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Laponite/PVA pervaporation membrane for desalinating simulated RO high-salinity by-product

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ABSTRACT

In this study, pervaporation (PV) was used as a great promise for freshwater production from high-salinity water. Laponite nanodisc/poly (vinyl alcohol) (PVA) membranes were produced by simple exfoliation method of the nanoclay in the polymer solution using glutaraldehyde (GA). The surface morphology of the produced membrane and the influence of the addition of the nanoclay were investigated using a scanning electron microscope. The effect of the laponite addition on thermal stability and membranes properties as well as swelling measurements was discussed. The pervaporation desalination water flux and salts rejection characteristics of the prepared membranes were observed at different laponite concentration up to 10 wt%, under operating temperature of 30°C–70°C and salt solution concentration (0–10 wt%) in the feed were determined at constant feed and permeate pressure of 1 and –8 mbar, respectively. The salt rejection for all membranes was more than 99.9% with significant-high flux. The highest water flux of 49.25 kg/m^2 h was obtained using the membrane with 2 wt% loaded-laponite with a rejection of 99.94% when desalinating 5 wt.% NaCl solution at 70°C. Overall, the salinity of the feed solutions varied from 0% NaCl to 10 wt.% NaCl (0 to 100 g/L) solutions while the salinity of the permeate was from 0.01 to 0.2 g/L.

Keywords: Nanoclay; Mixed matrix membranes; Pervaporation; Desalination; Poly (vinyl alcohol)

1. Introduction

Nowadays, water shortage is one of the most serious threats to human beings and social developments. Due to the high population and shortage of pure clean water finding a new technology to treat high salinity water and provide clean water became an essential issue [1,2]. Nowadays, the most-considered solution to eliminate water shortage threat and to produce freshwater from different sources is desalination [3]. Generally, desalination processes can be divided into thermal traditional processes such as distillation and non-thermal processes such as reverse osmosis (RO), pervaporation (PV), and membrane distillation (MD). Nowadays, penetration of membrane technology into desalination field is much faster, owing to the high efficiency, low capital and energy costs and ease of integration and scale-up in comparison with competing traditional distillation processes [4,5]. Currently, RO is considered the dominant method for desalinating used for about 60% of the world desalination capacity.

In addition to the high pressure and several pretreatment processes required for RO as well as the incompatibility for high salinity feeds and the fouling issues, RO desalination by-product such as high concentrated solution

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has been classified as threat waste to the environment and ecological life especially when it goes back to the ocean [6]. Therefore, it is necessary to find new engineering solutions to provide fresh water from high salinity water [7,8]. Over the last years, PV and MD seemed to be considered strongly as a promising and emerging tool for desalination process as well as to their anti-fouling ability. However, the crucial problems in using MD such as wetting and fouling lead to convert it to non-economical option particularly for long term [9]. On the other hand, PV provides a potential option for freshwater production from high-saline solutions owing to the low energy consumption during the desalination process [10–12].

In the PV process, the well-known solution-diffusion model of mass transport is approved. Basically, the feed mixture is heated to a certain temperature then penetrate through the membrane to be converted to gas and leave from the permeate side. By maintaining vacuum, the collected vapors are condensed by cold medium [13]. Subsequently, PV is able to provide a high percentage of rejection due to using dense membranes and non-volatility of salt. Moreover, hydrophilic dense PV membranes ensure high level of anti-fouling besides their ability to reject VOCs providing high-quality water [14]. Therefore, The most considered pervaporation membranes for desalination process are the hydrophilic dense polymeric membranes owing to their high water solubility as reported [11,15,16], and most used is poly(vinyl alcohol) [12,17,18].

Poly(vinyl alcohol) PVA is one of the most used polymers for pervaporation process, due to its advantages in resisting pollution, easy forming, environmentally friendly and stability [19–21]. Nowadays, using nanofiller from the silicate clay type for pervaporation based PVA membranes such as clinoptilolite, montmorillonite, and Bentonite is well established [22–24]. Laponite nanoclay is a new synthetic silicate clay having a layered structure with dimensions as shown in Fig. 1, with empirical formula $Na^{+0.7}[(Mg_{5.5}Li_{0.3})Si_8\,O_{20}\,(OH)_4]^{-0.7}$. Hence, Laponite nanodiscs clay has been well-established as nanofiller in several fields such as drug delivery, biochemistry, and tissue engineering due to their significantly high surface area, biocompatibility in addition to their high cationic exchangeability [25–27]. Additionally, the nanodiscs have shown extreme hydrophilicity behavior and are easy dispersed in water and widely reported in enforcing nanocomposite and hydrogels by improving their mechanical and physical stability

Additionally, the nanoclay has been widely reported as enforcing material for the mechanical and physical stability for nanocomposites and hydrogels, as well as its extreme hydrophilicity behavior and ease exfoliation in water [28–31].

In our last paper [32], we have observed that using laponite nanoclay as a nanofiller in crosslinked PVA produce a new pervaporation membrane by facile dispersing process. Based on contact angle and water uptake analysis, the new membranes have higher hydrophilicity with respect to the pristine crosslinked membrane. The kinetic desorption method has been applied to investigate salt transport properties. In addition to enhancing the thermal and mechanical stability of PVA membranes, the incorporation of 2 wt% laponite could achieve the highest flux for desalinating aqueous saline solution of 3 wt% NaCl at 70°C.

The aim of this work is to eliminate the high concentrated RO by-product using 2 wt% laponite membranes which previously achieved the highest flux. The thermal and surface properties for higher clay content membranes were evaluated using thermogravimetric analysis (TGA) and scanning electron microscope (SEM), respectively. The effect of laponite content on swelling behavior of the membrane and pervaporation desalination performance in relation to permeate flux and salt rejection at the RO by-product concentration was studied. Influence of feed concentration change on the desalination performance of PVA with was determined. The effect of feed temperature on desalinating 5 wt% NaCl solution using 2 wt% laponite membrane was determined.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (MW of 85,000–124,000 g/mol and 99%+); glutaraldehyde (Grade II with 25% in H_2O) were supplied by Sigma-Aldrich (Schnelldorf, Germany). Sodium chloride was purchased from Reanal Chemicals Ltd. (Budapest, Hungary). Laponite XLG was provided from Byk Additives and Instruments. All chemicals were used as such without further purification.

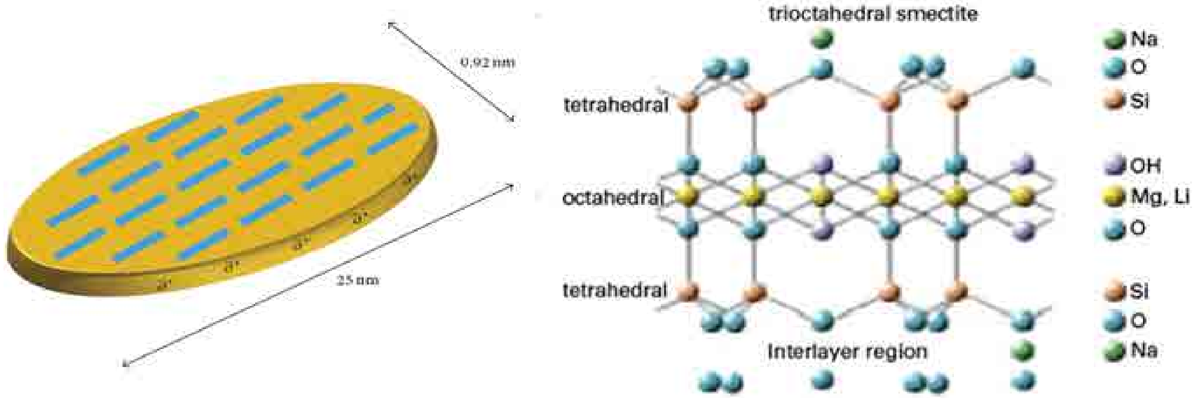

Fig. 1. Chemical structure of synthesis laponite nanoclay (from Southern Clay Products product information website).

2.2. Membrane fabrication

The solution-casting procedure was used to synthesize all the membranes, containing 5% PVA containing 0.3 v/v% of glutaraldehyde and different laponite content via phase inversion. For pristine membrane, 5 g of the polymer was dissolved in 100 ml of DI and stirred at 90°C when a clear homogenous solution is obtained 0.3 v/v% GA and few drops of 37% HCl solution were added and continues stirred for 3–5 min. The 5 wt% polymer solution was cast onto a Poly (methyl methacrylate), (PMMA), and plate and dried in air followed by 3 h of annealing in an oven at 40°C. For the laponite-loaded membranes, a clay solution with different Laponite content varied from 2 to 10 wt% with respect to the dry PVA weight was mixed with the PVA solution after sonicated for 3 h. The mixed solution was stirred for 24 h obtaining a homogenous PVA/GA/laponite solution. Afterward, the casting solution was following same steps as plain PVA membrane. The scheme for the preparation procedure is shown in Fig. 2 [32].

2.3. Morphological studies

The morphology of the clay, the surface of all the membranes as well as the cross-section of 2wt% laponite membrane were determined using a JEOL JSM-5500LV SEM. The samples were covered by sputtering with gold.

2.4. Thermal stability

Thermal stability of the powder clay, Pristine cross-linked PVA, as well as all the MMMs were studied by TGA (PerkinElmer TGA-6, Rodgau, Germany) in the temperature from 35°C to 700°C at 10°C/min^{-1} under nitrogen. The average mass of the sample was 10 mg. Temperature and sample weight were recorded.

2.5. Swelling degree

The hydrophilicity of the membranes was examined by the swelling measurements. The totally dry known weight membrane was immersed in simulated RO by-product (5 wt.% NaCl) solution for 10 h. at room atmosphere. All membranes then were taken from the water, and the surface water was totally removed using a filter paper and weighed. The swelling degree (SD) of the membrane is calculated using the following equation:

$$\text{SD}\% = \frac{W_{\text{swollen}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \tag{1}$$

where W_{swollen} (g) and W_{dry} (g) are the weight of swollen and dry membrane, respectively.

2.6. Desalination pervaporation performance

As our previous papers, the pervaporation desalination experiments were conducted using the synthesized membranes [13,32]. All the membranes were cut to have an effective area of 28 cm^2 then kept in the membrane cell on mechanical support. A feed solution of 50 g/L NaCl (5 wt.%), representative of an RO by-product solution was used. The mixture was circulated at a flow rate of ~182 L/h through the cell after adjusting the temperature between 40°C and 70°C. The permeate side was at low pressure of 6 torrs using VACUUMBRAND PC2003 VARIO vacuum pump to maintain the required driving force across the membrane. On the permeate side, a liquid nitrogen cold trap was used to collect the output solution. To investigate the membrane efficiency for the desalination process, water flux and salt rejection were calculated using the following equations:

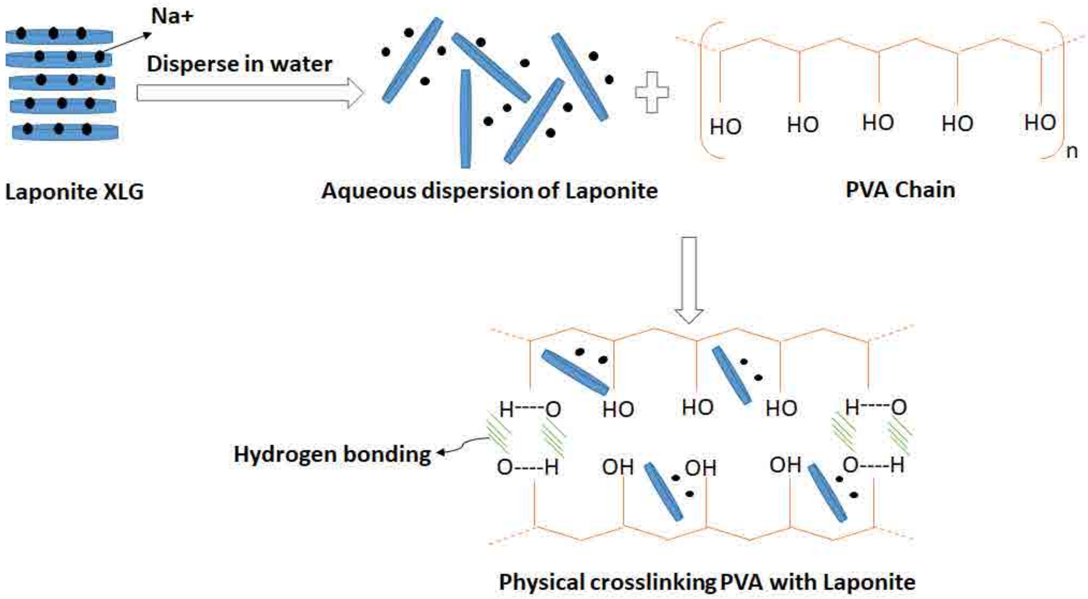

Fig. 2. Simple scheme for the production of PVA-Laponite mixed matrix membranes.

$$J = \frac{W}{A \times t} \tag{2}$$

The salt rejection (R) was determined from the concentration of the feed (C_f) and the permeate (C_p), which were calculated from the measured conductivity using an electrical conductivity meter (Mettler Toledo FiveEasy, Leicester-UK) using the following equation:

$$R = \frac{C_f - C_p}{C_f} \times 100\% \tag{3}$$

3. Results and discussion

3.1. Morphology

As shown by the SEM image, the surface micrograph in Fig. 3a represents the smooth and dense PVA pristine membrane. The surface SEM images of 2, 5, 7 and 10 wt.% laponite-loaded PVA are shown in Figs. 3b–e, respectively. The homogeneous dispersion of the laponite with no cracks or void around them can be clearly distinguished from the surface micrograph of the membranes. However, the roughness and the density of the surface increased by incorporation of the laponite clay. The higher the laponite content is, the higher roughness and agglomerations on the surface in addition to increasing the surface roughness (Fig. 3e). The cross-section of the 2 wt% laponite membrane Figs. 3f and g display the uniform and homogenous dispersion of the clay in the polymer matrix indicating perfect exfoliation process; additionally, it shows the average thickness of the membrane to be 122 μm.

3.2. TGA

Thermal properties were studied for laponite clay, PVA and laponite-loaded PVA mixed matrix membranes in the temperature range of 35°C–700°C and under nitrogen. Fig. 4 shows the TGA curves of laponite, Plain PVA membrane and 10 wt.% laponite mixed matrix membrane. The water release or the dehydration process weight loss could be observed at about 150°C for both pristine and laponite membrane [27]. Hence, TGA analysis was done till 700°C, the laponite layers did not show any thermal degradation. Pristine membrane demonstrates polymer side chain decomposition between 200°C and 350°C. Finally, the third thermal degradation related to the decomposition of the backbone of PVA and the carbonated residue such as glutaraldehyde split to two stages between 350°C and 450°C, and 450°C and 580°C

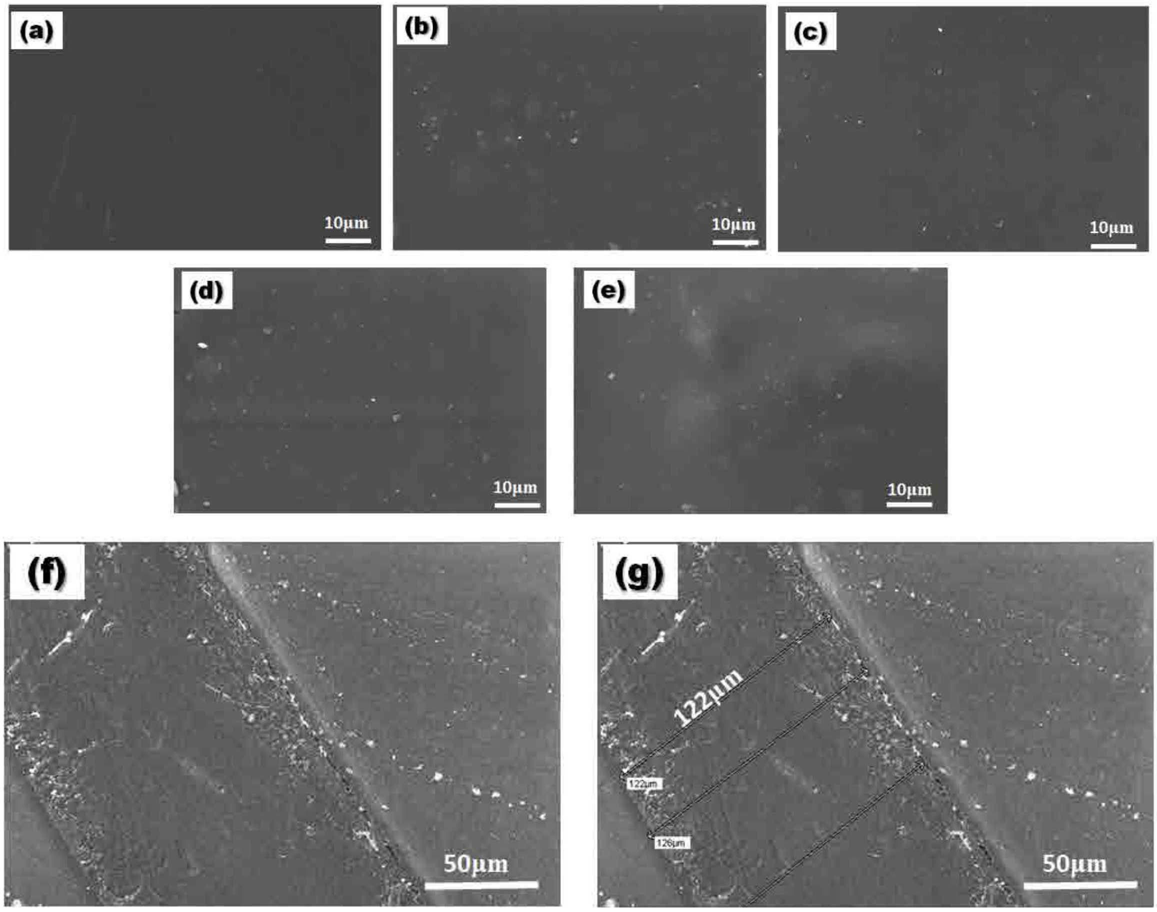

Fig. 3. SEM images of laponite powder (a) pristine PVA (b) 2 wt.% laponite (c) 5 wt.% laponite, (d) 7 wt.% laponite (e) 10 wt.% laponite, and (f,g) cross-section 2 wt.% laponite.

respectively [33,34]. With the addition of laponite, both the residual weight and the thermal degradation temperature of the laponite/PVA membrane increased. When the clay content was increased from 0 in PVA to 10 wt%, the residual weight increased from 4.36 wt% to 15.4 wt%. Additionally, the 10 wt% laponite-loaded mixed matrix membrane showed approximately 40°C higher degradation temperature or 30% weight loss in comparison with the pristine membrane.

3.3. Hydrophilicity of the membranes

Hence, the hydrophilic membranes swell in aqueous solution, the polymer chain becomes more flexible hence producing a higher permeation rate through the membrane, and therefore the degree of swelling is an essential factor for the pervaporation desalination process. The degree of crystallinity, the diffusion coefficient of the solvent and the rate of diffusion is the most critical factor causing the swelling of any polymer [35]. Influence of incorporating different laponite content on the swelling behavior of the membranes was investigated in 5 wt.% NaCl solution during 10 h at atmospheric condition and results are presented in Fig. 5. The results show that the swelling degree first increases with loading laponite and then decrease with further addition of the clay. The initial increase could be due to the higher hydrophilicity behavior of the membrane [30], while the decrease with increasing laponite content can be associated with decreasing the polymer free-volume and confined the active sorption sites of the laponite [36].

3.4. Desalination experiment

3.4.1. Influence of laponite content

Fig. 6 shows the impact of doping different laponite concentration in the PVA matrix on the desalination pervaporation performance. It is easily recognized that the flux first increased from 20.25 to 34.1 kg/m^2 h when the laponite nanodiscs incorporated then slightly decreased to 32 and 31.17 kg/m^2 h for 5 wt% and 7 wt% laponite, respectively, for desalinating 5 wt.% NaCl solution at 40°C. However, 10 wt.% loaded laponite membrane is still showing higher flux compared with the flux of the plain PVA membrane. Therefore, the contribution of the nanoclay in the PVA matrix led to an increase in the membrane water permeability. This result is consistent with the swelling measurements.

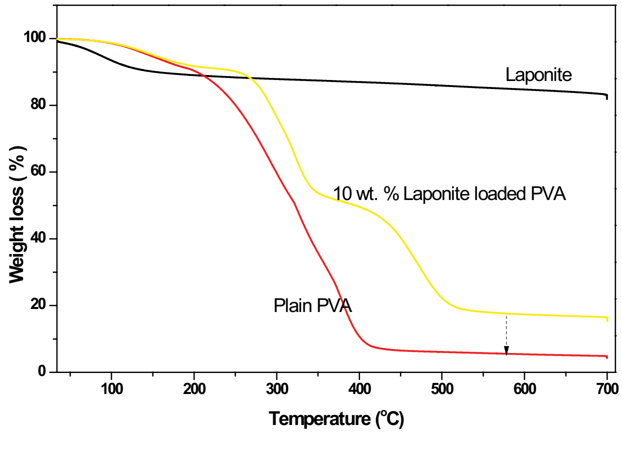

Fig. 4. TGA curves of laponite clay (black), Plain PVA (red), and 10 wt.% laponite-loaded PVA (yellow) mixed matrix membranes.

On the other hand, the salt rejection is also shown in Fig. 6 preserves increase the salt rejection from 99.5% for the plain PVA to 99.94% for the 2 wt.% laponite-loaded membrane. Moreover, further incorporation of laponite resulted in a slight increase in the salt rejection to a maximum of ~99.98% for 7 wt.% laponite then was hindered at 10 wt% laponite. The size exclusion mechanism during the desalination could be the main reason for this trend [37,38]. Hence, the free space in the polymeric chain could be restricted. Therefore, the smaller molecules (H_2O with 0.27 nm) will easily penetrate while the bigger size ions (Na^+ with 0.712 nm and Cl^- with 0.664 nm) will be rejected [39].

3.4.2. Effect of feed concentration on the desalination rejection

Fig. 7 represents the effect of the feed concentration (NaCl %) on the desalination performance of the 2 wt.% laponite-loaded membrane at 40°C. The results show a declination in the flux from 42.7 to 26.4 kg/m^2 h with increasing the salt concentration from 0 to 10 wt.% in the feed solution, however, the salt rejection show a modest increase from 99.90% to ~99.95% at the same conditions.

The charge exclusion theory gives a clear explanation of the drastic decrease in the flux, hence membrane surface will reject all the same charged ions and keep them in the feed side [39]. On the other hand, laponite nanoclay surface is negatively charged and edges are positively charged, consequently, when desalinating NaCl aqueous solutions the surface of laponite will be positively charged with the sodium ions, and only Cl^- will be rejected. Accordingly, increasing the salt concentration in the feed solution will result in decreasing the permeation through the membrane.

3.4.3. Effect of operating temperature

As the operating temperature could actuate the water permeability and diffusivity through the membrane, the temperature is considered as a prevailing feature in the pervaporation process [40]. Moreover, due to the vacuum pressure on the permeate side, the vapor pressure is neglected, therefore changing the temperature has a considerable impact on water vapor pressure. Consequently, higher temperature results in significantly higher driving force and accordingly higher water permeation through the membrane [41]. Additionally, temperature affects the thermodynamic properties of the feed as well as the polymer chain mobility. Fig. 8 represents the influence of feed temperature on the desalination pervaporation process.

It can be noted that the flux is dramatically increased by approximately 44% with increasing the feed temperature by 40°C. On the other side, salt rejection remains over 99.9% regardless of the feed temperature is, whilst the increase in temperature led to an obsolete decrease in membrane retention. This could be assigned to increase the water vapor pressure on the feed side, therefore, increase the driving force across the membrane. Consequently, increase both the

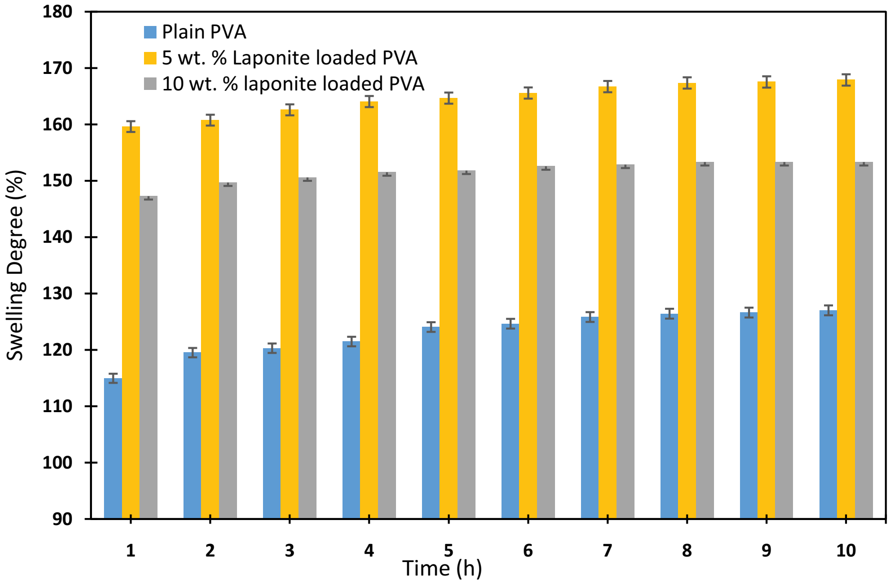

Fig. 5. Swelling measurements of PVA and laponite-loaded PVA mixed matrix membranes.

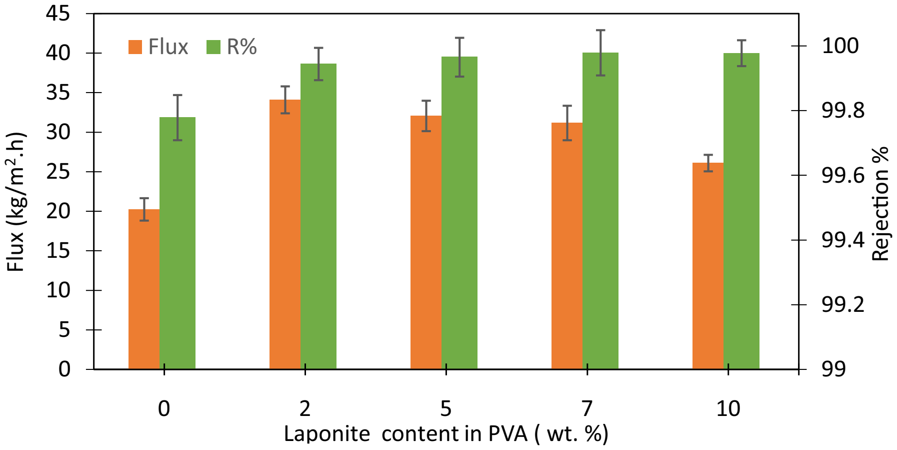

Fig. 6. Influence of laponite content on pervaporation desalination performance with 5 wt.% NaCl feed at 40°C.

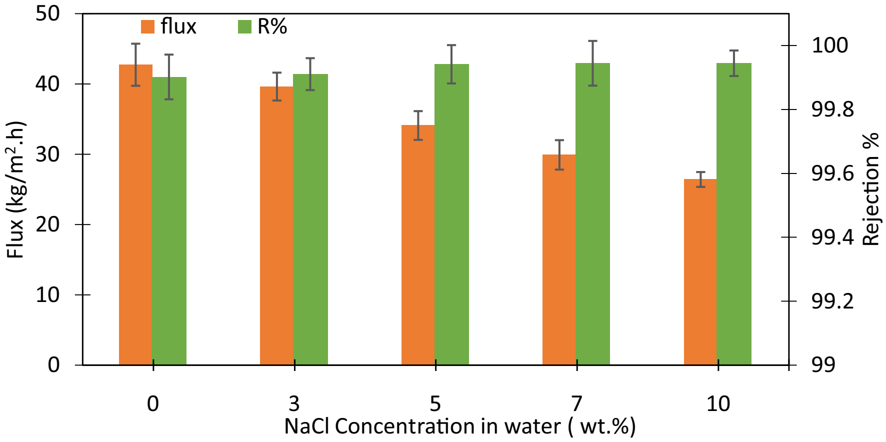

Fig. 7. Influence of NaCl concentration on desalination performance, (2 wt.% laponite-loaded membrane, at 40°C).

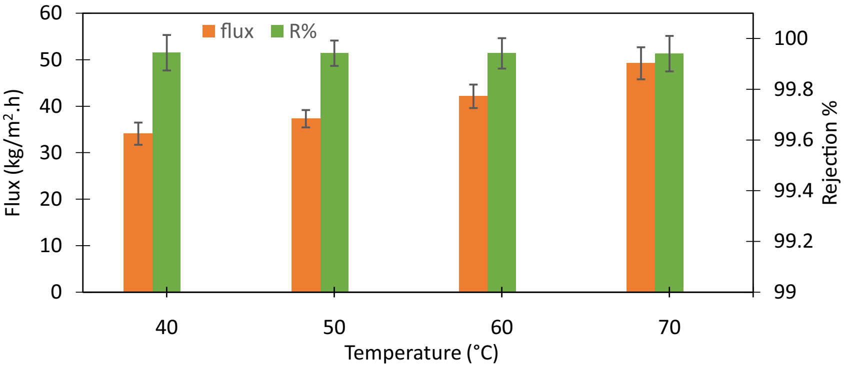

Fig. 8. Pervaporation desalination performance at different temperatures of 2 wt% laponite-loaded PVA mixed matrix membrane with 5 wt.% NaCl feed solution.

Table 1
Comparison of other membranes reported in the literature for Pervaporation desalination

Membrane material	Temperature	NaCl	Flux	Rejection	Reference
	(°C)	(g/L)	(kg/m² h)	(%)	
PVA/PS HF	70	50	6.5	99.9	[17]
PEPA Co-Polymer	65	50	1.5	99.9	[16]
CS/GO-1	75	50	25.8	99.99	[42]
PVA/PAN/PET	Room	50	8.51	99.8	[12]
Cellulose Acetate	70	50	~3.5	>99.8	[15]
S-PVA/PAN	40–70	50	~11–21	99.8	[18]
2 wt.% Laponite /PVA	40–70	50	34.1–49.2	>99.9	This study

diffusivity and solubility of water through the membrane. Additionally, increasing the temperature led to increasing the free volume in the polymer chain mobility result in increased water permeation [39]. These desirable results incarnate the advantages of increasing the feed temperature on the desalination pervaporation of high-salinity water.

Table 1 shows a brief comparison between several reported pervaporation desalination performance membranes in the literature.

4. Conclusion

Concluding that, mixed matrix crosslinked membranes based on laponite nanoclay, PVA and GA were fabricated via exfoliation method. Pervaporation desalination performance of different NaCl solution was investigated using different laponite-loaded PVA mixed matrix membranes. Both the thermal degradation temperature and the residue weight of the PVA membrane were improved upon the laponite incorporation. The swelling degree of the laponite/PVA mixed matrix membranes in brine solution was substantially amplified by the addition of 2 wt% laponite. However, all the mixed matrix membranes showed fluxes higher than the PVA plain membrane and salt rejection over 99.9%. A membrane with 2 wt.% laponite loaded obtained the highest water flux of 34.1 kg/m² h while the higher salt rejection of ~99.98% obtained by 7 wt.% laponite for desalinating 5 wt.% NaCl solution at 40°C. The feed concentration and feed temperature had a significant effect on the flux permeation of water through the membrane, where increasing the operating temperature from 30°C to 70°C led to remarkable increase in the water flux by approximately 44%, while the salt rejection remained higher than 99.9%. This work concluded that the incorporation of nano-layered silicate clay in the PVA matrix could be a promising membrane for high-salinity solutions pervaporation desalination application.

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