

# Treatment of wastewater containing volatile organics using hollow fibre PDMS-polysulfone membrane system: recovery of organics and water reclamation

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**Chlorinated volatile organic compounds (VOCs) from industrial facilities cause serious environmental problems. VOCs present in industrial wastewater are highly toxic to humans but can be valuable if it is recovered safely. A large membrane surface area is required for the treatment of dilute aqueous effluents containing dissolved VOCs. Hollow fibre membrane systems can provide a large membrane surface area per unit module. Here, we study the preparation of PDMS-polysulfone hollow fibre membrane system for application in separation of volatile organics from the aqueous stream. Dichloromethane, chloroform and dichloroethane of 300–5000 ppm in water, is used as model feed solution of aqueous effluent for the experiments. The results demonstrate that dissolved organics could be efficiently recovered from the aqueous stream, along with reclamation of water using the hollow fibre membrane system.**

**Keywords:** Hollow fibre membrane system, organic recovery, volatile organic compounds, wastewater, water reclamation.

VOLATILE organics in air or water are a result of solvent discharge in the environment during industrial processing and organic coatings. These discharged volatile organics are an environmental concern as they are toxic to human health<sup>1</sup>. Removal of these organics from aqueous streams can solve pollution. At the same time, these organics can be valuable, if they are recovered efficiently. Separation of volatile organics from aqueous stream using membranes is a promising method. The membrane separation process is a compact, modular and low-energy process compared to energy-intensive conventional separation processes, such as distillation, air stripping and absorption. The membrane determines the overall cost and economy of the process. Two main characteristics of membranes which govern the performance of the process are separation efficiency and flux. For example, when

separating volatile organics from aqueous streams, the organic components can be selectively collected if they preferably absorb and diffuse through membranes. Secondly, the flux of organics through the membrane, which is the volume of the organic permeation rate per unit area and unit time, is required to be high for a faster separation. One possibility for preparation of high-performance membrane is the fabrication of the selective membrane layer in the form of a film as thin as possible, over a porous support. The thin membrane film allows optimal transport of the organics while the support will provide mechanical strength.

PDMS is known to be a hydrophobic rubber-like material with high affinity for absorption of volatile organics. Preparation of the thin PDMS membrane is desirable as the membrane thickness is inversely proportional to the flux. Various PDMS membranes supported on porous substrate have been prepared by different methods, such as PDMS-PTFE and PDMS-polystyrene composite membranes, by pouring the coating solution on membrane support<sup>2,3</sup>; dip-coating preparation method of the PDMS membranes using various supports<sup>4-6</sup> and PDMS membrane preparation by solution casting technique<sup>7-12</sup>.

It is difficult to coat thin PDMS layer, as the initial coating solution is viscous due to the cross-linking reaction between the pre-polymer liquid and cross-linker. Thus, the PDMS composite membranes prepared on a porous polymer support using viscous coating solution have a PDMS layer of about 10  $\mu\text{m}$  thickness or above. A decrease in PDMS membrane film thickness could be obtained from evaporation casting of dilute solution; however, such membrane exhibits loose structure containing polymer aggregates and crystalline domains<sup>12</sup>. A preparation technique for polymer composite membrane film via sequential absorption–reaction–evaporation, with a top PDMS layer and bottom flat-sheet polysulfone support was reported earlier<sup>13</sup> and this composite membrane exhibits improved performance in terms of high flux and organic selectivity over water. However, a large surface area of the membrane is required for its practical use in the treatment of dilute aqueous streams containing

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VOCs. Hollow fibre membrane can provide a large membrane surface area per unit module. In the present study, we report preparation of high-flux hollow fibre composite membrane using an approach described earlier in case of flat-sheet composite membranes<sup>13</sup>. Dichloromethane (DCM), dichloroethane (DCE) and chloroform (CHCl<sub>3</sub>) of about 300–5000 ppm in water is used as model feed solution for the separation experiments.

## Experimental

### Preparation of membranes

Preparation of composite hollow fibre membrane includes two main steps: (i) preparation of hollow fibre polymer support; and (ii) coating it with PDMS. To prepare hollow fibre polymer support, polysulfone, polyvinylpyrrolidone and poly(acrylonitrile-co-methacrylic acid) were mixed by dissolving the desired amount of polymers in *N,N*-dimethylformamide to prepare a transparent spinning dope. The spinning dope was extruded under a nitrogenous environment through a double orifice spinneret. The water flowing through the inner nozzle of the spinneret acted as bore former, causing phase inversion in the inner part of the extruded hollow fibre. The outer surface of the extruded hollow fibre was then gelled in water bath. The hollow fibre was washed thoroughly with water followed by methanol. Further details of spinning conditions can be found in ref. 14.

Coating of polysulfone hollow fibre with PDMS: For the coating process, a hydroxyl terminated PDMS liquid of 18,000–22,000 cSt viscosity was used as base polymer liquid, while poly(methylhydro)siloxane (PMHS) of 12–45 cSt viscosity was used as cross-linker along with a catalyst-dibutyltindilaurate (Sigma-Aldrich Chemical Co). In the first step, the coating solution was prepared by cross-linking with a base polymer liquid and cross-linker in *n*-heptane solvent, with a ratio of 10:1 (w/w). The catalyst (3%) was added to the weight of polymer. Cross-linking solutions of varying polymer concentrations as 5%, 10%, 20% and 50% were prepared (Scheme 1).

In the second step, the cross-linking solution was absorbed into the porous polysulfone hollow fibre support by immersing it in the solution of a desired concentration. The immersion time was 10 min for equilibrium absorption of the solution into the support. In the final step, the support was removed from the cross-linking solution, transferred immediately into a glass chamber and then sealed. The glass chamber with the sample was heated at 40°C for 45 min. This resulted in the formation of a thin PDMS layer over the porous polymer support. The composite membrane was then taken out from the glass chamber and finally cured at 80°C in an oven for 1 h. The hollow fibre membrane modules hereafter designated as M-5, M-10, M-20 and M-50 were prepared by coating

polysulfone hollow fibres with PDMS of varying thickness from 5%, 10%, 20% and 50% initial polymer concentration respectively.

The morphology of the prepared membrane was characterized by scanning electron microscopy (SEM) LEO 1430VP at 10 kV accelerating voltage. Samples were freeze-fractured by immersing in liquid nitrogen and dried at room temperature to obtain a smooth cross-section of coated membranes. The broken section was coated with a conductive layer of sputtered gold. Thickness of the surface coat of the sample was fixed to about a few nanometers by sputtering for 150 sec at 1 kV, so that the membrane pore morphology was not affected by the coating.

The pervaporation experiments were carried out with a fabricated laboratory unit as shown schematically in Figure 1. Feed solution (300 ml) was circulated through the hollow fibre module with a membrane surface area of 33 sq. cm at fixed temperature ranging from 25°C to 60°C. A downstream pressure of about 5 mbar generated by a vacuum pump was continuously measured by a pressure transducer and displayed by the micro pirani gauge readout. The permeate was collected in cold traps and cooled in liquid nitrogen. The experiments were carried out at room temperature using an initial feed water containing 300–5000 ppm dissolved VOCs. DCM, DCE and CHCl<sub>3</sub> were taken as representative samples of VOCs. The concentrations of the feed and permeate were analysed by gas chromatography (GC) (GC ultra, thermo) equipped with a polar capillary column HP-5 (cross-linked 5% PHME siloxane, length 15 m, ID 0.53 mm × 1.5 μm). The separation factor of mixture was expressed as

$$\alpha = \frac{P_o/F_o}{P_w/F_w}, \quad (1)$$

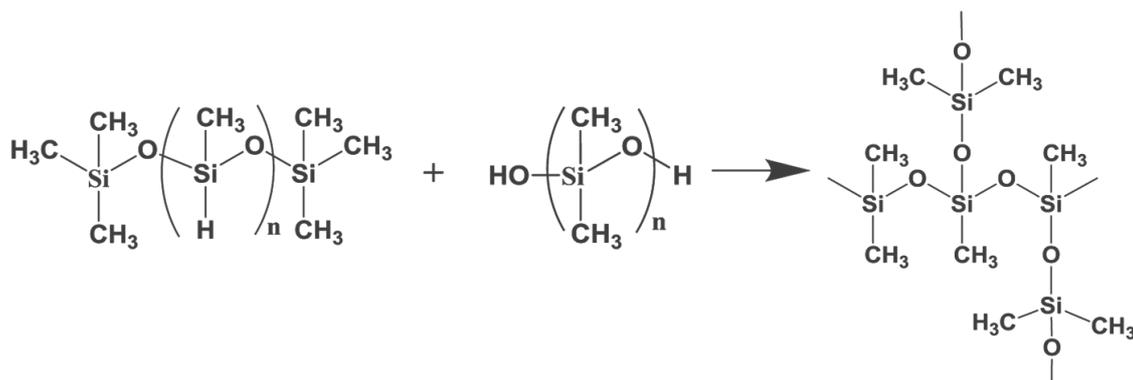
where  $P_o$  and  $P_w$  represent the organic and water concentrations (wt%) in permeate respectively;  $F_o$  and  $F_w$  represent the organic and water concentrations (wt%) in feed respectively.

## Results and discussion

### Preparation of PDMS membranes supported on polysulfone hollow fibre

The asymmetric polysulfone hollow fibre prepared was of 1.1 mm outer diameter × 0.8 mm inner diameter. Cross-sectional SEM images of the hollow fibre are shown in Figure 2. The molecular-weight-cut-off (MWCO) value of the hollow fibre was 100,000 g/mol based on >90% rejection of polyethylene oxide for this molecular weight.

Coating of the polysulfone hollow fibre support with top-layer of the cross-linked poly(dimethylsiloxane) (PDMS) membrane led to formation of composite



Scheme 1.

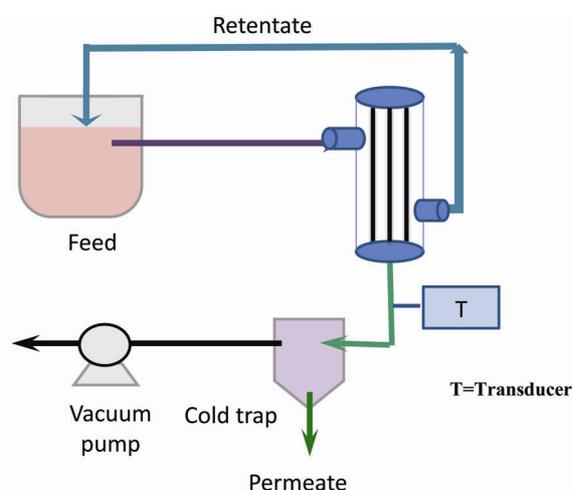


Figure 1. Schematic drawing of a fabricated laboratory test unit for pervaporation experiment.

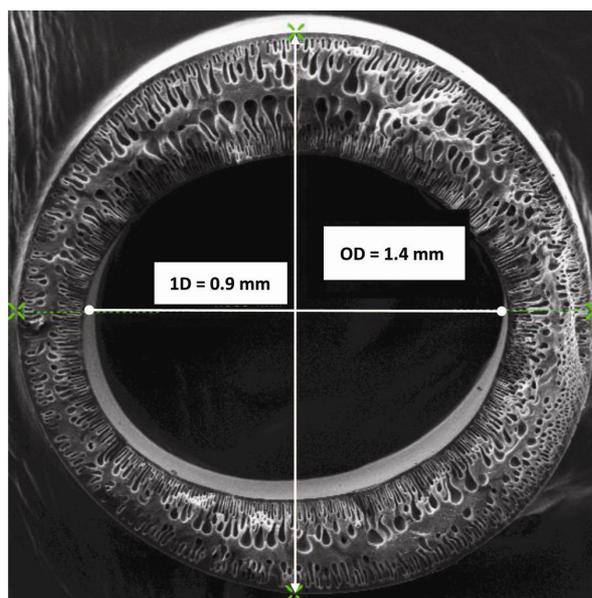
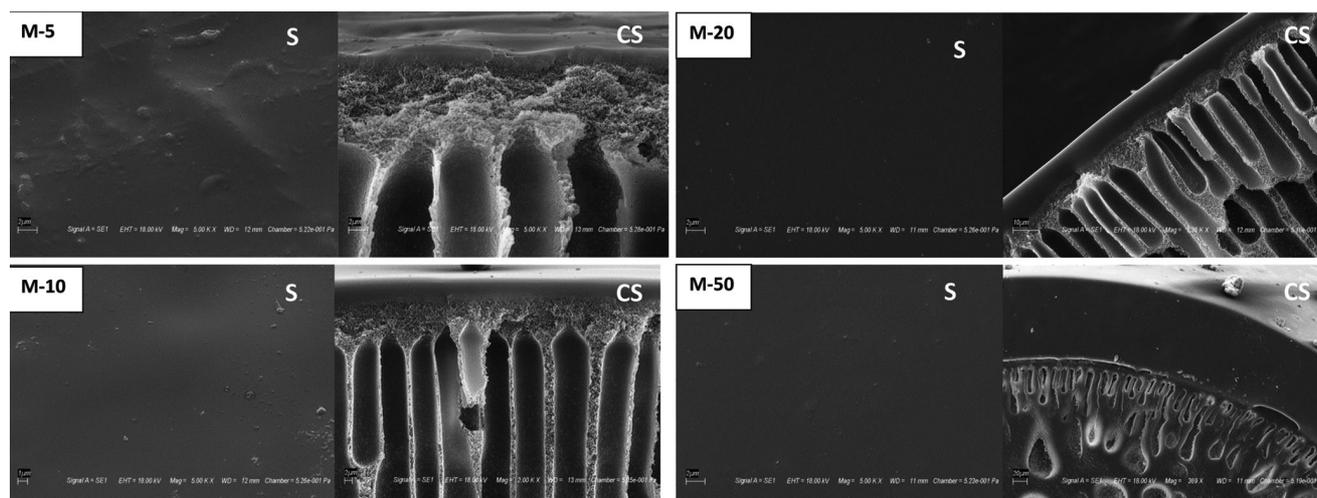


Figure 2. Cross-sectional SEM images of polysulfone hollow fibre support.

membranes. The cross-sectional SEM images of the composite membrane samples are shown in Figure 3, where formation of dense PDMS membrane on the hollow fibre support is clearly visible. M-5, M-10, M-20, M-50 composite membranes had average PDMS layer thickness of 1, 3, 10 and 70  $\mu\text{m}$  respectively. The M-5, M-10, M-20, M-50 membranes were prepared from 5, 10, 20 and 50% (w/w) coating solution, implying that PDMS layer thickness is directly proportional to the coating solution concentration. The results thus indicate that PDMS membranes of different thicknesses over porous polysulfone support could be prepared. The liquid permeability for the composite membrane depending on the top PDMS membrane layer thickness was observed by single liquid permeation data of water, ethanol and isopropanol. The comparison of liquid permeation data for the membranes is shown in Figure 4. In all cases, alcohol flux is higher than water by about 4 times for the M-5, M-10 and M-20 and about 9 times for the thickest M-50 membrane. This indicates that more polar water molecules are less preferentially permeated through membranes. Maximum isopropanol flux of 1900  $\text{g m}^{-2} \text{h}^{-1}$  was observed for the thinnest M-5 membrane. This is to be expected as the PDMS membrane is hydrophobic in nature.

#### Pervaporation performance of membrane modules

The pervaporation separation performances of the membrane modules, using feed solution containing 300–5000 ppm chlorinated VOC in water, were examined. The membrane performance results in terms of flux and separation factor of organics over water ( $\alpha_{\text{organic/water}}$ ) are given in Table 1. There were differences in the separation performance of the membranes of different PDMS layer thickness. The M-5 module with thinnest PDMS membrane layer of 1  $\mu\text{m}$ , exhibited an average permeate flux of 820  $\text{g m}^{-2} \text{h}^{-1}$  while the M-50 module with thickest PDMS membrane layer of 70  $\mu\text{m}$  showed the average permeate flux 66  $\text{g m}^{-2} \text{h}^{-1}$ . The M-10 and M-20 modules

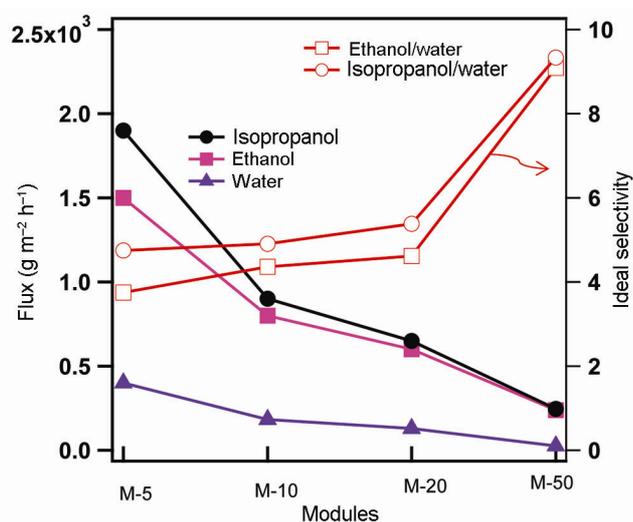


**Figure 3.** Surface (S) and cross-section (CS) images of hollow fibre composite membranes.

**Table 1.** Performance of the membrane modules in terms of the average flux and the average separation factor of organic over water from the feed water containing 300–5000 ppm volatile organic compound (VOC)

VOC	Flux ( $\text{g}/\text{m}^2 \text{ h}$ )				$\alpha$			
	M-5	M-10	M-20	M-50	M-5	M-10	M-20	M-50
DCE	826 (38)	380 (6)	157 (21)	66 (1)	66 (6)	228 (10)	1042 (77)	10759 (1104)
DCM	853 (7)	449 (1)	223 (7)	74 (1)	63 (14)	164 (19)	400 (53)	5498 (1328)
$\text{CHCl}_3$	783 (24)	229 (8)	169 (3)	59 (1)	47 (17)	155 (62)	325 (50)	2578 (1481)

Numbers in parenthesis are standard deviation values.



**Figure 4.** Single liquid permeance (water, ethanol and isopropanol) and ideal selectivity of alcohol/water for the membranes (condition: feed side = room temperature and atmospheric pressure; permeate side pressure = 5 mbar).

of 3  $\mu\text{m}$  and 10  $\mu\text{m}$  PDMS layer thicknesses showed the average flux of 353  $\text{g m}^{-2} \text{ h}^{-1}$  and 183  $\text{g m}^{-2} \text{ h}^{-1}$  respectively. The changes in average flux of the membrane can

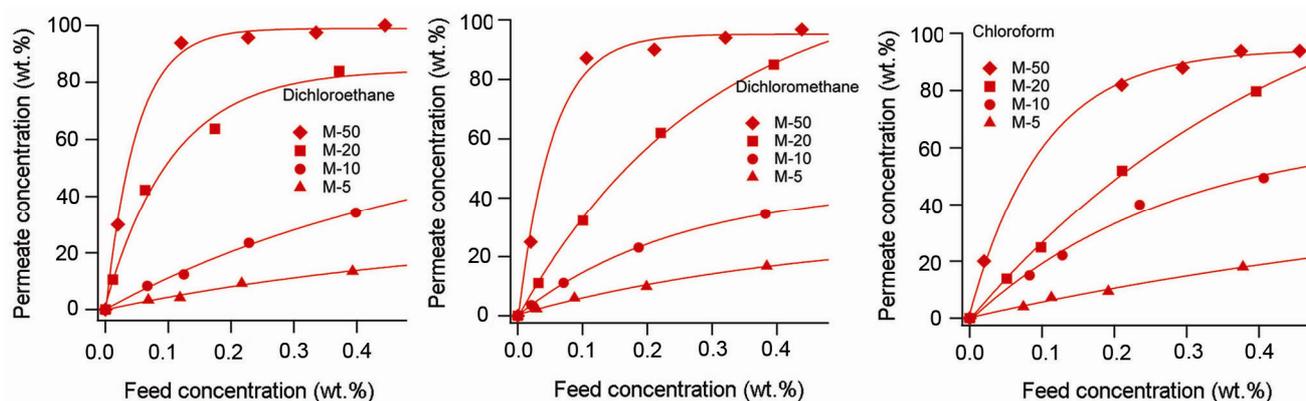
be thus related with the thickness of the PDMS membrane layer. The organic selectivity of membranes measured in terms of the  $\alpha$  values, increased with increase in PDMS membrane layer thickness  $\text{M-5} < \text{M-10} < \text{M-20} < \text{M-50}$ . The M-5 module exhibited  $\alpha_{\text{DCE}/\text{water}}$  and  $\alpha_{\text{DCM}/\text{water}}$  and  $\alpha_{\text{CHCl}_3}/\text{water}$  values of 66, 63 and 47 respectively while the M-50 module exhibited  $\alpha_{\text{DCE}/\text{water}}$  and  $\alpha_{\text{DCM}/\text{water}}$  and  $\alpha_{\text{CHCl}_3}/\text{water}$  values of 10,700, 5500 and 2600 respectively. The differences in separation selectivity of the chlorinated VOC for the membrane are explained based on the transport phenomena of VOC over these membranes as discussed below.

Pervaporation separation process is usually described by a solution-diffusion model in which the transport of molecules takes place from a combined effect of solubility and diffusivity of the molecules through the membrane. The degree of solubilization of the molecules in the polymer membrane material determined the solubility factor, depending on the difference of solubility parameter ( $\Delta\delta$ ) between membrane material and permeating molecule (permeant). The diffusivity of a permeant through a polymeric membrane is generally dependent on its molecular size, therefore, the small molecules are favoured over the large ones. The overall permeability of the membrane in the pervaporation separation process is

**Table 2.** Physical properties for the chlorinated VOCs tested in the membrane separation

VOC	Molecular weight (g/mol)	Molar volume (cm <sup>3</sup> )	Solubility parameter, $\delta$ (MPa <sup>1/2</sup> )	$\Delta\delta$	Solubility in water (ppm)	Saturated vapour pressure (mm Hg)
DCE	99.0	78.8	20.9	4.3	8690	115
DCM	85.0	64.5	20.2	3.6	19,450	430
CHCl <sub>3</sub>	119.5	81.1	18.7	2.1	7800	199

$\Delta\delta$ , Solubility parameter of VOC – solubility parameter of PDMS (16.6 MPa<sup>1/2</sup>).



**Figure 5.** Plots of VOC concentration (wt.%) in permeate as a function of its concentration in feed for the modules.

therefore influenced by the molecular size of permeate,  $\Delta\delta$ , solubility of VOC in water and vapour pressure of VOC. The physical properties of the chlorinated VOCs tested for membrane separation in the present work are given in Table 2.

Table 2 shows that the molar volume of the VOC is in decreasing order of CHCl<sub>3</sub> > DCE > DCM, implying that diffusion rate of DCM is the fastest. Similarly, the saturated vapour pressure is maximum for DCM, which is twice that of CHCl<sub>3</sub>, while DCE vapour pressure is nearly similar to that of CHCl<sub>3</sub>. This indicates the highest feed partial pressure of DCM-water mixture among the VOC-water mixtures tested. Therefore, diffusivity of DCM through the membrane should be comparatively higher than the others. Thus, the observed flux for VOCs in the order DCM > DCE > CHCl<sub>3</sub> may be influenced by the effect of molecular size and saturated vapour pressure.

Furthermore, the solubility of VOC in water may also influence permeability since affinity of VOC towards the membrane depends on its hydrophobicity. Less soluble VOC in water indicates more affinity towards the hydrophobic PDMS material. In water, solubility of CHCl<sub>3</sub> (7800 ppm) is slightly lower than the solubility of DCE (8690 ppm), whereas the solubility of DCM is more than twice the DCE. The solubility factor of VOC in the PDMS membrane is compared based on the difference of solubility parameter ( $\Delta\delta$ ) between the VOC and the PDMS material. Smaller values of  $\Delta\delta$  indicate more absorption of VOC in the PDMS. The calculated  $\Delta\delta$  values are in the decreasing order of DCE > DCM > CHCl<sub>3</sub>,

implying maximum absorption of CHCl<sub>3</sub> in the PDMS in the order of DCE < DCM < CHCl<sub>3</sub>. The absorbed VOC molecule can swell the polymeric membrane, depending on affinity of the VOC to the membrane. This action of the absorbed VOC increases polymer chain mobility leading to larger voids between the polymer chains. Among all, the affinity or solubility of DCE toward the PDMS membrane is the lowest, therefore we can expect minimum swelling of the polymer by DCE. Furthermore, the molar volume of DCE (78.8 cm<sup>3</sup>) is similar to that of CHCl<sub>3</sub> (81.1 cm<sup>3</sup>) but much larger than 64.5 cm<sup>3</sup> molar volume of DCM. Therefore, the observed highest selectivity of DCE for the membrane over water may be because of lesser membrane swelling by DCE and its large size.

#### *Recovery of chlorinated VOC from wastewater and water reclamation*

Variation of VOC concentration (wt%) in permeate as a function of its concentration in feed for different membranes, is plotted in Figure 5. The organic concentration in permeate increases with increase in organic concentration in feed for all membranes. Organic concentration in permeate increases by 200–1500 fold of organic concentration in feed for the M-50 module, whereas the increment was about 40–80 fold, 90–170 fold and 200–800 fold in case of M-5, M-10 and M-20 modules respectively. This may be due to difference in organic selectivity of the

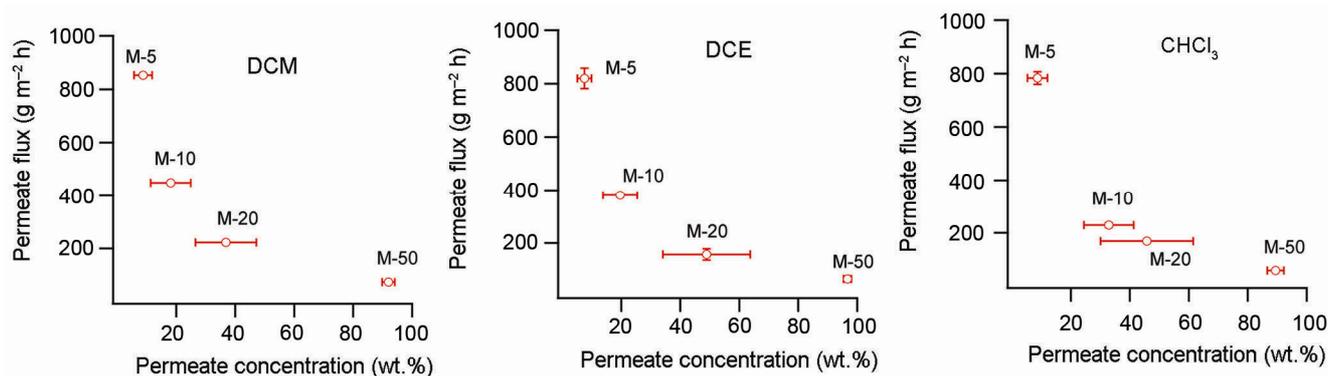


Figure 6. Plots of permeate flux against VOC concentration in permeate for the modules.

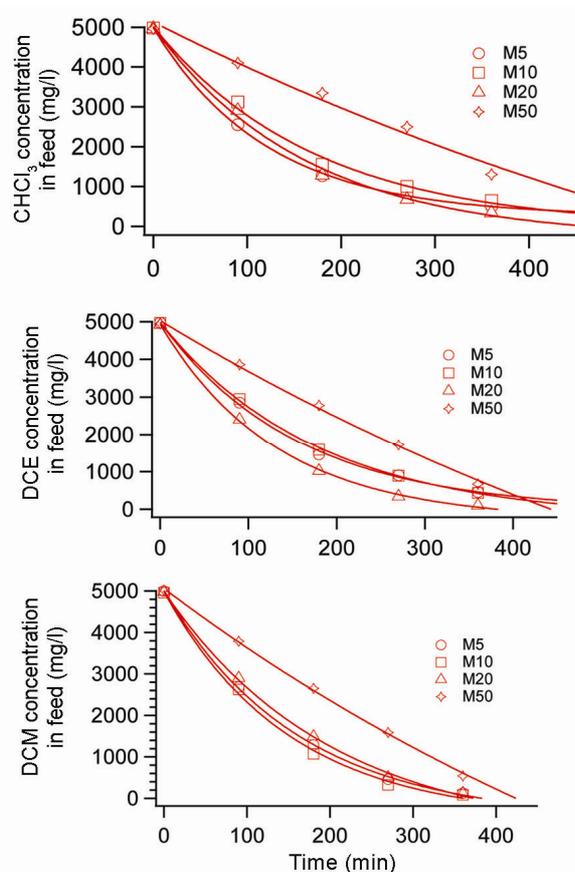


Figure 7. Changes in organic concentration in feed water as a function of run time for the modules.

modules of different PDMS membrane layer thicknesses. DCE concentration in permeate was relatively higher than the rest. Over 99 wt% DCE concentration in permeate was observed from the run of feed concentration with 0.5 wt% DCE for the M-50 module.

Plots of permeate flux against VOC concentration in permeate for the membranes are shown in Figure 6. The M-5 module flux is over 10 times of the M-50 module flux. Therefore, despite its low organic selectivity

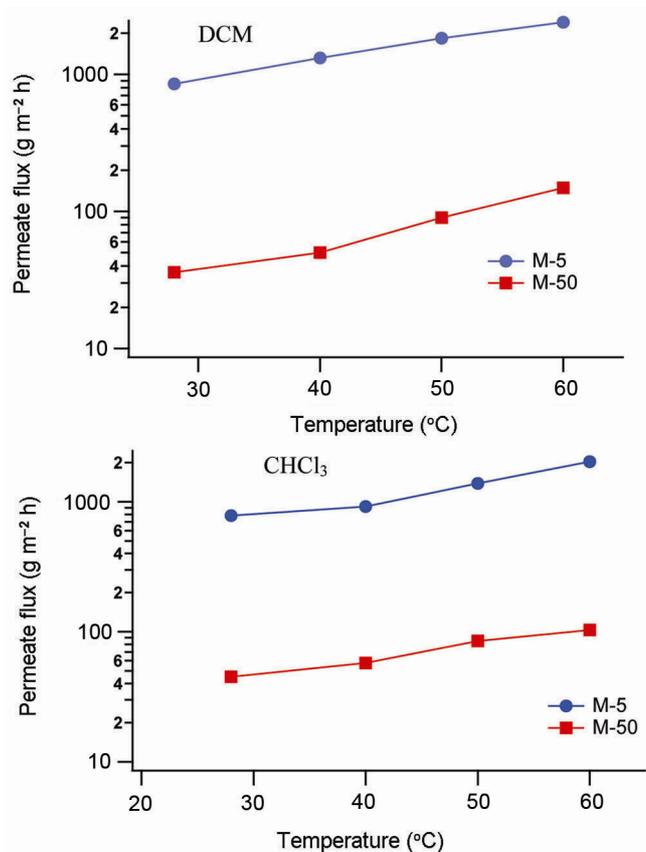


Figure 8. Effect of operating temperature on the flux of M-5 and M-50 modules using aqueous feeds containing 5000 ppm  $\text{CHCl}_3$  or 5000 ppm DCM.

compared to the other modules M-5 can quickly remove the organic present in the aqueous feed stream because of its high flux throughput. It is important to measure how quickly the membrane separation can purify the wastewater for practical uses of the membrane in treating industrial aqueous effluents. To compare the performance of the membrane modules in water reclamation from wastewater, separation experiments were conducted using modules and the organic concentration in feed was measured

at periodic intervals of run time. The changes in organic concentration in feed water as a function of run time for the membrane modules are shown in Figure 7. A larger run time is required for the M-50 module despite its high organic selectivity compared to the other modules, for water reclamation under similar operating condition. Based on these data, a water treatment plant capable of treating 1 cubic meter of wastewater containing 5000 ppm volatile organic in about 6–7 h at room temperature may require M-5/M-10/M-20 module of membrane area 10 sq. m. The flux of the membrane modules can be increased by operating the separation experiments at higher temperature. Figure 8 shows the effect of operating temperature on the flux of thinnest M-5 and thickest M-50 membrane modules, using aqueous feeds containing 5000 ppm  $\text{CHCl}_3$  or 5000 ppm DCM. When the operating temperature was increased from 25°C to 60°C, the flux increased from 40 to 150  $\text{g m}^{-2} \text{h}^{-1}$  and 800 to 2400  $\text{g m}^{-2} \text{h}^{-1}$  for the M-50 and M-5 module respectively. The increase in flux with increase in operating temperature is found to be exponentially related which agrees with the Arrhenius relationship of temperature dependence of flux.

## Conclusions

The composite PDMS-polysulfone hollow fibre membranes were prepared by depositing thin PDMS film over polysulfone ultrafiltration hollow fibre support. The selectivity of the membranes for chlorinated VOCs relative to water is high. The composite membrane comprising of top PDMS membrane layer and bottom polysulfone hollow fibre support exhibited high-flux with moderate organic selectivity. The separation factor of organics to water was found to be increased with increase in the PDMS membrane layer thickness. Organic concentration in permeate increased by about 200–1500 fold of organic concentration in feed, for the M-50 module while the increment was about 40–80 fold, 90–170 fold and 200–800 fold in the case of M-5, M-10 and M-20 modules respectively. Thus, VOCs can be concentrated from contaminated water and at the same time the water can be purified by the membrane systems at ambient condition. Based on the test results, the following conclusions are drawn: (i) depending on membrane thickness, 20–99 wt% VOC in permeate can be recovered in a continuous mode from feed water of 5000 ppm VOC concentration and (ii) 5000 ppm VOC feed water of 1 cubic meter water volume can be purified over 10 sq. m. of membrane area within 6–7 h of operation at room temperature.

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