Full paper

Effect of Zeolite Synthesized from Rice Husk Silica Towards Mixed Matrix Polysulfone Ultrafiltration Membrane

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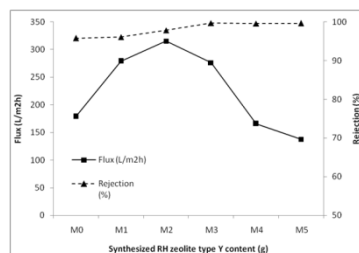
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Graphical abstract

Abstract

In the present work, polysulfone (PSf) ultrafiltration membranes were prepared by solution casting via phase inversion process. The effects of synthesized rice husk (RH) zeolite on the properties and performance of the casted PSf membrane were observed and investigated. Characterization of synthesized RH zeolite and morphology of membrane were conducted by using X-ray diffractometer (XRD), field emission microscopy (FESEM) and scanning electron microscopy (SEM). XRD analysis shows a mixture of zeolite A, Y and P, while FESEM images showed agglomeration of cubic-shaped morphology of the synthesized RH zeolite. SEM analysis on membrane morphology indicates that the addition of synthesized RH zeolite obviously changed the microstructure of the membrane sub layer. At 2g RHY content, the membranes held the highest water permeability (315.29 $Lm^{-2}h^{-1}$) and continuously decreased with higher RHY content. The incorporation of the RHY particles beyond 2% causes declination to the membrane flux and increment to the humic acid rejection from 95.8 to 99.6%.

Keywords: Polysulfone (PSf); rice husk ash; zeolite, ultrafiltration

■1.0 INTRODUCTION

The requirement of sustainability in line with economy development nowadays crucially needs in a water treatment process [1, 2]. As the requirement of sustainability, membrane separation technology (i.e. ultrafiltration, microfiltration etc.) provides an economical and simple technique in way of water treatment or recycling of wastewater process. However, membranes mostly fabricated with polysulfone (PSf) [3], poly(ethersulfone) (PES) [4] and poly(vinylidene fluoride) (PVDF) [5] struggling with hydrophobic nature, which limit their performance in term of flux and rejection. Intensive efforts have been made to improve the performance of this hydrophobic property by providing greater hydrophilicity via physical or chemical method [6-9]. The incorporation of inorganic materials into organic polymer matrix blend received most attention due to the effectiveness and simple technique compared to others.

Various types of inorganic particles ranging from nanometer to micrometer sizes incorporated to the polymer structure have been conducted to improve membrane performance and properties. For example, Mierzwa *et al.,* reported that nanoclay particles improved the permeability and fouling resistance of PES membrane by changing the membrane internal pore structure due to hydrophilicity of the clay [10]. Indeed, Harun *et al.* [11] and Jamalludin [12] have been used the amorphous rice husk (RH)

silica to improve the performance of PSf membrane. It was noticed that membrane permeability and fouling resistance increased due to formation of continuous finger-like macrovoid from top to the bottom of the membrane. Based on this observation, confirmation work was conducted by changing RH silica to zeolite. Zeolite materials possess a unique transport and an adsorption property because of it has a well-defined crystalline framework with the pore size at molecular level [13]. In fact, due to better selectiveness properties of zeolite pores for different-sized gas molecules, therefore it preferably used for most gas application. In some cases, the low silica represented by zeolites A and X are, aluminum saturated that have the highest cation concentration and give optimum adsorption properties and strongly hydrophilic surface selectivity [14]. This hydrophilic zeolite has received attention in preparing composite membrane either in gas separation or water treatment application in the last few years [15-17]. Thus, in this work, the effect of synthesized zeolite particles from RH based on PSf polymer from 1 to 5% were observed and investigated.

Table 1 Composition of dope solution

Membrane	PSf	NMP	PEG 400	RHY zeolite
M0	18	82	10	-
M1	18	82	10	1
M2	18	82	10	2
M3	18	82	10	3
M4	18	82	10	4
M5	18	82	10	5

■2.0 EXPERIMENTAL

2.1 Preparation of Synthesized RH Silica

RH ash, pellets of sodium hydroxide (NaOH) (Emory), Sodium aluminate (NaAl$_2$O$_3$) (Riedel-de Haën), and distilled water were used as the starting materials in the initial mixture of the synthesis of Na-Y zeolite. This RH source used in this experiments was obtained from Malaysia rice mill (Jelapang Selatan). The process involved burning of RH at 700ºC for 5 h in atmosphere, and continued with sieving process to get a desired particle. In the hydrothermal synthesis, the sodium solution was prepared by dissolving sodium aluminate (1.888 g) with NaOH solution (2.361 g in 26 mL water). Silicate solution was prepared by adding RHA (0.18 g) into 270 mL water and was left for 2 hr in stirred condition. The progressive addition of silicate solution and sodium aluminate was carried out with stirring using magnetic stirrer until they dissolved, and homogenized in the reaction gel for 2 hours. The molar composition of the reaction gel was 3.4Na$_2$O: Al$_2$O$_3$: 9.5 SiO$_2$: 136H$_2$O.[18] The reaction gel was poured into Teflon-lined stainless steel autoclaves and left for ageing process in 24 hour. Then, it was heated at 100ºC for 24 hour at autogenic pressure. After hydrothermal reaction, the prepared powder were collected by centrifugation (5000 rpm) followed by washing with distilled water repeatedly until the washing liquid become almost neutral as observed by the pH meter. The powders were dried at 100ºC for 24 hours.

2.2 Membrane Preparation

PSf membranes were prepared by using the phase inversion method. Casting solution were prepared by dissolving PSf in N-methyl-2-pyrrolidone (NMP) under mechanism stirring for 4 h. Then, PEG and synthesized RH zeolite at different loading (Table 1) was subsequently added with continuous stirring and heating at 60°C until the solution was completely homogeneous. Subsequently, the casting solution was sonicated for 1 h to release any bubbles in dope solution. The dope solution was then casted by using flat sheet membrane casting system and immersed in a coagulation bath containing distilled water. Finally, the flat sheet membranes were dried for 24 h.

2.3 Zeolite Analysis

The crystal phases of the powder were identified using powder diffraction technique by Bruker XRD (Model: D8 Advance) with Ni-filtered Cu-K$_a$ radiation (λ=0.15418 nm), operating at 40 kV and 40 mA. The morphology of the synthesized particles was examined by FESEM (Model: JEOL JSM 7600F) operating with an accelerating voltage of 1 kV.

2.4 Membrane Analysis

Membrane morphology of the membrane was examined by scanning electron microscope SEM (Model: JEOL JSM 7600F) operating with an accelerating voltage of 10 kV. The cross section area of the membrane was prepared by submerged and fractured the membrane in liquid nitrogen. All the specimens were coated with thin layer of gold before examined with SEM. While, the performance of prepared membrane was evaluated in terms of PWF and rejection of humic acid. Membrane pure water flux (PWF) and rejection (%R) was measured by using the ultrafiltration cross flow water permeability testing unit. The experiment was conducted at pressure of 2 bar and permeate was collected for every 10 minutes. The PWF was carried out by using distilled water and rejection was performed by using humic acid. The membrane was cut into 5.5 cm diameter before testing. The permeation flux was defined as Equation (1).

$$PWF = Q/(Ax\ \Delta t) \tag{1}$$

where PWF is the pure water flux (LMH), Q is the permeate volume, A is the membrane area (m2), and Δt is the time (h). Rejection was measured with 200 mg/L humic acid aqueous solution. The concentration of humic acid was measured by using a Perkin-Elmer Lamda 25 UV-Vis spectrophotometer at the wave length of 254 nm. The rejection was defined as Equation (2).

$$R\ (\%) = [1- (Cp/Cf)]\ x\ 100 \tag{2}$$

where Cp is solute concentration in permeate stream, C$_f$ is solute concentration in feed stream

■3.0 RESULTS AND DISCUSSION

3.1 Properties of Zeolites

The XRD pattern of synthesized zeolites in this study is shown in Figure 1(a). As noticed in Figure 1(a), this synthesize process produce a mixture of zeolite A, Y and P. This zeolite Y formation was referred to JCPDS number 38-0240 data by matching the diffractograms pattern. Due to the fact that zeolite Y is metastable, some of the crystallites were transformed to zeolite P with JCPDS number 39-0219 as clearly shown in Figure 1(a).[19] In fact, the result also shows that the existence of Zeolite type A with JCPDS number 40-1646 due to remaining water. According to Turnbull[20] zeolite A, X and P have the structure of faujasite where all of these types are naturally exist as mineral, and are commonly denoted as FAU. Figure 1(b) shows the FESEM microstructure of RH zeolite particles obtained at 100ºC/24 hr with magnification of 10,000 that show cubic shape particles of NaY with agglomerated condition.
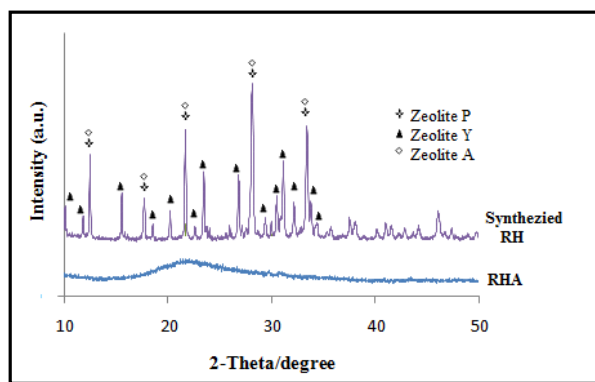
(a)
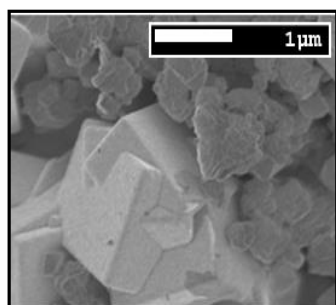
(b)

Figure 1 (a) XRD patterns of RH zeolite powders synthesized at 100°C, (b) FESEM-image of synthesized rice husk ash powders

3.2 Membrane Morphology

Figure 2 shows that the increment of percentage of synthesized RH zeolite significantly affect the cross sectional morphology on polysulfone membrane. As can be seen from the Figure 2, the asymmetric tend to be more porous with spongy microporous structure at the wall of membrane when RHY zeolite content is added from zeolite 1 to 5 g. This may induced by hydrophilic RHY zeolite particles that has tendency to cause instantaneous liquid-liquid demixing [21]. The faster exchange rate between solvent (NMP) and non-solvent (water) during phase inversion process occurred as the hydrophilic particles is added more to the dope solution which leading to the development of bigger macrovoid at the bottom surface and spongy porous structure at the wall.[22] However as the amount of RH zeolite content is increased (>2wt%), the agglomeration tends to be occurred and the interaction between zeolite particle with dope solution also increased. The latter effect significantly can increase the viscosity of dope solution and can delay the instantaneous demixing,[23] which cause denser top separation layer and bottom layer as shown in Figure 2. In fact, the excessive loading of synthesized RH particles (>3.0 wt%) lead to agglomeration effect that potentially can reduce the effective area of hydroxyl groups that acting to the hydrophilic mechanism [22].

3.3 Membrane Performance

Figure 3 shows that the pure water flux is increased from 178.57 $Lm^{-2}h^{-1}$ as the RHY zeolite content was added to 2 g at 315.29 $Lm^{-2}h^{-1}$ and slightly decreased after the zeolite exceeded more than 2 g. Early increment indicates that low content of RHY zeolite could lead to homogenous distribution silica that potentially can create hydrophilic effect and produce smaller finger like structure that allows better permeation path. Similar observation was found by Liu *et al.* [23] that showed by adding 3 g of zeolite 4A particle gave better result of pure water flux. However, addition RHY zeolite content more than 3 g promote the decrement of pure water flux which possibly could due to the formation of denser top separation and bottom layer along together with the entrapment of zeolite in the macroporous structure that create further blocking of the pore as can be observed in Figure 3. Studied by Mousa (2007)[24] revealed that the flux decline caused bypore blockage condition. Reported by Han *et al.* [25] that revealed the flux experienced to decrease when hydrophilic particles of 2.5 µm NaA were added.

However, the denser surface and pore blocking can enhance the rejection performance and thus is shown humic acid rejection value is increased from 95.537 to 99.732% when synthesized RHY zeolite is continuously added from 0 to 5 g as shown in Figure 3. As mentioned before, dense layer, at the top cross section membranes provides a selective skin layer causes higher rejection as the RH zeolite is increased. Instead of dense layer, the strong agglomeration of particles especially above 2 g of RH zeolite creates smaller pore radius at top layer and restrained the free permeate flow which contribute to excellent rejection value.

■4.0 CONCLUSION

Incorporation of synthesized RH zeolite with PSf/PEG membrane was successful prepared by phase inversion method, with different percentage ranging from 1-5%. (percentage of RHY weight). The RHY zeolite was synthesized by static hydrothermal condition at 100°C/24 hr. The transformation of metastable zeolite crystalline phase from amorphous phase gives a mixture of crystalline zeolite A, Y and P. The membrane morphologies using SEM indicates that the addition of synthesized RH zeolite at low concentration can create smaller finger-like structure due to better interaction area of hydrophilic particle. However, the excessive loading of synthesized RH particles (>2.0 wt%) lead to significant agglomeration on the finger-like structure and higher dope viscosity[23] that lead to worst reduction of flux value. Thus, the concentration at 2wt% was recommended for PSf membrane modification which offers good permeability and rejection mechanism.

(a)   (b)   (c)

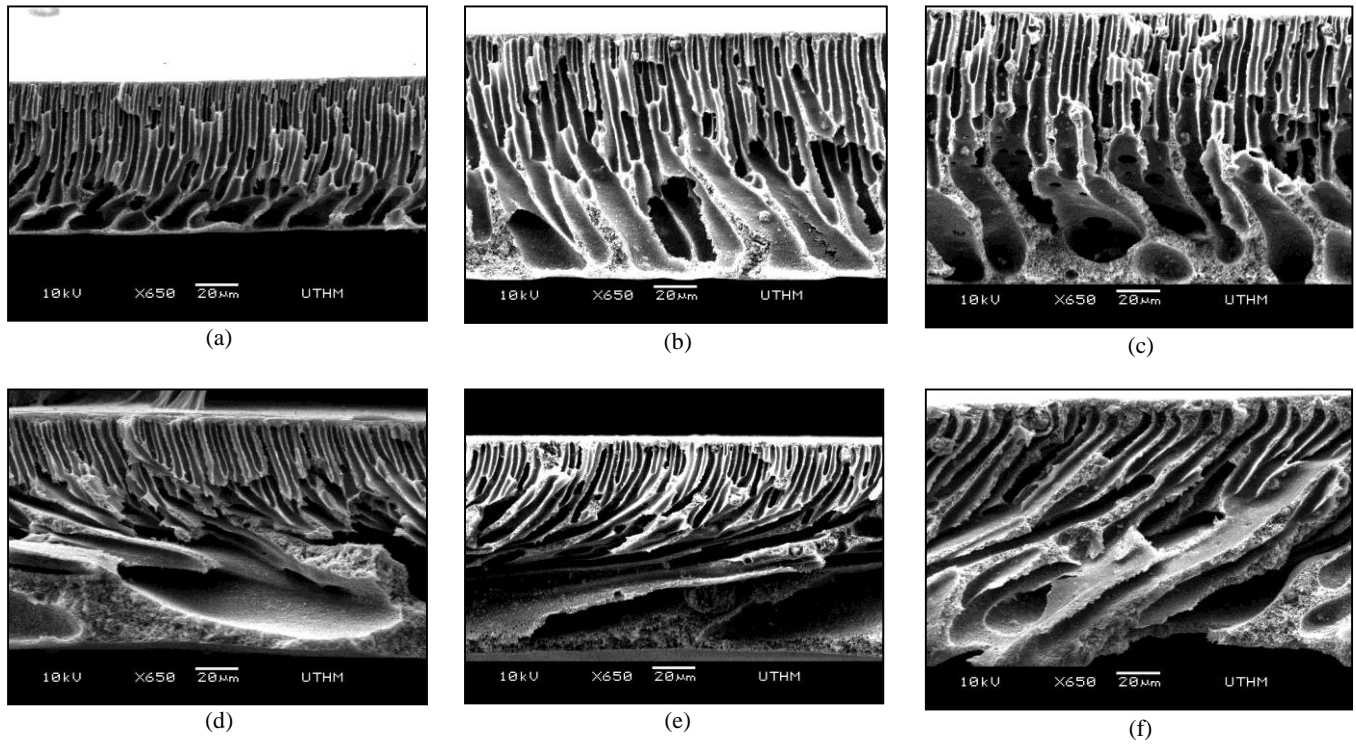(d)   (e)   (f)

Figure 2 SEM cross-section of PSF membrane with different percentage zeolite. a) M0. b)M1, c)M2, d)M3, e)M4, f)M5
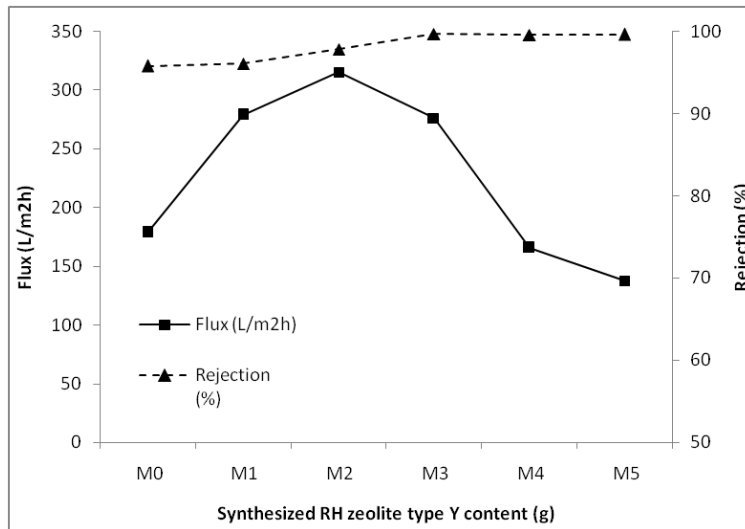

Figure 3 Effect of synthesized RH zeolite type Y content on the performance of PSf UF membrane

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