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Purification of emulsified oil by Bentonite loaded polyvinylidene fluoride/polyvinylpyrrolidone membrane

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Abstract

In this study, a Bentonite clay incorporated polyvinylfluoride (PVDF) and polyvinyl pyrrolidone (PVP) based adsorbent membrane was produced for the selective separation of oils from simulated wastewater. This membrane was produced as an intelligent material that selectively separates emulsified oils from water when it is used as adsorbent and purifies water when it is used in continuous membrane filtration. The affinity of the membrane to oil components was determined by water-oil uptake tests. The uptake experiments were conducted for soybean oil, hazelnut oil, lubricant oil and other volatile oils. As a result, membranes absorbed greater than 200 wt.% of oil when the membranes were immersed in the soybean oil, hazelnut oil and lubricant oil. When the same membranes were used for continuous filtration, greater than 85% of oil rejection values were obtained. As the PVP ratio in the membrane increased, flux values enhanced gradually. Bentonite incorporation simultaneously improved flux values and oil rejection remarkably. The soybean rejection increased from 69.1% to 90.9%, hazelnut oil rejection increased from 78% to 99.98%, and lubricant oil rejection enhanced from 80.5% to 96.5% when the bentonite amount was increased from 0 wt.% to 15 wt.%.

Key words: adsorbent membrane, Bentonite, oil removal, polyvinylfluoride

INTRODUCTION

Industrial wastewater contains many hazardous substances (Grüttner 1997). Many harmful components such as plastic residues, toxic components, heavy metals, volatile organic components, and oil extracts are released from the wastewater of industrial plants and discharged to natural resources such as seawater. Oil based components are found in the wastewater of food, pharmaceutical, polymer, automotive, electronics, and petrochemical industries (Doshi *et al.* 2018; Nthunya *et al.* 2019). Besides petroleum-derived oils such as lubricating oils, engine oils, and diesel, vegetable-derived oils are also found in the effluents of different industries. These kinds of oils are created by extracting from different plant seeds or fruits such as soybean and hazelnuts. In general, vegetable oils are used in the food industry. Moreover, soybean and hazelnut oil are used in biodiesel production as a waste vegetable oil (Celikten *et al.* 2012). The amount of oils in wastewater increases in line with the usage areas of oils in industry and daily life. One liter of waste oil contaminates one million liters of water. Hence oil separation from water is attracting attention for the environmental-chemical scientist. Depending on the lower density of oil components over water, the oil-based molecules accumulate on the water surface (Barron 2012). In addition to the industrial waste discharges, oil species spill from the defective pipes of petrochemical plants and sea vessels (Brody *et al.* 2010; Cui *et al.* 2019).

There are many techniques to separate oils from waters (Droste & Gehr 2019). The diversity of these techniques varies according to the structure of oils (whether they are emulsified or not, and drop size) and the area where oils are emitted. For example, oils are spilled by petroleum accidents and can be removed by *in situ* separation techniques such as adsorption and chemical methods. Biological, electrochemical treatment, coagulation, flocculation, vacuum evaporation, absorption, precipitation, and membrane filtration techniques are used for the separation of emulsified oil from water (Doshi *et al.* 2018; Nthunya *et al.* 2019). The most preferred methods are adsorption and membrane separation.

The membrane is defined as a barrier that selectively separates the two phases and allows the controlled passage of the target component. Membrane technology is known as a promising technique for the treatment of oil-based wastewater (Seo *et al.*1997). Especially for the removal of emulsified oil droplets, the purification is carried out without any de-emulsification process (Ang *et al.* 2015). Recently, studies on the separation of oil-based compounds have been performed by means of low-cost polymeric membranes having high oil absorption capacity and good oil-water selectivity. Microfiltration, ultrafiltration, and nanofiltration techniques are mostly used to remove oil from water (Hoslett *et al.* 2018). Selection of the appropriate technique changes depending on the concentration of the oil in water, the type of treated water, and the operating parameters. Each of these techniques is categorized according to the pore size of the membrane and trans-membrane pressure. The membrane-based separation has important advantages such as low energy consumption, and high separation efficiency. Compared to the adsorption technique, membrane separation can be conducted continuously.

In this study, a poly (vinylidene fluoride) (PVDF)/Polyvinylpyrrolidone (PVP) blend membrane was produced by the phase inversion method for separation of oil-emulsion water mixtures. Poly (vinylidene fluoride) is a hydrophobic polymer that is used in membrane separation processes due to its superior mechanical strength, heat resistance, chemical resistance and good film formation capability (Kang & Cao 2014). Polyvinylpyrrolidone acts as a pore-forming polymer in membranes prepared by the phase inversion technique (Amin *et al.* 2018). PVP content in the membrane influences the surface morphology of the blended membrane.

In our study, PVDF/PVP-based membrane was prepared to adsorb oil from water in the case where the membrane is used for the batch adsorption process. The membrane is also appropriate to remove water when it is used for the continuous water separation process. Therefore, in the present study, both the adsorption and separation characters of membranes were determined using uptake and filtration experiments. The simulated wastewater was prepared by using soybean, hazelnut, and lubricating oils, and toluene. In order to increase the water flux, Bentonite clay was added to the membrane matrix. Bentonite is a natural clay and a smectite-derived clay mineral that has high montmorillonite content (Adeboje *et al.* 2020). Bentonite clay has the advantages of large surface area, adsorptive capacity, rheological properties, chemical purity and low toxicity (Favero *et al*. 2019). In addition, Bentonite clay is a low-cost clay type that is abundant in nature. Bentonite shows a strong affinity towards water and increases the swelling character of the material (Kumar *et al.* 2015, 2016). This feature may increase the water flux when used as a membrane main material or filler. In the present study, the effects of PVDF/PVP ratio, Bentonite amount, and oil types on the uptake, flux, and rejection were evaluated.

MATERIALS AND METHODS

Membrane preparation

Blend membranes were prepared using the phase inversion technique. A certain amount of PVDF was dissolved in dimethylformamide (DMF) solvent with a concentration of 10 wt.% PVDF in DMF. PVP was also added to the polymer-DMF solution. The blend membrane solution was homogeneously mixed at 55 °C for four hours. The mixture was allowed to remove bubbles at room temperature for 24 hours. The mixture was poured onto a glass surface and a casting knife was used to obtain a homogeneous membrane thickness. Then, the glass plate was immersed in a water bath for two minutes. The PVDF/PVP weight ratios were varied as 90/10, 80/20, 70/30, 60/40.

For the preparation of Bentonite-incorporated membranes, a polymer solution containing 80 wt.% PVDF and 20 wt.% of PVP was prepared. The determined amount of Bentonite clay (concentration varied from 0 wt.% to 15 wt.% according to the total weight of PVDF and PVP) was added to the polymer solution and stirred at room temperature for four hours. The mixture was poured onto a glass plate and the thickness of the membrane was adjusted with an adjustable micrometer film applicator. The stainless-steel knife blade was fitted into slots in the end section to allow vertical adjustment of the blade. This way, the thickness of the membrane was adjusted. Then, the glass plate was immersed in a water bath. Table 1 shows membranes with codes. The amount of Bentonite was arranged according to the total weight of polymers. The thickness of all prepared blend membranes was measured with a digital micrometer (Dasqua 4310). The average thickness of the membrane was measured as $100 \pm 5\ \mu m$.

Membrane characterization

The surface hydrophobicity of the membrane was characterized using Contact Angle Measurements (KSV). The angle measurements were done by measuring the angle between the water droplets and the membrane surface. Each test was repeated three times and the average angle values were recorded. The chemical structure of the membrane was analyzed by using Fourier Transform Infrared Spectroscopy (FTIR) (Perkin Elmer, ATR mode). The wavelength of the spectroscopy was arranged between 650 and 4,000 cm^{-1}. The surface morphology of membranes was determined using scanning electron microscopy (SEM).

Oil/water uptake

The effect of polymer concentration and clay incorporation on the membrane-oil affinity were determined by means of uptake experiments. In order to determine the oil-water uptake capacity of different membranes, the membrane samples were immersed in water, soybean, hazelnut, lubricating oils, and toluene, separately. The uptake experiments were carried out for 90 minutes until the samples reached a constant weight. The uptake measurements were done by measuring the initial (W_i) and final (W_f) weight values of the membrane as shown in Equation (1).

$$Uptake\ (\%) = \frac{W_f - W_i}{W_i} * 100 \qquad (1)$$

Table 1 | Membrane identification

Membrane code	PVDF content (%)	PVP content (%)	Bentonite content (%)
PVDF90-PVP10	90	10	–
PVDF80-PVP20	80	20	–
PVDF70-PVP30	70	30	–
PVDF60-PVP40	60	40	–
Clay-0 wt.%	80	20	–
Clay-5 wt.%	80	20	5
Clay-10 wt.%	80	20	10
Clay-15 wt.%	80	20	15

Filtration test

The filtration test was carried out in a vacuum filtration test unit. Experiments were carried out at room temperature by using 1 wt.% of oil-containing water solution. Before the experiments, the oil-water solution was sonicated for three hours and a milky-like color was obtained. The prepared membranes were settled on a porous glass support and the oil/water solution was fed onto the prepared membrane. A 630 mmHg vacuum was applied at room temperature. The oil concentration of the permeate and the retained solution was determined using a UV-Vis spectrophotometer (Hach DR 5000). The filtration and separation performance of membranes were evaluated as a function of flux (F) and oil rejection (R) (%), as shown at the following Equations (2) and (3).

$$F = \frac{M}{t.A} \tag{2}$$

$$R(\%) = \frac{C_f - C_p}{C_p} * 100 \tag{3}$$

where M (g) is the weight of permeate water on the downstream side of the membrane, t is the filtration time (min), A is the effective membrane area. C_f and C_p are the concentration of oil-water solution at feed and permeate side, respectively.

RESULTS AND DISCUSSION

Membrane characterization

Figure 1 shows the surface micrographs of PVDF80-PVP20 membranes with different magnification. The pore distribution and pore size are homogeneous and the pore size changes between nanometer to micrometer.

Figure 2 shows comparative SEM images of PVDF80-PVP20 (Figure 2(a)) and PVDF60-PVP40 (Figure 2(b)) membranes. As seen in the figure, the pore diameter is increasing as the PVP content increases in the membrane. It is an expected result due to the fact that polyvinylpyrrolidone is a hydrophilic polymer (Amin *et al.* 2018) that is used as a pore-forming agent to produce a porous membrane.

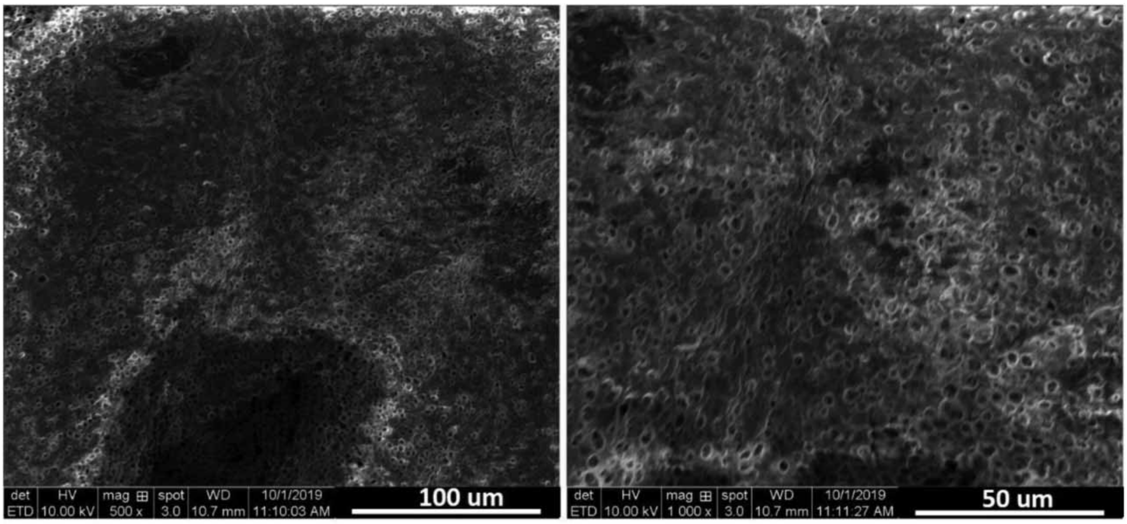

Figure 1 | Surface SEM micrographs of PVDF80-PVP20 membranes.

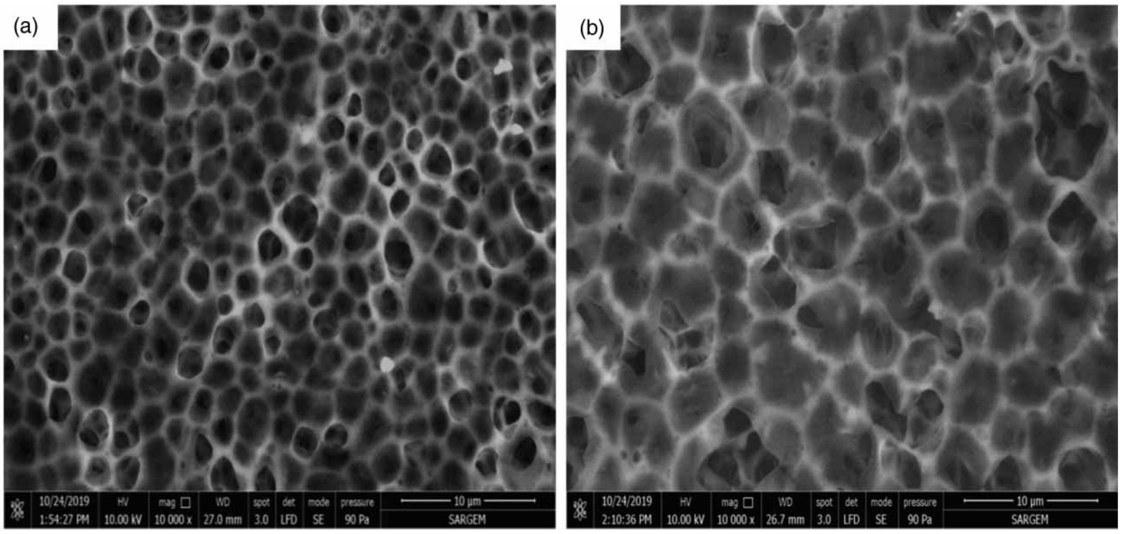

Figure 2 | Surface SEM images of PVDF80-PVP20 (a) and PVDF60-PVP40 (b) membranes.

Figure 3 shows the surface morphology of 10 wt.% (Figure 3(a)) and 15 wt.% Bentonite (Figure 3(b)) loaded membranes. The smallest clay particles are clearly seen in Figure 3(a). It is obvious that the Bentonite was intercalated into the polymer matrix when the amount of Bentonite was 10 wt.%. Increasing clay concentration prevented the molecular distribution of the fillers into the matrix.

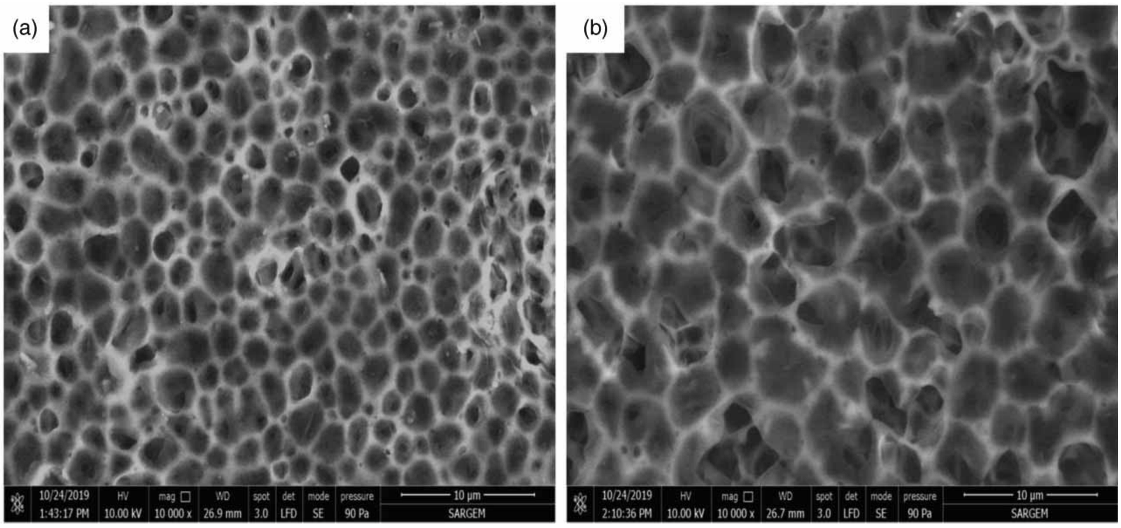

Figure 3 | Surface SEM images of 10 wt% (a) and 15 wt% (b) clay-loaded membranes.

In the present study, PVDF and PVP blend membranes were prepared, characterized and used for removal of oil from simulated oil-water mixtures. The chemical structure of the produced membranes was determined using FTIR analysis. Figure 4 shows the FTIR spectra of membranes having different PVDF/PVP ratios. Peaks at 1,680 cm^{-1} are assigned to the carbonyl stretching in membranes. The characteristic –CH2– deformation peaks are revealed at 1,400 cm^{-1}. The peaks from 760 cm^{-1} to 1,190 cm^{-1} correspond to CF and CF_2 stretching. The intensity of CF-based peaks decreased due to the PVP addition.

The surface hydrophobicity of the membranes was determined using contact angle measurements. The contact angle of the surface decreased as the PVDF ratio in the membrane increased (Table 2).

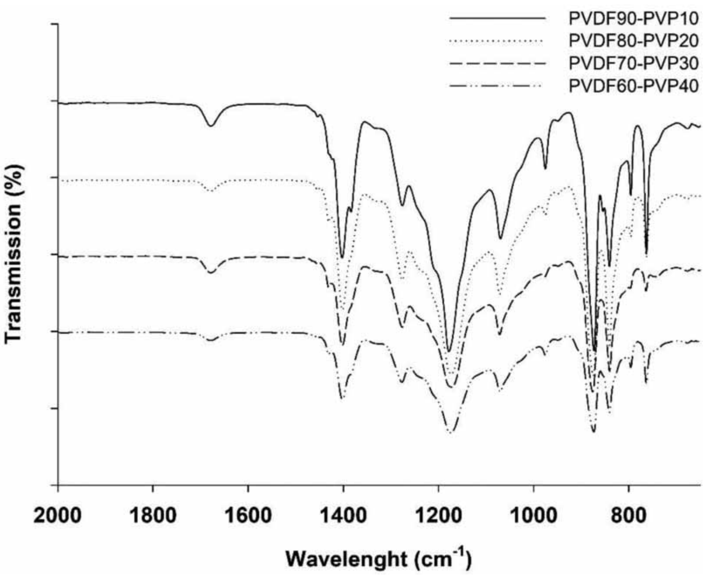

Figure 4 | FTIR spectra of membranes.

Table 2 | Contact angle of membranes with water droplets

Membrane code	PVDF60-PVP40	PVDF70-PVP30	PVDF80-PVP20	PVDF90-PVP10
Contact angle (°)	64	75	83	88

This is due to the hydrophobic character of the PVDF. It is also related to the hydrophilicity of PVP. Moreover, during the phase inversion process, the porosity of the membrane increased by increasing the PVP ratio. Thus, the water penetration on the surface of the membrane increased as expected.

Uptake and filtration test results

In this study, the affinity of PVDF/PVP membranes to oils and water were investigated. The produced membrane is expected to absorb oils when it is used as an adsorbent membrane in a batch adsorption process. Moreover, membranes are expected to permeate water when used in a continuous membrane separation process. Therefore, the usability of the adsorbent membrane was determined by swelling tests and the water permeability performance was determined by means of filtration tests.

Figure 5 shows the effect of PVDF/PVP concentration on the uptake results. It is clear from the figure that the water uptake capacity of the membrane enhanced with an increasing amount of PVP in the PVDF matrix. This is due to the hydrophilic structure of PVP polymer (Kao *et al.* 2003). PVP is a water-soluble hydrophilic and polar polymer. Therefore, it is expected that water uptake capacities will increase as the PVP ratio increases in the matrix. The highest uptake value of 266 wt.% was obtained when the PVDF ratio was kept at 60%. Compared to the water and soybean, the hazelnut oil uptake showed a variable trend. The highest uptake value was calculated as 325 wt.% when the PVDF concentration in the membrane was 80%. Therefore, it can be evaluated that the 80% of PVDF polymer ratio is more appropriate where the membrane will be used as an adsorbent membrane. In Figure 5, the increasing PVP ratio in the matrix reduced the lubricant oil uptake results. The highest lubricant oil uptake of 267 wt.% was obtained with the membrane having 90 wt.% PVDF concentration. The figure also illustrates the uptake results of petrochemical-based volatile oil, toluene. Toluene has a uniform molecular structure and has smaller molecular size than those of other oils

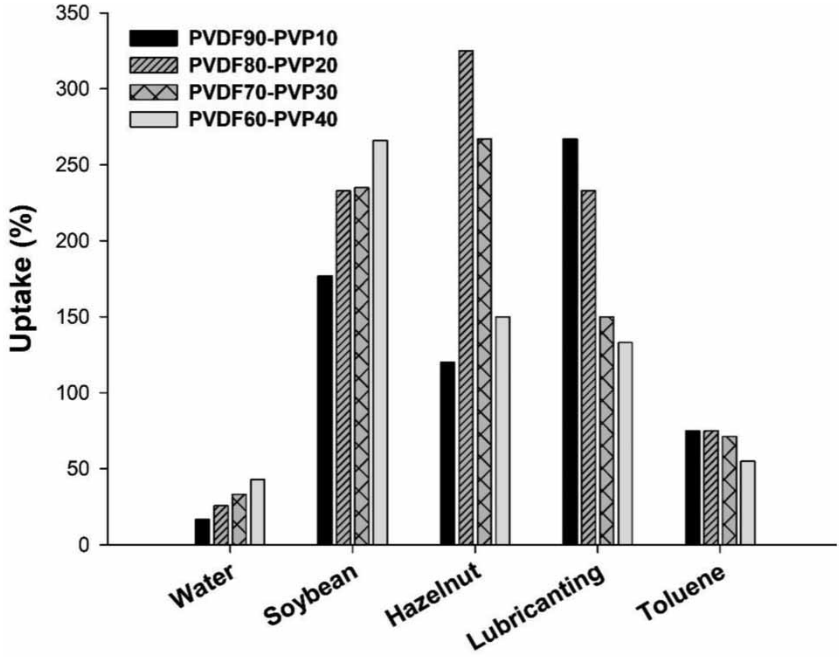

Figure 5 | Effect of PVDF/PVP ratio on uptake.

such as lubricant, hazelnut, and soybean. As shown in Figure 5, the increasing PVP ratio in the matrix reduced the toluene uptake slightly.

In Figure 6, the effect of Bentonite clay incorporation on oil uptakes was also investigated when the PVDF ratio was kept constant at 80 wt.%. Bentonite concentration was changed from 0 wt.% to 15 wt.% according to the total polymer weight. It is clear from Figure 6 that the clay addition has a positive effect on water uptake and has a negative effect on oil-based chemical uptake results. Due to the fact that the oil swelling capacity of the polymeric structure was higher than that of the clay, the uptake values decreased as Bentonite content increased in the membrane.

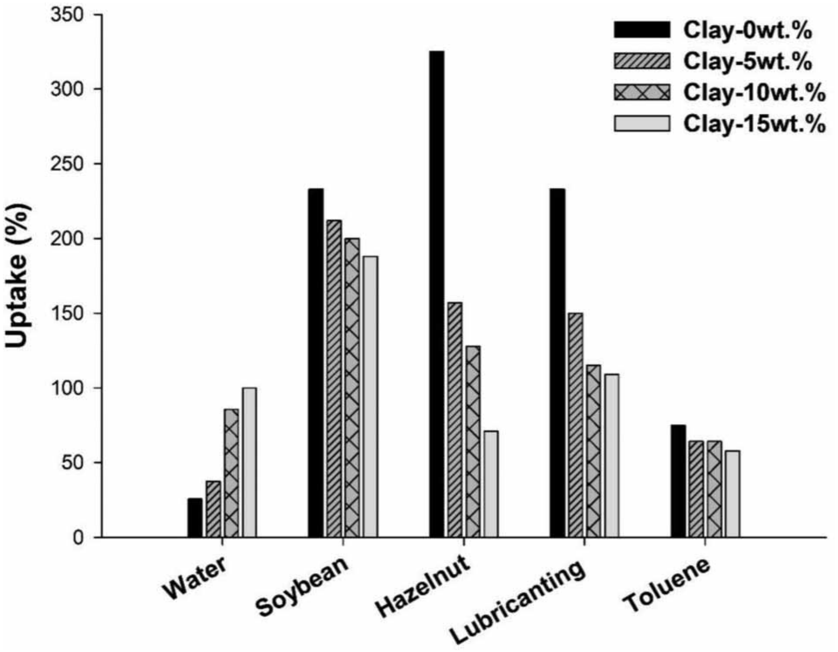

Figure 6 | Effect of clay content on uptake.

Figure 7(a) shows the effect of the PVDF/PVP ratio on flux when the oil concentration was kept constant as 1 wt.% in deionized water. In the case of the soybean oil, the flux enhanced from 0.0124 kg/s · m^2 to 0.23 kg/s · m^2 when the PVP ratio increased from 10 wt.% to 40 wt.%. The hazelnut oil-water flux also increased from 0.045 kg/s · m^2 to 0.15 kg/s · m^2. The lubricating oil-water flux increased from 0.13 kg/s · m^2 to 0.67 kg/s · m^2, and the toluene-water flux increased from 0.093 kg/s · m^2 to 0.82 kg/s · m^2. The increase in flux results should be related to the increasingly porous structure of the membrane with an increasing amount of PVP. In the literature, PVP polymer is used as a pore-forming agent to enhance the membrane porosity during the phase inversion technique (Amin *et al.* 2018). Depending on the porous structure, water flow increases as the PVP concentration increases in the membrane matrix.

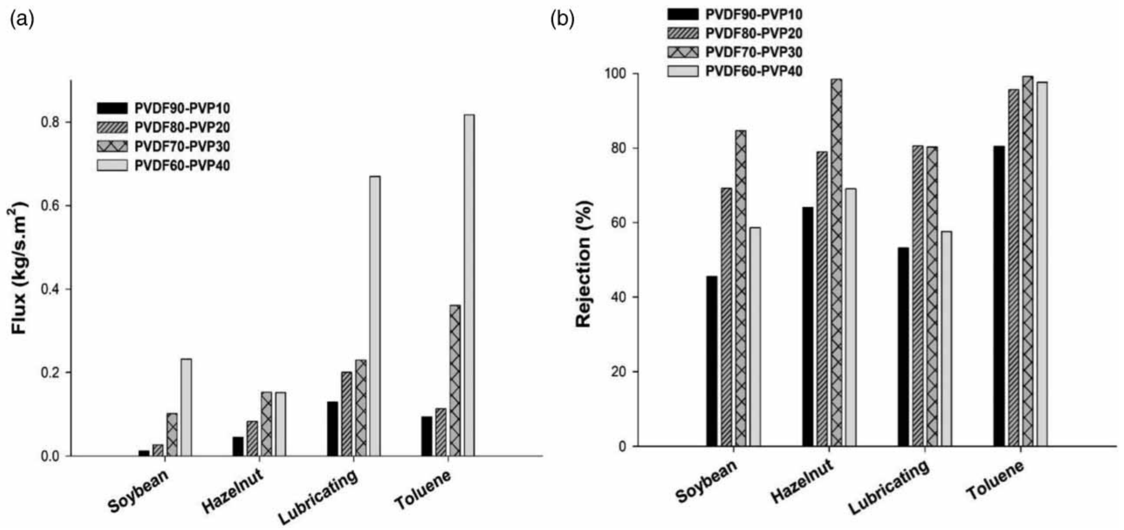

Figure 7 | Effect of PVDF-PVP concentration on flux (a) and rejection (b).

The effect of the PVDF/PVP ratio on rejection results is given in Figure 7(b). The soybean oil-water rejection increased from 45.5% to 84.6% with increasing PVP concentration up to 30 wt.%. However, the rejection drastically decreased when the PVP concentration was 40 wt.%. As the size of the pore enlarges, the oil molecules may be dragged with the water molecules and the oil rejection reduces, as also obtained in the present study. The hazelnut oil rejection values increased from 64% to 98.4%. when the PVDF ratio was decreased from 90 wt.% to 70 wt.%. In the case of the lubricant oil, the rejection of 80.5% was obtained when PVP ratio was 80 wt.%. The toluene rejection results also enhanced by increasing the PVDF ratio. In particular, the permeation results showed that 70 wt.% and 80 wt.% of PVDF-containing membranes had superior separation performance for removing oil species from the simulated wastewater. Oil rejection results were lower for 60% PVDF-40% PVP containing membrane due to the increasing porosity.

Figure 8 indicates the influence of Bentonite addition on the flux and rejection. Figure 8(a) shows the effect of Bentonite concentration on flux results. There is a significant increase in the flux values of the membranes with the increasing amount of clay. The soybean oil-water flux value increased from 0.027 kg/s · m^2 to 0.12 kg/s · m^2, hazelnut oil-water flux enhanced from 0.15 kg/s · m^2 to 0.34 kg/s · m^2, lubricant oil-water flux increased from 0.2 kg/s · m^2 to 1.09 kg/s · m^2, and toluene-water flux enhanced from 0.11 kg/s · m^2 to 0.54 kg/s · m^2 when the clay concentration increased from 0 wt.% to 15 wt.%. This is due to the super hydrophilic character of the clay. Bentonite has close-packed platelets which consist of tetrahedral–octahedral–tetrahedral layers. These layers are composed of metal ions that are responsible for the negative charge of the membranes. Bentonite exhibits a strong affinity

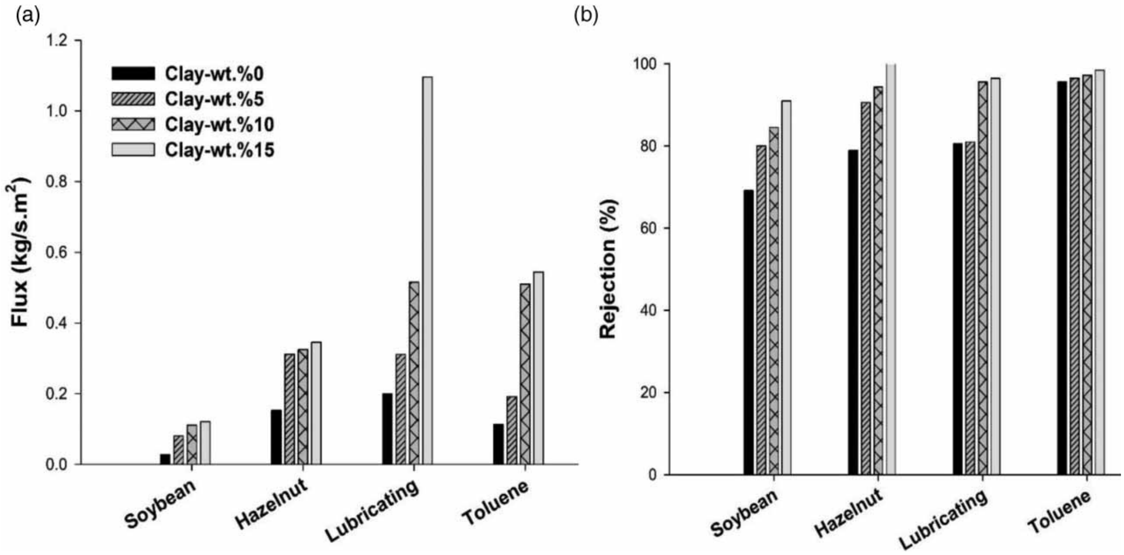

Figure 8 | Effect of clay concentration on flux (a) and rejection (b).

to water and increases the swelling character of composites (Kumar *et al.* 2015, 2016). This property may cause an increase in the water flux when it is used as a membrane main material or filler. Very few studies have also reported that Bentonite clay is effective to remove oil/water compared to activated carbon (Moazed & Viraraghavan 2005; Sun & Chung 2013; Zheng *et al.* 2017). Therefore, in the present study, Bentonite was used to increase water flux and to enhance oil rejection as well.

In the preliminary experiments, flux values decreased when the Bentonite concentration exceeded 15 wt.% concentration. The reason for the decrement should be attributed to the overloading of clays that causes aggregation. The agglomeration causes a reverse effect on the separation performance. Therefore, the maximum clay content was determined as 15 wt%.

Figure 8(b) indicated the effect of Bentonite on the rejection results. In addition to membrane flux, oil rejection values were also positively affected by Bentonite incorporation. The soybean rejection increased from 69.1% to 90.9%, hazelnut oil rejection increased from 78% to 99.98%, and lubricant oil rejection enhanced from 80.5% to 96.5%.

CONCLUSIONS

In this study, PVDF/PVP blend membranes were prepared for the separation of oily components from seawater or wastewater. Bentonite clay was added to the membrane to increase the water flux and enrich the oil rejection. The effect of PVDF concentration, Bentonite content and oil type on separation performance was investigated. PVDF ratio has a direct effect on oil uptake capacity, flux, and oil rejection. Especially for soybean oil, the flux increased significantly as the PVP ratio increased. There was also a significant increase in oil rejection values. The most suitable PVDF ratio was found to be 70 wt.% and 80 wt.%. When Bentonite was added to the membrane, the separation performance became superior.

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