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PES Membrane Performance for Triethylene Glycol (TEG) Removal of Wastewater from Natural Gas Separation Process

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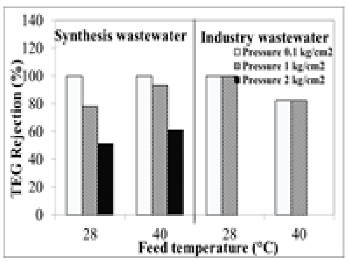
Graphical abstract



Abstract

In the natural gas separation plant, triethylene glycol (TEG) is used as a liquid desiccant dehydrator to absorb water vapor from the gas stream. Even though TEG can be recovered and reused in the process by evaporation and distillation, some of TEG still remains in wastewater of this recovery process. In this work, the polyethersulfone (PES-NTR 7450) membrane was chosen to test for TEG removal capacity on both cross-flow filtration and pervaporation systems. The morphology of membrane and the content of TEG were characterized by scanning electron microscope (SEM) and gas chromatography (GC), respectively. The synthesis wastewater with average TEG content of 5%, 10%, and 20% were used as feed. The increase of feed concentration was trend to increase of TEG rejection (17.49%, 43.29%, and 62.22%). In case of industrial wastewater, the average TEG content of 10.7% was monitored for feed. The high effectiveness of PES-NTR 7450 membrane to remove TEG was performed in pervaporation system. TEG rejection of 99% was achieved at the operation condition of feed temperature 28ºC and applied pressure 1 kg/cm^2.

Keywords: Triethylene glycol; membrane filration; pervaporation

1.0 INTRODUCTION

Triethylene glycol (TEG) is widely used as antifreeze, as raw material for making polyesters and as desiccant, especially the natural gas separation process to remove water from the natural gas stream in order to meet the pipeline quality standards[1,2]. Conventionally, the TEG removal from water can be removed by multi-stage distillation or multi-effect evaporation, which required intensive energies due to the high boiling point of TEG (285°C)[3,4]. Pervaporation has received considerable attention for this application. It is membrane separation process applied to separate liquid mixtures. The feed liquid diffuses through the membrane and vaporizes on the other side, where the applied pressure is lower than the saturated vapor pressure.[5] Nam *et al.*[6] reported that the crosslink chitosan/polyethersulfone composite membrane could be selective removal of water from aqueous ethylene glycol (EG) solutions by pervaporation. At 80°C and 80 wt% feed EG concentration, the permeation flux of 1130 g/m^2.h and water concentration of permeate greater than 99.5 wt% were achieved. Hu *et al.*[6] prepared the chitosan/poly(acrylic acid) complex membrane for pervaporation dehydration of EG aqueous soluions. From his result, the membrane exhibited the high separation performance with a water/EG separation factor of 105 and a flux of 216 g/m^2 h at 70°C for 80 wt% EG aqueous solution. Feng *et al.*[4] found that the chitosan/polysulfone composite membrane possess a permeation flux of 300 $g/m^2{\cdot}h$ and permeate water concentration higher than 92 wt% at 35°C and 60 Pa downstream pressure with a feed concentration of 10 wt% EG. The TEG resulting from the separation process can be reused, depending on the purification of TEG.

Thus, membrane is attractive method for TEG separation because of its simplicity and low energy cost[2]. The aim of this work is to study the effective separation of TEG in synthesis and industrial wastewater from natural gas process using cross-flow and pervaporation membrane filtration.

2.0 EXPERIMENTAL

2.1 Materials and Methods

The synthesis wastsewater was prepared at various TEG content of 5%, 10%, and 20%. The industrial wastewater collected from natural gas processing plant contained approximately 10% of TEG. Both synthesis and industrial wastewater were used as feed samples for this study. The polyethersulfone (PES-NTR 7450) membrane was supplied from Nitto Denko. The molecular weight cut-off (MWCO) of membrane is around 600-800 Dalton. The effective membrane area in contact with feed was 28 cm^2. For cross-flow filtration system, the applied feed pressure was 5 kg/cm^2. For pervaporation system, the vacuum pressure was maintained at 0.8 kg/cm^2, and permeate was collected in iced-cold traps. The feed temperatures were varied at 28°C, and 40°C, and the feed applied pressure were varied at 0.1, 1 and 2 kg/cm^2

2.2 Characterizations

The pH, turbidity, COD, BOD, and TDS of industrial wastewater were analyzed. Moreover, the metal content and the TEG content of wastewater were characterized by an inductive couple plasma (ICP, Perkin Elmer, Optima 7300) and a gas chromatography (GC, Hewlett Packard, Agilent HP 6890), respectively.

The morphology of membrane was observed by a field emission scanning electron microscope (FE-SEM, Jeol, JSM 6340F). The surface and cross-section of the samples were coated with gold by a sputtering coater. The membrane performance was determined in terms of permeation flux for both cross-flow and pervaporation filtration. The distilled water and TEG wastewater were used to measure the permeation resistance of the membranes. The permeation flux can be calculated using the following Equation 1,

$$J = \frac{Q}{A \cdot t} \tag{1}$$

where J is the permeation flux ($L \cdot m^{-2} h^{-1}$), Q is the permeation volume (L), A is the filtration area (m^2), and t is the permeation time (h).

The TEG selectivity of membranes was evaluated in terms of percentage rejection. The feed and permeate were characterized via a gas chromatography to analyzed the TEG content, and the % rejection was calculated as Equation 2,

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) x100 \tag{2}$$

where C_f and C_p are the concentration of the feed and permeate (mg/l), respectively.

3.0 RESULTS AND DISCUSSION

3.1 Properties of Membrane and Wastewater

The NTR-7450 membrane have a thin-film composite structure as shown in Figure 1, which include a sulfonated polyethersulfone (SPES) as active layer. The cross-section morphologies of PES membrane indicates that the dense layer with the thickness of ~3 µm was on the top of the microporous layer with the thickness of 40 µm.

The wastewaters used as the feed in this study were the synthesis and the industrial wastewater. The synthesis wastewater consist of 5%, 10% and 20% TEG. The industrial wastewater collected from gas dehydration process in natural gas processing plant had properties as shown in Table 1

Table 1 Properties of the industrial wastewater

Properties	Value
pH	6.5
TEG (%)	10.7
Turbidity (NTU)	8.8
COD (mg/L)	214,302
$BOD_5^{20°C}$ (mg/L)	2,950
TKN (mg/L)	101
SS (mg/L)	22
TDS (mg/L)	214
Oil & Grease (mg/L)	11.7
Alkalinity as $CaCO_3$ (mg/L)	118
Na (mg/L)	0.05
SO_4 (mg/L)	<0.50
Cl^- (mg/L)	1.34
Fe (mg/L)	1.69

3.2 Cross-flow Filtration System

The pure water flux was tested to determine the performance of the PES-NTR7450 membrane using cross-flow filtration system. It was observed that water permeation was not occurred when the applied feed pressure was below 5 kg/cm^2. The pure water flux was 47.56 $L/m^2 \cdot h$ at feed pressure 5 kg/cm^2. The cross-flow filtration system, however, was not effective for TEG removal because of the low TEG rejection of 5.21%. It was showed that the high feed pressure results in the high feed flow rate. Thus, the time of feed to contact with the membrane was too short. As the concentration of TEG feed increased from 5 to 10 and 20% of TEG, the membrane NTR7450 could reject the TEG of 17.49, 43.49 and 62.22%, repectively.

3.3 Pervaporation Filtration System

The performance and selectivity of membrane on TEG removal using pervaporation system with variation of the feed concentration, applied feed pressure and temperature are shown in Figure 2 and Figure 3. The pure water flux was compared to both the synthesis and industrial wastewater feed at the same conditions. Due to the stronger affinity of SPES to water molecules and smaller molecular size of water as compared with triethylene glycol, the pure water flux performed greater than the wastewater flux.[9]

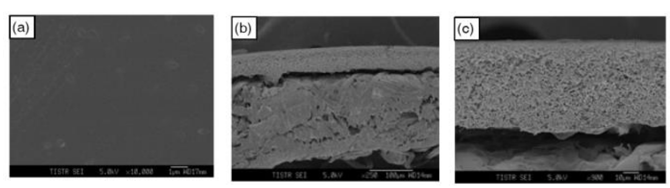
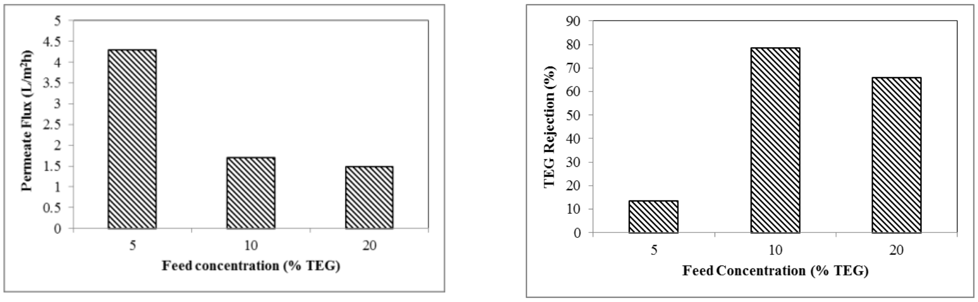


Figure 1 Microstructue of membrane PES (NTR7450), (a) surface, (b) cross-section and (c) cross-section of PES layer

As the feed concentration increased from 5 to 10, and 20% TEG, the permeate flux decerased. This is due to hydrophilicity of membrane NTR7450, the high concentration of water could be transferred to the membrane better than that the low concentration of water. For 10% TEG as a feed, the membrane had the TEG selectivity of 80% at 28°C and the applied feed pressure of 1 kg/cm^2.



(a) (b)

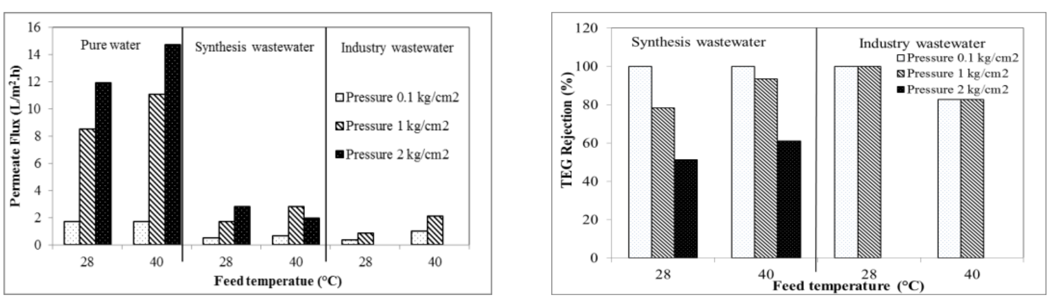
Figure 2 The effect of feed concentration on pervaporation system: (a) Permeate flux and (b) TEG Rejection

The effect of applied feed pressure on pervaporation performance was tested by carrying out the experiments at difference pressures (0.1, 1and 2 kg/cm^2). It can be seen that the pervaporation flux increased and TEG rejection decreased as the pressure in feed increased. The pressure could enhance water molecule transfering in wastewater through membrane and make polymer chain of membrane expansion, resulting in the permeation flux increased and rejection decreased. The permeation flux of synthesis wastewater was 0.51, 1.70 and 2.83 L/m^2.h for the applied pressure of 0.1, 1and 2 kg/cm^2 at 28°C, respectively.

The permeate flux of synthesis wastwater was trend to increased as the feed temperature increased. Generally, polymer possess larger free volumes at high temperature. If temperature increases, polymer chain composing the membrane and water molecule will move freely and thus free volume of the polymer increase resulting in an increase of the permeate flux and a decrease of TEG rejection.[10] However, high TEG rejections could be performed at the optimized of feed temperature and pressure. In figure 3-b, the appropriate condition for TEG removal of synthesis wastewater was the applied feed pressure of 0.1 kg/cm^2, and the feed temperature at 28°C. This condition could remove TEG more than 99% for the feed concentration of 10%TEG.

3.4 Pervaporation Filtration for TEG Removal of Industrial Wastewater

The wastewater from the natural gas separation industry was treated to remove TEG. The content of TEG in the wastewater was around 10.7%. The results showed that the flux increased as the applied feed pressure increased which was correspond to the treatment of synthesis wastewater. The increase of feed temperature affected the increasing of flux and the decreasing of TEG rejection. As the results, TEG removal of 99% in industrial wastewater using the pervaporation system was achieved at the operating condition of applied pressure 0.1 and 1 kg/cm^2 at feed temperature 28ºC. However, for providing higher flux, the applied pressure of 1 kg/cm^2, and 28°C was more proper to apply for pervaporation filtration system as shown in Figure 3.



(a) (b)

Figure 3 Effect of applied feed pressure and feed temperature on pervaporation system: (a) Permeate flux and (b) TEG rejection

4.0 CONCLUSION

The cross-flow and pervaporation filtration system were tested for wastewater treatment. The pervaporation system was more effective for TEG removal than the cross-flow system. The good TEG removal for pervaporation system performed at the feed concentration around 10%TEG. The applied feed pressure and the feed temperature influence on the flux and rejection of PES-NTR7450 membrane. As the applied pressure increased, the flux increased and TEG rejection decreased. The treatment of industrial wastewater using pervaporation system, TEG rejection of 99% was achieved at the operation condition of feed temperature 28ºC and applied pressure 1 kg/cm^2.

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