

Applying filled and unfilled polyether-block-amide membranes to separation of toluene from wastewaters by pervaporation

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Received 20 December 2006; accepted 3 January 2007

Abstract

One of the methods of achieving high selectivity or high flux for specific compounds is the modification of membrane such as filling, grafting or coating. The most common is adding fillers, especially high aspect ratio fillers. It improves physical properties such as increased stiffness or reduced creep and a variety of other purposes: improves thermal stability, high voltage resistance, electrical conductivity, radiation shielding and optical and aesthetic effects. In many cases, filled polymeric membranes show permeabilities much lower than the conventional unfilled membranes, and hence can serve as barriers for oxygen, water and other solutes. In the area of organophilic pervaporation membranes mostly tree types of fillers have been used: zeolite, silicate and carbon sieve.

This study focused on the removal of toluene from the wastewaters. The concentration of that solvent in the feed solution was close to its solubility in water — 500 ppm. The tests were carried out on a polyether-block-amide (PEBA) membrane filled with carbon black (PEBA + cb) and another without the filling (PEBA). Both membranes were made in a laboratory and were characterized by the same thickness (75 µm).

The removal of toluene from wastewaters for PEBA membrane after 5 h of the process was satisfactory, reaching approx. 65%. However, special attention should be paid to very high toluene concentration indicated by high enrichment factor and selectivity of the process. The final concentration of toluene in the retentate after 5 h of pervaporation with use of PEBA + cb membrane was about 100 ppm, (80% of removal), but much higher fluxes accomplished for that membrane (especially water flux) worsened the concentration of toluene in the permeate.

Keywords: Pervaporation; Wastewater; Toluene; Polyether-block-amide membrane; Filler

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Presented at the conference on Desalination and the Environment. Sponsored by the European Desalination Society and Center for Research and Technology Hellas (CERTH), Sani Resort, Halkidiki, Greece, April 22–25, 2007.

1. Introduction

Pervaporation, compared to the well-established pressure driven processes such as reverse osmosis, nanofiltration or ultrafiltration, is less common in the treatment of wastewater containing organic compounds. Until now, only one industrial-scale application of wastewater treatment using organophilic pervaporation for the recovery of VOCs has been reported [1]. Introducing pervaporation as part of hybrid processes can significantly enhance its prospects and help being adopted. Also, the emphasis on the recovery and reuse of solvents from aqueous solutions instead of their destruction can make organophilic pervaporation a considerable membrane technology [2].

Another method of making pervaporation a more attractive separation process is developing new membranes with good flux and selectivity properties. It can be achieved by functionalisation of membrane polymers [1], development of completely new polymers [3,4] or introduction of adsorber agents into polymer material [5–8]. All this improves, among others, stiffness, thermal stability, high voltage resistance, electrical conductivity, radiation shielding and optical and aesthetic effects [2].

Membranes which are usually applied to the separation of volatile organic compounds are made of elastomers, such as polyether-block-amide (PEBA), which is characterized by a high mechanical strength and a very good separation properties towards organic matter (Fig. 1). The properties of the polymer may be changed using different proportions of polyether and polyamide in its particle: more particles of the rodlike chain of polyamide increase the strength of the

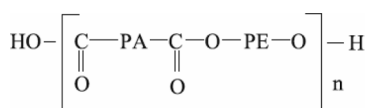


Fig. 1. The structure of PEBA. PA – polyamide, PE – polyether.

compounds while more flexible particles of polyether improve the separation properties.

2. Experimental

The study was aimed at removing of toluene from the wastewater coming from the chemical industry. It was a waste aqueous solution after distillation process of 4-toluenesulfonic acid. Toluene concentration in the effluent was about 500 ppm, which is close to its solubility in water limit. The tests were carried out on a polyether-block-amide membrane filled with carbon black (PEBA + cb) and another without the filling (PEBA). Both membranes had the same thickness (75 μm) and were made in a laboratory. A detailed description of their preparation was given in publication [9].

The apparatus employed in the tests is described in a study in Ref. [9]. The effective membrane area was 100 cm^2 and it was placed in the titan cell made by GKSS Forschungszentrum Geesthacht, Germany. The feed tank of the capacity of 2 dm^3 was filled with the wastewater. During the experiment the retentate was being recycled to the feed tank and the permeate was being collected in the cooling traps. Process parameters were:

- temperature of the feed: 25°C
- pressure on the permeate side: 100 Pa
- overall flow above the membrane: 1770 cm^3/min .

Each experiment lasted 5 h. Every hour, a sample was taken from the feed tank and the concentration of the toluene content was determined by gas chromatography using SRI chromatograph equipped with FID detector and 30 m capillary column MXT-5 made by Restek. The concentration of toluene in the permeate, followed by the sample dilution with water, was determined in the way similar to the feed samples. The permeate mass was determined before the dilution using a balance.

To evaluate the efficiency of the process following equations were used:

(1) Mean separation factor α (selectivity):

$$\alpha = \frac{\overline{Y a_i} / \overline{Y b_i}}{\overline{X a_i} / \overline{X b_i}}$$

(2) Mean enrichment factor β :

$$\beta = \frac{\overline{Y a_i}}{\overline{X a_i}}$$

(3) Permeate flux J_m :

$$J_v = \frac{m_r}{S_m * t}$$

(4) Removal degree D_r :

$$D_r = \left(1 - \frac{m_t}{m_0}\right) * 100\%$$

where:

a: primary mixture component transferred through the membrane,

b: secondary mixture component,

\overline{X}_i : geometric mean of the concentrations of component a or b in the feed,

\overline{Y}_i : concentration of component a or b in the permeate,

m_r : permeate weight (g),

S_m : membrane surface area (m²),

m_t : weight of removed component after t time,

m_0 : weight of removed component in time $t = 0$

t : time (h).

J_m values shown in the tables were calculated as mean fluxes obtained during a 5 h experiment, whilst α and β factors were calculated for 5 h stage, assuming that the concentration of the feed was the value averaged by the geometric mean.

3. Discussion

The first stage of the research dealt with the determination of separation properties of the

homogenous PEBA membrane. The results obtained in the experiments are shown in Table 1 and Figs. 2 and 3.

A careful observation of the decrease in toluene concentration in the feed stream revealed

Table 1

Total, toluene and water fluxes achieved during pervaporation of wastewater using 75 μ m PEBA membrane without carbon black

Total flux, g/m ² h	Toluene flux, g/m ² h	Water flux, g/m ² h
29.62	13.20	16.42

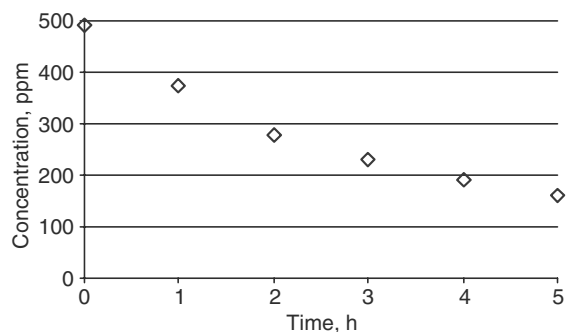


Fig. 2. Decrease in toluene concentration in the feed as a function of time for PEBA membrane without carbon black.

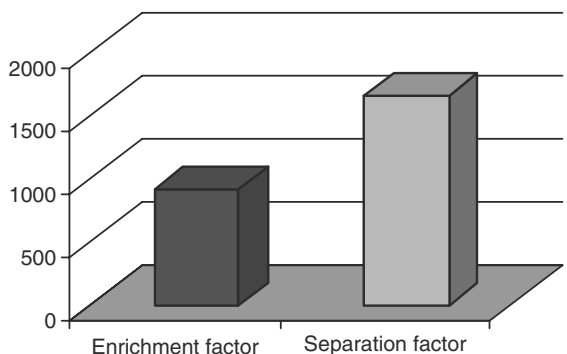


Fig. 3. Factors α and β for toluene obtained during pervaporation of wastewater solution.

Table 2

Total, toluene and water fluxes achieved during pervaporation of wastewater using 75 μm PEBA membrane with carbon black

Total flux, $\text{g}/\text{m}^2 \text{h}$	Toluene flux, $\text{g}/\text{m}^2 \text{h}$	Water flux, $\text{g}/\text{m}^2 \text{h}$
48.50	16.14	32.36

that half of the impurity was removed as soon as 2 h after the experiment started. Another 3 h showed a further reduction of toluene in the feed, however, the rate of the process dropped rapidly with the decreasing concentration of toluene in the feed. As a result, the final concentration of toluene in the retentate was approx. $150 \text{ mg}/\text{dm}^3$, which was equal to 70% removal. Since the membrane was relatively thick (75 μm), individual fluxes were low (Table 1), however, the percentage of toluene flux in the total flux was very high and reached 46%. This resulted in a very high concentration of toluene in the permeate as well as good selectivity of the process which was also proved by high separation coefficients and enrichments factors (Fig. 3).

In order to see the effect of the hydrophobic filling on the separation properties of the membrane, a PEBA membrane with carbon black

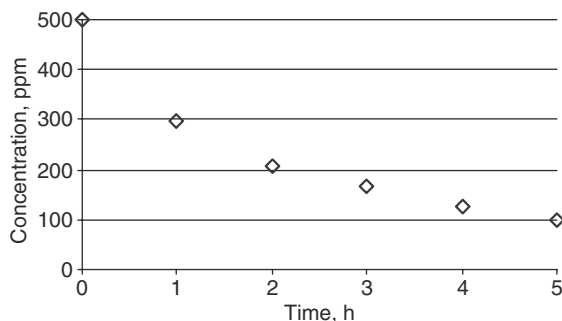


Fig. 4. Decrease in toluene concentration in the feed as a function of time for PEBA membrane with carbon black.

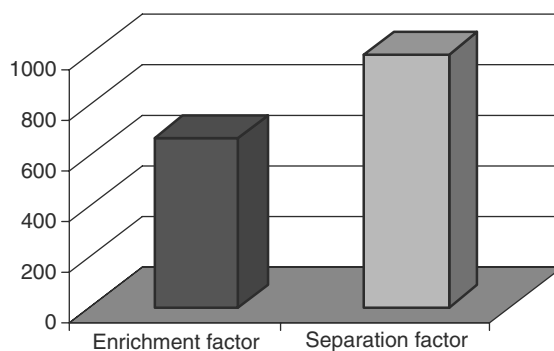


Fig. 5. Factors α and β for toluene obtained during pervaporation of wastewater solution.

was prepared and tested. The results obtained in the experiment are given in Table 2 and Figs. 4 and 5.

The comparison of the results for PEBA and PEBA + cb membranes revealed much higher fluxes of the components of the mixture for the filled membrane which resulted from both the higher rate of toluene removal from the feed and its lower concentration in the retentate. Therefore, its removal was slightly better for PEBA + cb than PEBA (Fig. 6).

This phenomenon is described by the images obtained from an electron microscope after the experiments (Fig. 7). They revealed that the

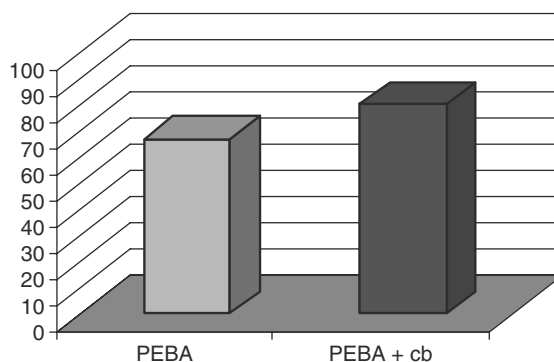


Fig. 6. Removal degrees of toluene achieved during 5 h of pervaporation of wastewater solution, using PEBA membranes.

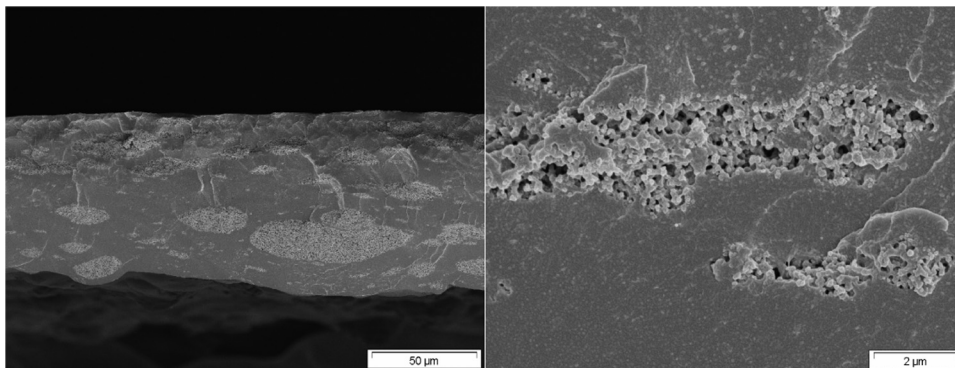


Fig. 7. SEM pictures of PEBA membrane with carbon black.

structure of PEBA + cb membrane was not continuous. Despite numerous attempts to form the membrane, the particles of the filling formed agglomerates which resulted in micropores and this effect increased the permeation of mixture components.

Unfortunately, the increase in the permeating water flux against a considerably small increase in toluene flux reduced the separation properties of PEBA + cb membrane. Both selectivity of the process and toluene concentration in the permeate were slightly lower for this membrane which was proved by the separation coefficient and enrichments factor (Fig. 5). However, they are high enough to regard the membrane as an attractive alternative for the treatment of wastewater fluxes.

4. Conclusion

The results yielded by the pervaporation of wastewater produced by the chemical industry using PEBA and PEBA + cb membranes are very promising. Although the wastewater was characterized by a very high toluene concentration (500 mg/dm^3), PEBA and PEBA + cb membranes removed 67 and 81% of toluene during one 5 h experiment. Moreover, the high enrichment factors and selectivity coefficients which indicate good separation properties of the membranes

prove their suitability for the pervaporation of industrial wastewater.

Acknowledgements

The financial support of the Polish Committee of Science, Grant number 3T09D 003 29, is greatly appreciated.

The authors wish to thank GKSS Germany particularly Dr Gisela Bengtson for all the help and support connected with that work.

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