Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Yahaya, Garba O.(2009) 'Separation of Phenol from Aqueous Streams by a Composite Hollow Fiber Based Pervaporation Process Using Polydimethyl siloxane (PDMS)/Polyether-Block-Amide (PEBA) as Two-Layer Membranes', Separation Science and Technology, 44: 12, 2894 — 2914

To link to this Article: DOI: 10.1080/01496390903018103

URL: http://dx.doi.org/10.1080/01496390903018103

Separation Science and Technology, 44: 2894–2914, 2009
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ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390903018103

Separation of Phenol from Aqueous Streams by a Composite Hollow Fiber Based Pervaporation Process Using Polydimethyl siloxane (PDMS)/Polyether-Block-Amide (PEBA) as Two-Layer Membranes

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Abstract: In order to simultaneously achieve both high permselectivity and permeability (flux) for the recovery of aromatic compounds such as phenol from aqueous streams, a composite organophilic hollow fiber based pervaporation process using PDMS/PEBA as two-layer membranes has been developed. The process employed a hydrophobic microporous polypropylene hollow fiber, having thin layers of silicones (PDMS) and PEBA polymers coating on the inside diameter. The composite membrane module is used to investigate the pervaporation behavior of phenol in water in a separate study; and that of a mixture of phenol, methanol, and formaldehyde in an aqueous stream (a typical constituent of wastewater stream of phenol-formaldehyde resin manufacturing process) in another study. The fluxes of phenol and water increase relatively linearly with increasing concentration especially at low feed concentration, and exhibit a near plateau with further increase in concentration. As a result, the phenol/water separation factor decreases as the feed concentration increases. Significant improvement in phenol/water separation factor and phenol flux is achieved for this two-layer (PDMS/PEBA) membranes as compared to that achieved using only PDMS membrane. The phenol and water fluxes and the separation factor are highly sensitive to permeate pressure as all decrease sharply with increase in permeate pressure. For this membrane, an increase in temperature increases the separation factor, and also permeation fluxes of phenol and water. An increase in

Received 7 November 2008; accepted 30 March 2009.

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feed-solution velocity does not have a significant effect on phenol and water fluxes, and also on the separation factor at least within the range of the feed-solution velocity considered. In the study of pervaporation behavior of a typical constituent of wastewater stream of phenol-formaldehyde resin manufacturing process, phenol permeation shows a much higher flux and a higher increase in flux with increase in concentration is also exhibited as compared to that exhibited by methanol permeation. This thus indicates that the membrane is more permeable to phenol than to methanol and formaldehyde.

Keywords: Composite hollow fiber membrane, pervaporations, phenol, poly(ether-block-amide) (PEBA), polydimethylsiloxanes (PDMS)

INTRODUCTION

Phenol and phenolic derivatives are chemical products commonly encountered in aqueous effluents from manufacturing processes. Phenol is used in the production of phenol-formaldehyde resin, caprolactum, adipic acid, and aniline which are required for the production of a wide range of consumer goods and product materials. This involves the production of a wastewater stream with up to 3 wt.% phenol and other minor components such as formaldehyde, methanol etc., which are miscible with water at this concentration (1). The limit for discharging phenol is set to 5–10 ppm (2). The toxicity of phenolic effluents is well known, and their treatment must be accomplished, depending on the nature of the phenols, the volume and rate of discharge, and the nature and volume of the receiving water. On the other hand, phenol is a valuable chemical. Therefore, recovery of phenols from phenolic effluents can achieve the dual objective of removing unwanted phenols from waste streams and obtaining valuable phenolic compounds. Currently, degradation methods (chemical and biological oxidation) and recovery methods (adsorption, solvent extraction, and liquid membranes) are widely used for treating phenolic waste effluents (3–9). Degradation methods involve a high cost because of the large consumption of chemicals and major investment in equipment required and the fact that phenols are converted into substances that are nontoxic and satisfactory for release to the environment means another costly loss of a valuable material. Thus, degradation processes are only used for treatment of waste phenolic streams at low concentration or in mixtures, and often as the last treatment stage. The need for frequent regenerations makes carbon adsorption economically unattractive for high phenol concentration streams and the loss of solvent is usually serious in solvent extraction, especially with phenols having a low distribution coefficient in water. Instability of the liquid membrane is a major problem in the recovery of phenol from waste stream.

Pervaporation, an emerging separation technology, appear to be both technically and economically, a viable method for removing phenols and other organic liquid mixtures from wastewater to yield a phenol and other organics concentrates, which can either be destroyed by conventional means, such as incineration and oxidation, or be recycled for reuse (10–14). In either option, the volume reduction of the original wastewater by two to three orders of magnitude is attainable. However, at the present stage of development, the main problem in commercializing pervaporation for wastewater treatment is the high cost of the process. However, if organics in the waste streams need to be recovered for their value or if the alternative treatment technologies either cannot do an adequate job or are also expensive, pervaporation may be the solution.

The most widely used polymeric material for organic extraction are poly(dimethyl siloxane) (PDMS) and to a much lesser extent, the so-called poly(ether-block-amide) (PEBA) materials (15–31). PDMS exhibits high permselectivity and permeability towards especially nonaromatic organic compounds, such as VOCs with low solubility in water (15–18) and therefore is preferred when the extraction by pervaporation involves such compounds. However, PDMS exhibits low permselectivity, but high permeability (flux) towards aromatic hydrocarbons and their derivatives, such as phenol and aniline (19–22,27). PEBA is a thermoplastic elastomer comprised of rigid (hard) polyamide and flexible (soft) polyether blocks. The combination of these two segments yields a block copolymer that exhibits a two-phase structure on a microscopic scale: a crystalline phase due to the polyamide and an amorphous phase due to the polyether. It has attracted great interest as a promising material for membranes (23–32), because of its excellent chemical, mechanical, and thermal stabilities as well as good permselectivity towards especially aromatics compounds and their derivatives, such as phenol and aniline. Permeability is however low for these compounds (27,31).

A good polymer material for membrane should have high permeability and selectivity, and long-term stability to maintain its original permselectivity under operating conditions. Since a trade-off between the flux and separation factor usually exists, the development of membranes is often targeted to achieve good fluxes with high separation factors simultaneously. In order to simultaneously achieve both high permselectivity and permeability for the recovery of aromatic compounds such as phenol from aqueous streams, a composite organophilic hollow fiber based pervaporation process using PDMS/PEBA as two-layer membranes has been developed. These two polymers combine their unique features to achieve these two important properties. PDMS exhibits low permselectivity, but high permeability towards aromatic hydrocarbons and their derivatives, such as phenol and aniline. However, PEBA show good permselectivity, but low permeability towards the same compounds.

In this work, a technique has been sought in our laboratory to develop pin-hole free composite hollow-fibers membranes. The process employed hydrophobic microporous polypropylene hollow fiber, having thin layers of silicones (PDMS) and PEBA polymers coating on the inside diameter. A very good performance can be achieved with the membrane as the fluid to be processed can now be passed through the inside diameter of the fiber or bore-side feed flow rather than shell-side feed flow. The advantage of this bore-side feed mode over the shell-side feed mode is that, very little pressure drop is produced in the permeate side, enabling almost all of the driving force to be applied across the skin layer. The composite membrane module was used to investigate the permeation behavior of phenol in water in a separate study, and that of the mixture of phenol, methanol, and formaldehyde in an aqueous stream (a typical constituent of wastewater stream of phenol-formaldehyde resin manufacturing process) in another study. In each case, very good separation efficiency and membrane permeation performance have been achieved. The influence of feed concentration, permeate pressure, temperature, and feed-solution velocity on the membrane separation efficiency and permeation behavior were systematically investigated.

EXPERIMENTAL

Materials and Membrane Preparation

This work focused on investigations of pervaporation behavior of phenol, and that of the mixture of phenol, methanol, and formaldehyde (Sigma-Aldrich) in distilled water across hydrophobic microporous polypropylene hollow fiber membranes (Membrana) coated with silicones (PDMS) (RTV-141, Rhodia: Rhone-Poulenc Inc.) and PEBA (Atochem) polymers. The PDMS is composed of two parts; part A is mainly PDMS oligomers terminated with vinyl groups and part B a mixture of Pt catalyst and PDMS oligomer with active hydrogens. A casting solution of PDMS was prepared by dissolving part A and part B with a ratio of 9:1 in n-hexane and other additive solvents. The PEBA, a thermoplastic elastomer comprised of rigid, crystalline phase polyamide and flexible, amorphous phase polyether block copolymer. The casting solution of PEBA was prepared by dissolving the copolymer in a 4:1 mixture ratio of n-butanol – n-propanol at about 80°C. These silicone and PEBA solutions were used separately and one after the other as thin coating on the inside diameter of hydrophobic microporous polypropylene hollow fibers. The fibers have a maximum pore diameter of about 0.64 μm, and a measured ID of 1.65 mm and OD of 2.54 mm. The PDMS/PEBA two-layer composite hollow fiber membranes were made by first making a module and then coating the fibers. The module was about 31.5 cm long, containing 100 fibers inside a PVC tube, all bonded together and potted by polyurethane or epoxy resin. The effective membrane surface area was 0.1 m^2.

The lumens or bore-side of the hollow fibers were coated as follows: PDMS was first coated and for this case, the prepared PDMS casting solution was pushed upwards through a vertical hollow fiber module until the solution filled the fibers up to the top of the module. The filled module's shell was allowed to stand for about 3–5 minutes, after which, the module was drained of the solution, and nitrogen gas was blown through the fiber lumens for about 25 minutes to dry. The module was then reverted and the above procedure was repeated for the other side of the module. The module was then cured overnight by placing it in an oven at about 60°C to ensure complete cross-linking. PEBA was then next coated on top of the already PDMS coated fibers and for this case, the prepared PEBA casting solution was used while still hot (e.g. at 60°C) and the same procedure as described above for PDMS coating was also followed for this case. The solvent was evaporated at about 60°C in an oven for about an hour and the module was then cured overnight by placing it in an oven at about 50°C to ensure complete cross-linking. A second thin layer coating of PDMS was then coated on top of the PEBA following the same procedure as described above. Thus separate thin coating layers of PDMS/PEBA/PDMS (one on top of another) were achieved on the surface of the lumens or bore-side of the hydrophobic microporous polypropylene hollow fiber membranes. All chemicals were used without any further purification as they were all extra pure grade.

Pervaporation

The module was tested for any fibers leaks or pinholes and possible leaks in the epoxy resin and polyurethane potted tube sheet before they were put into use. Two types of tests were carried out and these have been described in our previous publication (33). Apparently in view of our thorough coating procedure, no leak was detected and thus confirming that our module is free of pin-holes or leaks in the fibers and potted sections. The basic apparatus used here is shown schematically in Fig. 1. The module was attached via a pump (March orbital magnetic drive with TE-5C-MD model) through a 6 liter reservoir tank filled with

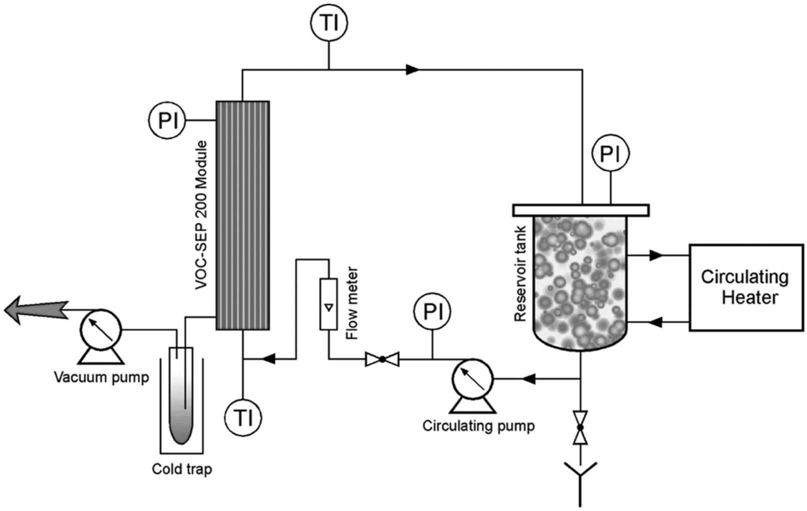

Figure 1. Pervaporation apparatus.

a liquid mixture of phenol-water solution in one study, and a liquid mixture of phenol, methanol, and formaldehyde-water solution in another study. The feed solution of known composition was pumped past the bore-side of the membrane module and then returned back to the reservoir tank at a controlled flowrate. The phenol, methanol, and formaldehyde concentrations in the reservoir were each measured vs time with a gas chromatograph (Varian 3300) equipped with a thermal detector and integrator. Transmembrane fluxes were generated by a downstream vacuum pump and the permeation measurement was carried out under vacuum on the downstream side of the membrane, and the upstream pressure was maintained at atmospheric pressure. The other side of the membrane was normally attached through a liquid nitrogen cold trap to a vacuum pump to condense and collect the permeate vapor. The weight and concentration of the accumulated permeate in the cold trap were also determined with time, by measurement of the sample weight collected and by gas chromatography analysis respectively. In a typical pervaporation experiment, membrane fluxes were allowed to stabilize for ≅2–3 hours before the permeate samples were collected over a period of 1–3 hours. The pervaporation experiments were performed for different permeate pressure (0–50 mmHg), temperature (40–70°C), feed-solution velocity (0.1–1.70 m/s) and for different feed concentrations. The flux, the separation factor, and the Reynolds (Re) number were calculated using similar equations as described in our previous publication (33).

RESULTS AND DISCUSSION

Effect of Feed Concentration

The influence of feed concentrations studies were performed to see how varying the concentration affects fluxes and separation factor, using the membrane module earlier described, which was carried out for different feed concentrations, feed-solution velocity of 0.64 and 1.7 m/s and at permeate pressure of 5 and 10 mmHg. As shown in Figs. 2–3, the flux of phenol increases relatively linearly with increasing concentration especially at low feed concentration, and exhibits a near plateau with further increase in concentration as depicted in Fig. 3. However, water flux increases dramatically as the feed concentration increases, and a near plateau value is obtained for water flux with further increase in concentration. As a result, the phenol/water separation factor decreases as the feed concentration increases as shown in Fig. 4. The corresponding separation diagram of phenol-water for the membrane is depicted in Fig. 5. The results show that the concentration of phenol in the permeate is always higher than that of the feed, i.e., phenol permeates this membrane preferentially. In general, the flux of most organic compounds

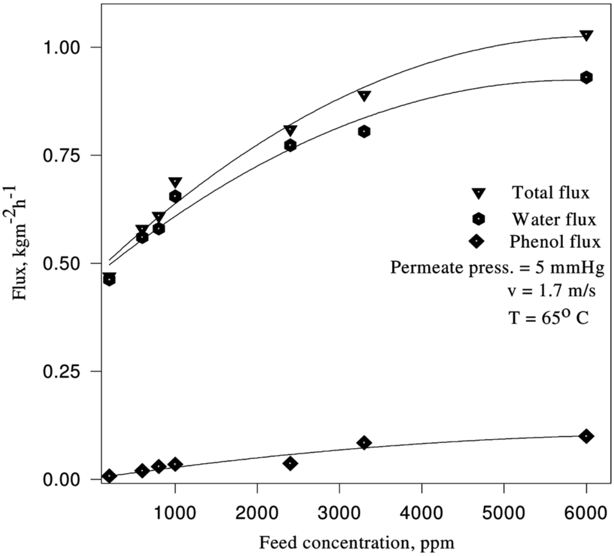

Figure 2. The effect of feed concentration on the phenol, water and total fluxes obtained at feed solution velocity of 1.7 m/s; permeate pressure of 5 mmHg and at 65°C, for the initial feed concentration of 1 wt% phenol.

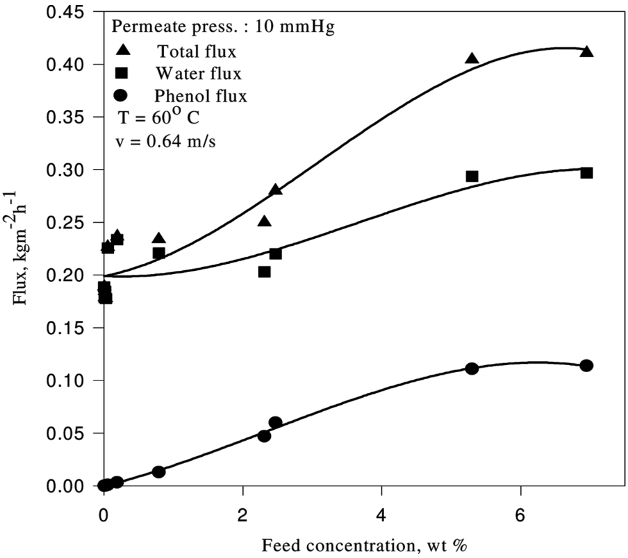

Figure 3. The effect of feed concentration on the phenol, water and total fluxes obtained at feed solution velocity of 0.64 m/s; permeate pressure of 10 mmHg and at 60°C, for the initial feed concentration of 8 wt% phenol.

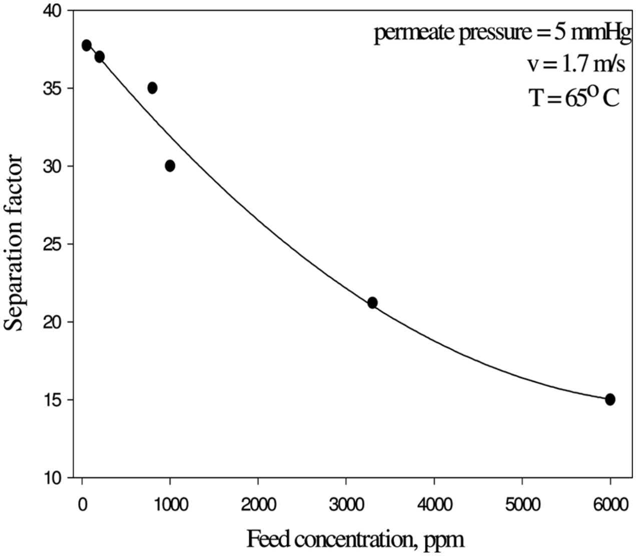

Figure 4. The effect of feed concentration on the separation factor of phenol/water obtained at permeate pressure of 5 mmHg, feed solution velocity of 1.7 m/s and at 65°C, for initial feed concentration of 1 wt% phenol.

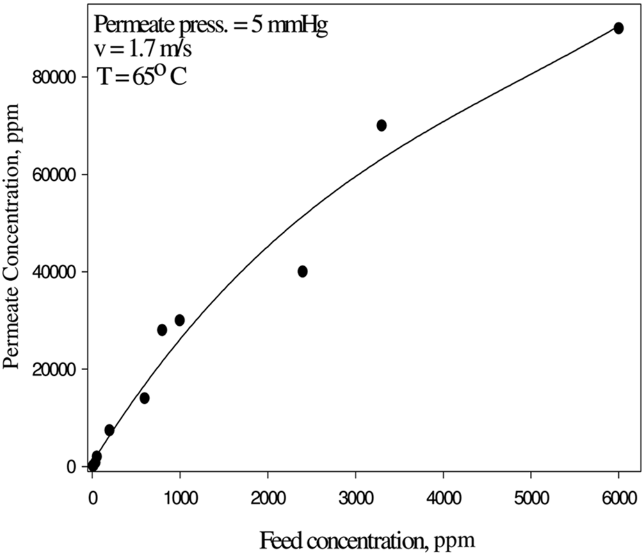

Figure 5. The separation diagram of phenol-water for the membrane obtained at feed solution velocity of 1.7 m/s and at 65°C, for feed concentrations of 1 wt%.

through organophilic rubbery membranes increases relatively linearly with increasing feed concentration especially for a race amount of the compound in solution (21,24,26,30). This linear dependence is expected, especially for phenol, which is known to swell and plasticize organophilic rubbery membranes. It should also be noted that, the increase in phenol flux with increasing feed concentration is partly due to an increase in the phenol vapor pressure difference driving force across the membrane. The dramatic increase in water flux with feed concentration could be attributed to swelling and plasticization of the PDMS/PEBA membrane by the phenol. However, a near plateau value obtained for water flux with further increase in concentration could be attributed to the balance of plasticization and swelling effects (which could contribute to water flux increase) and water clustering effect (which could contribute to reduction in water flux). This phenomenon has also been observed in our previous publication (33–35), and detailed explanation has been given.

As depicted in Fig. 4, the highest phenol/water separation factor obtained for this blend (PDMS/PEBA) membrane is about 37, which is much higher than the one reported using only the PDMS membrane. For the separation of phenol using only the PDMS membrane, the phenol/water separation factor of about 12–18 has been reported (19–21). Furthermore, even though PDMS membrane is known to exhibit high flux for phenol, a significant improvement in phenol flux (about 0.1 $\mathrm{kgm^{-2}h^{-1}}$ obtained for 5 wt% feed concentration as shown in Fig. 3) is achieved with the two-layer membranes as compared to that achieved (about 0.07 $\mathrm{kgm^{-2}h^{-1}}$ obtained for 5 wt% feed concentration reported elsewhere) (21) using only the PDMS membrane. This thus indicates that the two-layer membranes combine the unique features of PDMS (exhibiting high permeability) and PEBA (exhibiting high perm-selectivity) to achieve this significant improvement in both fluxes and selectivity for phenol separation.

Effect of Permeate Pressure

The influence of permeate pressure studies were next performed to see how varying the permeate side pressure affects the flux and the selectivity. Figures 6–8 depict the influence of permeate pressure on fluxes and selectivity. The data were obtained from the pervaporation experiment of phenol in aqueous streams using the membrane module earlier described, which was carried out at 60°C, feed solution velocity of 0.5 and 0.92 m/s, different feed concentration and at permeate

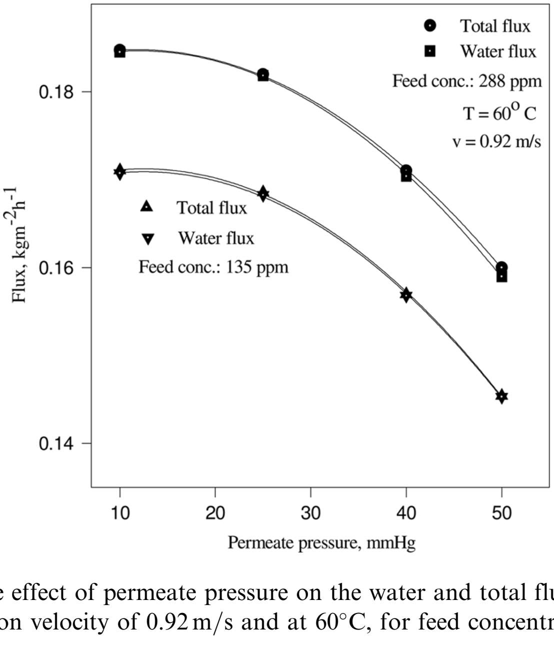

Figure 6. The effect of permeate pressure on the water and total fluxes obtained at feed solution velocity of 0.92 m/s and at 60°C, for feed concentrations of 135 and 288 ppm.

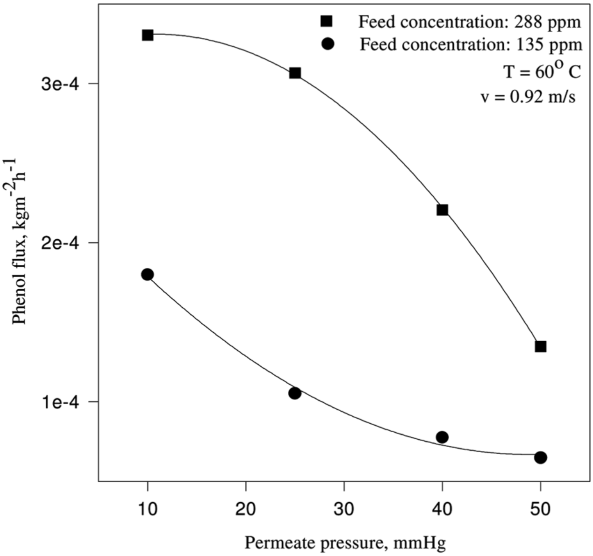

Figure 7. The effect of permeate pressure on the phenol flux obtained at feed solution velocity of 0.92 m/s and at 60°C, for feed concentrations of 135 and 288 ppm.

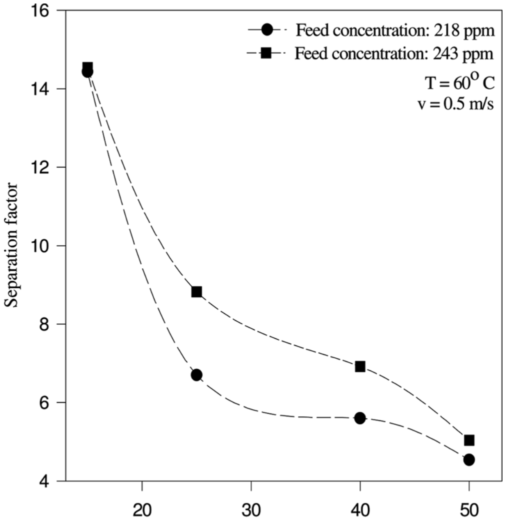

Figure 8. The effect of permeate pressure on the separation factor of phenol/water obtained at feed solution velocity of 0.5 m/s and at 60°C, for feed concentrations of 218 and 243 ppm.

pressure in the range of 10–50 mmHg. As shown in Fig. 6, the total and water fluxes decrease with increasing permeate pressure. The resulting fluxes decrease rapidly due to decreasing activity of permeants. The phenol flux and separation factor shown in Fig. 7 and Fig. 8 respectively also decrease sharply with increasing permeate pressure. This could be attributed to phenol having much lower vapor pressure than water, and thus its flux is highly sensitive to permeate pressure.

Effect of Operating Temperature

The studies of the influence of operating temperature were performed to see how varying the temperature affects fluxes and selectivity, using the membrane module earlier described, operated at a feed-solution velocity of 0.92 m/s and at a permeate pressure of 10 mmHg, different feed concentration and at various temperatures ranging from 50 to 70°C. The results are shown in Figures 9–11. As depicted (Figs. 9–10) an increase in temperature increases the permeation fluxes of both phenol and water. A similar trend has also been observed in our previous publication (33), and detailed explanation has been given. In

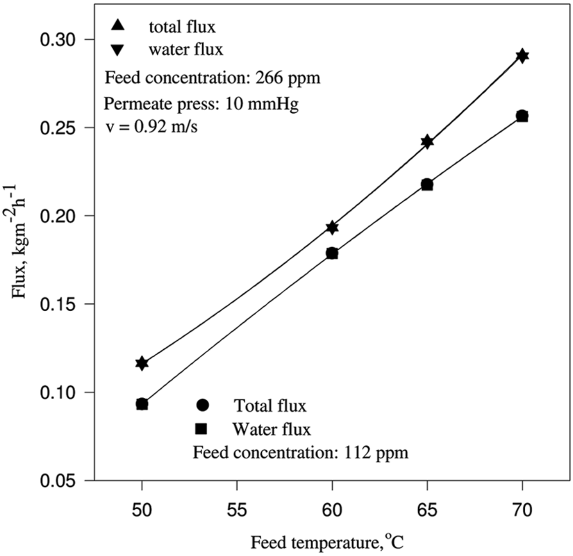

Figure 9. The effect of operating temperature on the water and total fluxes obtained at feed solution velocity of 0.92 m/s and at permeate pressure of 10 mmHg, for feed concentrations of 112 and 266 ppm.

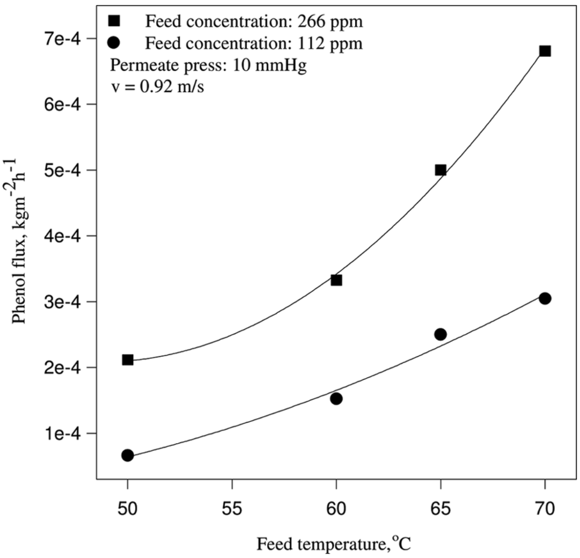

Figure 10. The effect of operating temperature on the phenol flux obtained at feed solution velocity of 0.92 m/s and at permeate pressure of 10 mmHg, for feed concentrations of 112 and 266 ppm.

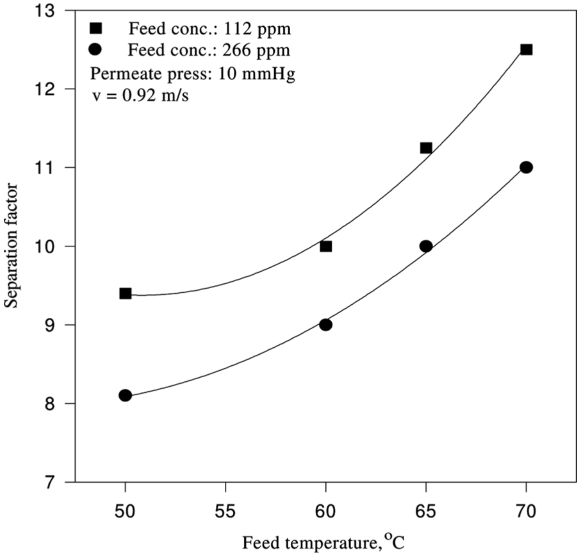

Figure 11. The effect of operating temperature on the separation factor of phenol/water obtained at feed solution velocity of 0.92 m/s and at permeate pressure of 10 mmHg, for feed concentrations of 112 and 266 ppm.

pervaporation, permeating molecules diffuse through the free volumes of the membrane. The thermal motion of the polymer chain in the amorphous regions randomly produces free volume. As the temperature increases, the frequency and amplitude of the polymer chain jumping increase. As a result, the free volume in the membrane increases. Thus, when the temperature increases, the diffusion rate of individual permeating molecules also increase. This leads to a high permeation flux. The usual trend for this kind of membrane with large free volumes is less capability of separation and thus resulting in a lower separation factor. However, in this study, the separation factor increases with increasing temperature as shown in Fig. 11. This could be attributed to the predominance of the water clustering effect that usually occurs at high temperature over the creation of large free volumes. Water flux reduces due to these large water clusters and could thus enhance phenol flux. Water clustering is developed in the membrane arising from repulsive interaction between water and the organic component absorbed. It has actually been shown that the permeation of water through polymer membranes can be hindered by the formation of a water cluster (33–35). Water itself exists in the form of hydrogen-bonded clusters, depending on its circumstance. Thus, "free" water molecules may diffuse accompanied by clustered molecules. This implies that as the diffusion size of water increases, the diffusion coefficient decreases. The extent and size of clustering also depend on the nature of solutes and on the chemical and physical nature of the membrane barrier. Hydrophobic solutes and membranes tend to repel water molecules, forcing them into larger, more ice like, and therefore, less easily permeating clusters especially at high concentration of organics and temperature. This effect could also be attributed to increase in the solubility of the phenol in the membrane as the temperature increases (which is probably due to the creation of more free volumes and/or increase interaction between the permeate and the membrane; permeate and permeate). In addition, the membranes would also be more hydrophobic.

Effect of Feed-Solution Velocity

Table 1 shows the results obtained for the studies of the influence of feed solution velocity on fluxes and separation factor, using the membrane module earlier described, which was operated at 60°C, feed-solution velocity in the 0.64–1.5 m/s range, different feed concentrations, and at a permeate pressure of 10 mmHg. As shown in the table, there are no significant changes in the phenol, water, and total fluxes, and the separation factor with an increase in the feed-solution

Table 1. Effect of feed solution velocity on fluxes and Separation Factor (S.F.) for temperature of 60°C and permeate pressure of 10 mmHg

	Fluxes & S.F. for phenol feed conc. of 31 ppm ($kgm^{-2}h^{-1}$)				Fluxes & S.F. for phenol feed conc. of 276 ppm ($kgm^{-2}h^{-1}$)			
Feed solution velocity (m/s)	Total flux	Water flux	Phenol flux	S.F	Total flux	Water flux	Phenol flux	S.F
0.64	0.1780	0.1776	0.0003719	11.32	0.1889	0.1888	0.0000552	11.16
0.92	0.1935	0.1932	0.0003316	11.84	0.2016	0.2015	0.0000612	10.16
1.50	0.1813	0.1809	0.0004073	11.35	0.1853	0.1852	0.0000549	11.63

velocity, at least within the range of the feed solution velocity considered. These results cannot be attributed solely to the effect of concentration polarization in the liquid boundary layer adjacent to the membrane surface. As a matter of fact, the boundary layer effect is significant, as the flow regime is close to Laminar (i.e., $Re = 836–1960$, for the range of feed-solution velocity investigated). Thus, perhaps much higher feed-solution velocity may be needed to be investigated on this membrane to see if the concentration polarization is having an influence on the fluxes and the separation factor. Concentration polarization tends to decrease the permeation rate of the more permeable component (which in this case is phenol) and increase the permeation rate of the less permeable component (i.e., water in this case), resulting in a lesser extent of separation (15). However, an increase in the feed-solution velocity could reduce the effect of concentration polarization, and thus the phenol flux should increase.

Pervaporation Behavior of Mixture of Phenol, Methanol and Formaldehyde in Aqueous Stream

The membrane module, which was operated at 60°C, feed-solution velocity in the 0.64–0.86 m/s range, different feed concentrations, and at a permeate pressure of 10–20 mmHg was also used to investigate the pervaporation behavior of the mixture of phenol, methanol, and formaldehyde in an aqueous stream (a typical constituent of wastewater stream of phenol-formaldehyde resin manufacturing process) as shown in Figures 12–15. Phenol, methanol, water, and total fluxes slightly increase with increasing feed concentration (Figs. 12–14). Phenol permeation shows a much higher flux (by 3 orders of magnitude) and a higher increase in flux with increase in concentration is also observed as

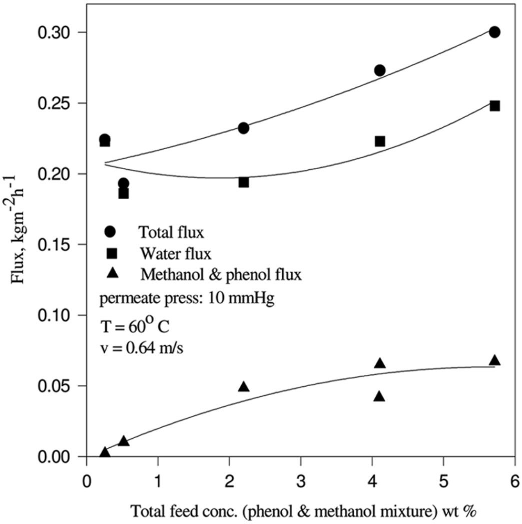

Figure 12. The effect of mixture of phenol and methanol feed concentration on the methanol and phenol, water and total fluxes obtained at feed solution velocity of 0.64 m/s; permeate pressure of 10 mmHg and at 60°C, for initial feed concentration of 8 wt% (phenol and methanol mixture).

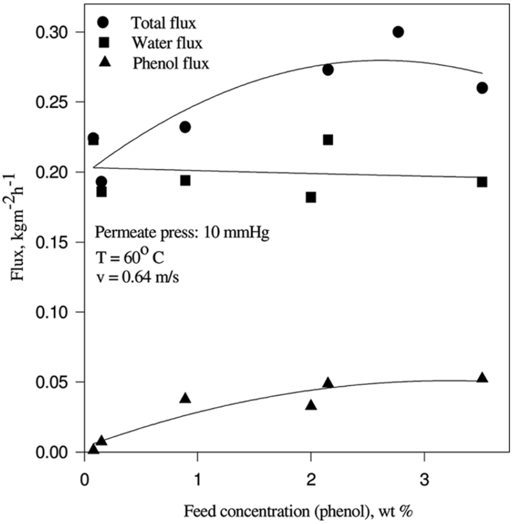

Figure 13. The effect of phenol feed concentration (in the mixture of phenol and methanol) on the phenol, water and total fluxes obtained at feed solution velocity of 0.64 m/s; permeate pressure of 10 mmHg and at 60°C.

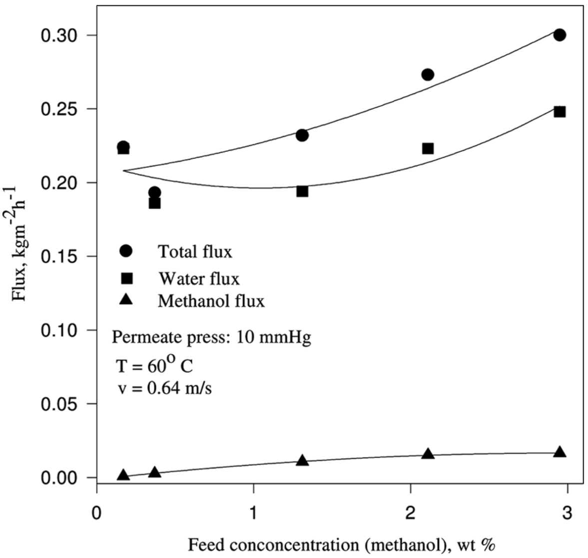

Figure 14. The effect of methanol feed concentration (in the mixture of phenol and methanol) on the methanol, water and total fluxes obtained at feed solution velocity of 0.64 m/s; permeate pressure of 10 mmHg and at 60°C.

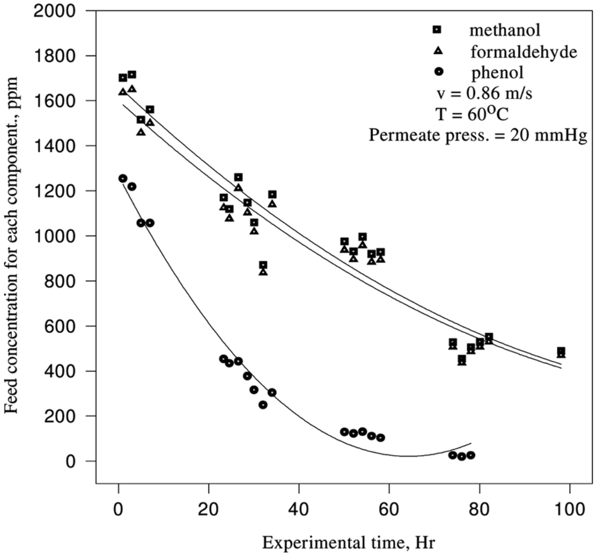

Figure 15. Pervaporation behaviour of mixture of phenol, methanol and formaldehyde in aqueous stream obtained at feed solution velocity of 0.86 m/s; permeate pressure of 20 mmHg and at 60°C.

compared to that exhibited by methanol permeation. This thus indicates that the membrane could be more permeable (expressed in term of flux and selectivity) to phenol than to methanol. The membrane is more efficient and performed better for phenol permeation than that of methanol, even though methanol molecules may be much smaller than that of phenol. Phenol permeability is probably enhanced due its much higher sorption effect in the membrane as compared to that of methanol. Figure 15 shows the pervaporation behavior of the mixture of phenol, methanol, and formaldehyde in an aqueous stream, and as can be observed, phenol concentration reduced sharply to less than 40 ppm; however, methanol and formaldehyde concentrations reduced slightly to about 800 ppm in about 60 h of the permeation experiment. This again indicates that the membrane is much more permeable to phenol than to methanol and formaldehyde.

CONCLUSIONS

A good polymer material for membrane should have high permeability and selectivity, and long-term stability to maintain its original permselectivity under operating conditions. Since a trade-off between the flux and the separation factor usually exists, the development of membranes is often targeted to achieve good fluxes with high separation factors simultaneously. In order to simultaneously achieve both high permselectivity and permeability for the recovery of aromatic compounds such as phenol from aqueous streams, a composite organophilic hollow fiber based pervaporation process using PDMS/PEBA two-layer membranes has been developed. From the pervaporation experiments using the composite membrane module, it was found that the fluxes of phenol and water increase relatively linearly with increasing concentration especially at low feed concentration, and exhibit a near plateau with further increase in concentration. As a result, the phenol/water separation factor decreases as the feed concentration increases. Significant improvement in the phenol/water separation factor and phenol flux is achieved for this two-layer (PDMS/PEBA) membranes as compared to that achieved using only the PDMS membrane. This thus indicates that the two-layer membranes combine the unique features of PDMS (exhibiting high permeability) and PEBA (exhibiting high permselectivity) to achieve this significant improvement. The phenol and water fluxes and the separation factor are highly sensitive to permeate pressure as all decrease sharply with increase in permeate pressure. For this membrane, an increase in temperature increases the permeation fluxes of phenol and water, but the increase in water flux is more significant than that of phenol. The usual trend for this kind of membrane with large free volumes has less capability of separation thus resulting in a lower separation factor. However, in this study, the separation factor increases with increasing temperature. An increase in feed-solution velocity does not have a significant effect on phenol and water fluxes, and also on the separation factor at least within the range of the feed-solution velocity considered. In the study of pervaporation behavior of a typical constituent of the wastewater stream of phenol-formaldehyde resin manufacturing process, phenol permeation shows a much higher flux, and a higher increase in flux with increase in concentration is also exhibited as compared to that exhibited by methanol permeation. This thus indicates that the membrane is more permeable to phenol than to methanol and formaldehyde.

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