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Porous polyurethane urea membranes for pervaporation separation of phenol and chlorophenols from water

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Abstract

Porous hydrophobic polyurethane urea (PUU) membrane was prepared for pervaporation separation of phenol and two chlorophenols namely *p*-chlorophenol (PCP) and 2,4-dichlorophenol (DCP). Polyurethane urea was synthesized by reacting hydroxy terminated polybutadiene (HTPB) with 2,4-toluene diisocyanate (TDI) using oxydianiline (ODA) as chain extender. Porosity was generated in the dense PUU by incorporating lithium chloride (LiCl) during PUU formation and then leaching out LiCl after PUU membrane formation. Both the pore size and number of pores per unit area was found to increase with increase in amount of LiCl addition during synthesis of membrane. The porous PUU showed better pervaporation separation efficiency than the dense PUU. The porous polyurethane membranes performed separation of phenol and chlorophenols with separation factors ranging from about 570 to 1760 at total permeate fluxes of 7.7–14.1 kg/m^2 h over feed concentrations of 1000–4000 ppm (0.1–0.4%, w/v) at 30 °C. Phenol and chlorophenol fluxes have been increased remarkably by incorporation of porosity in the membrane. But the separation factor has not been increased to the extent of increase in flux.

Keywords: Pervaporation; Flux; Separation factor

1. Introduction

Pervaporation is a promising technique in the separation of organic pollutant from water present in very low concentration but it suffers from a disadvantage of providing lower flux value compared to other membrane separation processes. By incorporating pores or channels in the membrane flux can be enhanced by membrane pervaporation. Many researchers have shown the suitability of using different porous and dense membranes in various membrane separation processes, such as gas separation, reverse osmosis, nanofiltration and pervaporation [1–6]. The porous membranes are particularly promising due to their high fluxes. In recent years microporous polymer films have been widely used for practical purposes, such as filtration and separation of liquid mixtures, and also as separation membranes in many processes. The use of microporous membranes for filtration imposes a number of requirements on the filtration material, such as a high permeability to liquids and gases and good mechanical properties. A material to be suitable for permeation of liquids and gases, its structure must contain flow channels. The value of the permeability will depend on the sizes and number of these channels, i.e., on the bulk structural characteristics of the material, which are controlled by the formation process parameters of the porous membranes [7]. There are many methods to prepare porous polymers such as electrospinning [8,9], solvent casting/salt leaching [10,11], phase inversion [12], laser excimer [13], and thermally induced phase separation [14]. Among these methods phase inversion method is mostly used for making porous membrane. Asymmetric porous ceramic-polymer membranes were prepared by dry and wet phase inversion processes using dispersions containing cellulose acetate, acetone, water and colloidal alumina particles by Wara et al. [15]. Using this phase inversion technology, porous membranes for gas separation, reverse osmosis, ultrafiltration, and microfiltration were produced from a variety of materials, including cellulose derivatives, polyamides, polyimides, and polysulphones [16]. Yamaguchi et al. [17] developed a membrane composed of a porous polyethylene substrate, to which poly(methyl acrylate) was grafted. The porous substrate was inert to organic liquids, a factor that minimized the swelling. The selectivity of the membrane was 7–14.8 for benzene/cyclohexane systems. Porous polyurethane–polyacrylate polymers were prepared by Huang

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et al. [18] by emulsion polymerization. The prepared membrane was a good material for solid polymer electrolytes or gel polymer electrolytes. Sakohara et al. [19] developed a dimethylaminoethylmethacrylate gel membrane, formed in the pores of inert silica and separated benzene–cyclohexane mixtures using the prepared membrane. Okui et al. [20] prepared porous organic/inorganic hybrid membranes for CO_2/N_2 separation using mixed sols consisting of tetraethylorthosilicate (TEOS) and phenyltrimethoxysilane. Gas permeability through this membrane was in the range of 10^{-8} [cc(STP) cm/(cm^2 s cmHg)] at 25 °C. Kusakabe et al. [21] synthesized hybrid sols using various ratios of silica and polyamic acid. They immersed a porous alumina support tube in the hybrid sol and then formed a silica-polyimide membrane by heat-treatment at 350 °C. The prepared membrane showed a high gas permeance and retained a high permselectivity inherent to the polyimide.

Pervaporation is an energy efficient combination of membrane permeation and evaporation and is considered an attractive alternative for many separation processes [22,23]. This technique is also being utilized for the removal of toxic organic compounds from industrial effluent [24]. In pervaporation membrane separation process generally dense membrane is applied instead of porous ones whereas in other separation processes both dense and porous membranes are used. In pervaporation both the chemical and the physical natures of the membrane material control separation. Separation occurs because of differences in size, shape, chemical properties, or electrical charge of the substances to be separated. Porous membranes control separation by size, shape and charge discrimination, whereas nonporous membranes depend on sorption and diffusion. In pervaporation it is expected that using porous membrane flux should be increased. Therefore we were interested to see the change in pervaporation separation performance after incorporating pores in dense membrane. Dense polyurethane urea is an excellent membrane material for selective separation of organics from water by pervaporation. Many researchers have found that some types of polyurethane ureas are more selective toward aromatic than aliphatic components [25–27]. We incorporated pores in dense polyurethane urea membrane and interested to separate phenol and chlorinated phenols from their aqueous solution by pervaporation. Phenol, *p*-chlorophenol and 2,4-dichlorophenol are used in the manufacture of fertilizers, explosives, paints and paint removers, drugs, pharmaceuticals, textiles and coke. As chlorinated phenolic compounds are widely used in pesticide industries, effluents generated by such industries and water in agriculture fields get contaminated with such toxic compounds. Chlorinated phenolic compounds are more severe than phenol. At low concentrations in water both *p*-chlorophenol and 2,4-dichlorophenol are highly toxic. Environmental protection agency (EPA) has limited the maximum contamination level of chlorophenols in water to 0.3 ppm. So their separation is highly essential when they are present in low concentration in water.

The main aim of this work is to increase flux of phenol and chlorophenols during separation of them by membrane pervaporation from their dilute aqueous solution. In order to fulfill this aim we have prepared both dense and porous hydroxyterminated polybutadiene (HTPB)-based diamine chain extended polyurethane urea (PUU) membranes. Our main objective in this study was to increase flux by incorporating the porosity in the dense membrane. Porosity was generated in polyurethane urea membrane by incorporating lithium chloride (LiCl) in viscous PUU solution followed by membrane casting and leaching out the LiCl from the PUU membrane. The advantage of using LiCl as a pore forming material in a membrane lies in its crystallizing tendency in a controlled crystallizing rate to a solid crystal formation during membrane casting. After obtaining solid membrane such LiCl crystal particles can be removed by simply leaching with water leaving behind pores of different size distribution. Even this method can lead to nanometer to micrometer sized pores. This process is very simple and economic. Whereas other porous membrane forming processes may be more complicated [28]. In this paper the pervaporation separation results of phenol and chlorophenols by both dense and porous membrane were reported and compared.

2. Experimental

2.1. Materials

Hydroxy terminated polybutadiene (HTPB) [functionality 2.4, hydroxyl value 43.2 mg KOH/g, number average molecular weight 2580, received from VSSC, India], 2,4-toluene diisocyanate (TDI, E. Merck), catalyst dibutyltindilaurate (DBTDL, Fluka AG), 4,4′-diaminodiphenylether (ODA, Fluka AG), lithium chloride (LiCl, Fluka AG), tetrahydrofuran (THF, E. Merck), phenol (E. Merck), *p*-chlorophenol (E. Merck), 2,4-dichlorophenol.

2.2. Membrane preparation

For preparing dense polyurethane urea first a prepolyurethane was prepared by reacting HTPB with TDI in dry THF in presence of DBTDL catalyst, using a mole ratio of NCO:OH of 2:1. The reaction was continued at 30 °C for 60 min with careful and controlled stirring. PUU was obtained by chain extension of prepolyurethane using the diamine, ODA (10–30 mol% based on HTPB). The content was stirred for 30 min at 30 °C to form a uniform mixture during which time the prepolyurethane reacted with diamine to form chain extended polyurethane urea. This entire reaction was carried out under dry oxygen free nitrogen blanket. The end product was obtained as a viscous solution of PUU in THF. The solution of PUU in THF was subjected to vacuum to remove trapped nitrogen gas and excess solvent present in it. Then the highly viscous mass of PUU in THF was cast on a flat-base glass Petri dish and allowed overnight for moisture curing at room temperature (30 °C) and laboratory humid condition (72% RH). Then the membrane was heated in an oven at 80 °C for 5 h for thermal curing [29].

To prepare porous PUU membrane before casting of the membrane LiCl was dissolved in required quantities in the viscous PUU solution. The solution of PUU and LiCl in THF was subjected to vacuum to remove trapped nitrogen gas and excess solvent present in it. Then the highly viscous solution of PUU-LiCl in THF was cast on a flat-base glass petridish and allowed overnight for moisture curing at room temperature followed by heating at 80 °C for 5 h for thermal curing. Then the cured membrane was boiled with distilled water to remove the LiCl present in the membrane to make it porous.

2.3. Scanning electron microscopy

Study of surface morphology of the dense polyurethane urea and porous polyurethane urea membranes was done using JEOL-JSM 5800 scanning electron microscope (CRF, IIT Kharagpur, India). The polymer films were gold coated before the study. Photomicrographs were taken at 500 and 1000 magnifications.

2.4. Mercury porosimetry

Mercury intrusion porosimetry is the only way of reliably determining the pore size distribution in porous films. The pore size and distribution analysis is based on the increasing intrusion of mercury into the porous material with increase in pressure. The coarser pores are the ones that get filled with mercury at the lowest pressure with finer pores getting filled at higher pressures. The process of pressurization depends on the external pore access diameter, pore shape and complexity of the pore geometry. The pore size distribution in porous polyurethane urea membrane was analyzed using mercury intrusion porosimetry (Pore master P33, Quantachrome, Materials Science Centre, IIT Kharagpur, India). A solid penetrometer having bulk volume 3 ml and 2 ml stem volume was used as a sample cell for measurement. The volume of mercury started to intrude to the sample at a pressure of 0.5 psi and continued to 50 psi. Within this pressure range, all samples got saturated completely with mercury and reached in a plateau region. The pore diameter distribution was obtained using the Washburn equation:

$$D = -\frac{4\gamma \cos\theta}{P} \tag{1}$$

where D is the pore diameter, γ the surface tension of mercury (480 dynes/cm), θ the contact angle between mercury and porous film and P is the pressure measured during the mercury intrusion process.

2.5. Swelling study

Small pieces of weighed dense and porous PUU membranes were kept immersed in pure water, aqueous phenol (0.4%) and chlorophenols (0.4%) separately at room temperature (30 °C). Since the membranes were found to achieve equilibrium swelling within 22 h, after 22 h of immersion the membranes were taken out and their weights were measured immediately after wiping out the surface liquid by soft tissue paper. The degree of swelling was calculated as follows:

$$\text{Percent degree of swelling} = \frac{W_w - W_d}{W_d} \times 100 \tag{2}$$

where W_d is the initial dry weight of membrane and W_w is the weight of the membrane after 22 h swelling (at equilibrium sorption).

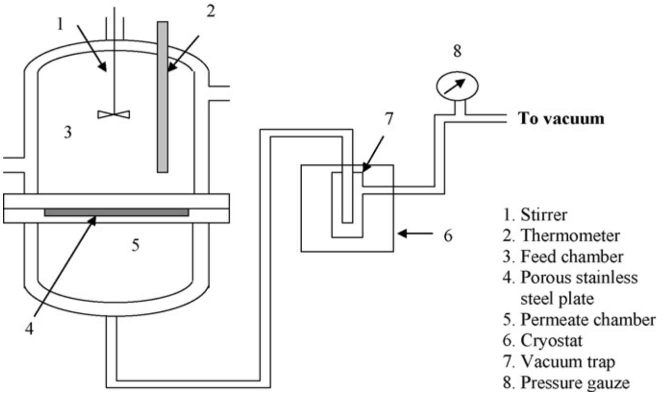

Fig. 1. Pervaporation setup.

2.6. Pervaporation setup

Pervaporation of phenol/chlorophenol–water mixture was carried out in a pervaporation cell (Fig. 1). It was assembled from two cylindrical half-cells made of stainless steel fastened together by nuts and bolts. The membrane was supported on a sintered (perforated) stainless steel plate placed at the joint of two cells. The membrane area was 2.9×10^{-3} m^2. For all measurements, the downstream pressure was maintained at 666.61 Pa (5 mm Hg) by applying vacuum. The permeate vapor was condensed in a glass trap suspended inside a cryogenic bath kept at −40 °C. Pervaporation separation was carried out at varying feed composition of 0.1–0.4% phenol/chlorophenols in water.

2.7. Permeate flux

The permeate flux was calculated from the weight of the permeate collected after pervaporation run using the following equation:

$$J = \frac{Q}{A \cdot t} \tag{3}$$

where Q is the quantity in kg of permeate collected in time t and A is effective area of membrane.

2.8. Determination of permeate composition

The concentrations of phenol and chlorophenols in permeate were estimated by volumetric redox titration. The permeate containing either phenol, *p*-chlorophenol or 2,4-dichlorophenol was diluted and acidified with HCl. Then a known volume of standard BrO_3^-/Br^- solution was added to this diluted and acidified permeate solution. After the liberated bromine completely brominated the chlorophenol, the excess bromine was estimated by iodometric titration [30]. From the amount of bromine consumed by the chlorophenol the quantity of cholorophenol in the permeate was calculated. An average of three consecutive titrations was taken.

2.9. Separation factor

The separation factor of permeation is expressed as

$$\alpha_{p(\text{phenol or Cl-phenol/water})} = \frac{C^{2}_{\text{phenol or Cl-phenol}}/C^{2}_{\text{water}}}{C^{1}_{\text{phenol or Cl-phenol}}/C^{1}_{\text{water}}} \quad (4)$$

where C represents concentration term and superscripts 1 and 2 represent feed and permeate, respectively.

3. Results and discussion

3.1. Preparation of porous polyurethane urea (PUU) membrane

By varying the amount of LiCl in PUU membrane three types of membrane were prepared. LiCl amount was varied from 1 to 5 wt.%. Maximum up to 5 wt.% of LiCl could be incorporated within the membrane. The membrane composition and characteristics are shown in Table 1.

3.2. Scanning electron microscopy (SEM)

It has been stated in the introduction that polyurethane urea is an excellent membrane material for selective separation of organics from water by pervaporation and earlier researchers have observed that these membranes are more selective toward aromatic than aliphatic components. As per our objective to increase the permeate flux we have prepared porous PUU membrane by incorporating LiCl. In order to visualize the porous microstructure we have analyzed the membrane by SEM and mercury porosimetry. SEM photographs of membrane surfaces were taken at 500 and 1000 magnifications for both dense and porous membranes. The scanning electron micrographs of dense and porous polyurethane urea membranes are shown in Fig. 2. The study of the surface morphology by scanning electron microscopy revealed the presence of pores on the surface of the membranes. From Fig. 2a and b no porous structure is visible on the surface of dense PUU membrane. Fig. 2c–h show the surface morphology of porous PUU membranes prepared by using different amounts of LiCl as given in Table 1. The SEM photographs taken at 500 and 1000 magnifications show distinct presence of pores on the surface. Although the membrane core is not visible from surface but there must be pores in the core since LiCl was dissolved in the viscous PUU solution in THF. In PORPUU-1 membrane (Fig. 2c and d), where 1% LiCl was used, the number of pores formed was less than those in PORPUU-3 (Fig. 2e and f), where 3% LiCl was given. In PORPUU-5 (Fig. 2g and h), when the maximum possible amount of LiCl (5%) was given more number of pores were formed and the pore size was also increased due to bigger crystal formation from more number of LiCl molecules during membrane solidification by solvent evaporation and curing of PUU by atmospheric moisture. Fig. 2 also demonstrates a uniform distribution of pores of different sizes throughout whole membrane surface. So it can be said that by increasing the amount of LiCl, both number and sizes of pores can be increased.

3.3. Porosity measurement

The average pore diameter and pore size distribution in porous PUU membrane were determined from mercury intrusion porosimetry. Porosity data of the membranes are included in Table 1. As was observed in SEM photographs, from the mercury intrusion porosimetry data given in Table 1 it is also evident that both the average pore diameter as well as void fraction is highest in PORPUU-5 membrane formed using 5% LiCl compared to other two porous membranes. In Fig. 3 pore number distribution is shown for PORPUU-1, PORPUU-3 and PORPUU-5 membranes. From the distribution curve of pore number fraction versus pore size it is clear that the distribution curves become broader from PORPUU-1 to PORPUU-5. It clearly indicates that number of pores increase from PORPUU-1 to PORPUU-5. The morphology of porous PUU membranes visualized from SEM pictures and mercury porosimetry clearly indicates the possibility of obtaining improved pervaporation flux over that of dense PUU membrane.

3.4. Swelling of membranes

Percent degree of swelling of dense and porous polyurethane urea membranes in 0.4% aqueous phenol, *p*-chlorophenol and 2,4-dichlorophenol solutions was studied and results are shown in Fig. 4. The percent degree of swelling for PUU, PORPUU-1, PORPUU-3 and PORPUU-5 membranes in pure water is only 1.1%, 1.13%, 1.18% and 1.23%, respectively. Whereas more than 8% degree of swelling was achieved in 0.4% aqueous phenol and chlorophenol solution. It is due to preferential sorption or solubility of phenol and chlorophenols in the membrane. With incorporation of porosity in the membrane the degree of swelling increases. It is due to the formation of pores, which provide high surface area of sorption of permeants. Out of three different solutions under study, 2,4-dichlorophenol solution (0.4%) showed highest degree of swelling due to its more polarity.

Table 1
Physical characteristics of dense and porous polyurethane urea membranes

Membrane designation	Membrane thickness (μm)	LiCl (wt.%)	Average pore diameter (μm)	Void fraction	Number of pores/m^2 × 10^{-9}
PUU	250	0	–	–	–
PORPUU-1	250	1	0.2	0.05	3.7
PORPUU-3	250	3	1.1	0.08	4.4
PORPUU-5	250	5	2.4	0.11	6.2

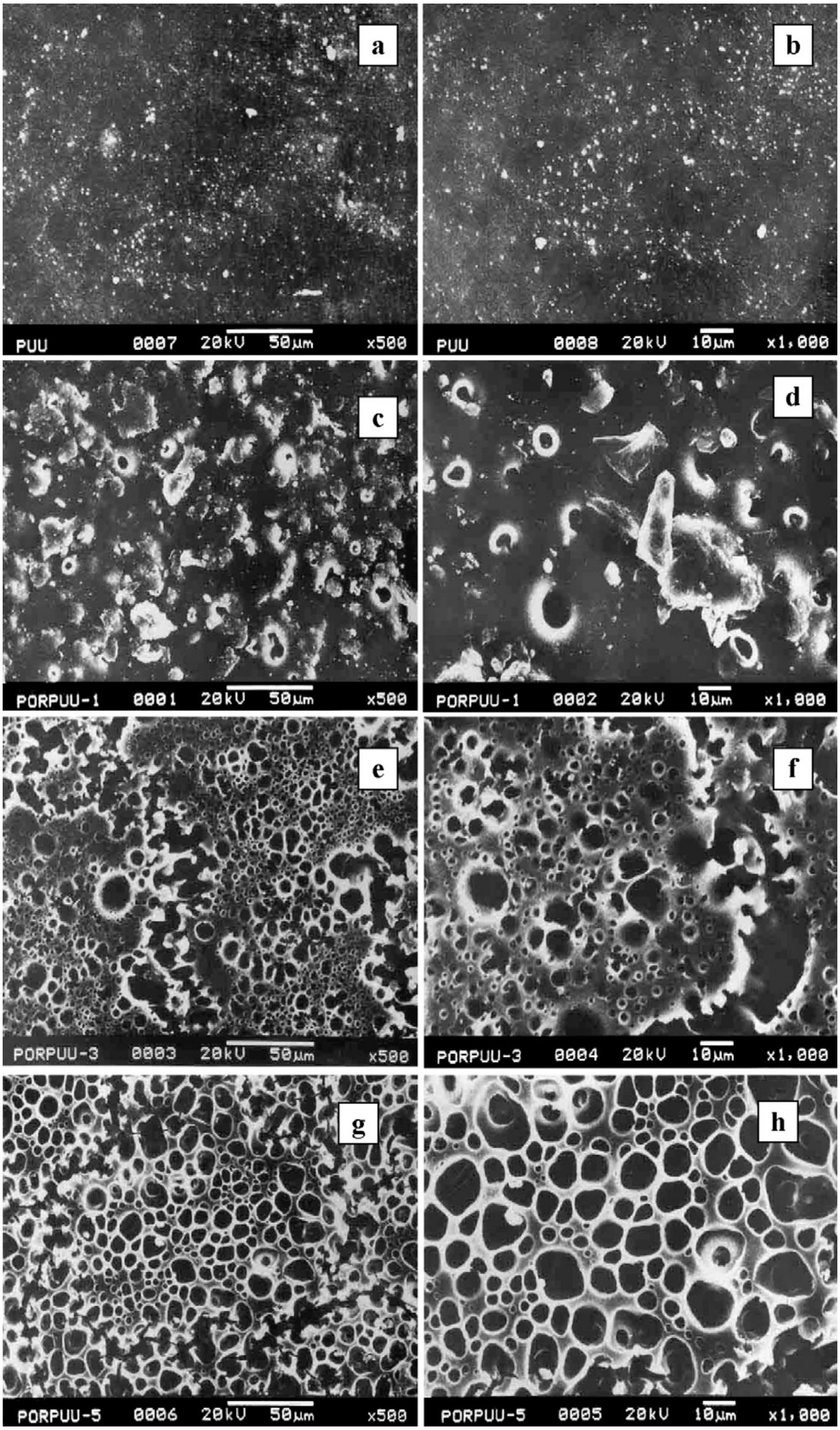

Fig. 2. SEM photographs of (a and b) dense PUU, (c and d) porous PORPUU-1, (e and f) porous PORPUU-3 and (g and h) porous PORPUU-5 membranes.

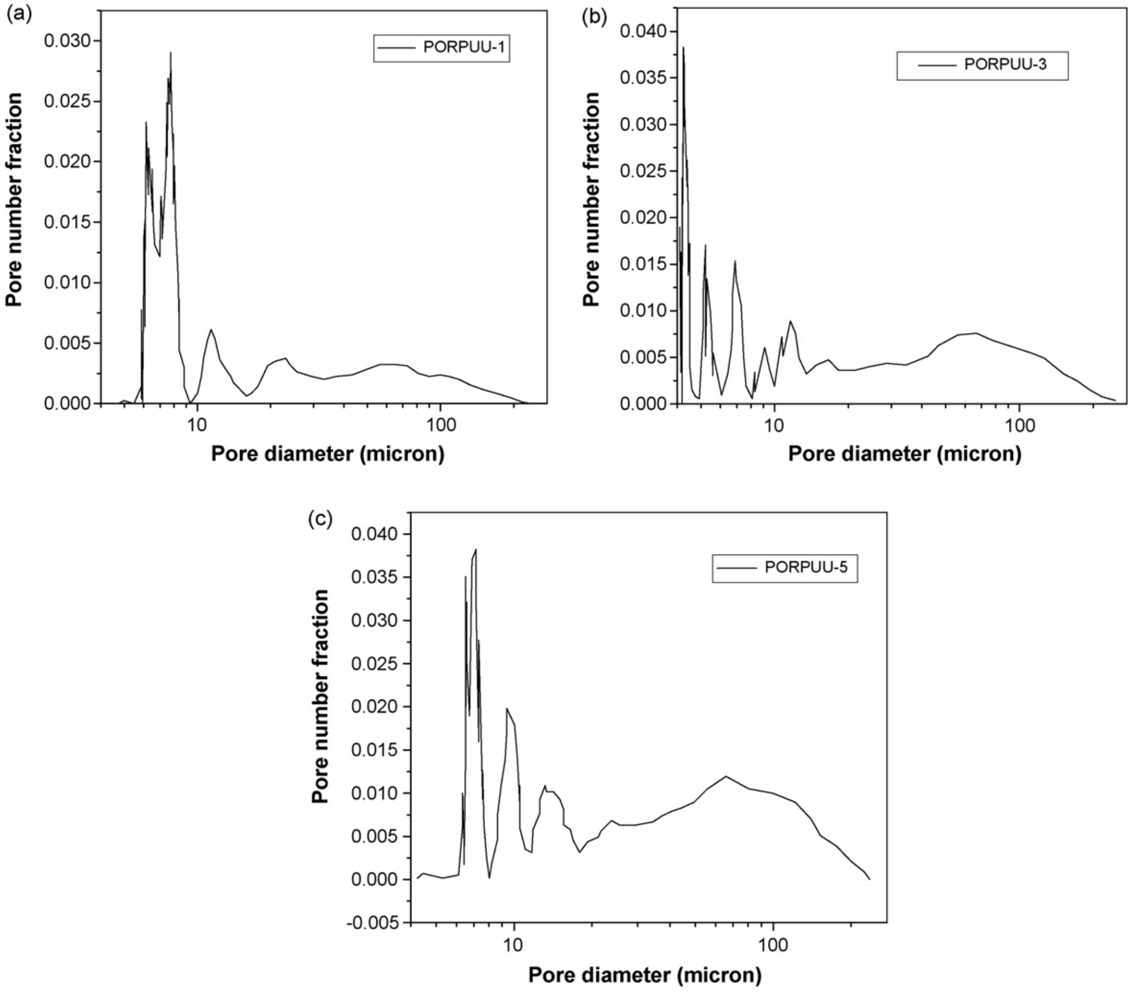

Fig. 3. Pore number distribution curve of (a) PORPUU-1, (b) PORPUU-3 and (c) PORPUU-5 membranes.

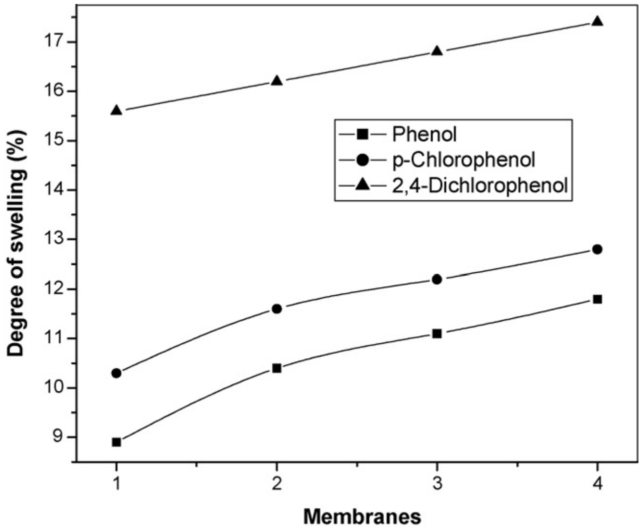

Fig. 4. Swelling of dense and porous polyurethane urea membranes at 30 °C (the numerals on the *X*-axis stand for membranes: 1, PUU; 2, PORPUU-1; 3, PORPUU-3; 4, PORPUU-5).

3.5. Pervaporation flux

Using both dense and porous PUU membranes pervaporation experiments were performed for the separation of phenol, *p*-chlorophenol and 2,4-diclorophenol from their dilute aqueous solutions. Pervaporation studies were done using varied feed concentration of the above chemicals from 0.1% to 0.4%. The extent of separation of the components under study were evaluated in terms of total as well as individual fluxes and separation factor of the permeated components in the down stream side at a low pressure [666.61 Pa (5 mm Hg)]. The variation of fluxes of permeating components for the phenol–water and chlorophenol–water systems with feed concentration for dense PUU and porous PUU membranes are shown in Fig. 5. From the flux data it is clear that with increase in porosity of the membrane permeating component flux was increased. That the prepared PUU membranes are selective to phenol, *p*-chlorophenol and 2,4-dichlorophenol is evident from their concentrations in permeate as well as their flux data shown in Table 2. In pervaporation both the chemical and the physical natures of the membrane material control separation. Porous membranes control separation by size, shape and charge discrimination, whereas dense membranes depend on sorption

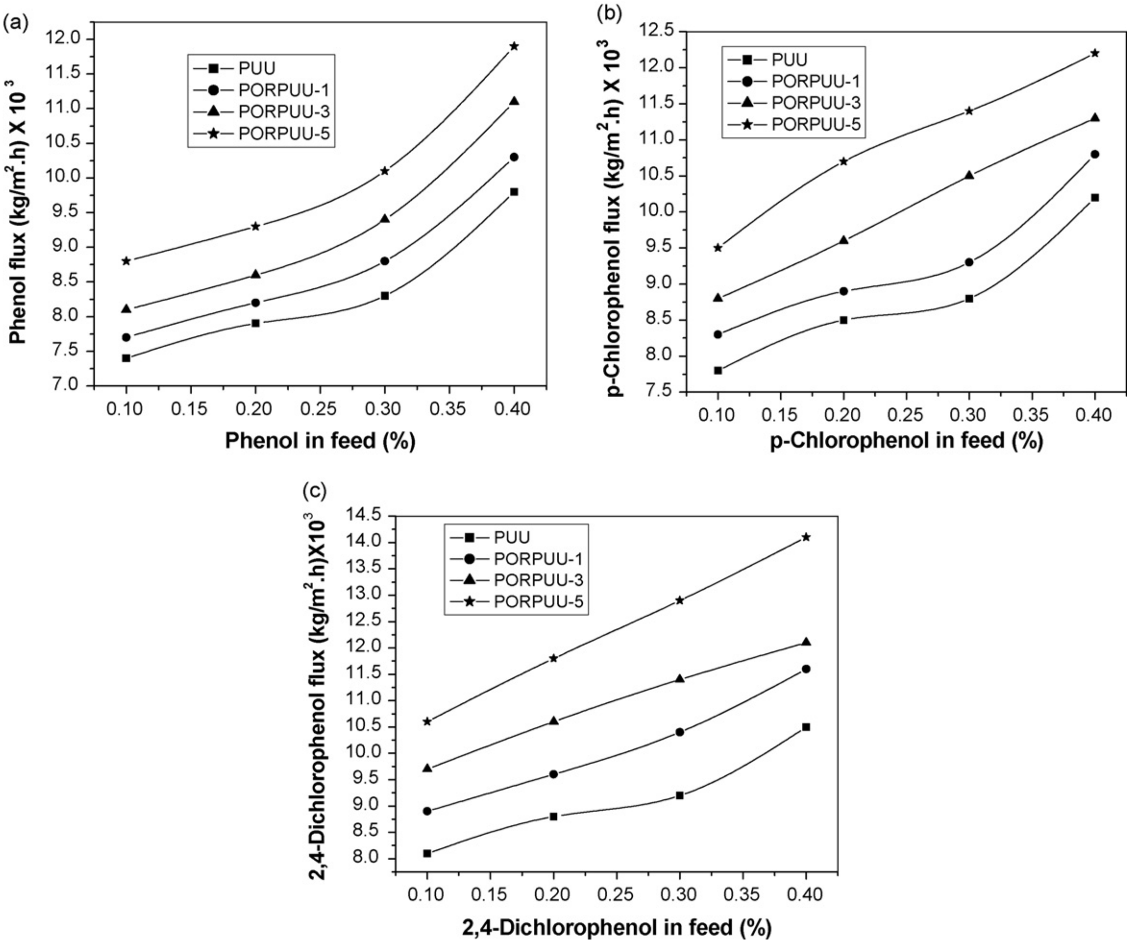

Fig. 5. Variation of fluxes of (a) phenol, (b) *p*-chlorophenol, (c) 2,4-dichlorophenol with change in feed concentration for different membranes.

Table 2
Separation of phenol, *p*-chlorophenol and 2,4-dichlorophenol by pervaporation using PUU, PORPUU-1, PORPUU-2, and PORPUU-3

Membrane (void fraction)	Phenol			*p*-Chlorophenol			2,4-Dichlorophenol		
	In		Flux ($\times 10^3$ kg/m^2 h) (% increase)	In		Flux ($\times 10^3$ kg/m^2 h) (% increase)	In		Flux ($\times 10^3$ kg/m^2 h) (% increase)
	Feed (%)	Permeate (%)		Feed (%)	Permeate (%)		Feed (%)	Permeate (%)	
PUU (0)	0.1	60.1	7.4 (–)	0.1	60.8	7.8 (–)	0.1	61.5	8.1 (–)
	0.2	64.3	7.9 (–)	0.2	65.1	8.5 (–)	0.2	66.4	8.8 (–)
	0.3	66.7	8.3 (–)	0.3	67.2	8.8 (–)	0.3	68.3	9.2 (–)
	0.4	68.7	9.8 (–)	0.4	69.3	10.2 (–)	0.4	70.8	10.5 (–)
PORPUU-1 (0.05)	0.1	61.4	7.7 (4.1)	0.1	62.3	8.3 (6.4)	0.1	62.9	8.9 (9.9)
	0.2	65.2	8.2 (4.2)	0.2	65.7	8.9 (6.7)	0.2	66.7	9.6 (10.1)
	0.3	67.8	8.8 (6.0)	0.3	69.1	9.3 (7.6)	0.3	68.8	10.4 (13.0)
	0.4	69.6	10.3 (7.1)	0.4	70.2	10.8 (7.9)	0.4	71.2	11.6 (14.4)
PORPUU-3 (0.08)	0.1	61.9	8.1 (9.5)	0.1	62.8	8.8 (12.8)	0.1	63.4	9.7 (19.8)
	0.2	66.8	8.6 (9.8)	0.2	67.1	9.6 (13.0)	0.2	67.5	10.6 (20.5)
	0.3	68.8	9.4 (13.2)	0.3	68.9	10.5 (19.3)	0.3	69.4	11.4 (23.9)
	0.4	70.7	11.4 (16.3)	0.4	70.4	11.3 (20.8)	0.4	71.6	12.1 (25.2)
PORPUU-5 (0.11)	0.1	62.7	8.8 (18.9)	0.1	63.5	9.5 (21.8)	0.1	63.8	10.6 (30.8)
	0.2	67.6	9.3 (19.4)	0.2	68.1	10.7 (25.9)	0.2	68.7	11.8 (34.1)
	0.3	69.9	10.1 (21.6)	0.3	70.4	11.4 (29.5)	0.3	71.6	12.9 (40.2)
	0.4	71.8	11.9 (22.4)	0.4	72.3	12.2 (30.6)	0.4	73.1	14.1 (44.3)

and diffusion. Prepared dense PUU membranes are highly selective for phenol and chlorophenols. With this selectivity when pores are incorporated in PUU membrane flux of phenol and chlorophenols was enhanced. More amount of phenol, *p*-chlorophenol and 2,4-dichlorophenol were present in permeate when separation was done from a very dilute solution of phenol and chlorophenols. So with this selectivity of membrane towards phenol and chlorophenols when pores are generated inside the membrane, the permeating component got channel to pass through the membrane. Presence of pores in the membrane facilitates the transport of permeants. Thus in case of PORPUU-5 membrane highest flux was achieved. In Fig. 6 it is shown that dense PUU membrane gave highest flux for 2,4-dichlorophenol and lowest flux for phenol. So the selectivity of PUU membrane towards phenol and chlorophenols followed the order phenol < *p*-chlorophenol < 2,4-dichlorophenol. This result also corroborates the swelling characteristics of the membranes in the corresponding aqueous solutions.

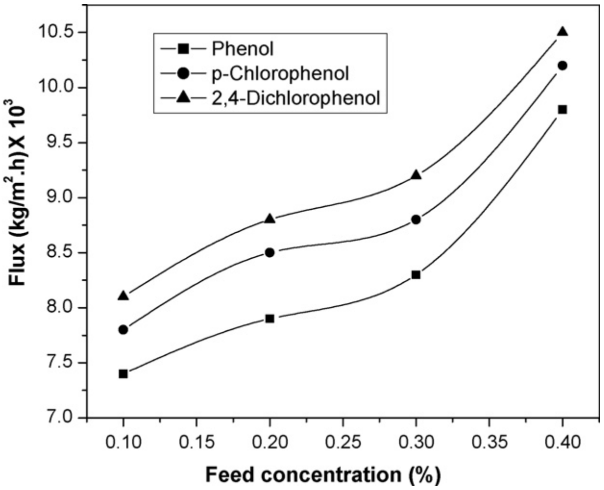

Fig. 6. Variation of flux of phenol and chlorophenols for dense PUU membrane with change in feed concentration.

3.6. Separation factor

The variations of phenol and chlorophenol separation factors for the porous and dense PUU membranes are shown in Fig. 7. It is evident that the separation factor for permeation of phenol and chlorophenol in permeate increase from PUU to PORPUU-5. As the porosity increases, the spacing between two polymer chains becomes narrower. The penetration of less interactive water molecules through hydrophobic chain becomes more difficult and, as a result, separation factor was observed to

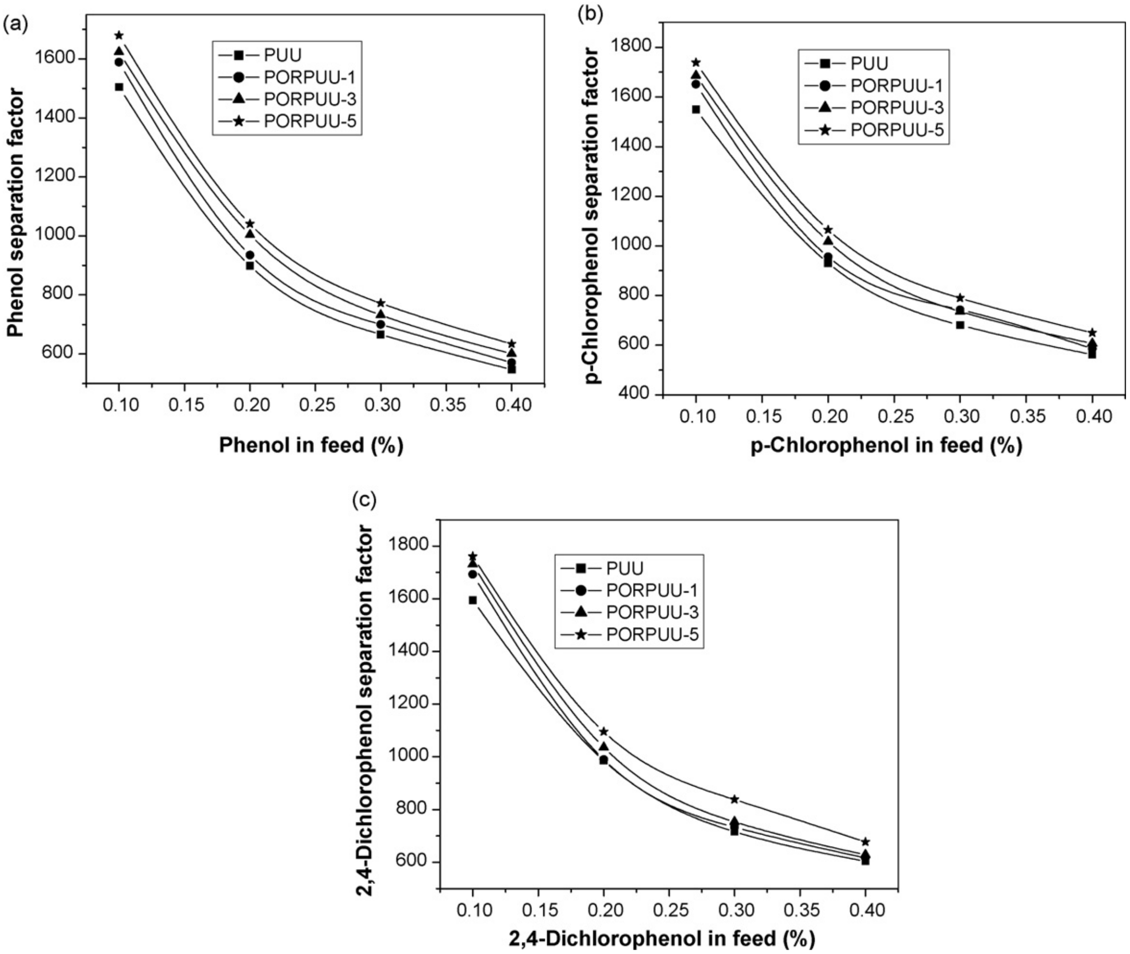

Fig. 7. Variation of separation factor of phenol (a), *p*-chlorophenol (b), 2,4-dichlorophenol (c) with change in feed concentration for different membranes.

increase. But the separation factor did not increase so much as flux increased. It is due to the transport of permeants through pores.

4. Conclusion

In this investigation we have got higher flux by incorporation of porosity in PUU membranes with the help of LiCl. By variation of LiCl amount, porosity in the membrane can be varied. Pore formation was studied by scanning electron microscopy and mercury intrusion porosimetry. Pores in the membrane have provided high surface area of sorption of permeants. As the sorption of permeants in the membrane increased more amounts of permeants were present in permeate side and thus phenol and chlorophenol flux increased. Both dense and porous PUU membrane fabrication was very easy and the membrane can be scaled up easily to use in commercial purpose.

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