Recovery of cutting oil from wastewater by pervaporation process using natural clay modified PVA membrane

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ABSTRACT

In this study, the pervaporative dehydration of the cutting oil 'diethylene glycol' (DEG) through a hydrophilic PVA membrane was investigated at various operation temperatures in the range of 333–363 K with a feed mixture containing 0.5–2.0 wt% water. The pervaporation (PV) performance of poly(vinyl alcohol) (PVA) is enhanced by the addition of natural clay kaolin into the pristine membrane. The thermal stability of the membranes was analyzed by thermal gravimetric analysis (TGA). The morphological analysis of the membranes was performed by scanning electron microscope (SEM). Separation success was determined by calculation of flux, selectivity, and PSI. These values were investigated as functions of the clay amount, feed concentration and feed temperature. The obtained results show that PV is an effective method for recycling waste cutting oil from wastewater.

Key words | cutting oil, diethylene glycol, kaolin, pervaporation, PVA

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INTRODUCTION

The solar energy and semiconductor sectors need more and better wafers. The general cutting process cannot satisfy these demands, so the wire saw process has been enhanced. In this process, a material called a cutting oil is used in the wire saw instrument. The cutting oil consists of SiC particles, solvent, and additives. The used solvent must have two properties: it can be easily cleaned using water and the solvent must not have an abrasive effect for the suspended particles in the solvent. Ethylene glycol (EG), diethylene glycol (DEG), and polyethylene glycol (PEG) are often used as solvents for cutting oil.

DEG has the necessary characteristic properties of cutting oil. DEG ($(HOCH_2CH_2)_2O$) is a co-product with ethylene glycol and triethylene glycol. It is a colorless and odorless liquid that is miscible in water and alcohol (Schep *et al.* 2009). The only disadvantage of DEG has been the high boiling point of 245.3 °C. The recovery of the DEG is difficult due to the high boiling point and its miscibility with water. Tons of waste cutting oil are produced in the wafer slicing process. The waste cutting oil contains the original cutting oil, water, and Si particles. SiC and Si particles can be separated by the solid–liquid technique, but the solvent recovery is possible with the dehydration method. The conventional method for dehydration is distillation, but distillation requires high energy and cost. Also, the obtaining of high-purity DEG by distillation is not possible. Therefore, a new separation technique must be developed. Pervaporation is an important alternative to the distillation process in the treatment of waste cutting oil (Chen & Huang 2018).

Pervaporation is one of the promising techniques among the membrane processes. The pervaporation process is used to separate azeotropic mixtures and organic–organic mixtures (Shaban 1997; Abdallah *et al.* 2013; Oh *et al.* 2013; Suhas *et al.* 2013). The advantages of the pervaporation process are low cost, low energy consumption, and high separation efficiency. The pervaporation process is carried out under mild operation conditions (Assabumrungrat *et al.* 2003; Park & Tsotsis 2004; Unlu & Hilmioglu 2016; Sha *et al.* 2018). Membrane selection is an important point of the pervaporation process. Hydrophilic membranes are used in the dehydration operation of aqueous–organic mixtures. Poly(vinyl alcohol) (PVA) is a frequently used membrane material in the dehydration process. PVA is a non-toxic, water-soluble, biocompatible and biodegradable polymer (Zheng *et al.* 2001; Rashidzadeh & Olad 2013).

In recent years, filler materials have been used to improve the water adsorption capacity of the PVA membrane. Various filler materials such as zeolite, silica, carbon molecular sieve, activated carbon, and clay have

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been used in the improvement of the separation performance of the pristine membrane. Among these, polymer–clay hybrid membranes are attracting a great deal of attention because of their unique properties, synthesis with low cost and the abundance of clay in nature (Choudhari & Kariduraganavar 2009). The kaolin clay in the membrane is used to enhance the water adsorption capacity and mechanical, thermal, and chemical strength of the membrane (Pradhan *et al.* 2015; Rekik *et al.* 2019).

In the literature, there is no study about the pervaporation process for the dehydration of cutting oil by using clay loaded membranes. Therefore, the obtained pervaporation dehydration results by using composite clay/PVA or kaolin/polymeric pervaporation membranes in literature are summarized. Ravindra *et al.* (2016) studied the pervaporative separation of aqueous–organic mixtures by using natural clay clinoptilolite loaded PVA membrane. The effects of feed concentration, operation temperature and clay content on the separation performance were investigated for each membrane in the pervaporation. While the flux and selectivity values were 0.264 kg/m^2 h and 79.32 for the PVA membrane for 10 wt% feed water concentration at 30 °C, these values were 0.251 kg/m^2 h and 4,081 for the 5 wt% clay loaded PVA membrane under the same conditions. Banerjee & Ray (2018) prepared unfilled PVA membrane and sodium montmorillonite (NaMMT) filled PVA membrane for the dehydration of acetic acid by pervaporation. Process parameters such as feed concentration, temperature and permeate pressure were optimized by similar factorial design of RSM. The prepared membranes showed much higher flux and separation factors than most of the reported PVA membranes in the literature. For clay filled membrane, the obtained separation factor was 584 at 1 wt% of water amount in the feed mixture, which decreased with the increasing of feed water concentration. For 10 wt% water concentration, the separation factor decreased to 203, but flux rose to 0.520 kg/m^2 h from 0.403 kg/m^2 h for the same membrane. Adoor *et al.* (2006b) synthesized pristine PVA and sodium montmorillonite clay loaded PVA membranes. Poly(vinyl alcohol) membranes loaded with 5 and 10 wt% of sodium montmorillonite clay particles were fabricated by the solvent casting method. The synthesized membranes were utilized in pervaporation (PV) dehydration of aqueous solutions of isopropanol and 1,4-dioxane at 30 °C. Poly(vinyl alcohol) membranes loaded with 5 and 10 wt% of sodium montmorillonite membranes showed separation factors of 1,130 and 2,269 with flux values of 0.049 and 0.073 kg/m^2 h for 10 wt% of feed water concentration of water + isopropanol mixture. However, the pristine PVA membrane displayed a separation factor of 65 with a flux value of 0.108 kg/m^2 h. In pervaporative separation of a water + 1,4-dioxane feed mixture, separation factors were found to be 221 and 377, whereas the flux values were 0.065 and 0.088 kg/m^2 h, respectively. These values were found to be 40 and 0.137 kg/m^2 h for the pristine PVA membrane, respectively.

In this study, synthetic wastewater 'DEG–water mixture' was tested in the pervaporation system. PVA membrane modified with natural kaolin clay has been used in the process. This study presents a new solution in pervaporative dehydration of cutting oil by using the natural clay filled hydrophilic membrane. No study is available in the literature on the pervaporative recovery of cutting oil by the usage of PVA incorporated kaolin clay membranes. Clay improved the dehydration performance of the membrane. The optimum clay amount, optimal operation temperature and optimum feed water concentration were determined. According to the author's knowledge, this study is the first study on pervaporative dehydration that deals with the usage of clay/PVA membranes in dehydration of cutting oil.

MATERIALS AND EXPERIMENTAL METHODS

Materials

Polyvinyl alcohol (PVA), diethylene glycol with a purity of 99%, hydrochloric acid and glutaraldehyde were purchased from Sigma Aldrich. Kaolin clay was provided by Karabacak Mining Industry.

Membrane preparation

A 6 wt% PVA aqueous solution was mixed at 90 °C to obtain a homogeneous solution. A certain amount of kaolin clay (1 wt%, 3 wt%, 5 wt%) was dispersed in 10 ml of deionized water by sonication for 2 h. The prepared clay solutions with different concentrations were mixed with the pristine PVA solution. The clay amount in the membrane was defined with respect to the dry polymer weight. After mixing of the clay loaded membrane solution for 24 h, the membrane was cross-linked in situ. A certain amount of glutaraldehyde and HCl were added to the solution for cross-linking and stirred for 1 h. Then the final solution was cast onto a glass plate and dried at room temperature.

Membrane characterization

The cross-section images of the pristine and clay loaded membranes were investigated by using a JEOL/JSM-6510-LV scanning electron microscope. Scanning electron microscopy for the pristine PVA membrane was operated at an accelerating voltage of 5 kV and zoomed in 100×; clay loaded PVA membrane was analyzed at an accelerating voltage of 10 kV and zoomed in 3000×. The membrane samples were cooled in liquid nitrogen and broken. Broken means that the membrane is fractured perpendicular to the surface. Breaking the membranes in liquid nitrogen is done to avoid damage to the cross-sections of the membrane and to obtain clear images of them. After being broken, the membrane sample was coated with gold and placed on the scanning electron microscope (SEM) sample holder for analysis.

A Mettler Toledo TGA 1 Star System thermal analyzer was used for determination of the thermal stability of the pristine PVA and clay loaded membranes. Membrane samples having weights of 8 mg were prepared. The samples were placed in an aluminium pan. Then, the closed pan was put into a heating tunnel and the experiment was started. The membrane samples were heated from 25 °C to 600 °C at a constant rate of 10 °C/min under a nitrogen flow of 10 ml/min.

Waste cutting oil pervaporation experiment

The scheme of the laboratory-scale pervaporation unit is shown in Figure 1.

The membrane surface area is 9.61 cm^2. The volume of the feed solution is 70 ml. The pressure at the permeate side was reduced to 5 mbar by a vacuum pump. Separation experiments were carried out for 5 h. Structural deformation was not observed in membranes during the experiments. Membranes displayed mechanical strength and chemical stability in the separation process. Total flux was calculated by weighing the liquid mixtures collected in the trap for each 60 min. The recovery rate of cutting oil was obtained as approximately 75%. The flux (J), separation factor (α) and pervaporation separation index (PSI) were calculated by analysis of the compositions of both the feed and permeate streams with the Agilent 7820A model gas chromatograph and hand-held refractometer. The gas chromatograph was coupled with a thermal conductivity detector and an HP-INNOWAX column. Nitrogen was used as a carrier gas. The oven temperature was programmed as follows: the column was held initially at 70 °C for 3 min, then increased to 220 °C at 25 °C/min. The injector and detector temperatures were 230 °C each. The sample injection volume was 2 μL. The flux, separation factor and pervaporation separation index values were determined by the following equations:

$$J = \frac{m}{A.t} \tag{1}$$

$$\alpha = \frac{(y_a/y_b)_{\text{permeate}}}{(x_a/x_b)_{\text{feed}}} \tag{2}$$

$$PSI = J \times (\alpha - 1) \tag{3}$$

where J is the flux, m is the permeation mass, t is the time in Equation (1); y_a and x_a are the weight fraction of water in the

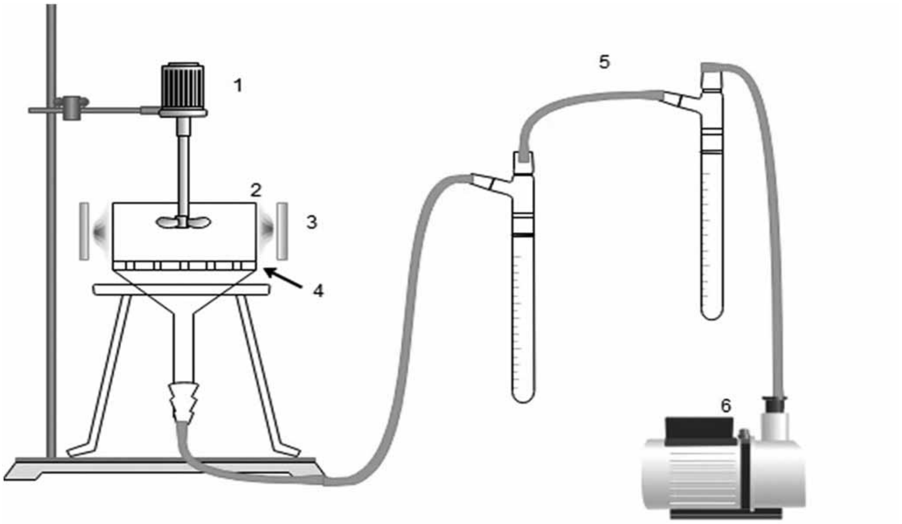

Figure 1 | PV configuration: (1) agitator, (2) membrane cell, (3) heating jacket, (4) membrane, (5) Dewar flasks, (6) vacuum pump.

permeate and feed streams, and y_b and x_b are the weight fraction of DEG in the permeate and feed streams in Equation (2).

The repeatability of flux and selectivity values is within ±1.5%. Experiments were replicated three times, and flux, separation factor and pervaporation separation index values were detected. The mean values of these parameters were determined and mean values were used in the figures. Also, analyses were repeated three times for each experiment. This means that each sample was analyzed three times for the determination of flux, separation factor and pervaporation separation index values.

RESULTS AND DISCUSSION

Membrane characterization

Figure 2 depicts the cross-section images of the pristine PVA membrane and the natural clay modified PVA membrane. The pristine PVA membrane has a smooth surface relative to the clay modified PVA membrane, because the pristine membrane represents a crystalline structure. The incorporation of clay destroys the crystalline structure of the polymer matrix and an amorphous structure is obtained.

Figure 3 shows the thermal gravimetric analysis (TGA) profiles for the pristine PVA membrane and PVA/clay membrane. The most weight loss is observed in the range of 150–400 °C for all membranes. This loss corresponds to the structural decomposition of the polymers. The thermal decomposition of kaolin loaded PVA membrane shifts toward a higher temperature range than that of the pristine PVA membrane. This confirms that the addition of clay enhances the thermal stability of the pristine membrane.

Recovery of cutting oil from wastewater by pervaporation

The flux, separation factor and PSI values of the binary mixtures were investigated at 333 K with varying the kaolin clay content in the range between 1 wt% and 5 wt%, and the results are shown in Figures 4 and 5.

In pervaporation, molecular diffusion is generally explained by the solution–diffusion mechanism. According to the solution–diffusion mechanism, molecules firstly dissolve on the membrane surface and then diffuse through the membrane as a result of the concentration gradient (Adoor *et al.* 2006a). However, the overall separation is related to the physical feature of the solvents, affinity of solvents to the membrane as well as the morphological structure of the membrane. PVA is a hydrophilic polymer and has many hydroxyl groups. With this approach, alcohols can be diffused into the PVA membrane due to hydrophilic–hydrophilic interactions, because alcohols have close polarity with water. The performance of PVA membranes can be improved by the addition of clay. The addition of clay in the membrane restricts the diffusion of organic molecules and thus excess swelling of the membrane is prevented. While the separation in the pristine PVA membrane occurs in the PVA polymer matrix, in the clay loaded PVA membrane the hydrophilic interactions between the clay and the PVA play a role in separation. Water molecules are adsorbed in the hydrophilic clay instead of the PVA. Therefore, diffusion becomes difficult. Clay avoids the diffusion of the organic molecules through the membrane, so selectivity increases. As can be seen in Figures 4 and 5, separation performance changes depending upon the clay content. The selectivity value of the pristine PVA membrane is 24 at 2 wt% feed water concentration. However, the water selectivity value increased to 134 for

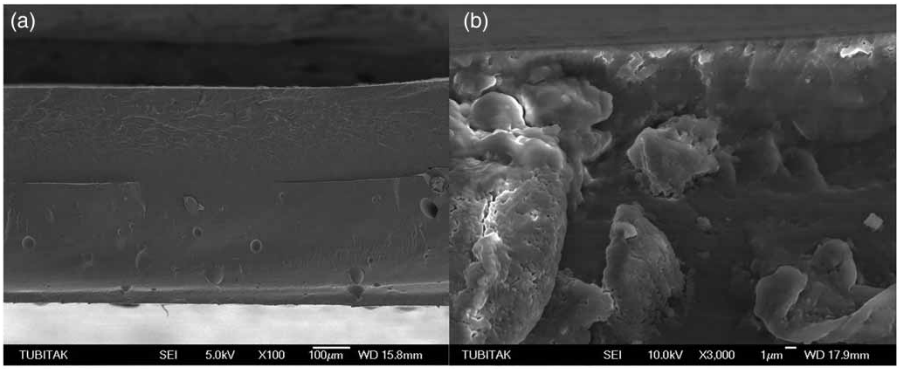

Figure 2 | Cross-section images of membranes: (a) pristine PVA membrane, (b) clay loaded PVA membrane.

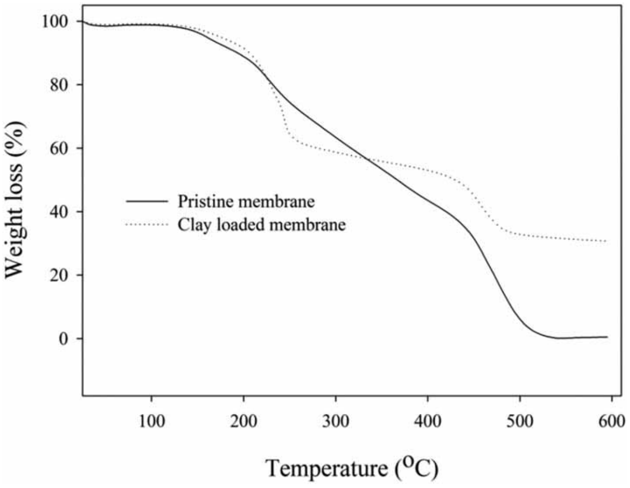

Figure 3 | TGA curves of membranes.

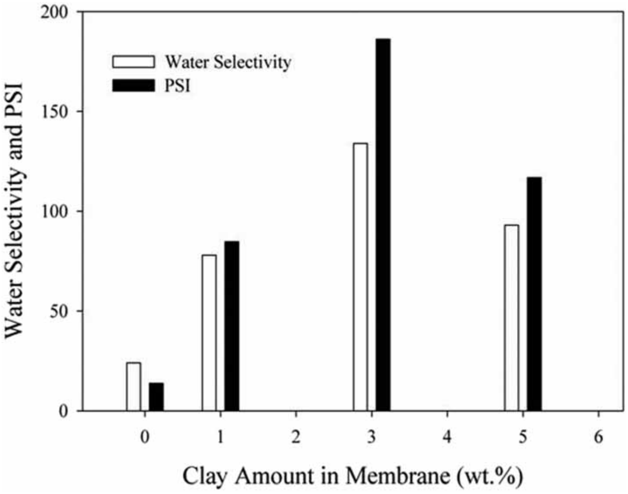

Figure 5 | Effect of clay amount on water selectivity and PSI (333 K, 2 wt% feed water concentration).

the same feed water concentration for the 3 wt% clay loaded PVA membrane. Compared with the pristine membranes, the water selectivity values of the clay loaded membranes are rather higher.

However, the flux is small at lower feed water concentration. A higher concentration of water in the feed mixture would result in a higher permeability. Under these conditions, the flux of the clay loaded membrane is higher than that of the pristine PVA membrane. The flux is decreased with an increase in the amount of clay beyond 3 wt%. It is observed that there is an increase in PSI values with an increase of the clay from 0 to 3 wt%, but further addition of more clay than 3 wt% reduces the PSI value. This result can be related to the aggregation of clay particles. When the clay amount is greater than 3 wt%, the compatibility of the additive and the polymeric matrix decreases. Therefore, the separation factor drops and permeation rate increases (Anilkumar *et al.* 2008).

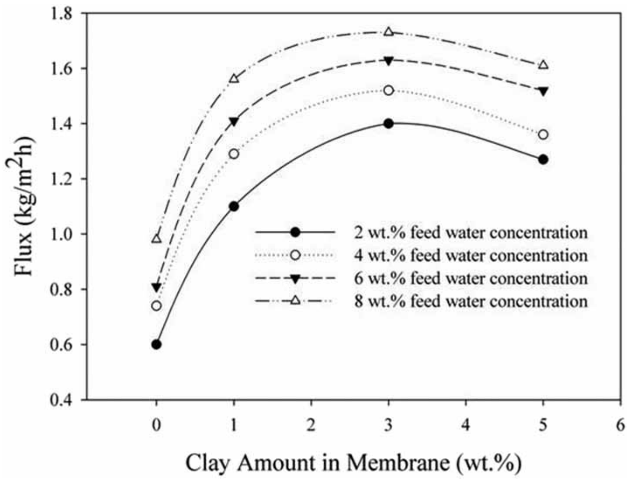

Figure 4 | Effect of clay amount on flux (333 K).

The effect of feed water concentration on the separation performance of the clay loaded PVA membrane was investigated, and results are presented in Figure 6. The flux increased with increasing of feed water concentration from 2 to 8 wt%. While the feed water concentration is 2 wt%, the observed selectivity value for dehydration of cutting oil is 134. The selectivity value decreased with increasing feed water concentration (see Figure 6). The clay loaded PVA membrane absorbed a greater amount of water molecules due to the plasticization effect of the polymer under the high feed water concentration (Devi *et al.* 2006). Furthermore, the degree of swelling and the flexibility of the polymer chains increase by the plasticization effect. Thus, the water diffuses easily through the membrane. However, the plasticized membrane also permits the diffusion of cutting oil due to the increased spacing between the polymer chains. Therefore, selectivity decreased, but flux increased considerably for the clay loaded PVA membrane. When the water concentration in the feed increased to 8%, the water selectivity came down to 78 and the flux value increased to 1.73 kg/m^2 h. In all cases, the flux and selectivity of PVA–clay membranes are higher than those of the pristine PVA membrane (0.6 kg/m^2 h and 24). The present study demonstrates the positive role played by clay upon incorporation into PVA to enhance membrane performance over that of the pristine PVA membrane.

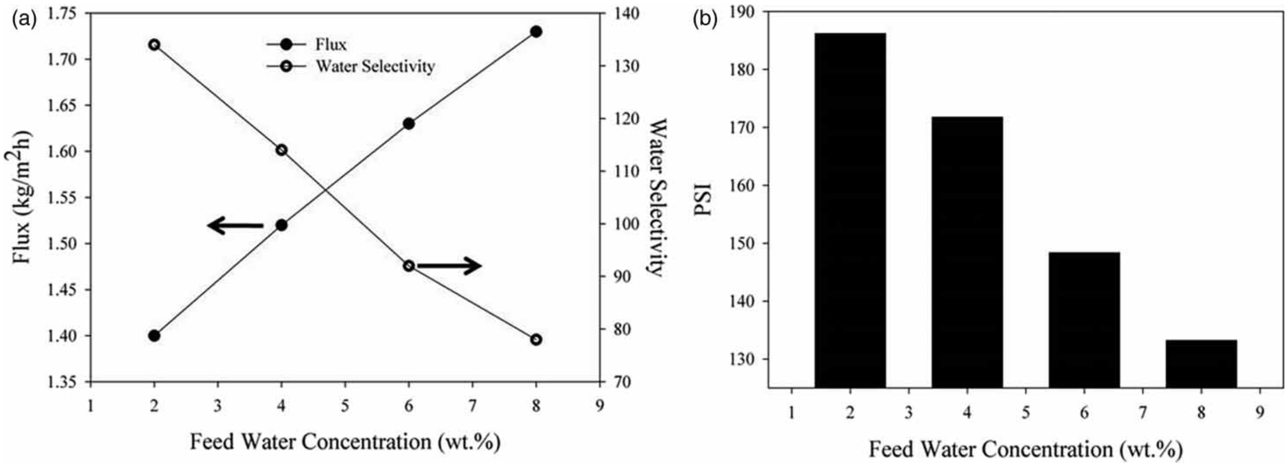

Figure 6 | Effect of water concentration on (a) flux and water selectivity, (b) PSI (333 K, 3 wt% of clay loaded PVA membrane).

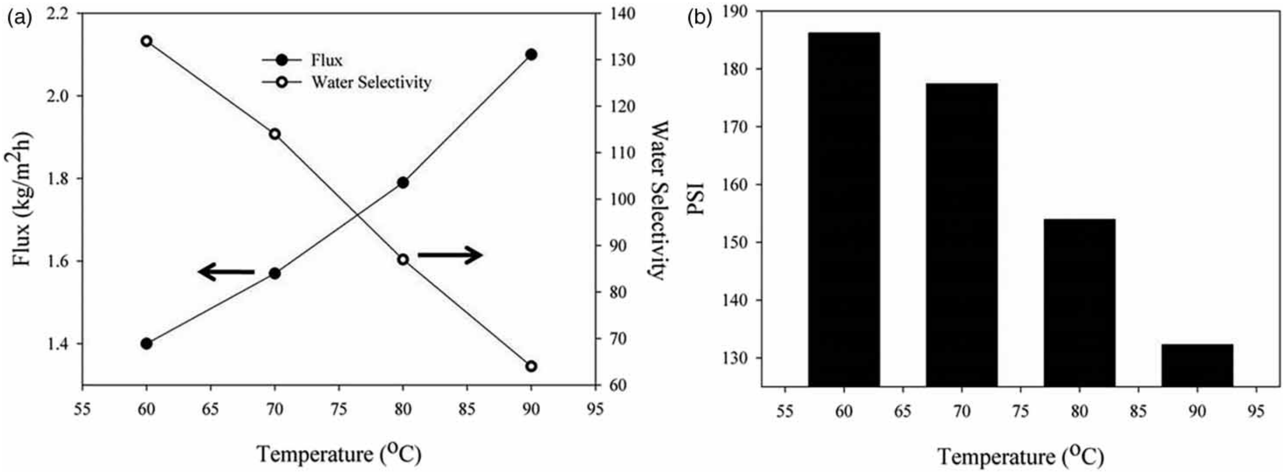

Figure 7 | Effect of temperature on (a) flux and water selectivity, (b) PSI (2 wt% feed water concentration, 3 wt% of clay loaded PVA membrane).

The results of the recovery of cutting oil from wastewater which were obtained at temperatures of 60, 70, 80 and 90 °C are presented in Figure 7. It is known that PVA has superior separation performance for the dehydration process, but temperature negatively affects the separation performance of PVA. Polymer mobility increases with temperature, with diffusion channels expanded. Flexible polymer chains allow the water molecules through the membrane easily. This fast and increased diffusion causes membrane swelling, flux increase and selectivity reduction. The driving force is created from a difference in temperature between the feed and permeate sides. As the feed temperature increases, the vapour pressure of the feed mixture also increases, but vapour pressure at the permeate side is not affected. Therefore, the driving force increases with increasing temperature (Wang *et al.* 2011; Hu *et al.* 2012; Ravindra *et al.* 2016).

CONCLUSION

PVA–clay composites containing different clay amounts were prepared, and the application of separation performance on the recovery of cutting oil from wastewater was investigated in the pervaporation system. The dispersion of particles in the membrane decreases with the increase in clay amount. Pervaporation experiments showed an excellent performance in selectivity in the case of the clay loaded membrane compared with the pristine membrane. Pervaporation experiments showed an excellent performance in selectivity in the case of the clay loaded membrane compared to the pristine membrane. This state can be explained in that while the transport in the pristine PVA membrane occurs in the polymer matrix, hydrophilic interactions between the clay and the PVA in the clay loaded PVA membrane acts with a role in separation. In brief, in that membrane, water molecules are adsorbed in the hydrophilic clay instead of the PVA. The 3 wt% clay loaded membrane showed excellent performance with a flux of 1.40 kg/m^2 h and water selectivity of 134 at 60 °C when the flux and selectivity values of pristine membranes were 0.6 kg/m^2 h and 24, respectively. However, a decrease in flux and separation factor values was observed when the clay amount became higher than 3% w/w. The excess clay usage results in the agglomeration of clay particles, and miscibility and homogeneity in the membrane decrease. Therefore, the separation performance of the membrane decreases. Consequently, natural clay modified PVA membrane which has a selectivity of water is highly effective in the recovery of cutting oil from wastewater by pervaporative separation.

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