate the membrane properties based on theoretical approach. Steric Hindrance Pore (SHP) Model was used to estimate the ion flux (reflection coefficient) inside a charged nanofiltration membrane by considering the steric hindrance parameter as stated by Ismail & Hassan, 2006. Pore radius could be estimated by the availability experimental data. Teorell – Meyer – Sievers model is an approach to describe the membrane electrical properties in term of effective charge density (X_d) and also electrostatic effect (ε). The values can be calculated based on experimental data. The equations can be referred as stated by Ismail & Hassan, 2006.

2.4 Membrane Performance Study

The membrane productivity and separation performance were assessed via vanillic acid separation experiments. 1000ppm of vanillic acid solution was prepared by dissolving vanillic acid powder into distilled water and was stirred overnight. The stock of 1000ppm was preserved at temperature 4 °C and stable to be used for two weeks. 250ml of vanillic acid solution was filled in dead end permeation cell. The flux was measured every 10 minutes within 120 minutes duration of filtration with operating pressure was at 10 bars. The vanillic acid flux was determined as below:

$$J_v = Q/At \quad (3)$$

Where, J_v = Vanillic acid flux (L/m².hr), Q = Volume of permeate solution collected (L), A = the effective area of the membrane (0.00146m²), T = time (0.1667hr).

2.5 Vanillic Acid Analysis

The vanillic acid concentration of retentate and feed solutions were determined using Folin – Ciocaltue method. 1.0mL of Folin – Ciocaltue was added to a 0.2mL sample aliquot. After 3 minutes at room temperature, 0.8mL sodium carbonate was added. The solution was incubated for 2 hours in dark place. The absorbance of the mixture was determined spectrophotometrically at a wavelength of 310 nm using UV-Vis spectrophotometer. The vanillic acids were quantified based on the constructed calibration curve using vanillic acid.

Rejection observation percentage of vanillic acid was calculated by using the below mentioned formulae:

$$\text{Percentages of rejection } R\ (\%) = \frac{Cp}{Cf} x100\% \quad (4)$$

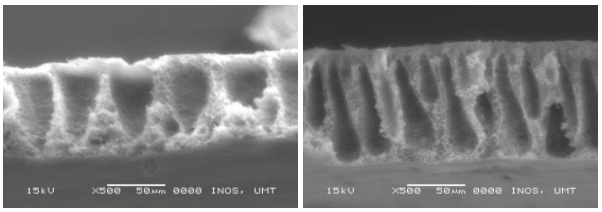
Where, C_p= the permeate particle concentration and C_f = the feed particle concentration.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of PES/HAP membrane

3.1.1 Scanning Electron Microscopy (SEM)

The membranes have asymmetric structures which show the heterogeneous structure compromising of a dense skin layer, a porous intermediate layer and macrovoids at the bottom. The pore size of the membrane decreases from the bottom to top layer of membrane. Based on Figure 1, the most significant difference between native membrane and modified membrane can be seen based on its finger-like structure of modified membrane was much smaller in size compared to the native membrane. Native PES membrane has larger microporous finger – like structure. Addition of hydroxyapatite leads to the increasing of viscosity of the dope solution. Thus, the phase inversion speed delays, resulting in formation of small pores [4].



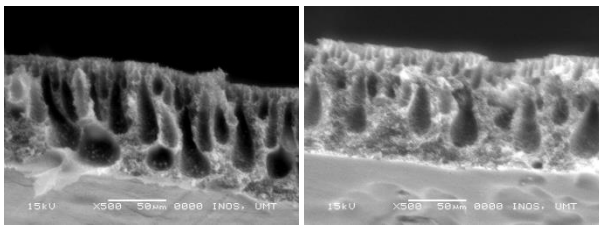


Figure 1 SEM images of 1) native PES membrane, 2) PES – HAP 1%, 3) PES – HAP 2%, and 4) PES – HAP 3% with x500 magnification

3.1.2 Pure Water Permeation (J_w) and Membrane Permeability (P_m)

Table 2 shows the pure water permeation at 10 bars, permeability coefficient and regression values. As the pressure increases up to 10 bars, the flux increased linearly. The membranes were stable at different operating pressure. It was found that the water flux for modified membranes were higher compared to unmodified one under all operating pressures. The pure water permeability as calculated were 1.909 L/m^2.hr.bar, 5.094 L/m^2.hr.bar, 6.612 L/m^{2}hr.bar and 10.05 L/m^2.hr.bar for unmodified and unmodified membranes respectively as shown in Table 2.

Table 2 Pure water permeation at 10 bars, permeability coefficient and the regression values

Membrane ID	PWP (L/m^2.hr)	Pm (L/m^2.hr.bar)	R^2
PES Native	19.05	1.909	0.999
PES-HAP 1.0%	71.06	6.612	0.995
PES-HAP 2.0%	95.76	10.05	0.991
PES-HAP 3.0%	37.56	5.094	0.997

3.1.3 Porosity and Contact Angle

Table 3 tabulated the porosity of the membrane. The most porous membrane was PES-HAP 2.0wt%, followed by PES-HAP 1.0wt%, PES-HAP 3.0wt% and native PES. PES-HAP 2% is more porous compared to the unmodified membrane. It can also be proved with the higher permeability of the membrane based on pure water permeation test. Based the result of contact angle, the more hydrophilic membrane was PES-HAP 2% compared to the other membranes. With addition of hydroxyapatite, the hydrophilicity increases as stated by Junfen & Lishun, 2014.

Table 3 Porosity and contact angle of the membranes

Membrane ID	Porosity (%)	Contact angle
PES Native	45.02	74.44
PES-HAP 1.0%	46.00	72.17
PES-HAP 2.0%	47.53	65.96
PES-HAP 3.0%	45.29	66.32

3.1.4 Determination of Structural Parameter Details of the Fabricated Membranes

Rejection ability was dependent on membrane pore size. According to Table 4, we can notice that, the highest λ value was PES-HAP 3.0%. σ value also dependent on membrane pore and membrane rejection. The higher the membrane rejection, results to a higher of reflection coefficient, σ. PES-HAP 3% also provides the highest value of X_d which providing the highest rejection value (Table 5).

Table 4 Membranes parameters and steric hindrance factors for modified and unmodified membranes

Membrane parameters	Membrane ID			
	Native PES	PES-HAP 1.0%	PES-HAP 2.0%	PES-HAP 3.0%
λ	0.1173	0.0811	0.0526	0.1628
σ	0.2335	0.1614	0.1048	0.3243
H_F	1.0245	1.0117	1.0049	1.0471
S_F	1.2040	1.1480	1.0994	1.2647
S_D	0.9862	0.9934	0.9972	0.9735

Table 5 Modeling result for membrane structural details for modified and unmodified membranes

Structural parameters	Membrane ID			
	Native PES	PES-HAP 1.0%	PES-HAP 2.0%	PES-HAP 3.0%
Ps (10^{-6}m/s)	0.7700	1.9974	2.9304	1.2038
r_p (10^{-12}m)	7.8591	5.4324	3.5242	1.0908
Δx(10^{-3}m)	2.0910	0.8061	0.5494	1.3374
A_k	1.0140	1.0070	1.0030	1.0270
ε	-0.4780	-0.3509	-0.2395	-0.6184
X_d	-0.0478	-0.0351	-0.0240	-0.0618

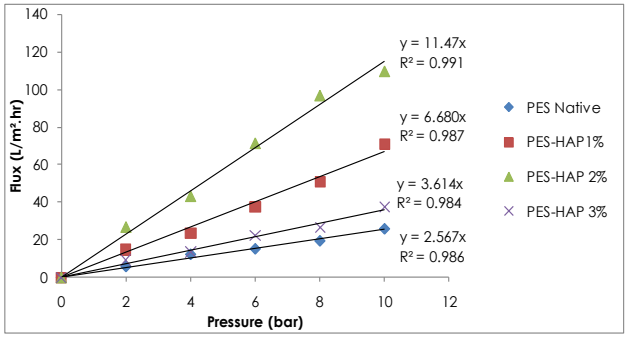


Figure 2 NaCl flux at different operating pressure for modified and unmodified membranes

Based on Figure 2, the graph of NaCl flux permeation at different operating pressure for modified and unmodified membranes show that, the flux increased with the increasing applied pressure which was similar to the pure water permeation flux behavior. The highest NaCl flux was PES-HAP 2%, followed by PES-HAP 1%, PES-HAP 3% and native PES

membrane (Figure 3 and Figure 4). The permeability coefficients for the membranes were 11.47 L/m^2.hr.bar, 6.680 L/m^2.hr.bar, 3.61 L/ m^2.hr.bar and 2.567 L/m^2.hr.bar respectively (Table 6).

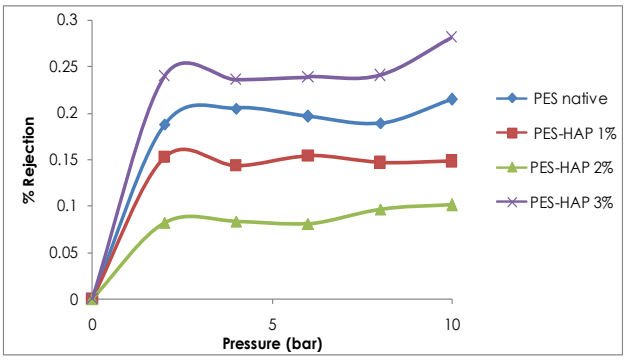


Figure 3 Graph of % Rejection of Nacl vs Pressure

Table 6 NaCl Rejection

Membrane ID	Rejection (%)	Pm (L/m^2.hr.bar)	R^2
PES Native	21.00	2.567	0.986
PES-HAP 1.0%	15.00	6.680	0.987
PES-HAP 2.0%	10.00	11.47	0.991
PES-HAP 3.0%	28.00	3.614	0.984

Modified (PES-HAP 1%, PES-HAP 2% and PES-HAP 3%) and unmodified membrane exhibits rejections up to 68.3%, 69.88%, 66.3%, and 66.59% respectively as shown in Table 7. The rejections of 4 different types of membranes does not show huge different due to the range of the membranes were lies on the nanofiltration. The permeate fluxes decreased as the time increases due to the concentration polarization and fouling occurred. However, with the addition of hydroxyapatite, it was shown that, the permeate fluxes was higher compared to unmodified membrane as well as the rejection of vanillic acid. This occurred due to the increasing hydrophilicity of the membrane with the addition of hydroxyapatite. Thus, it was shown that the hydroxyapatite can promotes the increasing of productivity in term of high flux.

Based on Figure 5, PES-HAP 2% shows the excellent result on initial flux and average flux. Addition of 2% hydroxyapatite was the optimum loading for mixed matrix membrane. This is because, with the addition of 3% of hydroxyapatite, the membrane structure became dense. Thus, the flux decreased.

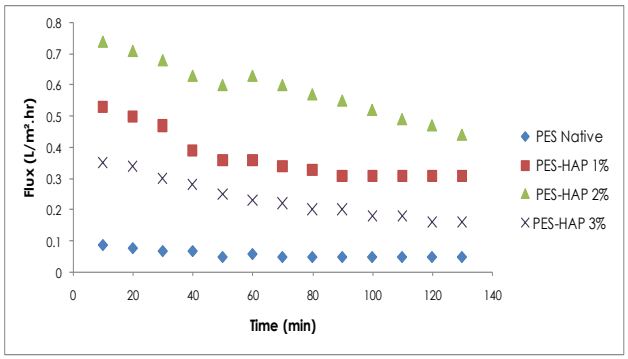


Figure 4 Vanillic acid separations

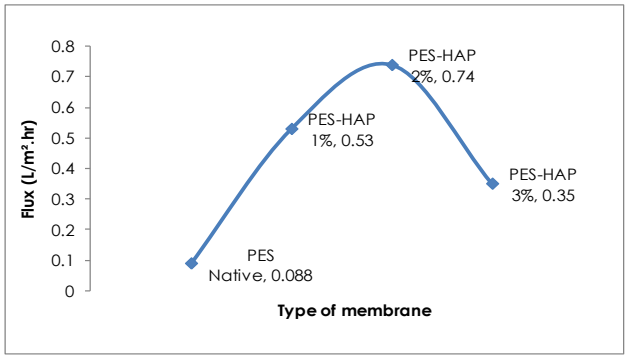


Figure 5 Flux versus different type of membrane

Table 7 Vanillic acid concentration rejection

Membrane ID	Rejection (%)	Initial Flux	Average Flux
PES Native	68.30	0.088	0.0683
PES-HAP 1.0%	69.88	0.530	0.4200
PES-HAP 2.0%	66.30	0.740	0.5900
PES-HAP 3.0%	66.59	0.350	0.2550

4.0 CONCLUSION

As the experiment was conducted, it was shown that the hydroxyapatite was very effective for improving the membrane hydrophilicity as its ability to reduce fouling, hence increase the flux permeation via diffusion. As the hydroxyapatite was added as additive in the composite membrane, the water flux increases to 95.76 L/m^2.hr compared to native membrane which is 19.05L/m^2.hr only. Both PES polymer and hydroxyapatite were combined synergically to increase the performance of the nanofiltration membrane for the vanillic acid separation.

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