Pesticides Removal Performance by Low-Pressure Reverse Osmosis Membranes

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ABSTRACT: Pressure driven techniques (*viz.* reverse osmosis and nanofiltration) have the potentiality to remove the pesticides from water. The observations revealed that pesticides removal mostly depends upon the molecular weight (size exclusion) and hydrophobicity (log P) of the pesticides. Interfacial polymerization of *m*-phenylene diamine (MPD) and trimesoyl chloride (TMC) on the polysulfone membranes impart the salt rejection property in it. It is shown that with the greater salt rejection property, the performance removal of pesticides also is in increasing trend. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3575–3579, 2006

Key words: membranes; polyamides; composites; pesticides

INTRODUCTION

Pesticides are designed for the welfare of human being, but sometimes, due to ignorance in proper handling, it may act as devil to the mankind. As water is one of the paths that often facilitate wandering, that takes the pesticides easier to threat mankind in direct as well as indirect manner.[1] The pesticides contaminate water through agricultural, domestic, and industrial activities. Water pollution by pesticides is of great public concern. The permissible limit of different pesticides has been set by different environmental and health organizations like Environment Protection Agency (US) and World Health Organization. Occurrence of pesticides in larger concentrations than permissible limits has been reported in the literature.[2–5]

There are various methods (e.g., granular activated carbon, ozonation) to separate pesticides from water. As they are expensive and bears limitations, membrane separation technique is the preferable one because of the inherent characteristics, low cost energy consumption, and simple operation.[6,7] Many researchers[8–18] have reported the removal performance by different commercial membranes like Desal DK (Osmonics), NF200 (Dow, Filmtec), NTR-729HF (Nitto Denko), and UTC 20(Toray) for different pesticides such as triazines, pyridinium compounds, organophosphorus compounds, etc. The separation ability of the membranes is mostly dependent upon the nature of the membranes as well as pesticides. The details regarding the performances of commercial membranes have been discussed in the recent review.[19] The limitation of the reports is that the chemistry linked with performance data is not available, as the composition of the membrane is really not disclosed for those commercial membranes. Here, in the present investigation, we have tried to correlate the performance data of polyamide membranes with the sodium chloride removal ability within it. The chemistry of polyamide membranes is also no longer concealed in this case.

EXPERIMENTAL

Materials and instruments

Polysulfone (Udel, M_w 35,000), dimethylformamide (Merck, India), sodium lauryl sulfate, *m*-phenylene diamine (Lancaster), and trimesoyl chloride (Lancaster, USA) are used in these experiments. The technical grade pesticides such as atrazine, simazine, and diuron are procured from Sigma Chemicals, USA.

For permeability and salt rejection measurement, laboratory-made pressure cell, and conductivity meters are employed. The experimental set up used for treating the solution is sketched in Scheme 1. The permeability is tested in 1.4 MPa. HPLC (Shimadzu LC-10A), and UV–vis spectrophotometric analysis is done to measure the concentration of the pesticides.

Methods

A two-step process is used in this investigation to prepare polysulfone–polyamide composite membranes. The steps are as follows: (i) Preparation of asym-
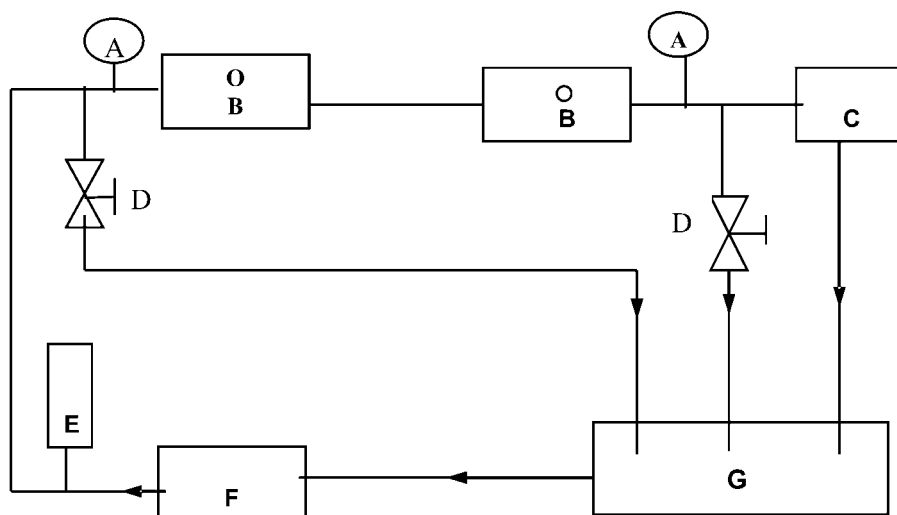
Scheme 1 Schematic diagram of testing unit for flat membrane (Pressure gauze A; Pressure test cell B; Back pressure regulator C; By-pass valve D; Pressure accumulator E; Pump F; Feed solution tank G).

metric polysulfone membrane; (ii) Thin film composite membrane (m-phenylene diamine, MPD based) over the polysulfone membrane. The processes are described and the schematic diagram (Scheme 2) is also presented.

Preparation of asymmetric polysulfone membrane

Polysulfone is a classical material for the preparation of polymeric asymmetric porous membranes by the phase inversion method. The polysulfone membranes of 15–17% w/w in dimethyl formamide are prepared over the nonwoven polyester fabric (1 m width) by phase inversion technique using a prototype casting machine. The polymeric solution, casted on the nonwoven fabric and then it is dipped into the nonsolvent bath (here, water). The schematic diagram of membrane formation is presented in Scheme 2. Here, ternary system is employed polysulfone as polymer, N,N-dimethyl formamide as the solvent, and water as the nonsolvent. Diffusion exchange of solvent by the nonsolvent from the interstices of a casted polymeric membrane in a gelling-bath is the basic methodology for the preparation of such asym-

metric membranes.[20–23] Sodium lauryl sulfate was used to control the uniformity of pores in the gelling-bath and also to improve antifouling properties of the membrane.

Preparation of thin film composite membrane

Polyamide composite membranes are prepared by the interfacial polymerization of MPD and trimesoyl chloride (TMC) on the surface of the prepared polysulfone membranes. First, the polysulfone membrane is coated with 2 wt % MPD solution of water, the excess amount of the MPD solution remaining on its surface is removed and then immersed into a 0.1 wt % TMC solution (in hexane) for the interfacial polymerization, after which it is cured at temperature 70–83°C. The selected concentrations of MPD and TMC have been optimized from the systematic studies on the basis of salt rejection ability of the membranes. The reaction between MPD and TMC results —CONH (bond formation in form of polyamide). The interfacial polymerization took place in the hexane (organic phase). Reaction does not take place in the water phase, because a highly unfavorable parti-
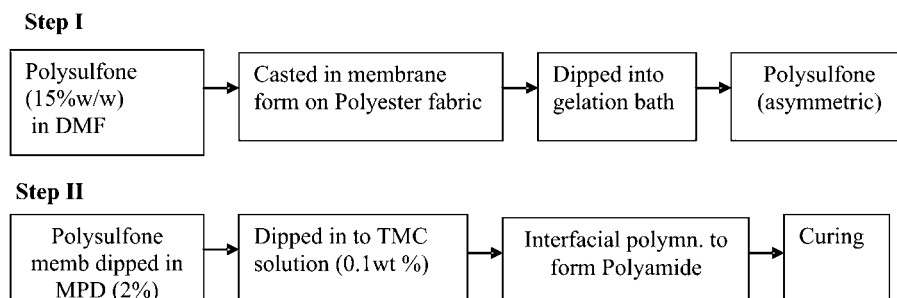
Scheme 2 Schematic diagram of the preparative way of polyamide membranes.

TABLE I
Preparation Conditions of Membranes

Membrane	Polysulfone in DMF (% wt/wt)	Conditions		
		Curing temperature (°C)	Coating temperature (°C)	% RH
MA3	15	70	15	89
MA2	16	83	16	90
MA1	17	83	16	90

TABLE II
Performance Evaluation of Pesticides for the Membranes

Membrane	Water flux ($lm^{-2} d^{-1}$)	Atrazine (% R)	Simazine (% R)	Diuron (% R)
MA3	1421	81.7 (1184)	75.5 (1150)	88.7 (884)
MA2	948	77.5 (537)	75.4 (895)	77.9 (758)
MA1	379	14.3 (711)	11.5 (474)	50.2 (252)

The values given inside parentheses are Flux ($lm^{-2} d^{-1}$).

tion coefficient for acid chloride limits its availability in the aqueous phase.[24] Thus, the polyamide film is formed on the organic solvent side. The details of the preparation conditions are described in Table I. The coating temperature has been maintained at a lower level to avoid undesirable evaporation of solvent resulting to a concentration gradient of TMC, which in turn produces a nonuniform network structure of polyamide. Though the interfacial polymerization occurs at low temperature, achievement of network structure as well as it's anchoring with the polysulfone substrate demands higher range of curing temperature (Table I).

Preparation of pesticides solution

The pesticides are dissolved in methanol solutions (300 mg/L). An appropriate amount of methanol solution is kept in open condition to evaporate and the residues are dissolved into water (already passed through R.O. module). The final concentration is 0.5 mg/L for the selected pesticides.

Analysis

The pesticide concentrations are analyzed with high performance liquid chromatography (HPLC) (reverse phase), using the direct injection method under the following conditions: Column, Shim Pack CLC-OPS (M) 4.6 × 250 mm × 5 μm, mobile phase acetonitrile/water (Rankem) (60 : 40 for atrazine, 70 : 30 for simazine, and 55 : 45 for Diuron), flow = 1.0 mL/min, and UV–vis detector (χ_{max} = 226 nm). In all the cases 20 μL pesticide solution is injected. The pesticides (*viz.* atrazine and simazine) concentration measurements are also crosschecked using UV–visible spectrophotometer at 226 nm. The total volume of pesticides solution taken is 5 L. The flow rate of the solution is 48 L/hr and the size of the membrane is 0.00152 m². The separation of NaCl (2.5 gm/L) is monitored from the conductivity relationship as it follows the linear corelation with the concentration.

The rejection (%) can be expressed by the general mathematical expression

$$R = (1 - C_p/C_r) \times 100$$

where R is the rejection in percentage, C_p and C_r are the concentration for permeate and the retentate, and the flux can be calculated from the relation:
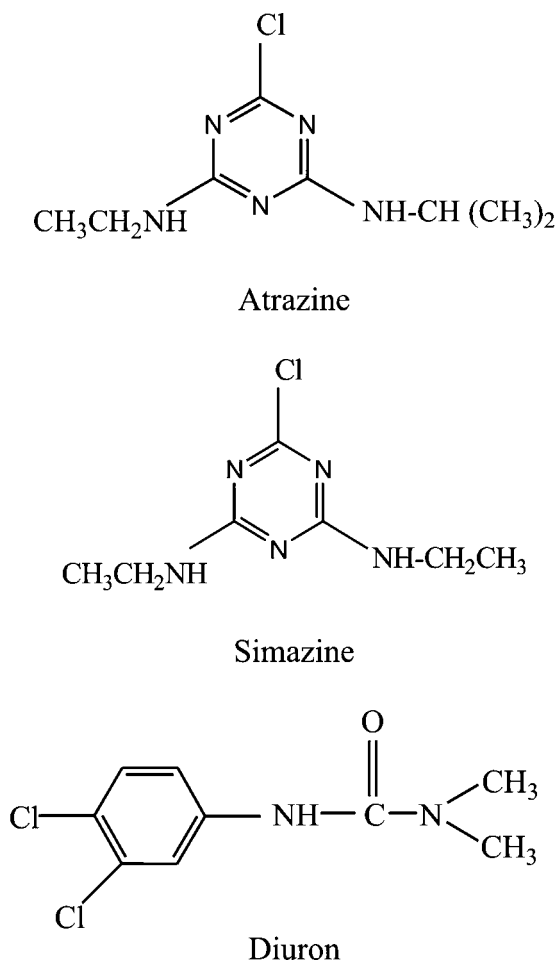
$$Flux = \frac{Volume\ of\ permeate\ (l)}{Time\ (day) \times Effective\ membrane\ area\ (m^2)}$$

RESULTS AND DISCUSSION

The performance of the membranes in terms of water flux can be corelated with the polysulfone concentration (Tables I and II). It has been observed that with the increase in polysulfone concentration (Table I), the water flux decreases. Higher concentration of polysulfone lowers the rate of diffusional exchange of solvent (DMF) and nonsolvent (water), and hence results in a dense matrix, which is reflected in the flux data. Moreover, the salt rejection order of the membranes follows the same trend that is, MA3 > MA2 > MA1, which indicates that MA3 is more responding in the preferential sorption of water[9] when compared with others, which reflects comparatively higher hydrophilicity of the same. In this case, low curing temperature facilitates the formation of loose network structure of polyamide and
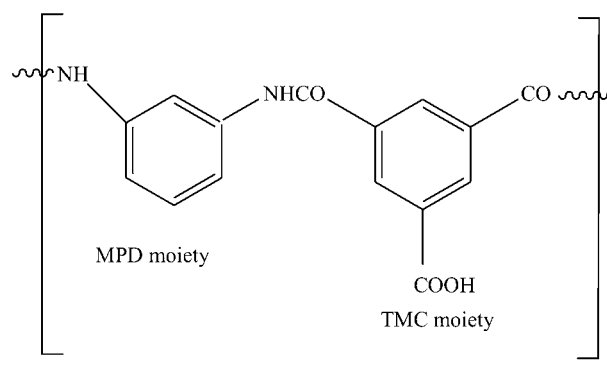
Figure 1 Chemical structure of polyamide, interfacially formed with the *m*-pheneylene diamine and trimesoyl chloride.

Cl

N N

CH$_3$CH$_2$NH   N   NH-CH (CH$_3$)$_2$

Atrazine

Cl

N N

CH$_3$CH$_2$NH   N   NH-CH$_2$CH$_3$

Simazine

O

Cl   NH-C-N   CH$_3$
                      CH$_3$

Cl

Diuron

Figure 2 Chemical structures of pesticides experimented.

may result in a comparatively higher content of unreacted —COOH (Fig. 1). In case of MA1, the low salt rejection is probably due to its denser base matrix (polysulfone) prohibiting the proper anchoring of the polyamide layer formed by the interfacial polymerization of TMC and MPD.

The chemical structures of the three pesticides are presented in Figure 2. Atrazine and simazine are similar in their respective heterocyclic structure, but the branched methyl groups in atrazine makes the difference. On the other hand, diuron is aromatic (homocyclic) with two chlorine groups attached to the benzene ring.

Pesticides removal can be explained by size exclusion or diffusion controlled mechanisms. Size exclusion mechanism dominates for the large molecules. Molecular charge, van der Waal's forces, or other surface interactions also act when the molecule is in size range to the pores. In this case, diffusion control may dominate. If the solute is so small that no significant interaction will occur with the membrane surface, then convection will dominate and no rejection will occur.[15]

The experimental results for the pesticides removal by the membrane are shown in Table II. The chromatograms of feed and permeate solutions of diuron, passing through all the three membranes are presented in Figure 3. As the molecular size is the descriptive factor to size exclusion by the membrane, it is logical to corelate the molecular size with the molecular weight. The removal performance of the three pesticides is according to the order diuron > atrazine > simazine for the membrane MA1, whereas for the membrane MA3, a 13.2% rejection difference is observed between diuron and simazine. The membrane MA2 retains the same rejection for all the three pesticides. The highest rejection of diuron with respect to atrazine and simazine is not observed in earlier cases.[15,17] As mentioned earlier, the removal of pesticides is dependent on the nature of the pesticides as well as membrane. There are several parameters like molecular weight, molecular width, dipole moment, and partition coefficient, etc, which coherently and solely controls the performances, may act in synergy or in opposition. Chen
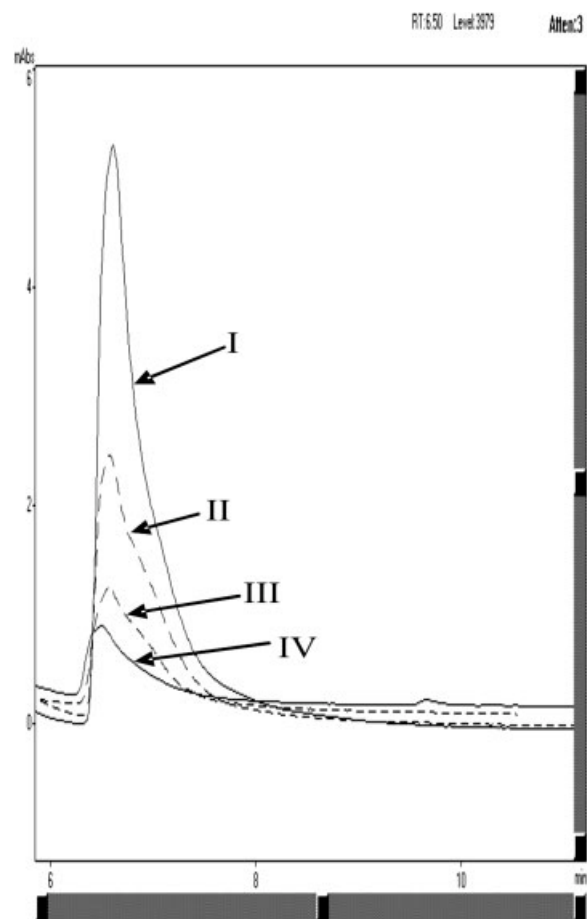
Figure 3 Chromatograms of feed/permeate solutions of diuron passing through three membranes (I-feed, II, III, and IV permeate through MA1, MA2, and MA3 respectively).

et al.[15] and Vander Bruggen et al.[17] justified their observations of comparatively low rejection of diuron in terms of dipole moment. In our case, the observation is quite different and it can be explained in terms of log P (*n*-octanol/water partition coefficient), which is a better descriptor. Kiso et al.[16] also justified the high rejection of chloropyrifos in terms of log P among other factors.

The log P is defined as log $P = \log (C_o/C_w)$, where C_o and C_w are the concentrations of solute in *n*-octanol and water layers.[11] The log P value of diuron is the highest among the three pesticides used in this experiment.[19,25]

The higher value of log P of diuron reflects the hydrophobicity of the same. It indicates that the diuron prefers the organic phase rather than the aqueous one. Hence it tends to keep away from the membrane, which is hydrophilic while in operation. It results higher concentration of diuron in feed, that is, higher rejection.

It is also observed that the removal of pesticides is remarkably corelated with the salt rejection property of the membranes. It shows (Tables II and III) that with the decrease in desalting property, the rejection ability of pesticides also decreases. For MA3 membrane, the rejection is the maximum and for MA1 membrane, it is of the minimum. The order is same for all the three pesticides.

CONCLUSIONS

In this study, we examined the rejection properties of pesticides with the low-pressure thin film composite polyamide membranes. Moreover, the rejection properties of NaCl were also examined. The obtained results are summarized as follows:

1. The NaCl rejection order for the polyamide membranes is MA3 > MA2 > MA1.

2. As the molecular sieving controls it, the molecular weight is the descriptor for this effect. For the membranes MA1 and MA3, the rejection of pesticides is following the order $R_{diuron} > R_{simazine} \approx R_{atrazine}$.

3. The removal performance of pesticides is of similar trend as salt rejection.

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