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Dehydration of monohydric alcohols via pervaporation using nano NaX zeolite/ polyvinyl alcohol mixed matrix membranes for biofuel production

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ABSTRACT

This paper focuses on the dehydration of monohydric alcohols via pervaporation process for using as biofuel additive. For this purpose, two-layer polyvinyl alcohol (PVA)/polyethersulfone (PES) mixed matrix membranes containing nano NaX zeolite were fabricated. The ATR-FTIR, SEM, AFM and swelling tests were employed to characterize surface properties and morphology of the prepared membranes. The results revealed that incorporation of nano NaX zeolites into the cross-linked PVA layer of membranes improved the separation performance. The total and water fluxes enhanced by increasing the zeolite content, whereas the water separation factor had a maximum at the zeolite concentration of 2%wt. for dehydration of a 90%wt. aqueous ethanol solution. The pervaporative dehydration of aqueous solution of methanol, ethanol and isopropanol indicated that the total permeation flux decreased in the order of methanol > ethanol > isopropanol, while the water separation factor had a reverse trend. Finally, the performance of the papered mixed matrix membranes was compared with a commercial hydrophilic PVA membrane and it was observed that the mixed matrix membrane containing 2%wt. NaX zeolite had higher permeation flux and separation factor than the commercial membrane.

Keywords: Pervaporation; Polyvinyl alcohol (PVA); NaX zeolite nanoparticles; Mixed matrix membrane; Bioalcohol dehydration

1. Introduction

Biofuels as alternative for fossil fuels are the one way to reduce the emission of the greenhouse gases. Today, different biofuels like bioethanol and biodiesel are used as fuel or as blending agent with fossil fuels throughout the world [1]. Monohydric alcohols such as methanol, ethanol, propanol and butanol are mostly used as an additive for gasoline to increase octane number and cut down carbon monoxide and other smog-causing emissions. Bioalcohols are naturally produced during the fermentation of biomass feedstocks [2]. The biological method leads to a final product with low alcohol concentration and needs to be concentrated. For the bioalcohols to be usable as a fuel, the majority of the water is mostly removed by the distillation process. However, for use as a fuel additive, the alcohols must be dehydrated in order to be miscible in all ratios with gasoline. Techniques including liquid-liquid extraction, adsorption, partial condensation, gas stripping, perstraction and pervaporation have been employed for the alcohol dehydration [3]. Pervaporation is a membrane-based separation process based on the selective sorption and diffusion through a non porous membrane. Compared with the conventional processes, pervaporation has many superiorities such as, moderate operating conditions, low energy consumption, no entrainer added, no regeneration needed, no heat damage to heat-sensitive compounds, high dehydration efficiency and easy installation and operation [3,4].

In the pervaporation, the properties of the membrane and permeating compounds determine the separation performance of the process. Different polymeric materials have been used for the preparation of the pervaporation membranes for dehydration of different solvents [5]. Among them, polyvinyl alcohol (PVA) was given more attention

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due to its special properties like good film forming, high hydrophilicity, good thermal and chemical stability as well as high tensile and impact strengths [6]. However, poor stability and swelling of pure PVA in water have limited its use as a membrane in aqueous systems because the membrane swelling has a great influence on the membrane separation performance in the pervaporation process. Generally, the swelling leads to an open structure membrane, consequently results in a higher flux and lower selectivity and loose the separation performance of the membrane. To overcome this problem, the PVA membrane is modified by grafting [7], copolymerizing [8], blending [9,10], addition of inorganic filler [11] and cross-linking [12]. Several cross-linking methods including chemical [13–17], irradiation [11,18] and heat treatment [19] have been used for cross-linking of the PVA membranes. In the chemical technique, the PVA molecules are cross-linked through the use of difunctional cross-linking agents. Aldehydes like glutaraldehyde (GA) [13–15] and formaldehyde [16,17] as well as carboxylic acids such as citric acid, malonic acid, maleic acid, oxalic acid and succinic acid [20,21] are the common cross-linking agents which have been utilized for the chemical cross-linking of the PVA membrane.

In recent years, mixed matrix membranes have been extensively used in the pervaporation process for various applications like dehydration of solvents. The hydrophilic mixed matrix membranes which are prepared by incorporating hydrophilic inorganic materials as dispersed phase into a polymeric matrix as continuous phase show high separation performance for pervaporative dehydration of alcohol/water mixtures. Another type of the advanced membranes employed in the pervaporation process is multilayer mixed matrix membranes. A multilayer mixed matrix membrane has an asymmetric structure consisting of different layers, generally, a thin active dense layer on a porous sublayer as a mechanical support for the selective top layer in which the inorganic fillers are loaded into the top layer to modify the membrane surface properties as well as the separation performance. For example, Amnuaypanich et al. [11] used zeolite 4A as inorganic filler into natural rubber (NR) and PVA as selective layer on a nylon membrane to prepare two-layer mixed matrix membranes for the pervaporative dehydration of aqueous ethanol solutions. Oh et al. [22] also employed the NaA zeolite particles as filler in the PVA mixed matrix membrane for separation of water/butanol mixtures. Huang et al. [23] fabricated three-layer mixed matrix membranes using PVA and polyacrylonitrile (PAN) as an active layer and sublayer, respectively, on polyester non-woven fabric support membranes. They studied the effect of different micro zeolites including silicalite, beta, 3A, 4A, 5A, NaY and NaX on the pervaporative dehydration of ethanol. Furthermore, Khoonsap and Amnuaypanich [24] prepared the mixed matrix membranes by casting the cross-linked PVA incorporated with the micro zeolite 4A-graft-PHEMA on a nylon substrate as the support layer for the dehydration on acetone/water mixtures. Fathizadeh et al. [25] fabricated polyamide thin film nanocomposite (TFN) membranes with NaX zeolite nanoparticles as inorganic filler for the dehydration of alcohols by pervaporation. Recently, Panahian et al. [26] prepared three-layer mixed matrix membrane by incorporating carbon nanotubes (CNTs) into the PVA as selective top layer on polyethersulfone (PES)/polyester membranes as support layer.

A search through the current literature revealed that there are no researches on the use of nano-NaX zeolite as filler in the mixed matrix membranes of PVA. The inorganic fillers in the micro form were utilized in most of the previous studies. In the present work, two-layer mixed matrix membranes were prepared by incorporating NaX zeolite nanoparticles into cross-linked PVA as the selective top layer on PES ultrafiltration membrane as the support layer. For this purpose, NaX zeolite nanoparticles were synthesized by a hydrothermal method using microwave heating and citric acid (CA) was utilized as a green cross-linking agent. The effect of zeolite content of the mixed matrix membranes and CA content of the casting solution on the membrane properties as well as swelling behavior and separation performance of the membranes were investigated. The fabricated membranes were employed for the pervaporative dehydration of alcohols such as methanol, ethanol and isopropanol for using as a biofuel additive. Finally, the pervaporative performance of the fabricated mixed matrix membranes were compared with that of a commercial PVA/PAN composite membrane for the dehydration of different alcohols.

2. Experimental

2.1. Materials

PVA with molecular weight of 145,000 g/mol, N,N-dimethyl-formamide (DMF) and citric acid which were purchased from Merck Co. Ltd. (Darmstadt, Germany) as well as commercial PES with molecular weight of 58,000 g/mol (E6020P, BASF, Ludwigshafen, Germany) and polyvinylpyrrolidone (PVP) with an average molecular weight of 360,000 g/mol (PVP-K90) that was supplied from Sigma-Aldrich (MO, USA) were used for the membrane fabrication. Also, fumed silica (7 nm, Sigma Aldrich, MO, USA), sodium aluminate ($NaAlO_2$) (Sigma Aldrich, MO, USA) and NaOH (Merck, Darmstadt, Germany) were used for the synthesis of zeolite nanoparticles. A commercial PVA/PAN composite membrane (PERVAP 2210) with a functional layer of PVA was supplied by Sulzer Chemtech Ltd. (Switzerland).

2.2. Synthesis of zeolite nanoparticles

The NaX zeolite nanoparticles were prepared by the hydrothermal method using microwave heating according to the procedure presented by Ansari et al. [27]. Typically, an aluminosilicate gel was prepared by mixing raw materials in the molar ratio of 5.5 Na_2O:1.0 Al_2O_3:4.0 SiO_2:190 H_2O. For this purpose, 2.67 g of NaOH was solved in 25 g of de-ionized water and stirred well. Before the next step, the obtained solution was cooled to room temperature, and then 1.21 g of $NaAlO_2$ was added to the solution and stirred continuously until all the powder is completely dissolved in the NaOH solution. Afterwards, 1.715 g of silica powder was slowly added to the solution until a homogeneous aluminosilicate reaction gel was obtained. The prepared gel was regularly stirred at room temperature for 24 h, and then transferred into a commercial microwave oven (CE1110C, Samsung, Korea) to perform the hydrothermal crystallization by microwave heating at 90°C for 3 h. The microwave oven was operated at wavelength of 2.45 GHz with 900 W output power.

The products were regained with centrifugation, washed with de-ionized water until pH reached below 8, and then for further characterization, dried at room temperature for 24 h.

2.3. Preparation of mixed matrix membranes

The two-layer nano NaX zeolite-PVA/PES mixed matrix membranes were prepared according to the following steps:

- The PES ultrafiltration membranes as the support layer were synthesized using the phase inversion technique by immersion precipitation as previously presented by Sadeghi et al. [28].
- The PVA top layer was fabricated on the PES support layer by solvent evaporation method. Typically, 10%wt. of PVA solution was prepared by dissolving the PVA in de-ionized water as a solvent. For cross-linking of PVA, different amounts of CA as a cross-linking agent were added to the PVA solution. Furthermore, a given amount of zeolite nanoparticles was added to the casting polymer solution of the fabricated mixed matrix membranes. The prepared solution was stirred for 2 h at 95°C and then de-aerated by a vacuum process to remove any bubbles. Afterwards, the bubble-free PVA solution was cast on the porous PES support membrane which was placed on a glass plate with a cast knife. The obtained film was allowed to dry in an oven at 37°C for 15 h. To complete the cross-linking reaction between PVA and CA, the membranes were put in the oven at 150°C for 1 h. The composition of the casting solution for the preparation of various membranes is given in Table 1.

2.4. Pervaporation experiments

The separation performance of the fabricated nano NaX zeolite-PVA/PES mixed matrix membranes was evaluated by the pervaporation experiments with 90%wt. aqueous ethanol, methanol and isopropanol solutions using the apparatus previously described in details [25]. The experiments were conducted using a cross-flow plate and frame membrane module with an effective area of 35 cm^2 at a feed temperature of 30°C and permeate pressure of 1 mmHg. The total mass flux (J) was determined by collecting the permeate stream and calculated as follows:

Table 1
The composition of casting solution for the preparation of various membranes

Membrane	PVA (%wt.)	CA (%wt.)	Nano NaX zeolite (%wt.)	Water (%wt.)
M1	10	0	0.0	90.0
M2	10	5	0.0	85.0
M3	10	10	0.0	80.0
M4	10	15	0.0	75.0
M5	10	10	0.0	80.0
M6	10	10	0.5	79.5
M7	10	10	1.0	79.0
M8	10	10	1.5	78.5
M9	10	10	2.0	78.0
M10	10	10	4.0	76.0

$$J = \frac{W}{S.t} \tag{1}$$

where W is collected permeate weight, S is membrane area and t is time duration of the pervaporation experiment.

Also, the water separation factor (α) was computed as follows:

$$\alpha = \frac{y_{H_2O} / y_{EtOH}}{x_{H_2O} / x_{EtOH}} \tag{2}$$

where x and y are components weight fraction in the feed and permeate streams, respectively.

The alcohol concentration of the feed and permeate streams were analyzed by a Gas Chromatography (Younglin 6000M, Anyang, Korea) equipped with a flame ionization detector (FID) and a 60 m × 0.32 mm × 0.5 μm TRB-Wax capillary column (Teknokroma, Barcelona, Spain). The carrier gas was helium with a column head pressure of 10 psi. Injector and detector temperatures were 200 and 220°C, respectively and oven temperature was adjusted at fixed temperature of 100°C.

2.5. Characterization tests

The X-ray diffraction (XRD) analysis was employed to determine the structure of the synthesized zeolite powder. The XRD test was performed using a Philips instrument (X'pert diffractometer using CuK radiation) with a scanning speed of 0.03° (2θ) min^{-1} at 25°C. The average crystal size of the zeolite powder was calculated based on the Scherrer's equation and the crystallinity was estimated from the peak areas of 6° (111), 16° (331) and 27° (642) [27]. The scanning electron microscope (SEM) analysis using a TESCAN SEM instrument (VEGA 3SB, TESCAN, Czech Republic) was utilized to evaluate the morphology of the NaX zeolite nanoparticles. The X-ray fluorescence (XRF) analysis performed on a Philips PW 1404 spectrometer (Philips X'pert, Eindhovan, Netherlands) was used to determine the elemental compositions of the prepared zeolite powder.

The surface and cross-sectional morphologies of the zeolite filled PVA/PES mixed matrix membranes were characterized by the SEM analysis using a TESCAN SEM. Before analysis, a sputtering system was utilized to coat a ~10–20 nm thin layer of gold on the surface of the membrane samples. The surface roughness of the prepared mixed matrix membranes was characterized by atomic force microscopy (AFM) analysis using a Hysitron TriboScope® nano-mechanical device (Hysitron Inc., Eden Prairie, MN, USA) with 2D transducer by semi-contact mode in the air. A 0.2 cm × 0.2 cm membrane sample was fixed on a metal support and a 5 μm × 5 μm area of each sample was scanned. Four different locations of each membrane sample were analyzed and the average values were reported. The surface roughness was expressed in terms of RMS (root mean square) and RA (average roughness) values. The attenuated total reflection-Fourier transforms infrared spectroscopy (ATR-FTIR) was also used to characterize the functional groups on the membranes containing different citric acid contents. The ATR-FTIR analysis was done using a Nicolet Nexus 670 spectrometer instrument (Nicolet Instrument Co., Madison, WI, USA) over a wave number range of 4,200–700 cm^{-1} with 4 cm^{-1} resolution. Furthermore, the swelling degree (SD) of the prepared mixed matrix membranes was measured via a well-known gravimetric procedure [29] and calculated using the bellow equation:

$$\mathrm{SD}\,(\%) = \frac{W_W - W_D}{W_D} \times 100 \tag{3}$$

where W_W and W_D are the membrane weight in the wet and dry state, respectively.

3. Results and discussion

3.1. Characterization of synthesized zeolite nanoparticles

The XRD pattern of the prepared zeolite is shown in Fig. 1(a). The observed XRD pattern matches very well with the standard XRD pattern for FAU zeolite [30] denoting that the obtained zeolite crystals are pure FAU zeolite. In addition, the XRD results show that the nano NaX zeolite sample has 93% crystalline. The average crystal size of the NaX zeolite that was calculated using the Scherrer's equation from the peak with 2θ of 6° was found to be 15 nm.

The result of the SEM analysis for the synthesized NaX zeolite is presented in Fig. 1(b). The SEM images show that the particles of the prepared zeolite powder were morphologically similar and the particle size of nano NaX was within a range of 55–120 nm. Moreover, the Si/Al ratio of 1.25 and the unit cell mass of $Na_{86}[Al_{86}Si_{106}O_{384}]$ were calculated for the synthesized NaX zeolite based on the results of XRF test.

3.2. Characterization of prepared mixed matrix membranes

The surface and cross-sectional SEM images of the neat PVA and zeolite filled mixed matrix membranes are indicated in Figs. 2 and 3, respectively. As indicated in Fig. 2, there are some bright spots on the surface of the zeolite incorporated PVA mixed matrix membranes, M9 and M10 membrane

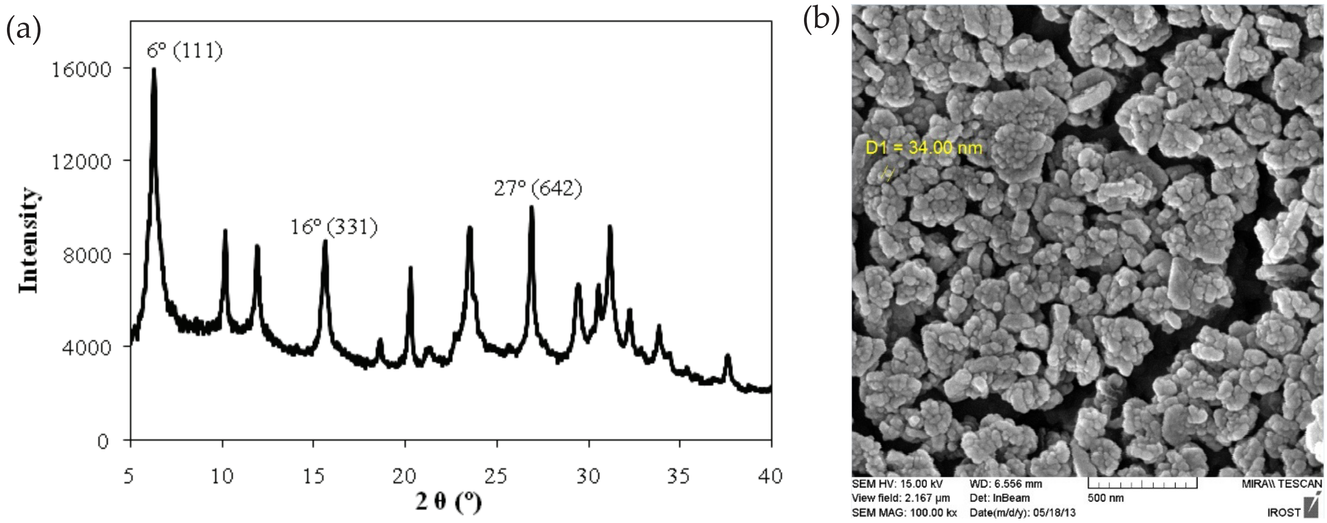
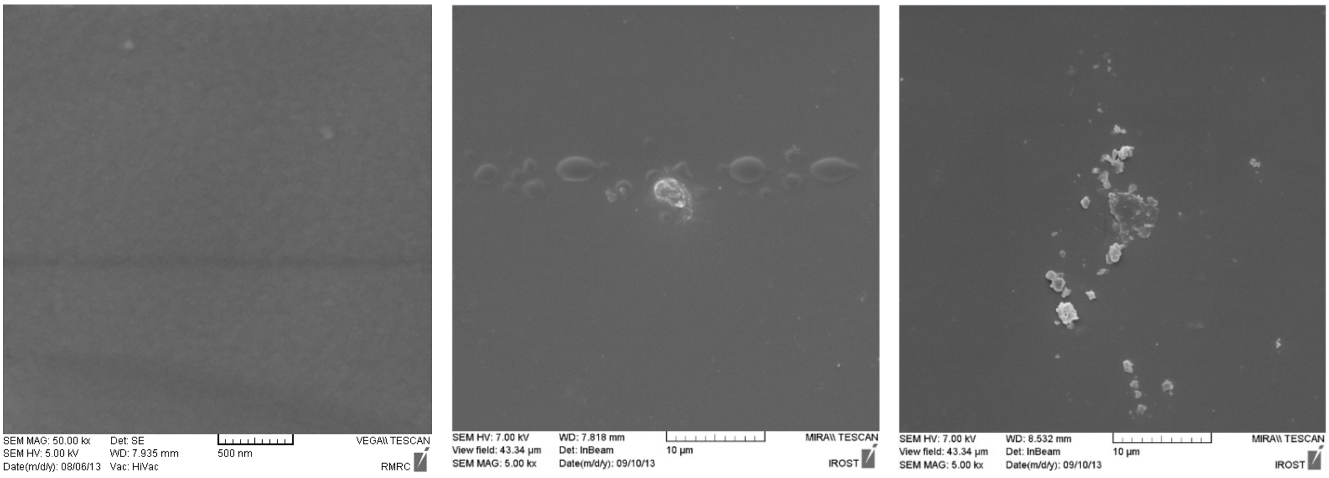
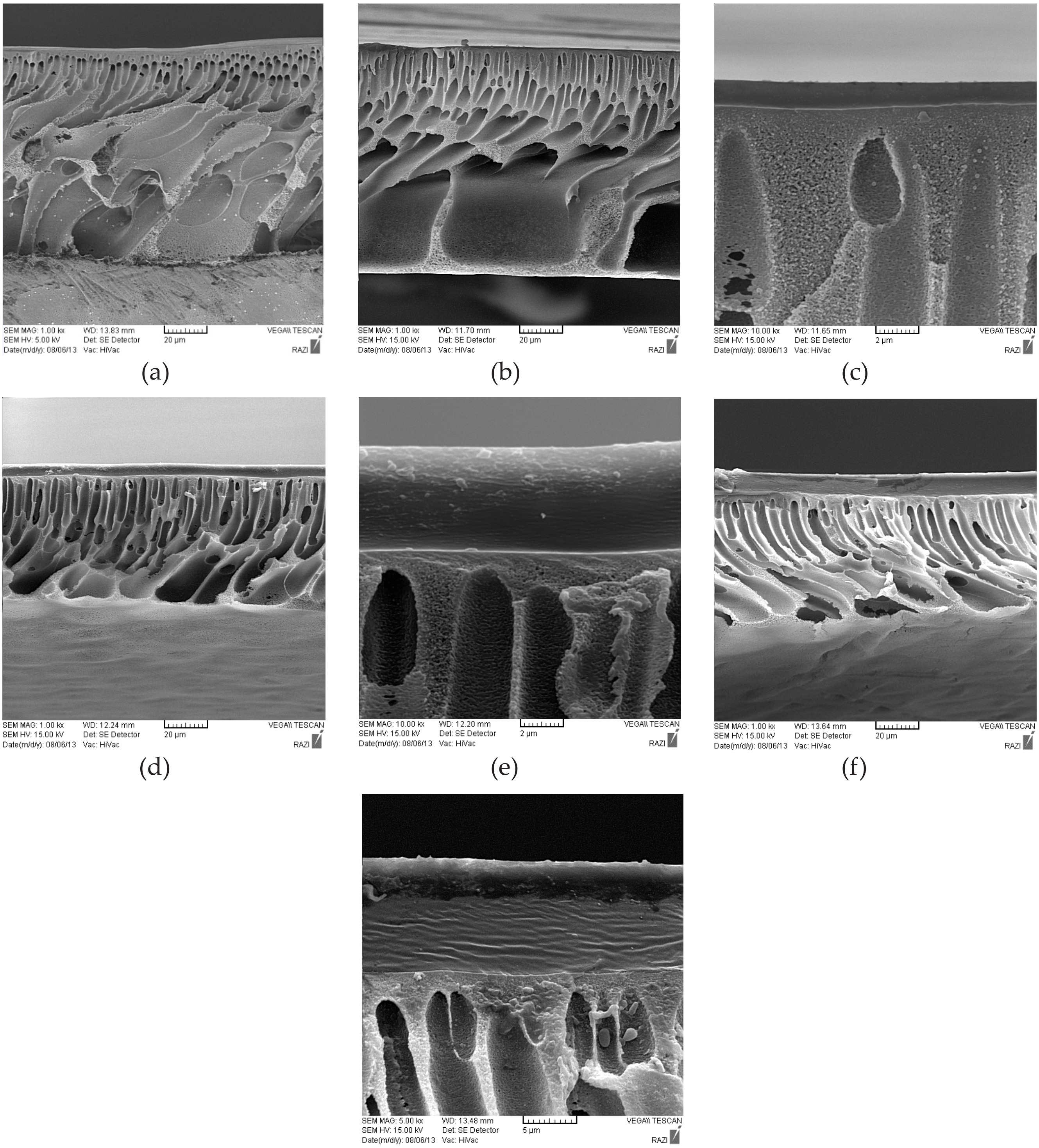


Fig. 1. The XRD pattern (a) and SEM images (b) of the synthesized NaX zeolite nanoparticles.



(a) (b) (c)

Fig. 2. The SEM images from the surface of the neat PVA and zeolite filled mixed matrix membranes: (a) M5, (b) M9 and (c) M10.



(g)

Fig. 3. The SEM images from the cross section of the neat PVA and zeolite filled mixed matrix membranes: (a) M5, (b and c) M6, (d and e) M7 and (f and g) M9.

samples. These spots represent the zeolite on the membrane surface. The SEM images of the zeolite filled mixed matrix membranes indicate that the zeolite nanoparticles were agglomerated and the amount of zeolite on the membrane surface increased with an enhancement in the zeolite content of the membrane. Also, the cross-sectional SEM images of the M5, M6, M7 and M9 membrane samples (Fig. 3) show that the dense PVA layer as the selective layer was formed on the top of the porous PES support layer with finger-like macrovoids and NaX zeolite nanoparticles were presented in the

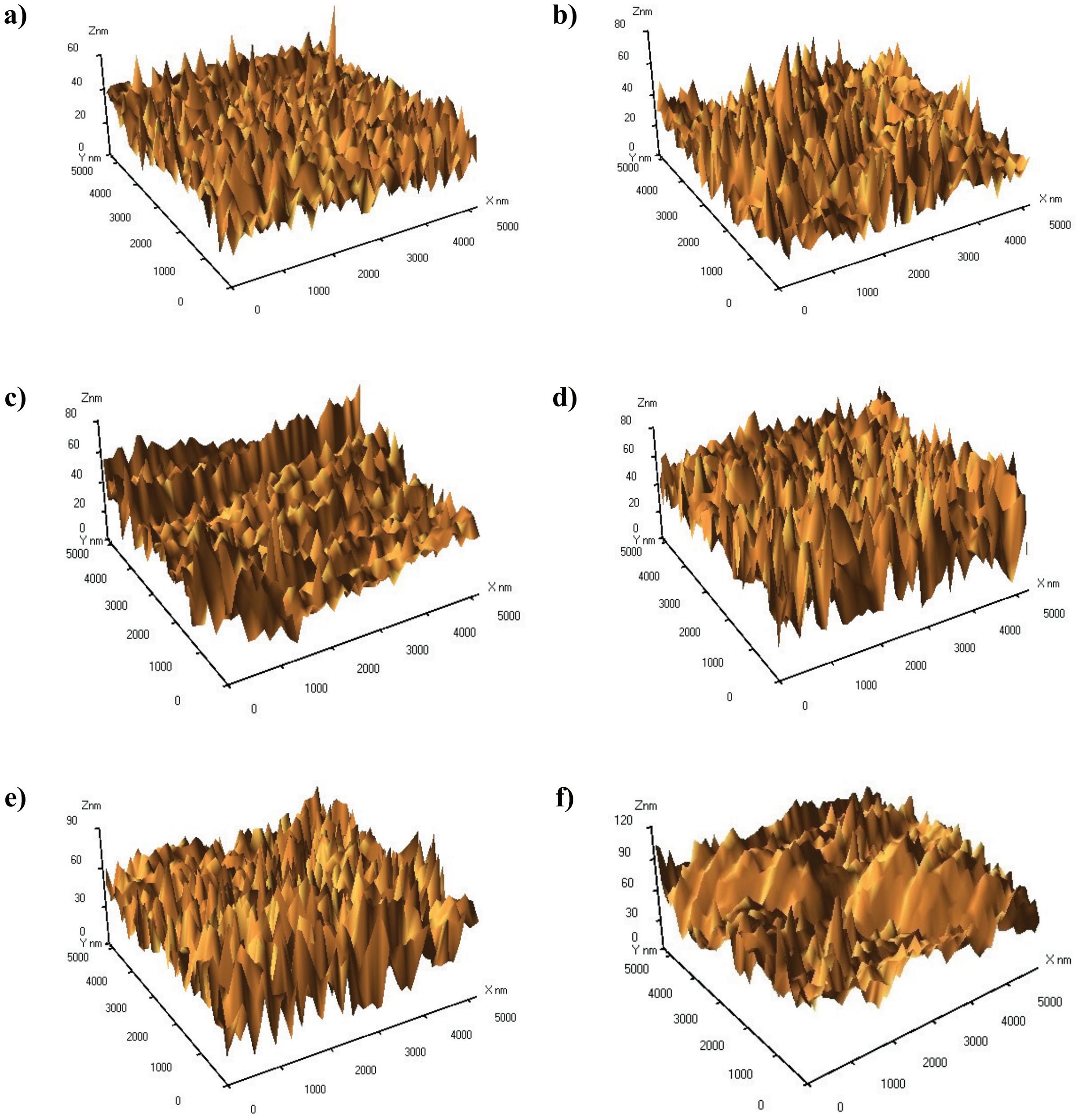


Fig. 4. The AFM images of the fabricated membranes: (a) M5, (b) M6, (c) M7, (d) M8, (e) M9 and (f) M10.

selective layer of the prepared mixed matrix membranes, M6, M7 and M9 samples.

The AFM analysis was also used to investigate the changes in surface roughness and morphology of the fabricated membranes due to presence of zeolite nanoparticles. The AFM surface topography of the neat and NaX zeolite incorporated PVA mixed matrix membranes are shown in Fig. 4. Also, the values of roughness parameters, i.e., RA and RMS values, for various membranes are given in Table 2. It is found that the surface roughness of the NaX zeolite filled membranes is higher than the neat PVA membrane and the membrane roughness faintly enhances as the zeolite loading of the mixed matrix membranes increases. On the other words, when the filler content of the membrane increased from 0 to 4%wt., the amount of the zeolite nanoparticles on the surface of the membrane increases and leads to a membrane with rougher surface. The AFM test results confirm variations in the surface roughness of the mixed matrix membranes which were observed in the SEM images.

The ATR-FTIR spectra of the fabricated membranes with different CA contents in the casting solution are presented in Fig. 5. The absorption bands at 2,850–3,000 cm^{-1}, 3,200–3,570 cm^{-1} and 3,600–3,650 cm^{-1} are attributed to the C-H, hydrogen bonded O-H and non-bonded O-H groups in the PVA molecules, respectively and the absorption bands at 1,700–1,725 cm^{-1} and 2,500–3,300 cm^{-1} are attributed to the

C=O and O-H groups in the citric acid molecules [31]. It can be seen that the intensity of some peaks changes with the variation in the CA contents of the membranes. Comparisons between spectra of the uncross-linked and cross-linked PVA composite membranes are given in Table 3. It can evidently be observed from Table 3 that the absorbance intensity at 1,710 cm^{-1} and 2,360 cm^{-1} which are attributed to C=O stretching vibration in carboxyl groups and stretching vibration of the hydroxyl groups increases as the CA concentration enhances. This is due to the number of hydroxyl and carboxyl groups enhanced as the citric acid concentration increased. Furthermore, the peak at 1,680–1,750 cm^{-1} is related to O=C-O groups in the cross-linked membranes. As shown in Fig. 6, the hydroxyl groups of the PVA react with the carboxyl groups of the citric acid to form the cross-links via formation of O=C-O bonds. It could clearly be seen that the peak intensity at 1,680–1,750 cm^{-1} enhanced with increasing the CA content of the membranes. The increase of the absorbance intensity of this peak is excellent evidence for the increase in cross-linking of the PVA membrane with an enhancement in the CA concentration. Similar results were observed in the previous researches [32].

Table 2
The roughness parameters of the prepared membranes

Membrane sample	RA (nm)	RMS (nm)
M5	6.9	8.5
M6	7.9	10.5
M7	9.9	12.9
M8	10.7	13.3
M9	12.7	15.5
M10	14.4	18.3

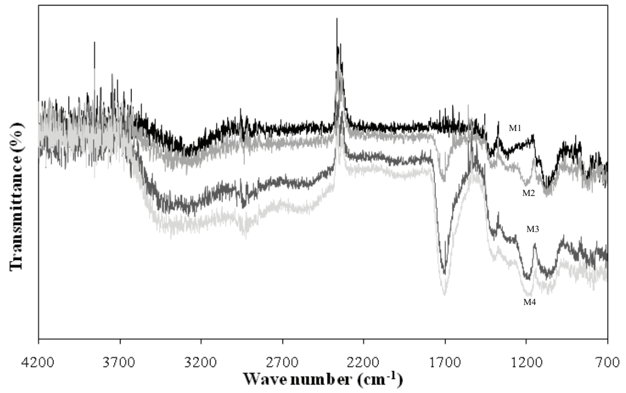


Fig. 5. The ATR–FTIR spectra of the PVA/PES composite membranes with various CA contents.

Finally, the swelling degree of the PVA layer of the fabricated mixed matrix membranes was determined by the gravimetric method and the results are represented in Fig. 7. It was observed that the NaX zeolite filled PVA membranes had lower swelling degree than the neat PVA membrane (M5 sample). It means that addition of NaX zeolite nanoparticles into the PVA top layer of the membranes decreased the swelling phenomenon and an increment in the zeolite content of the membrane led to a lower membrane swelling. This trend can be attributed to the reduction in the flexibility of the polymer chains and decreasing the membrane free volumes. In the mixed matrix membranes, the zeolite nanoparticles occupy the void spaces between the PVA chains and restrain the movement of polymer chains surrounding the zeolite. Therefore, the swelling degree of the membranes decreased by the addition of the NaX zeolite nanoparticles. These results agree well with the results reported by other researches. For instance, Khoonsap and Amnuaypanich [24] observed that incorporating 4A zeolite into the cross-linked PVA resulted in a lower degree of swelling. Kang et al. [33] reported that the swelling degree of neat chitosan (CS) membranes was significantly higher than the CS mixed matrix membranes loaded with the microporous ZIF-7 crystal particles as filler.

3.3. Pervaporation performance

3.3.1. Effect of cross-linking

The effect of cross-linking and cross-linker concentration on the separation performance of the two-layer PVA/PES composite membranes for dehydration of a 90%wt. aqueous ethanol solution was investigated and the results are shown in Fig. 8. As indicated in this figure, the non-cross-linked membrane (M1 membrane sample) has lower water separation factor and higher permeation flux in comparison with the cross-linked membranes. Furthermore, an increase in the CA content of the membrane led to a lower total flux and higher water separation factor. On the other hand, as the CA concentration enhanced from 0 to 15%wt., the total permeation flux decreased from 591 g/m^{2}h to 396 g/m^{2}h while the water separation factor increased from 3 to 61. This indicates that the degree of cross-linking of the PVA membranes enhanced with an increase in the CA concentration of the membrane casting solution. These observations are agreed well with the results of the ATR-FTIR and swelling analysis. The influence of CA content on the separation performance of the fabricated membranes may be related to

Table 3
The transmittance of some functional groups in the ATR-FTIR spectra of the fabricated membranes

Membrane	C=O (1,680–1,750 cm^{-1})	C=O (1,700–1,725 cm^{-1})	O-H (2,360 cm^{-1})	O-H (3,371 cm^{-1})
M1	85.85	99.45	153.75	92.63
M2	79.17	75.58	136.48	85.90
M3	44.56	30.25	112.14	63.37
M4	37.29	20.78	106.09	54.22

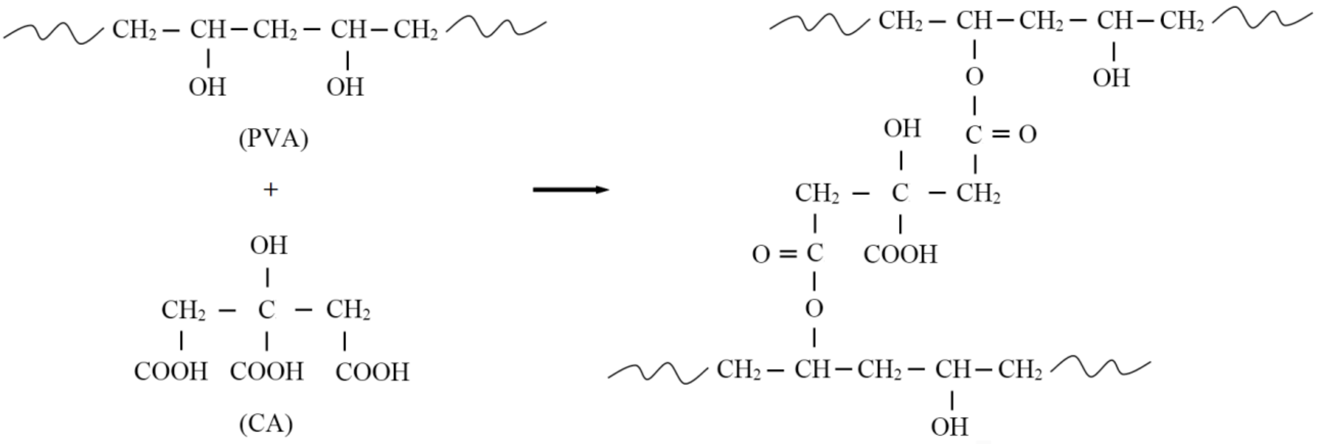


Fig. 6. Schematic cross-linking mechanism of the PVA with citric acid.

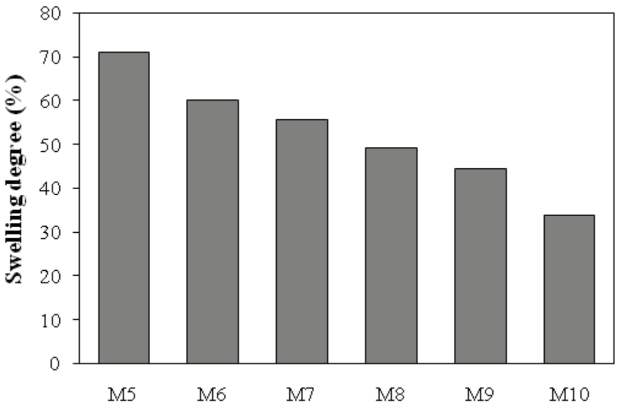


Fig. 7. The effect of zeolite concentration on the swelling degree of the fabricated membranes.

the degree of cross-linking and flexibility of the polymer chains. Based on the ATR-FTIR results, the cross-linking of the PVA membrane increased with an enhancement in the CA concentration. Cross-linking has a significant effect on the polymer network structure and the cross-linked polymer becomes rigid and more compact. Therefore, the cross-linked membranes possess high obstruction to the diffusion of permeants, especially the large molecules which lead to a lower permeation flux. As shown in Fig. 8(b), the water partial fluxes increased with enhancement in the CA concentration up to 2%wt., while the ethanol flux decreased by increasing CA concentration due to the larger molecular size of ethanol than water. Therefore, the ratio of the water flux to the ethanol permeation flux, which is proportional to the water separation factor enhanced when the CA concentration of the membrane casting solution goes to a higher level. In other words, when the PVA top layer of the composite membranes was cross-linked and by an increase in the concentration of the cross-linking agent, the obtained membrane became more selective to the water transport, and consequently the water separation factor enhanced. A similar trend was observed in the literature,

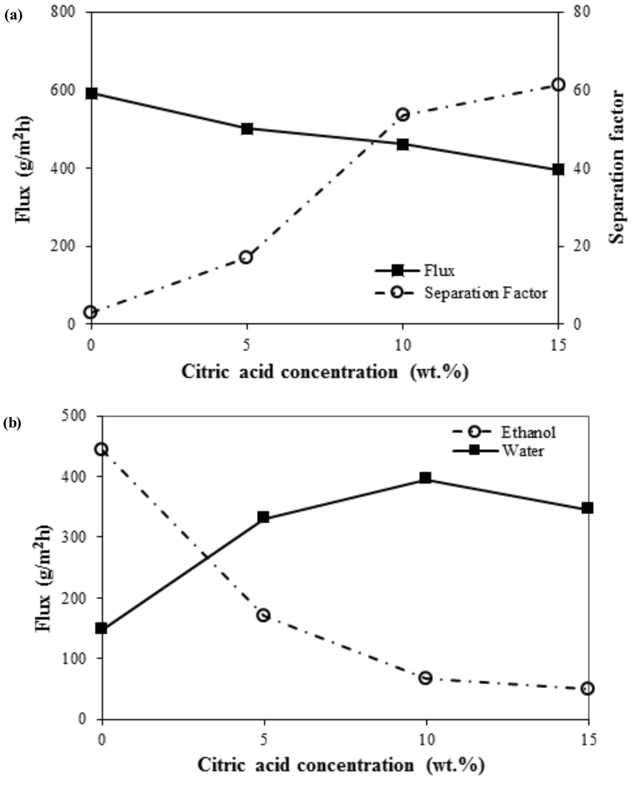


Fig. 8. The effect of citric acid concentration on the total flux and water separation factor (a) as well as on the water and ethanol partial fluxes (b).

i.e. cross-linking of the membranes results in lower permeation flux and higher selectivity and improves the membrane separation performance [16,17]. As indicated in Fig. 8, the M3 membrane sample has a reasonable permeation flux and water separation factor in comparison with other membrane samples, therefore the CA concentration of 10%wt. was used for the preparation of mixed matrix membranes.

3.3.2. Effect of NaX zeolite nanoparticles

The pervaporative separation performance of two-layer mixed matrix membranes for dehydration of a 90%wt. aqueous ethanol solution was studied. Fig. 9 shows the influence of NaX zeolite nanoparticles on the permeate flux and separation factor of the fabricated membranes. As shown in Fig. 9(a), all zeolite loaded mixed matrix membranes have higher permeation flux and separation factors than the neat PVA membrane. For instance, the total flux of the membrane increased from 461 g/m^{2}h for the M5 membrane to 843 g/m^{2}h for the M10 membrane sample, while the water separation factor enhanced from 53.6 to 95.8 for these membrane samples. Furthermore, an increase in the zeolite content of the membrane led to higher total permeation flux, whereas the water separation factor enhanced as the zeolite content varied from 0 to 2%wt. and a further increment in the zeolite content of the membranes resulted in a lower separation factor. The water separation factor increased from 53.6 to 122.1 with an increase in the membrane zeolite content from 0 to 2%wt., while increasing zeolite concentration from 2 to 4%wt. led to reduction in the separation factor from 122.1 to 95.8. Also, the water partial flux enhanced with increasing nano zeolite content as indicated in Fig. 9(b). The increase in the total and water fluxes can be attributed to the hydrophilic nature of the NaX zeolite. Generally, the addition of CA as a cross-linker agent and NaX zeolite as a hydrophilic filler into the PVA matrix have two contrary effects on the structure and chemistry of the obtained cross-linked mixed matrix membranes. The addition of CA into the PVA and the cross-linking reaction increase the membrane crystallinity and reduce the membrane hydrophilicity due to the consumption of hydrophilic groups on the gelatin chains. Also, the incorporation of zeolite nanoparticles decreases the membrane flexibility. Thus, the addition of CA and zeolite make the membrane more rigid and the permeation through the membrane becomes more difficult. On the other hand, both PVA and NaX zeolite are hydrophilic materials and loading hydrophilic NaX zeolite filler to the PVA layer of the mixed matrix membranes enhances the hydrophilicity of the membrane. The hydrophilicity, introduced by NaX zeolite along with the polymer itself, can make the prepared membrane able to form more specific interactions like hydrogen bonding between the water molecules and zeolite-filled membrane. The strong interactions between the water and membrane facilitate the water transport through the membrane. Therefore, the water and total permeation fluxes rise by incorporating more zeolite nanoparticles into the active layer of the mixed matrix membranes. Furthermore, Fig. 9(b) revealed that the ethanol partial flux slightly decreases by enhancing zeolite concentration up to 2%wt. and a further increase in the NaX zeolite content leads to higher ethanol permeation flux. The reason is that the agglomeration of zeolite nanoparticles occurs under high zeolite content. Generally, in the mixed matrix membranes well-dispersion of the inorganic filler particles into the polymer matrix makes it difficult to achieve a uniform membrane structure. Therefore, the agglomeration of zeolite particles leads to void volumes around zeolite and creates cracks in the membrane. The ethanol molecules pass easily through such defects and the ethanol permeation flux increases at zeolite concentrations higher than 2%wt. and consequently the water separation factor declines as the zeolite loading increases from 2 to 4%wt. Similar results have been reported in previous studies [11,24]. Amnuaypanich et al. [11] observed that increasing the filler content in 4A zeolite/NR-PVA mixed matrix membranes improved both the total flux and the separation factor for the dehydration of aqueous ethanol solutions. However, the total permeation flux and separation factor enhanced and reduced, respectively by further increasing the zeolite concentration.

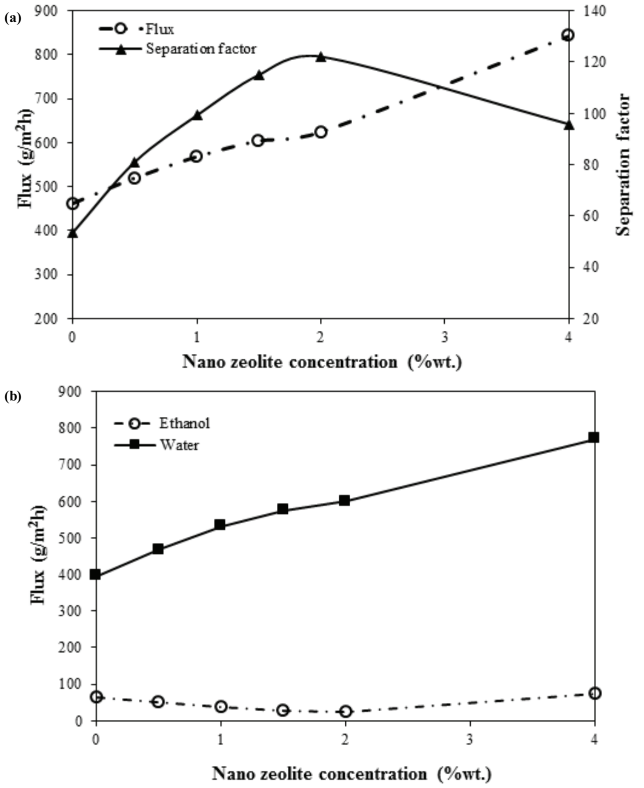


Fig. 9. The effect of zeolite concentration on the total flux and water separation factor (a) as well as on the water and ethanol partial fluxes (b).

Besides, the separation performance of the mixed matrix membrane containing 2%wt. zeolite (M9 membrane) was evaluated for the dehydration of other monohydric alcohols like methanol and isopropanol from their 90%wt. aqueous solutions and compared with the performance of the commercial hydrophilic membrane, i.e., PERVAP 2210. Fig. 10(a) indicates the total flux and separation factor of the M9 membrane sample for dehydration of methanol, ethanol and isopropanol. It was found that the total permeation flux increased in the order of isopropanol < ethanol < methanol and the water separation factor had a reverse trend. It is well-known that the molecular size of the monohydric alcohols enhances in the order of isopropanol > ethanol > methanol. Based on the solution-diffusion mechanism, the molecular size of the permeating components affects both sorption and diffusion steps through the membrane in the pervaporation process. As the size of the permeating molecules increases, the molecules become more hydrophobic [34] and its sorption into the hydrophilic PVA membrane decreases. On the other hand, increasing the size of the permeating molecules decreases the molecular mobility and leads to a lower diffusion coefficient through the membrane. Therefore, the permeation flux decreases and the water selectivity enhances from the methanol/water mixture to the isopropanol/water mixture.

The pervaporation performance of the commercial PVA membrane for 90%wt. aqueous solution of methanol, ethanol and isopropanol is given in Fig. 10(b). As observed in this figure, the PERVAP 2210 membrane had the same trend as the prepared mixed matrix membrane, while the permeation flux and water separation factor of the M9 membrane sample were significantly higher than those of the commercial membrane.

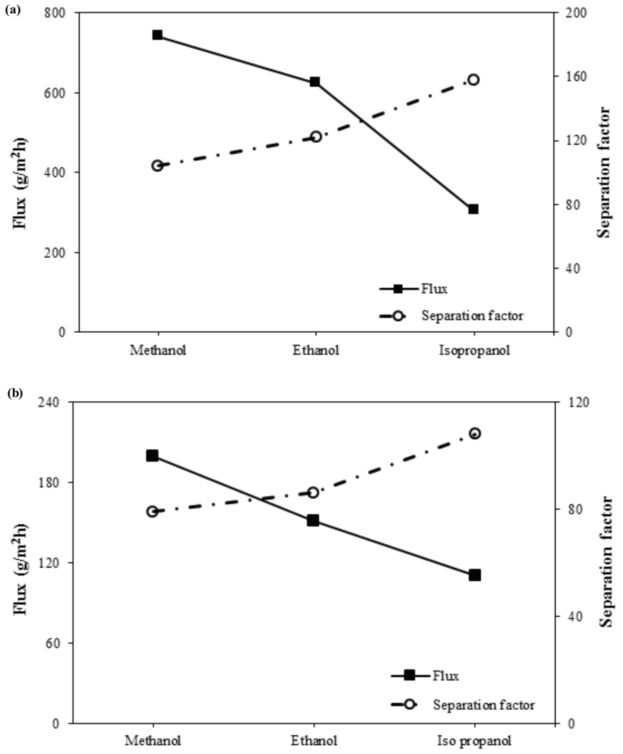


Fig. 10. The separation performance of the mixed matrix membrane containing 2%wt. zeolite (a) and PERVAP 2210 (b) for dehydration of 90%wt. aqueous solution of alcohols.

Furthermore, a 24-h pervaporation test was conducted using the M9 membrane sample in order to evaluate the long-term stability of the fabricated mixed matrix membranes. Fig. 11 shows the total permeation flux and ethanol permeate concentration of the M9 membrane sample for the long-term pervaporation test. The results indicated the mixed matrix membrane containing 2%wt. zeolite (M9 membrane) had good performance and stability for the long time with average separation factor of 122.

Finally, the pervaporation performance of the fabricated mixed matrix membranes were compared with the separation performance of different PVA membranes reported by other researches for ethanol/water separation and the results are presented in Table 4. It can be seen that the total flux of

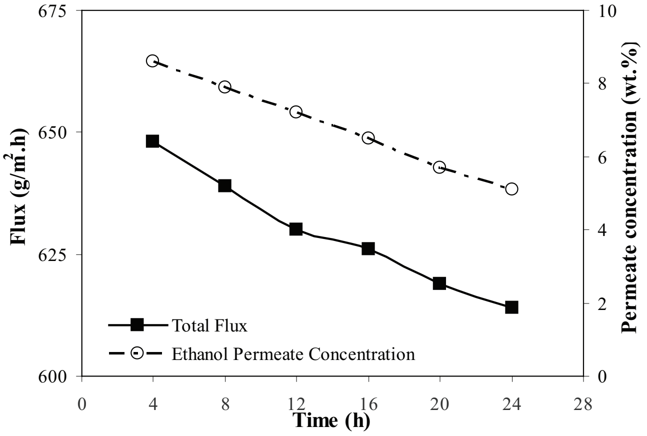


Fig. 11. The total permeation flux and ethanol permeate concentration of the mixed matrix membrane containing 2%wt. zeolite for the long-term pervaporation test.

Table 4
The pervaporation performance of different PVA membranes for the dehydration of ethanol/water mixtures

Membrane	Feed water concentration (%wt.)	Feed temperature (°C)	Total flux (g/m^2h)	Water selectivity	Ref.
PVA/Ceramic	10	50–70	330–1,050	38–56	[5]
PVA-NaX/PAN/Polyester	20	60	506	1,060	[23]
PVA-SA/PSf	10	45	391	387	[29]
PVA	10	50	232	30	[35]
PVA	10	60	50	4,200	[36]
PVA/PES	10	80	295	83	[37]
PVA-KA	20	50	140–288	5.74–40	[38]
PVA-TEOS	25	40	4–5	239–893	[39]
PVA/APTEOS	15	60	60	200	[40]
PVA-PAA/PES	20	40	250	11	[41]
PERVAP 2210	10	30	151	86	This study
NaX-PVA/PES (M9 sample)	10	30	624	122	This study

the mixed matrix membrane prepared in this work is higher than those of most PVA membranes with and without other inorganic filler particles reported in the literature and the nano NaX zeolite filled membrane has a reasonable water separation factor. For example, the mixed matrix membrane containing 2%wt. zeolite nanoparticles has a water separation factor of 122 and total flux of 624 g/m^{2}h for the dehydration of 90%wt. aqueous ethanol solutions at temperature of 30°C.

4. Conclusions

Two-layer mixed matrix membranes were fabricated by incorporating NaX zeolite nanoparticles into the cross-linked PVA as the selective layer on the porous PES ultrafiltration membrane as the support layer and the fabricated membranes were used in the pervaporation dehydration of aqueous monohydric alcohol solutions for biofuel production. The followings were observed during this research:

- The PVA layer was successfully cross-linked by citric acid as a green cross-linking agent. Based on the ATR-FTIR analysis and swelling measurement, the membrane became more cross-linked with an increase in the CA content of the membrane. The cross-linked membranes had lower permeation flux and degree of swelling as well as higher water separation factor in comparison with the non-cross-linked membrane.
- Incorporation of nano NaX zeolites into the PVA top layer of the membranes strongly affects the permeate flux and water selectivity of the membrane. An increase in the zeolite concentration of the membrane from 0 to 4%wt. resulted in higher total flux, while a maximum was found for the water separation factor at the zeolite concentration of 2%wt., the total flux of 461 and 624 g/m^{2}h and water separation factor of 53 and 122 were obtained for the M5 and M9 membrane samples, respectively. Furthermore, based on the SEM and AFM analysis, as the filler loading of the membrane changed from 0 to 4%wt., the amount of zeolite particles on the membrane surface increases and leads to a rougher membrane surface.
- Comparison of the flux and selectivity of the M9 membrane sample for dehydration of aqueous methanol, ethanol and isopropanol solutions revealed that the total flux reduced and the water separation factor enhanced in the order of isopropanol > ethanol > methanol.
- Finally, the pervaporative separation performance of the PVA/PES mixed matrix membrane contains 2%wt. NaX zeolite was compared with the commercial PVA/PAN membrane of PERVAP 2210 and it was found that the M9 membrane had higher permeation flux and water selectivity for dehydration of alcohols than the commercial membrane.

Finally, it can be concluded that the incorporation of NaX zeolite nanoparticles into the cross-linked PVA as a hydrophilic polymer successfully improved the membrane performance for the dehydration of alcohols as a fuel additive. However, more research should be conducted to modify the polymer–zeolite interface in the mixed matrix structure for well-dispersion of the filler nanoparticles into the polymer matrix, especially at high zeolite contents.

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