VOLATILE ORGANIC COMPOUND REMOVAL USING POLYURETHANE BASED SELECTIVE MEMBRANE

Filiz UĞUR NİGİZ[1, +], Nilüfer DURMAZ HİLMİOGLU[1, *]

[1]Kocaeli University, Faculty of Engineering, Department of Chemical Engineering

Kocaeli TURKEY

*niluferh@kocaeli.edu.tr; filiz.ugur@kocaeli.edu.tr

Abstract

In this study pervaporative separation capability of silica incorporated thermoplastic polyurethane (TPU) membrane was investigated at different case studies. Representative waste disposal for different industry was prepared synthetically. Toluene-water, chloroform-water, formic acid-water, isopropyl alcohol-water mixture were prepared in concentration of 3 wt. % and the pervaporation experiments were performed at 40 °C. Membrane morphology was analyzed using scanning electron microscopy and polarized optical microscopy. Effect of membrane preparation technique on membrane affinity to the organic mixture was also investigated and the results were evaluated as a function of degree of swelling. Better flux of 0.73 kg/m^2.h and a separation factor of 14.9 were obtained at chloroform-water pervaporation. Pervaporation was also effective in toluene-water mixture separation. The quantitative results of the flux was chloroform>toluene>formic acid>isopropyl alcohol.

Keywords: Thermoplastic polyurethane membrane, organic-water separation, hydrophobic pervaporation, mixed matrix membrane

UÇUCU ORGANIC BILEŞENLERIN POLIÜRETAN TEMELLI SEÇICI MEMBRANE KULLANILARAK AYRILMASI

Özet

Bu çalışmada silika partikülü katkılı termoplastik poliüretan (TPU) membranların farklı çözeltilerdeki ayırma davranışları incelenmiştir. Farklı endüstriyel tesislerin

atıksularında bulunan organik bileşenlerden yola çıkılarak sentetik sulu organik bileşen çözeltileri hazırlanmıştır. %3 oranında organik madde içeren toluen-su, kloroform-su, formik asit-su ve izopropil alkol-su çözeltileri hazırlanarak 40 °C sıcaklıkta pervaporasyon deneyleri yapılmıştır. Membran hazırlama tekniğinin membran-solvent ilgisine etkisi de ayrıca şişme testlerine bağlı olarak belirlenmiştir. Pervaporasyon deneylerinde en iyi sonuç kloroform-su testlerinde gerçekleşmiş olup 0.73 kg/m2.h akı değeri ile birlikte 14.9 ayırma faktörü sonuçları elde edilmiştir. Pervaporasyon metodunun ayrıca toluen-su bileşenini ayırmak için de uygun olduğu görülmüştür. Sayısal olarak değerlendirildiğinde, akı değerlerine bağlı olarak en yüksek performansın kloroform>toluen>formik asit>izopropil alkol organik bileşen sırası ile elde edildiği görülmüştür.

Anahtar kelimeler: termoplastik poliüretan membran, organik-su ayırma, hidrofobik pervaporasyon, karma matrisli membran

1. Introduction

Industrial waste disposal includes hundreds of contaminants such as ions, radioactive elements, bacteria, volatile organic compounds (VOCs) and these impurities have potential to show toxic effect on the living cell within water ecosystem. It is a legal obligation to treat waste water before discharging to the lake, oceans or seawater [1, 2].

The concentration of each contaminant changes according to the industrialization of the region. Based on these variables, there are several purification methods for VOC purification which are used in large scale [3-6]. Distillation, carbon adsorption, air stripping, biological oxidation, coagulation, chemical treatment, and membrane separation methods are used for water treatment. Either these units are employed in-place or the waste disposal is drained to a general purification plant. In both cases, it is hard to remove small amount of dissolved chemicals from water. Most of chemicals present in waste at very low concentration (<1000 pmm), therefore, it is needed to separate them selectively using selective purification technique such as the membrane process [7-11].

Membrane separation methods (nanofiltration, reverse osmosis, pervaporation) are known as cost-effective and environmentally friendly solution for water treatment.

For deep purification of dissolved or very dilute disposal waste, nano-porous or non-porous membranes are preferred. Separation system via membrane is defined in several ways based on the structural nature of the membrane and the driving force between the upstream and downstream of the membrane. For example, pervaporation is a chemical potential driven process in which non-porous polymeric, inorganic or mixed matrix membranes are used [12-16]. It is an appropriate method for deep water purification when the organic contaminants are very low scale (<1000ppm). In the case of the pervaporative separation, selected ions or solvent is adsorbed to the surface of the membrane and pass through it in vapor phase.

Hydrophobic materials such as polyether-block-amid, poly(dimethyl siloxane), polyurethane, natural rubber are used for organic removal. Uragami (2014) studied for chloroform-water pervaporation using PDMS-PMMA membrane and obtained a flux of 1.9*10-5 kgm/m2.h with a separation factor of 4850 [17]. Khayet and Matsura (2004) also studied for chloroform-water mixture by using PVDF membrane [18]. Satyanarayana et al. (2004) used two different commercial membrane for toluene-water pervaporation [19]. In a study by Simone et al. (2012) Ethylene–Chlorotrifluoroethylene copolymer membrane was fabricated and used for toluene separation from water. They reported a total flux of 0.193 kg/m2.h with a separation factor of 849 at the room temperature [20]. Isopropyl alcohol-water pervaporation is a most recent study in pervaporative study. However, a big part of these studies have been performed for isopropyl alcohol dehydration by using a hydrophilic membrane [21, 22].

In this study pervaporative separation capability of silica incorporated thermoplastic polyurethane (TPU) membrane was investigated at different case studies. Thermoplastic polyurethane has very unique feature. TPU consists of both the soft polyether/polyester segment and hard aromatic urethane segment that change the adjustable segmental properties of the TPU. When TPU is used as non-porous membrane, as its soft region allows to passage of organic molecules, the hard segment gives mechanical durability over the long term separation process under forcible conditions. Additionally amine bond of urethane enhances the hydrophobicity of TPU and it contributes increasing the organic selectivity. According to the membrane preparation method, period, and solvent type, phase separation can be occurred within TPU and the crystalline structure of TPU is directly affected [23]. Therefore, in this study it was aimed

to obtain high organic separation factor due to the selective nature of TPU. Representative waste disposal for different industry was prepared synthetically. Toluene-water mixture was selected for paint and resin industry, chloroform-water mixture was selected for pulp-paper and polymer industry, formic acid-water mixture was selected for textile, and isopropyl alcohol-water mixture was selected for pharmaceutical and semiconductor industry. Effect of crystalline structure on the degree of swelling was investigated at a given temperature and feed composition of organic-water mixture. The pervaporation performance of crystalline silica loaded TPU membrane was also investigated as a function of total flux and organic separation factor. In conclusion, the silica loaded TPU membrane showed high affinity to chloroform and toluene than that of isopropyl alcohol and formic acid.

2. Material and Method

2.1. Membrane Preparation

In this study silica-TPU membranes were prepared by using solution-casting method. 10 wt % TPU was dissolved in N,N-dimethylformamide and stirred for four hours at 65 °C. Then 5 wt. % silica (Ultrasil) (respect to the polymer's weight) was homogeneously dispersed into the polymer solution and stirred in ultrasonic bath. In order to determine the effect of crystalline structure on separation performance, membranes were dried in two different ways. In the first way, pre-membrane solution (TPU-DMF and silica) was dried slowly at the ambient temperature. In the second way, pre-membrane solution was dried in oven at 140 °C for four hours. The membranes dried rapidly in vacuum oven were entitled as PC-TPU for plain-crystalline TPU, SC-TPU for silica loaded crystalline TPU, and the membranes dried slowly at room temperature were entitled as PA-TPU for plain amorphous TPU, SA-TPU for silica loaded crystalline TPU.

2.2.Membrane Characterization

The surface morphologies of the silica loaded membrane which was dried in oven were determined by polarized microscope (POM)(Nikon Elipse) scanning electron microscopy (SEM) (JEOL JSM-6000).

2.3. Swelling experiment

The degree of swelling (DS) (%) test was done to evaluate the affinity of the membrane to the target component. For determination of the swelling degree, membranes were immersed in toluene-water, chloroform-water, isopropyl alcohol-water and formic acid-water solution with an organic concentration of 3 wt. %. Swelling degrees were calculated from the weight difference of the swollen (W_s) and dry (W_d) membrane as seen in Equation 1.

$$DS = ((W_s - W_d)/(W_d)) * 100 \qquad (1)$$

2.4. Pervaporation experiment

Pervaporation experiments were performed in a laboratory scale pervaporation unit with a volume capacity of 250 ml. The system was also defined elsewhere [24]. The upper side of the membrane was kept in atmospheric pressure and a pressure difference was occurred between the sides of the membrane with a vacuum pressure of 1mbar on the downstream side to maintain the chemical potential gradient. To create a chemical potential gradient between the sides of the membrane play a critical role on the performance of pervaporation. According to the solution-diffusion phenomenon which defines the pervaporative separation accurately, the target component dissolved on the membrane surface, diffuses through the membrane and desorbs to downstream side resulting the chemical potential created by pressure difference.

After the better membrane type had been selected with the results of swelling experiments pervaporation were carried out at 40 °C. Experiments were performed with binary water–organic mixtures of chloroform/water, toluene/water, formic acid/water, and isopropyl alcohol/water solutions when the organic concentration in water was 3 wt. %. Permeate solution was collected in cold traps with an hourly interval and weighted to determine the flux (J)(kg/m^2.h) as seen in Equation 2.

$$J = (W_p)/(A.t) \qquad (2)$$

where Wp (kg) is the weight of the permeate solution, t is pervaporation time (h), A is effective membrane area (m^2).

2.5. Analysis

The organic separation factor (β) was calculated for four types of organic component separately using Equation 3.

$$\beta = (y_i/y_j)/(x_i/x_j) \tag{3}$$

where y_i and x_i represent the organic concentration in the permeate and feed respectively. y_j and x_j show the water concentration in the permeate and feed respectively.

For this purpose, the concentrations of the organic compounds were determined in different methods. Formic acid concentration in water was determined using titration method. Isopropyl alcohol concentration in water was analyzed using gas chromatography equipped with a thermal conductive detector. Chloroform and toluene concentration in water were determined using UV-Vis spectroscopy.

3. Findings and Discussion

3.1. Characterization Results

Figure 1 indicates the surface morphologies of pristine (unfilled) and 10 wt. % silica filled TPU membranes. While the light phase represents the silica particle, the dark region indicates the TPU matrix. Figure 1a shows the smooth and dense structure of the unfilled TPU surface. Figure 1a indicates the homogeneous dispersing of the silica particle within the polymeric matrix. The interface regions between the silica and TPU clearly appear in Figure 1b. As seen in the figure, the filled membrane was fabricated successfully without any fractures or defects between the two different structures (organic polymer-inorganic silica). This observation is very important for non-porous selective membrane fabrication. Undesired defect-free region or voids between the polymer and inorganic particle would allow unselected passage of the other molecules with the target ones. Therefore, the mixed matrix, hybrid, and inorganic particle filled polymeric pervaporation membrane should be well fabricated without any adhesion-free region to achieve a selective separation.
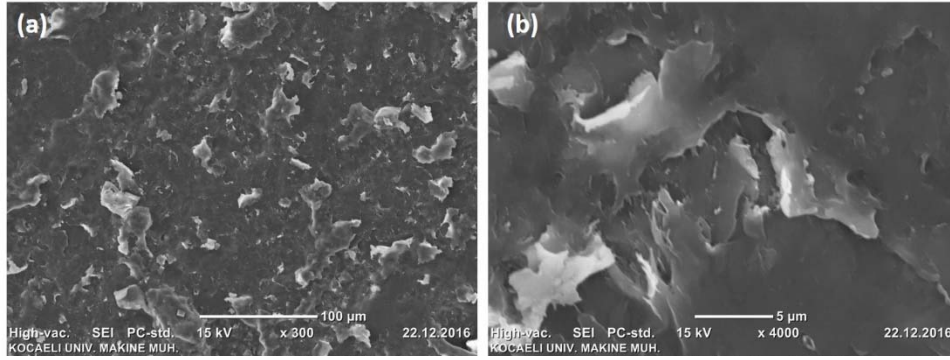
Figure 1: SEM micrographs of silica filled TPU membranes

The homogeneous silica distribution is also confirmed by the polarized microscope micrographs as it is indicated in Figure 2. Silica particles were well distributed within the TPU and this case would be expected to affect positively pervaporation performance of the organic-water solution.
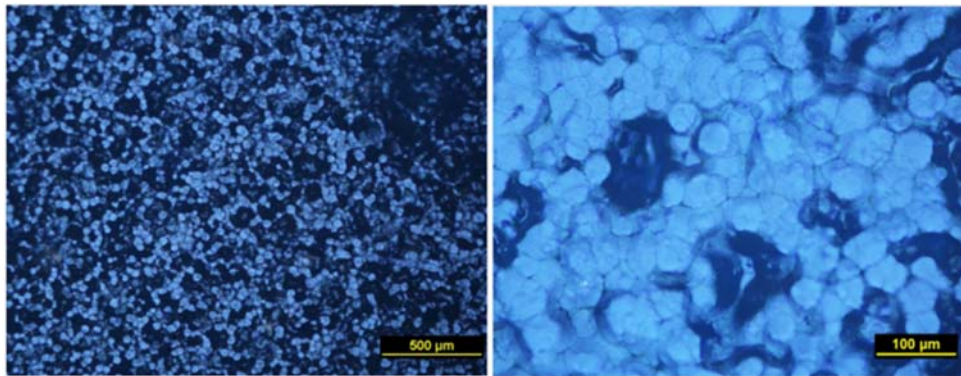

Figure 2: POM micrographs of silica filled TPU membrane

3.2. Swelling Experiment

As seen in Figure 3, thermoplastic polyurethane shows high affinity to chloroform compared to other organics. Hence it could be predicted that the separation capability of crystalline TPU would be chloroform>toluene>formic acid>isopropyl alcohol. When the membranes were dried at ambient conditions, amorphous structure of membrane showed higher swelling tendency to the solvent. Therefore, PA-TPU and SA-TPU exhibited higher swelling compared to PC-TPU and SC-TPU. Additionally, affinity of the amorphous membrane to isopropyl alcohol increased compared to crystalline.
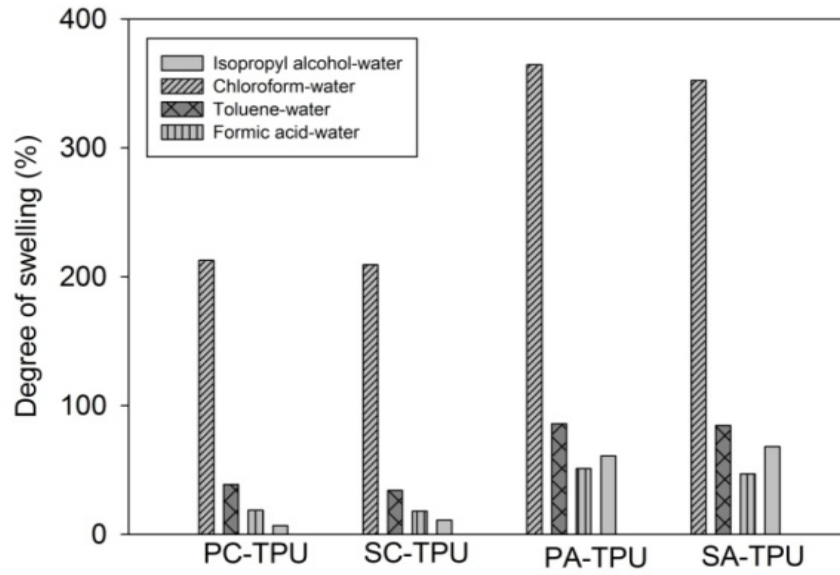
Figure 3: Swelling degree of membranes

However, the swelling degree results between the 300-400 % are very high for selective separation. Therefore, SC-TPU membrane was selected to be used for pervaporative separation of organic-water mixtures.

3.3. Pervaporation experiments of organic-water solutions

According to the swelling experiment, membrane separation studies were performed using SC-TPU membrane. Separation performances of the SC-TPU membrane in the pervaporative separation of isopropyl alcohol-water, formic acid-water, toluene-water and chloroform-water binary mixtures are presented in Figure 4 and Figure 5.

Figure 4 indicates the flux result comparison of the different binary solutions. The flux results confirmed the swelling results. The better flux result was obtained in chloroform-water solution as 0.73 kg/m^2.h. The quantitative results of the flux was chloroform>toluene>formic acid>isopropyl alcohol. This result was due to the interaction forces between the solvent and polymer. For better understanding this interaction Hensen solubility parameters were given in Table 1.
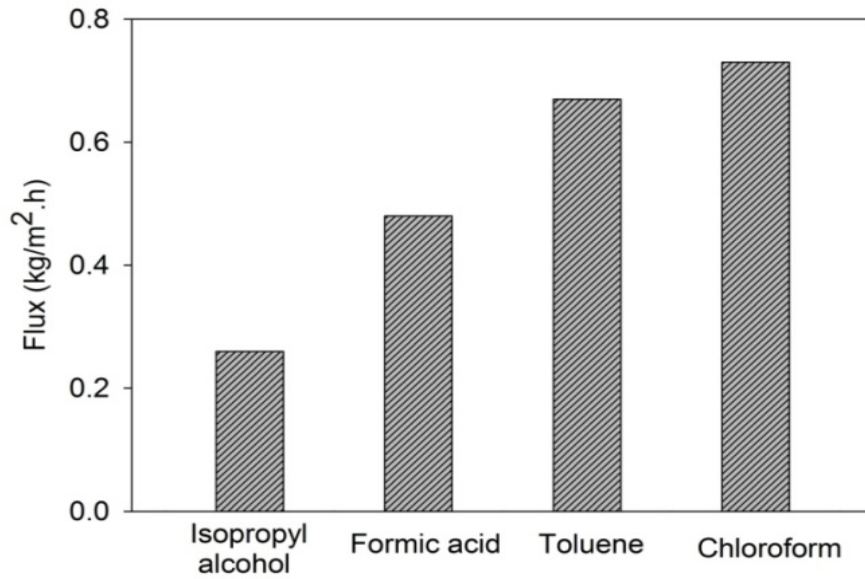
Figure 4: Total flux results of SC-TPU membrane for binary mixtures

Table 1: Hensen Solubility Parameters [25]

Components	δd	δp	δH	δ
Water	15.5	16	42.3	**48.8**
Isopropyl alcohol	15.8	6.1	16.4	**23.6**
Formic acid	14.3	11.9	16.6	**37.8**
Toluene	18	14	2	**18.2**
Chloroform	17.8	3.1	5.7	**18.9**
TPU	10	8.2	9.8	**18.8**

Where (δp) represents the polar component dipole–dipole interactions, (δH) represents hydrogen bonding forces, (δd) represents the dispersive force component, and the (δ) represents Hansen solubility parameter [26]. As can be clearly seen in the Table 1, Hensen solubility of the chloroform was almost the same with the TPU, therefore, the flux value of chloroform-water solution was the highest one resulting the higher affinity of the polymer to the chloroform. The quantitative order of the Hensen parameters were chloroform>toluene>isopropyl alcohol>formic acid>water. These results were almost the same with both the swelling results and flux results.
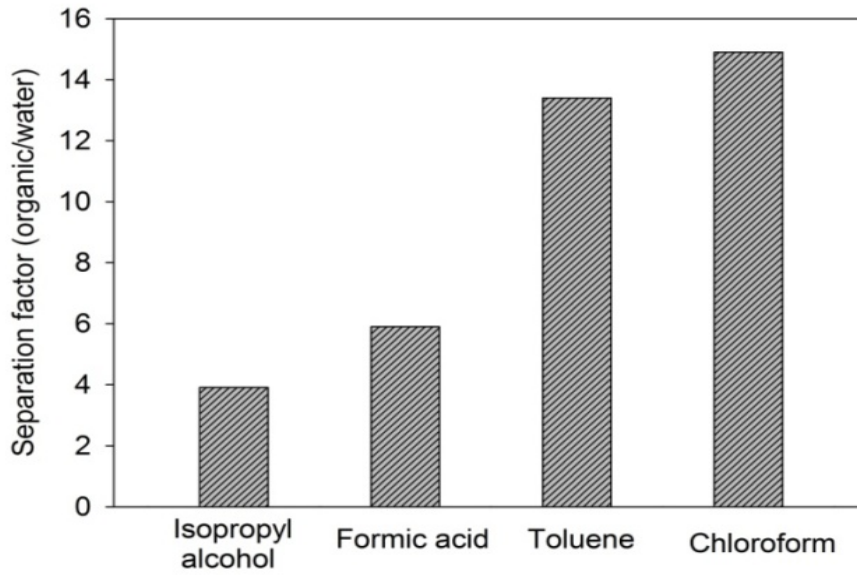
Figure 5: Separation factor results of SC-TPU membrane for binary mixtures

Better flux and separation factor was achieved in the case of chloroform-water and toluene-water solution. While the organic separation factor of 14.9 and 13.4 were achieved for chloroform-water and toluene-water binary mixtures, 5.8 and 3.7 separation factor were obtained for formic-acid and isopropyl alcohol-water binary mixtures respectively. This result attributed to affinity of the membrane to the chloroform and toluene as indicated before related to Hensen Parameters.

4. Results

In this study, an amorphous and crystalline pristine and zeolite distributed membranes were synthesized. Firstly, four different membranes were immersed in chloroform-water, toluene-water, isopropanol-water, formic acid-water binary mixtures to determine the sorption capability of the membranes to the target component. Following the swelling measurements, pervaporation experiments of the binary mixtures were performed at 40 °C temperatures with constant organic composition of 3 wt. % by using crystalline silica loaded TPU membrane. Better flux of 0.73 kg/m2.h and a separation factor of 14.9 were obtained at chloroform-water pervaporation. Pervaporation was also effective in toluene-water mixture separation. In conclusion, it can be concluded that the

silica loaded TPU membrane which was dried in oven was very effective for chloroform-water and toluene-water separation.

Abbreviations

DMF	:	N,N-dimethylformamide
PA-TPU	:	Pristine-amorphous thermoplastic polyurethane
PC-TPU	:	Pristine-crystalline thermoplastic polyurethane
PDMS	:	Poly(dimethyl siloxane)
PMMA	:	Poly(methyl metacrylate)
POM	:	Polarized optical microscope
PVDF	:	Polyvinylidene fluoride
SA-TPU	:	Silica loaded-amorphous thermoplastic polyurethane
SC-TPU	:	Silica loaded-crystalline thermoplastic polyurethane
SEM	:	Scanning electron microscope
TPU	:	Thermoplastic polyurethane
VOCs	:	Volatile organic components

Acknowledgment

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