ELSEVIER

Desalination 222 (2008) 197–201

DESALINATION

www.elsevier.com/locate/desal

Use of SAPO-5 zeolite–filled polyurethane membranes in wastewater treatment

Gabriela Ciobanu[a]*, Gabriela Carja[a], Octavian Ciobanu[b]

[a]*The Gh. Asachi Technical University of Iasi, Faculty of Chemical Engineering, Bvd. D. Mangeron, No. 71, Iasi, 700050, Romania*
Tel. +40 232 255649; Fax +40 232 271311; email: gciobanu03@yahoo.co.uk
[b]*The Gr. T. Popa University of Medicine and Pharmacy of Iasi, Faculty of Medical Bioengineering, Str. Universitatii, No. 16, 700115, Iasi, Romania*

Received 20 December 2006; accepted 13 January 2007

Abstract

The SAPO-5 zeolite-filled polyurethane membranes with perselectivity to the gases or liquids were prepared, characterized and utilized for the ultra- and, respectively, microfiltration (UF + MF) of synthetic wastewater containing colophony. The influence of the colloidal dispersion concentration on the membrane processes has been followed. Also, the conversion degree of colophony colloidal dispersions has been studied versus light diffusion through the dispersoid system. Filtration experiments were operated in cross-flow mode under 50 mm Hg of applied pressure. The influence of temperature on the membrane processes has been followed, the observation being made that, on increasing temperature, the membrane permeability (P) and retention capacity (R, %) increase. Thus, the conclusion to be drawn is that temperature influences considerably the colophony dispersion through the membrane. The temperature-dependent permeability parameter followed the Arrhenius relation from which the energy of activation has been obtained.

Keywords: Polyurethane membrane; SAPO-5 zeolite; Microfiltration; Ultrafiltration; Textile wastewater treatment; Colophony

1. Introduction

Textile processing is one of the most important industries in the world and it employs a variety of chemicals, depending on the nature of the raw material and product. Some of these chemicals are different types of dyes, acids, sodas, salts enzymes, resins, detergents etc. The extensive use of chemicals and water in textile industry results in generation of large quantities of highly polluted wastewater [1,2]. The wastewater generated by the different production steps contains high concentration of organic matter, non-biodegradable matter, toxic substances, detergents and soaps, oil and grease, sulphide, sodas, and alkalinity.

*Corresponding author.

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.

doi:10.1016/j.desal.0000.00.000

Recovery of some useful compounds from such waters is necessary not only for combating pollution, but also for the re-utilization of recovered products and of the released water. An example is colophony (rosin), a natural product derived from pine resin. The textile materials treated with colophony or mixtures with paraffin wax show a good behavior in contact with water. Consequently, a good resistance of the textile materials, in wet state, may be assured. The colophony deposited on the textile surface behaves like a moderator for the hydrophilic/hydrophobic ratio, which represents a quality parameter for textile materials. Therefore, textile wastewaters contain certain amounts of colophony.

On condition that the concentration of colophony is high, the conventional methods such as flocculation, coagulation, ion-exchange etc. for the recovery of colophony from the residual waters resulting from textile processing, are quite good.

For lower contents of colophony, especially for wastewater with colophony content in ranges between 0.01 and 0.1 g/L, membrane separation processes are recommended. The membrane separation processes are especially suited for removal of colloids from colloidal dispersions and emulsions by ultrafiltration and microfiltration [3]. The membrane treatment is widely used in industry because it offers several advantages over other processes. The major advantages of the process include: low-energy consumption, low space usage and easy process design [4–6]. Although there are many advantages offered by membrane, the application of membrane technology in separation processes is still limited. This is due to the fouling problem which reduces the membrane performances. The membrane fouling is dependent on several parameters such as membrane characteristics, feed properties, operational conditions and solution chemistry.

In this paper, the SAPO-5 zeolite-filled polyurethane membranes with perselectivity to the gases or liquids were prepared and characterized. The membranes have been utilized for the ultra- and, respectively, microfiltration of synthetic wastewater containing colophony. The influence of the colloidal dispersion concentration and temperature on the membrane processes has been studied.

2. Materials and methods

SAPO-5 zeolite, unfilled and zeolite-filled polyurethane membranes were prepared using the method and materials described elsewhere [7–9]. The silicoaluminophosphate SAPO-5 was synthesized by hydrothermal crystallization. The polyurethane (PU) membranes were prepared by casting a PU solution containing a calculated amount of PU polymer on a glass plate and allowing the solvent to evaporate under caloric radiation. We have prepared some pure membranes, the most performant was denoted MP. The composite membranes were obtained by adding a calculated amount of zeolite SAPO-5 (varying between 10 and 70 wt.%) into the polymer solution and by mixing thoroughly before casting. The casting and curing of the composite membranes are identical with those of the pure PU membranes. The most performant samples were denoted MPZ-1 and MPZ-2.

The membranes were characterized by SEM and Bubble-point methods. SEM pictures were taken on a TESLA-BS-300 instrument after silver coating. The pore diameters have been determined by Bubble-point method with a laboratory instrument. The features characteristics of the prepared membranes in our laboratory are summarized in Table 1.

Colophony solutions with various concentrations (in ranges between 0.01 and 0.1 g/L) have been prepared using colophony (from Sigma–Aldrich) and deionized water.

The ultra- and microfiltration processes of colophony dispersions were performed with a laboratory installation. Circular membrane discs were cut and mounted in a cylindrical membrane test cell. Effective permeation area of each

Table 1
Characteristics of the unfilled and zeolite-filled PU membranes

Characteristic	Membrane		
	MP	MPZ-1	MPZ-2
Zeolite content (wt.%)	0	30	50
Thickness[a] (μm)	300	220	170
Pore diameter (μm)			
In active layer[b]	4.5	2.5	2
In substructure[a]	2–10	8–25	2–5

[a]By SEM method.
[b]By bubble-point method.

membrane was 12.5 cm^2. Prior to testing, the pure water flux was measured to ensure that the used membranes were stable.

Parameters used to quantify the efficiency of membrane processes are flux (F) or permeability (P) and solute rejection (R), where the percentage of solute rejection is defined as:

$$R\ (\%) = \left[1 - \frac{C_p}{C_f}\right] \cdot 100 \quad (1)$$

where C_p is the permeate concentration in mg/L and C_f is the feed concentration in mg/L.

The concentration of colophony in solutions was determined on the basis of absorbance measurements by the spectrophotometric method at $\lambda = 660$ nm, using a spectrophotometer (Jasco V-550 UV/VIS, Japan).

3. Results and discussion

The formation of PU asymmetric membranes is the result of microphase separation phenomena that occur during an evaporation step and/or quench step of an initially thermodynamically stable polymer solution. Consequently, the membrane structure is affected strongly by the conditions of membrane preparation. The SEM images of the unfilled and zeolite-filled PU membranes evidence the asymmetry/heterogeneity of these systems [8,9]. All PU membranes obtained have an asymmetric structure consisting of two layers: the dense top layer (active layer) supported by the porous sub-layer (substructure). In the active layer, the estimated pore size is much smaller than that of the supported layer. Accordingly, the molecular sieve property of PU membranes appears to be determined by the pore size in the top layer of the PU membranes.

The incorporation of SAPO-5 zeolite in PU matrix induces some changes into membrane morphology. A good dispersion of the zeolite is important but difficult to obtain especially when small particles of zeolites are used. Interactions exist between zeolite and the used polymer. The SAPO-5 zeolite acted as a cross-linker on the PU polymer and, finally resulted material being a reinforced membrane [8,9].

The membranes have been utilized for the ultra- and, respectively, microfiltration of synthetic wastewater containing colophony. The influence of the colloidal dispersion concentration on the membrane processes has been studied. Table 2 shows the declination of permeability with the increase of colophony concentration at room temperature. This is due to the impact of membrane fouling that leads to an increase of hydraulic resistance and a reduction in filtration efficiency.

Table 2
Effect of colophony concentration in feed solution on membrane permeability (at 25°C)

Membrane	Colophony concentration (g/L)				
	0.01	0.03	0.05	0.07	0.09
	P (L/m^2 h)				
MP	201.5	147.2	111.4	102.3	98.7
MPZ-1	322.1	286.3	229.1	198.7	124.1
MPZ-2	237.7	200.1	135.5	114.6	99.9

Membrane fouling in ultra- and microfiltration is a key factor affecting the separation process. The membrane structure and the molecular weight cut-off have an important role on the performance of the separation process in terms of permeate fluxes. Membranes characterized by pores with lower dimensions than the size of suspended particles behave as support, promoting the formation of a particle layer during the early filtration period with the formation of a secondary membrane or cake. The thickness of this layer, which constitutes an additional resistance to the mass transport, can be controlled by choosing appropriate fluid-dynamic conditions [10]. In order to decrease fouling and to increase permeability and selectivity and also to influence the membranary performances, we studied the influence exercised by temperature on ultra- and microfiltration of colophony solutions.

The temperature will influence in a decisive manner the concentrated layer of colophony particles from the upper side membrane or internal side as well as their diffusion through the membrane [11]. The increase of temperature reduces the association tendency of the carboxylic acid molecules from the colophony composition. At the same time, the ratio of particles with molecular sizes permitting their diffusion through the membrane increases and consequently, the concentrated layer of colophony particles gets thinner. Table 3 shows an increase of permeability with the increase of the temperature, along with a rejection, for MPZ-1 membrane during ultra- and microfiltration of colophony solution with 0.07 g/L concentration. For all studied membranes, close results are obtained, showing that the fouling process is diminished.

Table 3
Effect of temperature on the MPZ-1 membrane permeability

Temperature (°C)	25	30	50	70	90
P (L/m^2 h)	198.7	226.5	341.2	632.1	2573.4
R (%)	20	42	61	87	100

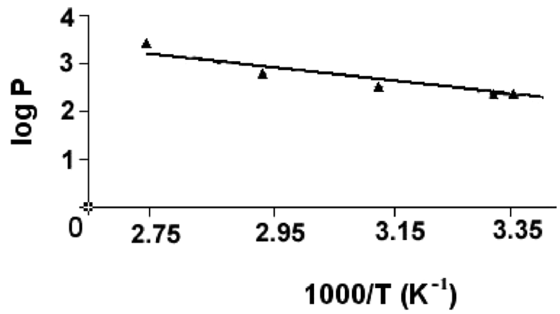

Fig. 1. Dependence of permeability on temperature, for ultra- and microfiltration 0.07 g/L concentrated colophony solution in MPZ-1 membrane.

The temperature dependence of permeability is given by the Arrhenius relationship:

$$P = P_0 \cdot \exp\left(\frac{-E_{ap}}{RT}\right) \quad (2)$$

where P is the permeability, P_0 is a pre-exponential factor, E_{ap} is the activation energy of permeation, R is the gas constant and T is temperature. Slope of linearized plot of log P versus $1/T$ (Fig. 1) is proportional to E_{ap}, consequently, the activation energy of permeation could be calculated, i.e. $E_{ap} = +5.133$ J/mol for MPZ-1 membrane during ultra- and microfiltration of colophony solution with 0.07 g/L concentration. For all studied membranes, close results are obtained. Low values of E_{ap} showed that separation process is rapid and efficient.

4. Conclusion

SAPO-5 zeolite-filled polyurethane membranes with permselectivity to the gases or liquids were prepared, characterized and utilized for the ultra- and, respectively, microfiltration of synthetic wastewater containing colophony.

The present study demonstrates the potential of the unfilled and zeolite-filled PU membranes for colophony removal from solutions with below 1 g/L concentrations.

Temperature influences considerably the colophony molecule dispersion and diffusion through the membrane. Membrane fouling may be controlled by operational temperature. The results show the declination of permeability with the increase of colophony concentration at room temperature. Temperature increasing produces a permeability increasing. Therefore, higher temperatures are recommended for preventing membrane fouling with colophony. Lower values of E_{ap} show that separation process is rapid and efficient.

Acknowledgement

The authors gratefully acknowledge the financial assistance from the Ministery of Education and Research, Romania (Grant CEEX, SINAPS, No. 69/2006).

References

[1] P.C. Vanndevivera, R. Bianchi and W. Verstraete, Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies, J. Chem. Technol. Biotechnol., 72 (1998) 289–302.

[2] I.M. Banat, P. Nigam, D. Singh and R. Marchant, Microbial decolorization of textile dye containing effluents: a review, Bioresour. Technol., 58 (1996) 217–227.

[3] M. Bezdadea and G. Ciobanu, Study of the conversion degree of a colloidal dispersion through membranes. Part I. The structure–performance relation, Analele Stiintifice ale Universitatii “Al.I. Cuza” Iasi, Tomul VI, (1998) 145–152.

[4] M. Marcucci, G. Ciardelli, A. Matteucci, L. Ranieri and M. Russo, Experimental campaigns on textile wastewater for reuse by means of different membrane processes, Desalination, 149 (2002) 137–143.

[5] P. Schoeberl, M. Brik, R. Braun and W. Fuchs, Treatment and recycling of textile wastewater — case study and development of a recycling concept, Desalination, 171 (2004) 173–183.

[6] Z. Badani, H. Ait-Amar, A. Si-Salah, M. Brik and W. Fuchs, Treatment of textile waste water by membrane bioreactor and reuse, Desalination, 185 (2005) 411–417.

[7] N. Balba and G. Ciobanu, Synthesis and characterization of some silicoaluminophosphate with SAPO-5 structure, in: 8th Deutsche Zeolith–Tagung, Berlin – Adlershof, R.F.G., Vol. Proceedings, 1996, pp. 1–3.

[8] G. Ciobanu and M. Bezdadea, SAPO-5 zeolite-filled polyurethane membranes. I. Preparation and morphological characterisation, Revista de Chimie, Bucuresti, 55 (3) (2004) 140–143.

[9] G. Ciobanu, G. Carja and O. Ciobanu, Preparation and characterization of polymer-zeolite nanocomposite membranes, Mat. Sci. Eng. C, in press.

[10] S. Todisco, L. Peña, E. Drioli and P. Tallarico, Analyses of the fouling mechanism in microfiltration of orange juice, J. Food Process. Preserv., 20 (1996) 453–466.

[11] M. Bezdadea and G. Ciobanu, Study of the conversion degree of a colloidal dispersion through membranes. Part II. Kinetic and thermodynamic aspects, Analele Stiintifice ale Universitatii, “Al.I. Cuza” Iasi, Tomul VI (1998) 153–158.