Petroleum and Coal

Article **Open Access**

EFFECT OF COMPOSITE MEMBRANE FOR DESULFURIZATION DIESEL IN PERVAPORATION PROCESS: FABRICATION OF POLYDIMETHYLSILOXANE AND USING TETRA-ETHYL-ORTHO-SILICATE AS CROSS-LINKING AGENT

Mohsen Farsi[1], Bizhan Honarvar[2], Amir Heydarinasab[1], Mehdi Arjmand[1]

[1] Department of Chemical Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran
[2] Department of Chemical Engineering, Marvdasht Branch, Islamic Azad University, Marvdasht ,Iran

Received April 4, 2018; Accepted June 25, 2018

Abstract

The multi composite membranes were fabricated through a blend of polydimethylsiloxane (PDMS), polyethyleneglycol (PEG), polyethersulfonic (PES) and cross-linked polyacrylnitrile (PAN) with tetra-ethyl-ortho-silicate (TEOS) to decrease the sulfur content in diesel fuel. The structural morphology of the composite membranes was characterized by scanning electron microscope (SEM). Experimental results indicated that 20% of the crosslinking agent amount was more preferable. The composite membranes were employed in pervaporation separation of thiophene mixtures in diesel. The pervaporation performances of the membranes under various crosslinking agent amounts, feed sulfur content, feed temperature, permeate pressure and feed flow rate on the separation efficiency and total flux was investigated experimentally. The increase of sulfur content in feed resulted in a higher total flux but a lower sulfur enrichment factor. By increasing the feed temperature, the total flux increased while sulfur enrichment factor decreased. Low permeate pressure and high feed flow rate were beneficial to improve total flux and sulfur enrichment factor. The prepared membrane displayed an optimum desulfurization performance with permeation flux of 9.98 kg/(m^{2}h) and the selectivity of 2.56 towards thiophene in model diesel.

***Keywords**: Composite Membrane; Sulfur Content Removal; Cross-linking Agent; PDMS; Pervaporation.*

1. Introduction

The presence of sulfur compounds in liquid hydrocarbons and its products creates various problems such as corrosion, poisoning factories catalyst receiving gas and liquid products, environmental problems, reduced heat value and reduced the price. Environmental concerns about fuel quality are one of the most important topics in oil refineries. Reducing sulfur below the 30 ppm for diesel and gasoline in many developed countries is according to the Environmental Protection Agency (EPA) rules that have been adopted in 2006 [1]. However, new methods for removing sulfur deeper may be necessary for the near future (sulfur content less than 10 ppm) [1-2]. (Common sulfur compounds can be founded in diesel and gasoline fuels contain mercaptans (RSH), sulfides (R2S), disulfides (RSSR), thiophene and its derivatives [1,3]). Thiophene compounds attributed itself more than 80% of sulfur impurities among other compounds of sulfur in gasoline and diesel [4].

The used membrane materials for removing sulfur are mostly including hydrophobic membranes such as polyurethane, polyurea/polyurethane, polyamide, natural rubber, polystyrene-butadiene and Polydimethylsiloxane. Hydrophilic properties of the membranes clearly increase the selectivity to the sulfur compounds which usually are more polar than hydrocarbons. The most common methods for making membranes with high selectivity and flux include cross-linking, blending, filling and copolymerization. Lin et al. studied the solubility of gasoline blending in polyethylene glycol [5]. They concluded that sulfur recovery rate by increasing the amount of cross-linking agent and the cross-linking time increases. Lin *et al.* [6] used polyethylene glycol and polyurethane polymers for fluidized bed catalytic cracking unit gasoline desulfurization. Wu *et al.* [7] improved the stability of the interface between the active layer of Polydimethylsiloxane and base layer of polyethersulfone by the aminosilane and amino propyl trimethoxysilane. Their results showed that with an increase of cross-linking agent penetration flux is uniformly reduced. The effect of tetraethyl ortho silicate on the increasing selectivity in the Polydimethylsiloxane membrane has been studied by Xu *et al.* [8]. In another study, manufacturing of *Polydimethylsiloxane* and polyamide composite membrane in separation heptane from thiophene was studied [9]. Rajesha et al. [10] synthesized oxide-zeolite composite membranes for benzophenone-3 removal from water. They concluded that membrane performances were significantly improved after the addition of ZnO-zeolite in the cellulose acetate solution. Ghasemian *et al.* [11] used polyvinylidene fluoride (PVDF) and nano-porous silica particle. Their results show that PVDF/SiO_2 nano-composite membranes exhibited enhanced antifouling property compared to neat PVDF membrane [11]. Xu *et al.* [12] manufactured a gradient cost-efficient composite membrane. They concluded that when the additive amount of OMWCNTs was 1wt%, the composite membranes presented an excellent flux.

Esfahan oil refining company operates in Iran. The company offers liquefied petroleum gas, solvents, unleaded gasoline, kerosene, gasoil, light and heavy fuel oil, light and heavy lubecut, and sulfur. In this study, the total sulfur in diesel product of Esfahan oil refinery was reduced from 6380 ppm to 1700 ppm by using composite membranes of PDMS, PDMS + PEG, PDMS + PES and PDMS + PAN, as well as the cross-linking technique by TEOS in a module of flat sheet membranes.

2. Materials and Methods

2.1. Materials

In order to manufacture the composite membranes, the following laboratory material was used: Tetraethyl ortho-silicate (TEOS) with an average molecular weight of approximately 208 g/mol (Merck, Germany); oligomers *of* polydimethylsiloxane (PDMS) with an average molecular weight of approximately 40000 g / mol and viscosity 5000 MPa.sec (Aldrich, USA); polyethylene glycol (PEG) with an average molecular weight of approximately 4000 g / mol (BASF, Germany); polyethersulfone (PES) with an average molecular weight of about 58000 g / mol (flakes, BASF, Germany); polyacrylonitrile (PAN) with an average molecular weight of about 45000 g / mol (Merck, Germany); polyvinylpyrrolidone (PVP) k90 as a filler with an average molecular weight of approximately 360000 g/mol (Merck, Germany); dimethyl acetamide (DMac) as a solvent (Merck, Germany); dibutyltindilaurate (Fluka, Switzerland); ammonia (Merck, Germany); the asymmetric nano filter based membrane of polyester (PlasmachemGmbH, Germany); n-heptane (Romil, UK); SPAN 80 (Merck , Germany); distilled water.

2.2. Composite membrane preparation

A certain amount of Span 80 as a surfactant, silicone propulsion (tetraethyl-ortho-silicate) with various weight percentages with oligomers of polydimethylsiloxane and polyethylene glycol in n-heptane (solvent) at room temperature for making homogeneously solution mixed together. Ammonia in water (anti-solvent) with half the molar concentration of the solution is solved to build a solution with pH = 9. However, a certain amount of this solution is added into a homogeneous solution under difficult conditions of stirring. The mass ratio between solvent to polymer is about 3.5, and the mass ratio between the polymers used in this study is equal. The use of ammonia as catalyst cause agglomerate silica has been done at the interface of water/homogeneous solution. After mixing for thirty minutes, a small amount of dibutyltindilaurate*as* bubble removing is added to this mixture. After removing bubbles in homogeneous solution, the solution is laying the base layer, and the film device is used. The solution to building a base film by deposition technique made by immersion; so, a 15% the mass of solution polyethersulfone and 3% the mass of the Polyvinylpyrrolidoneas filler in the dimethylacetamide solvent is made. This solution is built on the base of nano-filter asymmetric polyester, and after using the film immersed quickly in distilled water to remove residual dimethylacetamide. For other types of base layer, a 15% solution of polyethersulfone, 10% polyethylene glycol and 3% Polyvinylpyrrolidonein dimethylacetamide are used. Membranes initially are placed in the open air for 24 hours and then to complete the cross-linking process and evaporate the remaining solvent at the time of cross-linking (0.5-2.5 h) determined and at the time of cross-linking time (65-85℃) placed inside an electric furnace. Finally, the membranes are washed with distilled water and placed between sheets of filter paper and dried. All of the membranes before used in the membrane module and the membrane performance be measured should be placed in a free of dust and dry environment.

The other homogeneous solutions parallel with the above active membrane (PDMS + PEG) can be made only with this difference that the polyethylene glycol in the production of the homogeneous solution is removed from the environment and replaced with polyethersulfone and polyacrylicnitrile in each stage. In the entire process of construction of active membrane (derived from homogeneous solution), construction of basement membrane is the same way.

3. Membrane characterization

3.1. Scanning electronic microscopy spectroscopy

In order to investigate the membrane structure, SEM characterization of the prepared membraneshas been carried out. For this purpose, the membrane samples were fractured in liquid nitrogenand then coated with Au–Pd under vacuum conditions. The cross section and surface membranemorphology was taken by SEM (JSM-6301F scanning electron microscope). Membrane Characterization. In this study, a device with a model of VEGA3SBH\\TESCAN is used for the morphology of the cross-sectional structure of composite membranes. First, membrane samples are be broken in liquid nitrogen and then coated with a thin layer of gold in a vacuum.

3.2. Fourier Transform Infrared Spectra (FTIR-ATR)

Information about the presence of specific functional groups of the prepared membrane surfaceswas obtained by a Nicolet IR 560 spectrometer with horizontal attenuated total reflectance(ATR) accessory equipped with a ZnSe crystal. For evaluation, a total of 32 scans were performed at a resolution of 4 cm-1 at a temperature of 25±1°C. Meanwhile, Fouriertransform infrared (FTIR) spectra were recorded within the range of 4,000–400 cm^{-1}.

4. Pervaporation experiments

The schematic pervaporation apparatus is shown in Fig. 1. The feed solution was continuously circulated from a feed tank through the tube side of the membrane module using a variable speed feed pump. Vacuum on the permeate side was monitored by a digital vacuum gauge. The permeated vapor was collected by turns in liquid nitrogen traps. About 2 h after starting the PV process, a mass transfer equilibrium was established, and PV performance reached stable. At steady state, the weight of permeate collected in the cold trap was measured to obtain the total flux, J:

The total flux can be obtained from the following equation [13]:

$$J = \frac{m}{A \times t};\left[g.m^{-2}.h^{-1}\right] \qquad (1)$$

and partial flux, J_i:

$$J_i = w_i^p J \qquad (2)$$

where M is the total mass permeated; A the effective membrane area; t the experiment time interval, and w_i^p the weight fraction of component i in the permeate samples.

The total sulfur contents of the feed and permeated samples were analyzed by gas chromatography (GC-2014, SHIMADZU, Japan, equipped with FID). The sulfur enrichment factor, E, is defined as

$$E=w^p/w^f \qquad (3)$$

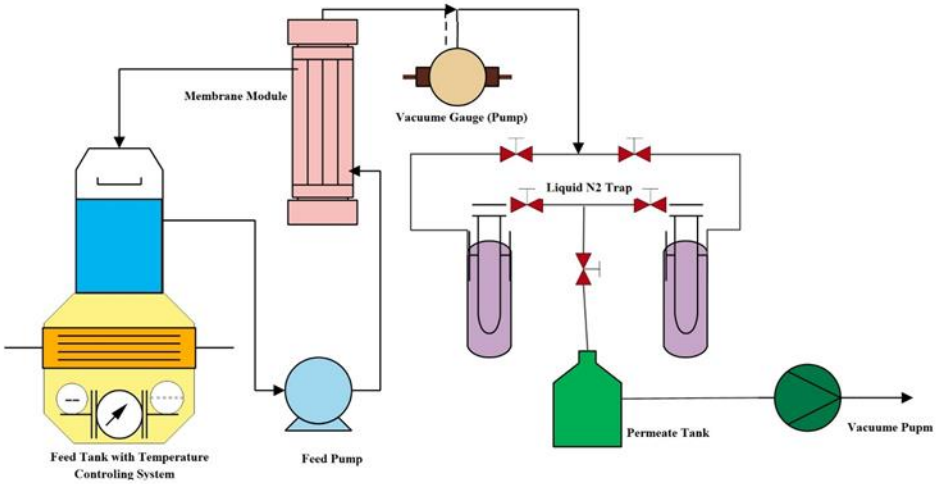


Fig. 1. Schematic diagram of experimental apparatus.

Feed is containing about three liters of diesel with the total sulfur content of 6380 ppm. After using any appropriate membrane, the remaining diesel is poured inside the feed tank and to experiment with new membrane will be replaced with a new diesel. The pump has been used that leads diesel with different flow rates and pressures set (5-9 times) into the membrane module. Membrane modules are manufactured from stainless steel and membranes used with an active area of 2100 cm. Membranes used to achieve steady state to be kept wet approximately one hour before the start of each test in the input feed to the modulus. For each test, approximately three hours were taken, and operating temperature range is between 30-50ºC.

5. Results and discussion

5.1. SEM Photographs of PDMS–TEOS composite membrane

As demonstrated in the SEM photographs, there is a clear boundary between the top layer and the support layer. Meanwhile, the cross-sectional structure of the composite membrane consisted of an ultrathin skin layer and a porous finger-like structure. The surface morphology of the composite membrane was shown in Fig. 3 and Fig. 4.

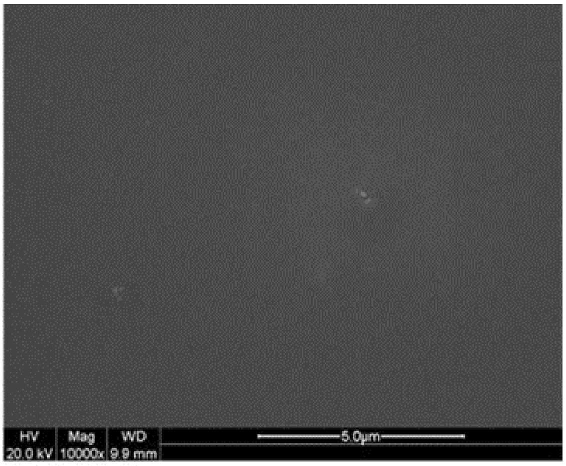


Fig. 2. The surface morphology of the PDMS composite membrane

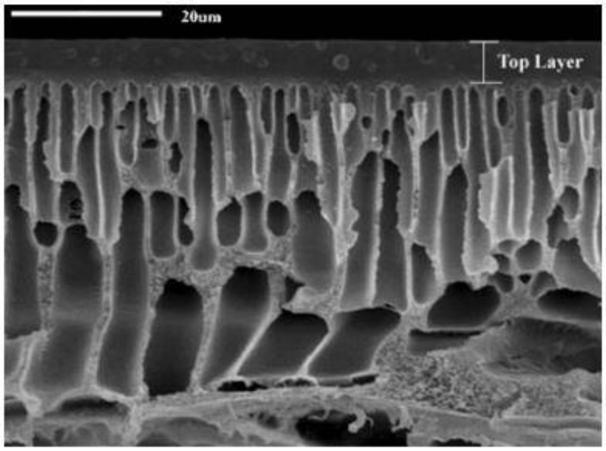


Fig. 3. The cross section morphology of the PDMS composite membrane

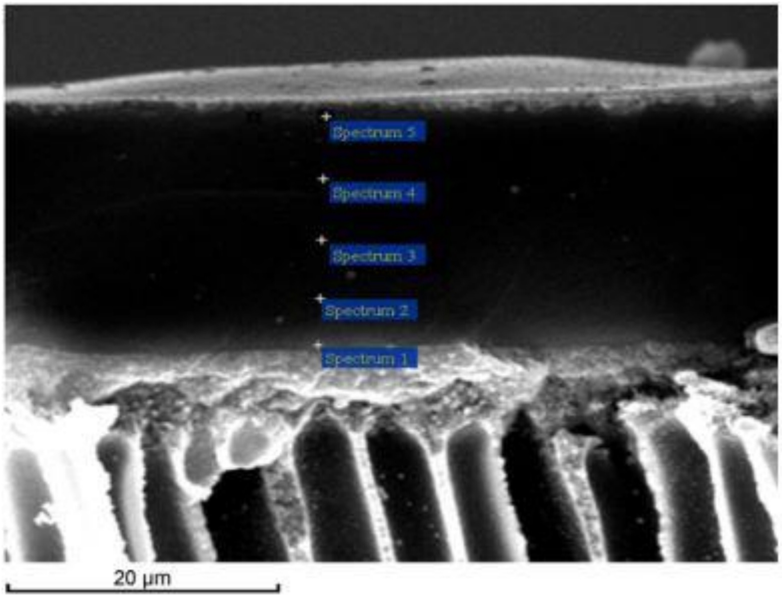
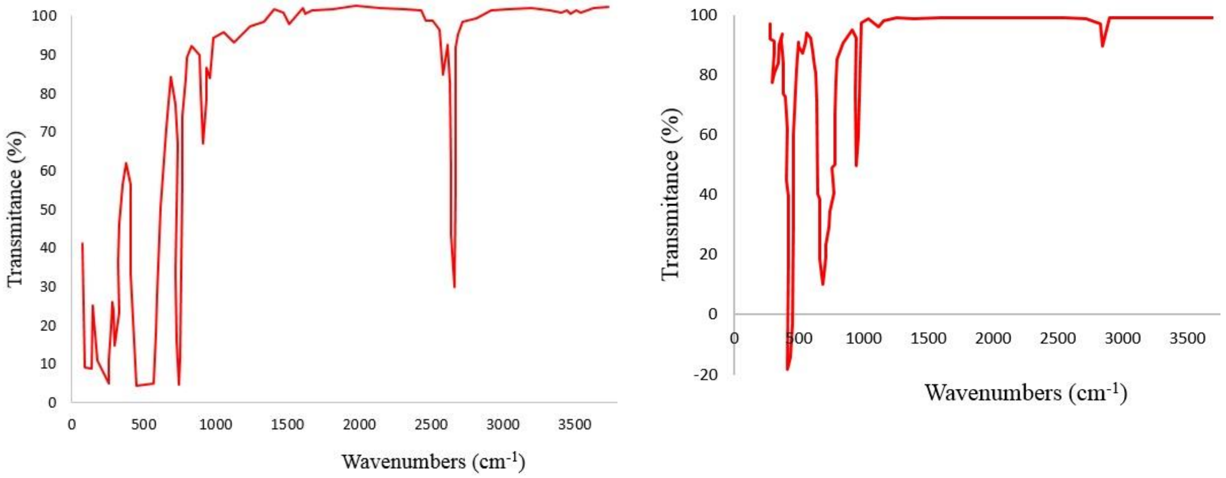


Fig. 4. SEM images of the cross-section of composite PDMS membrane

From these figures, the originally porous surface of the main substrate was covered by a flat, featureless layer, and the top PDMS layer, functioning as the basis of selectivity, had a nonporous and tight structure. The surface of the composite is dense, and there is no pinhole or crack, which is important for the practical application.

5.2. FTIR Spectra of PDMS composite membrane

The attenuated total reflection Fourier transform infrared spectroscopy is a commonly used method to characterize the chemical structure of the surface. The ATR technique enables the identification of specific molecules and groups located within 100 nm from the surface layer. In order to obtain accurate information about the structural changes of PDMS composite membranes resulting from cross-linking modification, FTIR spectra of the surface of PDMS composite membranes were recorded in Fig. 5 using the ATR technique.



(a) (b)

Fig. 5. FTIR spectra of PDMS composite membrane. (a) Before cross-linking modification, (b) after crosslinking modification

5.3. The effect of cross-linking agent amount on membrane performance

In order to improve the selectivity and limiting the swelling behavior of the active PDMS layer, the effect of crosslinking agent amount on membrane performance was investigated. From Fig. 6, the sulfur enrichment factor increased by increasing the amount of crosslinking agent as envisage, while the total flux decreased. When the crosslinking agent was added to the PDMS solution, the chemical connection occurred between macromolecules and reticular spatial structure formed, which was desirable for swelling resistance of membranes in diesel. And then the mobility of macromolecules and chain segments weakened with the inter chain free volume reduced, which estimated for the decline of permeation flux. However, because of thiophene species having a stronger affiliation to the membrane, the permeation flux of the thiophene species decreased more slowly than that of hydrocarbon species. Therefore, the sulfur enrichment factor increased with the addition of the crosslinking agent.

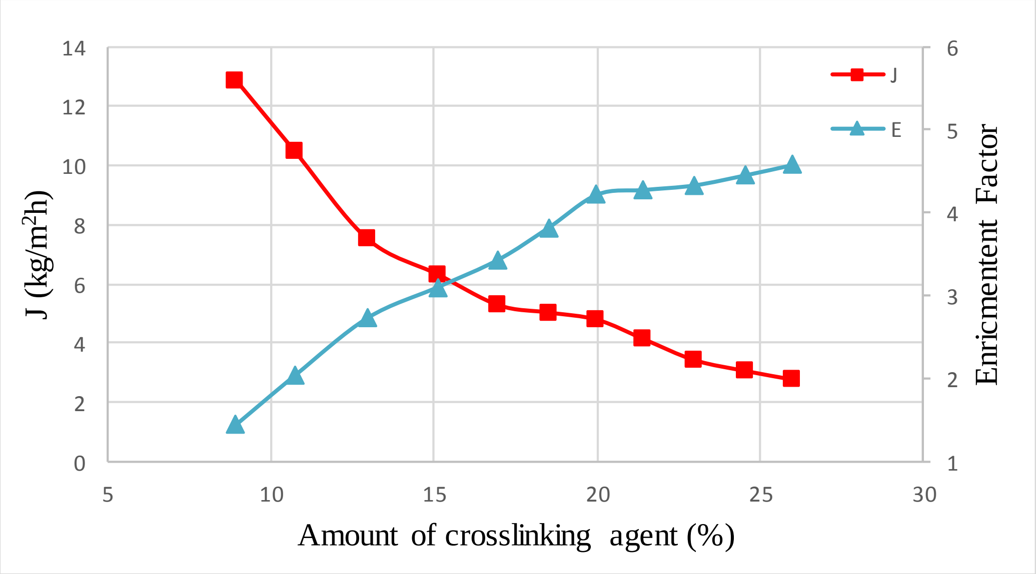


Fig. 6. Effect of crosslinking agent amount on the pervaporation performance of PDMS composite membrane

Meanwhile, excessive addition of crosslinking agent solution brought a higher viscosity solution, which was hard to be coated on the support layer uniformly. So the amount of crosslinking agent at 20% should be more practical due to the trade-off between permeation flux and sulfur enrichment factor.

5.4. Feed temperature

Feed temperature is an important factor in membrane separation performance for desulfurization. As shown in Fig. 7, when the temperature increased, the total flux increased, whereas the sulfur enrichment factor decreased. The increase of the feed temperature cause speed up the mobility of the polymer chains and prepared larger available free volume within the membrane for diffusion. In addition, higher temperature resulted in higher vapor pressure difference which would enhance the transport driving force.

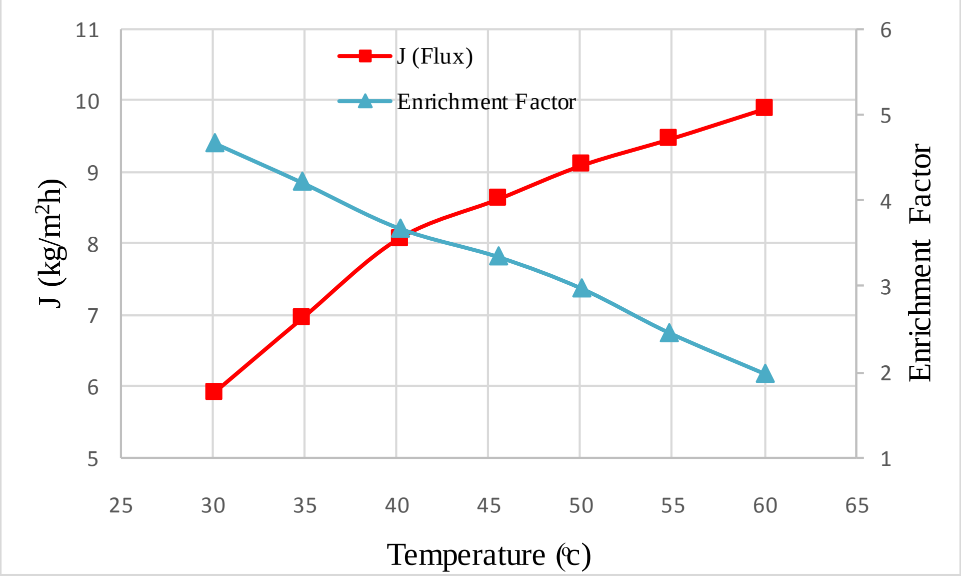


Fig. 7. Effect of operating temperature on the pervaporation performance of PDMS composite membrane

5.5. Permeate pressure

A vapor pressure difference through the membrane is the crucial driving force for pervaporation process. Fig. 8 shows the effect of permeate pressure on the membrane performance for desulfurization. As the permeate pressure increased, the total flux decreased significantly because there was a reduction of driving force for transport of components. In contrast, the sulfur enrichment factor decreased gently. The above results showed that relatively high vacuum (low permeate pressure) was useful to improve both total flux and sulfur enrichment factor.

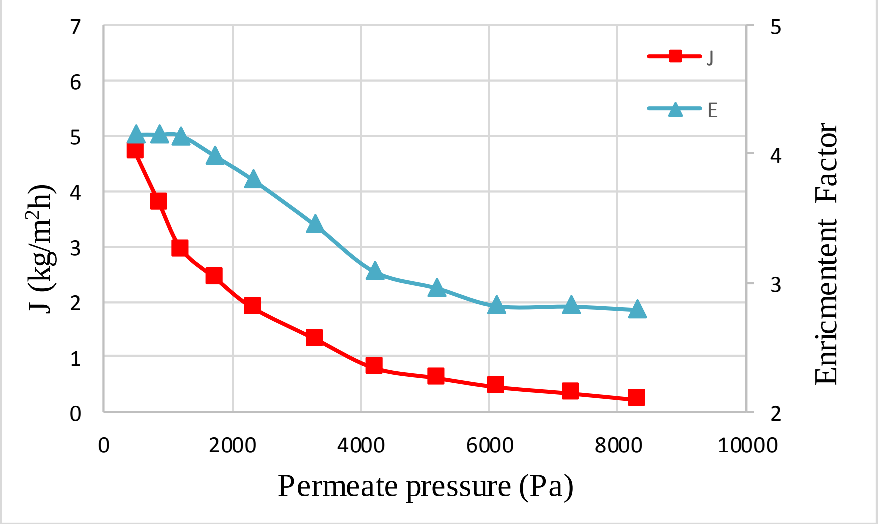


Fig. 8. Effect of operating pressure on the pervaporation performance of PDMS composite membrane

5.6. Feed flow rate

The effect of feed flow rate on pervaporation performance for desulfurization is representd in Fig. 9. Total flux and sulfur enrichment factor both increased with increasing the feed flow rate. The increase of feed flow rate was favorable to the reduction of concentration polarization and thickness of liquid boundary layer. Meanwhile, a reduction of concentration polarization meant that thiophene concentration near the membrane surface was close to that in bulk, which could enhance sorption and swelling of thiophene in the membrane. Consequently, both total flux and sulfur enrichment factor increases.

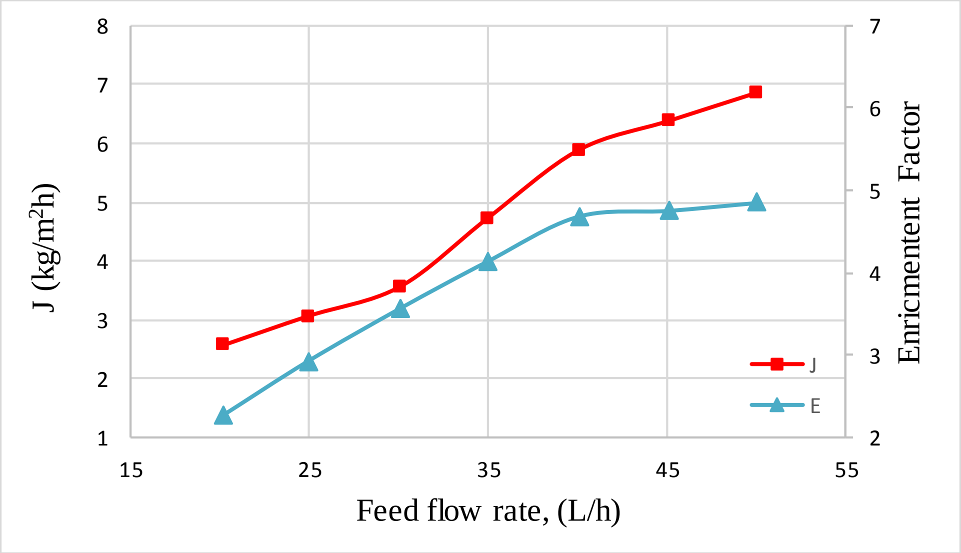


Fig. 9. Effect of feed flow rate on the pervaporation performance of PDMS composite membrane

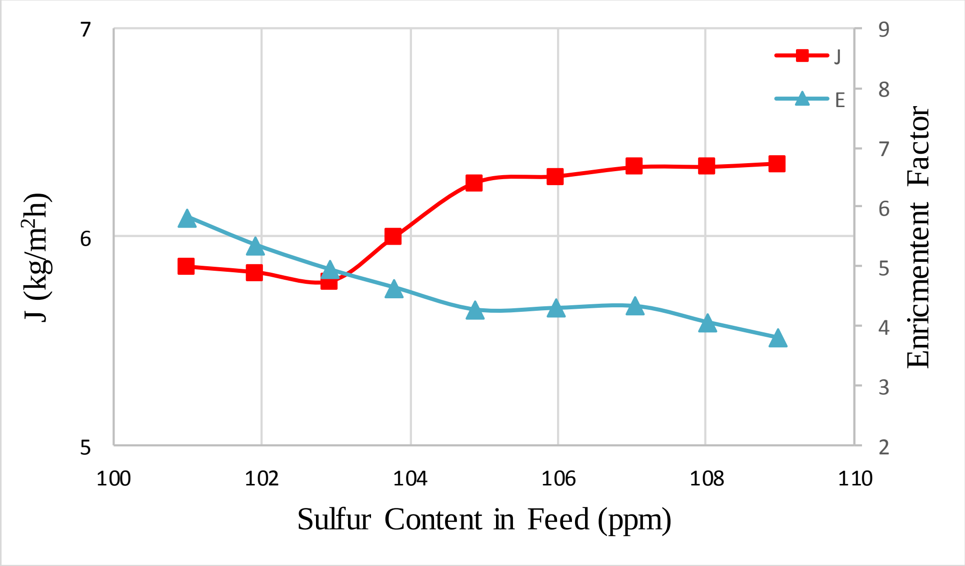


Fig. 10. Effect of sulfur content in feed flow on the pervaporation performance of PDMS composite membrane

5.7. Sulfur content in feed

Fig. 10 illustrates the effect of sulfur content on pervaporation performance for desulfurization. A higher feed sulfur content resulted in a higher total flux but a lower sulfur enrichment factor. while sulfur content increases, the thiophene molecules dissolve more and more in the polymer chains of the membrane, leading to the extensive swelling of the membrane. Consequently, the thiophene components permeated through the membrane easily, and total flux increases. The increasing swelling of the membrane would weaken difference of sorption and diffusion characteristics of the individual component. Therefore, the sulfur enrichment factor decreases.

6. Conclusions

Cross-linked PDMS composite membranes were utilized for removal of sulfur impurities from diesel by pervaporation process. Experimental results showed that the total flux increases with the increase of feed temperature and sulfur content, while in this situation the sulfur enrichment factor decreases. A relatively low permeate pressure was desirable for an optimal total flux and sulfur enrichment factor. On the other hand, both the total flux and sulfur enrichment factor increase s little with increasing the feed flow rate. Our study indicated that the cross-linked PDMS composite membranes had a good sulfur removal efficiency and were potential candidates to be used for practical and industrial desulfurization.

7. Acknowledgement

The authors gratefully acknowledge the scientific institutes and companies that they sincerely helped to this research. Among them can be mentioned the following: Esfahan Oil Refining Company, Iran Polymer and Petrochemical Institute (IPPI), Chemistry & Chemical Engineering Research Center of Iran (CCERCI), and Razi University.

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To whom correspondence should be addressed: Dr. Amir Heydarinasab, Department of chemical engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran, amir.heydarinasab@hotmail.com