

Studies on the Separation Performances of Chlorophenol Compounds from Water by Thin Film Composite Membranes

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Abstract: The pressure driven membrane process has been a breakthrough in the removal of pollutants from drinking water. These experiments examined the removal of chlorophenol compounds from water using low pressure membranes. The removal performance of the membranes was based primarily on size exclusion. Apart from size exclusion, the polarity and pKa of the compounds also influences the membrane performance. The molecular size and dipole moments of the respective molecules were calculated using a quantum chemical method. The rejection of pollutants also followed the same trend as salt rejection by the membranes.

Keywords: rejection, phenol compounds, polarity, molecular weight, molecular volume.

Introduction

To meet the increasing demand of consumers regarding the new food products, pharmaceuticals, chemicals different phenol compounds are used in significant quantities throughout the world. They are also favored in industry for production of resins, plastics, disinfectants, paints, antioxidants, perfumes.¹ But, they are considered harmful ecotoxins and possess carcinogenic, cytotoxic and teratogenic properties.² They have the ability to disorder the enzyme activity and cell metabolism. As water is one of the paths that often facilitate wandering, living organisms are affected through it.³ In the present study, our attention is focused on remediation of chloro-phenol toxicity from water. Usually the removal of the phenol compounds in water production chains is performed through activated carbon, ozone or ozone and hydrogen peroxide. But these techniques suffer with their limitations. Competitive adsorption and filtration results the saturation of carbon filters rapidly and it needs regular replacement. Ozone, the significant air pollutant is explosive, toxic and an irritant to the skin, eyes, respiratory tract and mucous membrane. Moreover, it must be generated and immediately applied at the treatment location.^{4,5} Hydrogen peroxide is an irritant, can cause chemical burns, and is an explosive hazard.⁶ Ultraviolet light can burn unprotected skin and the mercury in UV lamps can damage the central nervous system, along with inflaming the nose and throat area.

On the other hand, membrane separation process has become increasingly popular due to its low cost and environment friendly nature. Traditionally, high pressure membranes used in reverse osmosis resulted in a considerable energy cost. As a result, the low pressure reverse osmosis membranes are attractive in recent years. Membranes with lower rejections of dissolved components, but with higher water permeability would be a great improvement for separation technology. Few reports are there in the literature in the context.⁷⁻⁹ The limitation of the reports is that there is no chemistry linked with the performance data, as the composition of the membrane is really not disclosed for those commercial membranes. Here, in the present investigation, performances of thin film composite membranes in the removal of phenol and chloro-phenol compounds from water are studied. The performances in salt rejection of the membranes and their abilities to remediate the chloro-phenol compounds from water with the co-relation of their structures, polarities and pKa values are drawn. The rejection of two isomers having different polarities is also shown in the study.

Experimental

Materials and Instruments. Polysulfone (Udel, P-3500, Solvay Advanced Polymers, USA), dimethyl formamide (Merck, India), sodium lauryl sulfate were used to prepare the asymmetric membrane. *m*-Phenylene diamine (Lancaster, U.S.A), trimesoyl chloride (Lancaster, U.S.A), was used for interfacial polymerization. Pentachlorophenol

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(National Chemicals, India), phenol (Ranbaxy, India) were used for the performance test of the membranes. All other phenols were procured from S. D. fine chemicals, India.

Laboratory made pressure cell was used for testing permeability of the solution. Salt rejection measurement was done on the basis of conductivity data by using conductivity meters. The experimental set up used for the treating the solution was sketched in elsewhere.¹⁰ The permeability was monitored at 1.4 MPa. HPLC (Shimadzu, LC-10 A) analysis was done to measure the concentrations of the phenol organics. The topograph of all the membranes were carried by scanning electron microscope (Philips XL30 ESEM TMP).

Methods. The following two-step process was used in this investigation to prepare polysulfone-polyamide composite membranes.

Preparation of Asymmetric Polysulfone Membrane:

The polysulfone membranes were prepared on the non-woven polyester fabric (1 m width) by wet phase inversion technique using a proto-type casting machine. The polymeric solution, (of 14% and 15% in dimethyl formamide) casted on the non-woven polyester fabric and was dipped into the non-solvent bath (here water). Diffusion exchange of *N,N*-dimethyl formamide solvent from the interstices of polysulfone aggregates by the non-solvent water was taking place during the phase inversion.¹¹⁻¹⁴ The dense polymeric selective layer formed over the relatively more porous substrate of polysulfone. Typically the dense selective layer was quite thin to provide high flux. The porous support layer of polysulfone has a gradient in pore size from small to larger with increasing depth from membrane surface. 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 were prepared by the interfacial polymerization of *m*-phenylene diamine and trimesoyl chloride (TMC) on the surface of the prepared polysulfone membranes. The polysulfone membrane was coated with 2 wt% *m*-phenylene diamine solution of water, the excess amount of the *m*-phenylene diamine solution remained on its surface was removed and immersed into a 0.1 wt% TMC solution (in hexane) for the interfacial polymerization, after which it was cured at temperature 70-85 °C. The interfacial polymerization took place in the hexane (organic phase). Reaction did not take place in the aqueous phase, because a highly unfavorable partition coefficient for acid chloride limits its availability in the aqueous phase.¹⁵ Thus the polyamide film formed on the organic solvent side. The reaction between *m*-phenylene diamine and trimesoyl chloride formed -CONH- bond and results cross-linked polyamide structure on polysulfone. The preparation conditions of all the four membranes are shown in Table I.

Preparation of Phenol Solutions: Different phenol solu-

Table I. Preparation Conditions of the Membranes

	Polysulfone in DMF (% wt/wt)	Conditions
Memb I	15	Coating temp: 15 °C RH%: 90, curing temp : 70 °C
Memb II	15	Coating temp: 15 °C RH%: 85, curing temp : 83 °C
Memb III	15	Coating temp: 18 °C RH%: 85, curing temp : 82 °C
Memb IV	14	Coating temp: 16 °C RH%: 89, curing temp : 80 °C

tions were prepared in aqueous solutions (50 mg/L), 100 mg/L and 150 mg/L). Due to low solubility, solutions could not be prepared above 50 mg/L for the 2,4,6-trichlorophenol and pentachlorophenols.

Analysis: The phenol concentrations were analysed with high performance liquid chromatography (HPLC) using the direct injection method under the following conditions: Column: Nucleosil C 18 (Supelco) 250 mm × 4.6 mm × 5 μm, mobile phase acetonitrile/water (Rankem) (80:20) (containing 0.1% trifluoro acetic acid), flow = 1.0 mL/min, UV/Vis detector ($\lambda_{max} = 280$ nm).

The separation of NaCl and Na₂SO₄ (1 gm/L) was monitored from the conductivity relationship, as it follows the linear co-relation with the concentration.

The rejection (%) was calculated by the general mathematical expression

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

where R is the rejection in percentage, C_p and C_f are the concentration for permeate and the retentate.

For the strong electrolyte C_p and C_f is correlated with the conductivity relationship and the flux was calculated from the relation:

$$Flux = \frac{l}{t \times A}$$

Where l indicates the volume of permeate in liter, t in hours and A is effective membrane area (m²).

The concentrations for the phenol compounds in water were monitored from the HPLC technique.

Results and Discussion

It is observed from Table II, that the NaCl rejections order: Memb-I > Memb-II > Memb-III > Memb-IV. The salt rejection property develops in these membranes because of residual charge of the unreacted -COOH groups from the hydrolyzed trimesoyl chloride.⁷ The low curing temperature probably favors comparatively more content of -COOH group in the polyamide in case of Memb-I. In case of Memb-III,

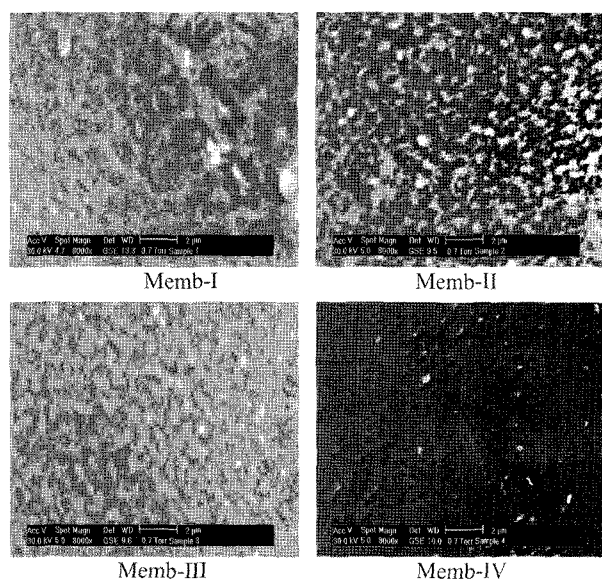


Figure 1. Scanning electron micrograph of all the membranes membrane I, II, III and IV.

coating temperature probably influences the property of the membrane (Table I). The scanning electron micrograph of the membranes (Figure 1) shows more or less similar pattern except for the Memb-IV. The micrographs show the pattern of formation of crosslinked polyamide on the polysulfone. The low curing temperature (for Memb-I) favors loose network compared to Memb-II and III. The difference in Memb-IV is probably because of the difference in base matrix (Polysulfone) which is of 14%. The rejection difference of Na_2SO_4 and NaCl , indicates that the membranes have the selectivity of rejection of bivalent ion with respect to monovalent. Different transport mechanisms are

there to explain the removal of electrolytes from the aqueous solution.¹⁶ Memb-IV is the most permeable membrane (observed from PWP and solution flux) among the four membranes.

The performances in removal of phenol compounds of all the four membranes are enlisted in Table III. There is a low rejection for all the phenol compounds in Memb-IV. The water permeability and the salt rejection data suggest that Memb-IV is not the appropriate for the separation of phenol compounds. The different influencing factors regarding the removal of phenol organics are described below.

Influence of Molecular Weight/Molecular Size of the Solutes. Figure 2 shows the variation of the rejection performances on the molecular weight. There is a positive correlation between rejection and the molecular weight of the phenol compounds. As the molecular weight of the dissolved solute phenol compounds increases, removal percentage through the membrane is higher. Pentachloro phenol is of being highest molecular weight (266.5) of all the phenol compounds used in the experiment, the rejection is high. The trend is followed for all the three Memb-I to III. For the different concentrations (100 ppm and 150 ppm) the trend is as similar like Figure 2 for the phenol compounds excluding pentachloro and 2,4,6-trichlorophenols, as both of the phenol compounds have the solubility problem beyond 50 ppm. The rejection difference of the isomers (2, 4/2,6-dichlorophenol) (2-chloro/4-chlorophenols) could not be explained from the molecular weight point of view.

Though generally molecular weight is the indirect parameter to get the idea of size of the solutes, molecular size is the better descriptive factor regarding the size exclusion by the membrane. A steric effect considered to be one of the prime factors, the determination of size of all the molecules is important. The molecular volume and the dipole moment

Table II. Performance Data of All the Four Membranes for NaCl and Na_2SO_4

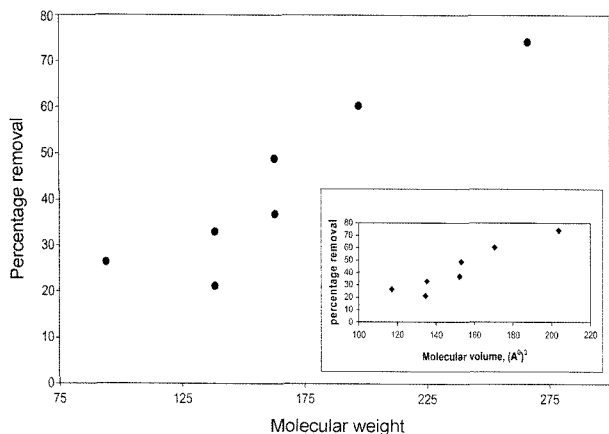
	PWP ($\text{l m}^{-2}\text{h}^{-1}$)	NaCl , 1,000 ppm (% R) (flux) ($\text{l m}^{-2}\text{h}^{-1}$)	Na_2SO_4 , 1,000 ppm (% R) (flux) ($\text{l m}^{-2}\text{h}^{-1}$)
Memb-I	592.2	77.3 631.7	82.2 710.6
Memb-II	750.1	56.75 671.1	77.4 710.6
Memb-III	671.1	43.24 437.7	60.74 434.3
Memb-IV	3947.9	5.55 2881.9	14.81 3316.2

Table III. Performance Data of Different Membranes for the Phenol Compounds (50 ppm)

	Pentachloro-phenol % R (flux, $\text{l m}^{-2}\text{h}^{-1}$)	2,4,6-Trichloro-phenol % R (flux, $\text{l m}^{-2}\text{h}^{-1}$)	2,6-Dichloro-phenol % R (flux, $\text{l m}^{-2}\text{h}^{-1}$)	2,4-Dichloro-phenol % R (flux, $\text{l m}^{-2}\text{h}^{-1}$)	2-Chloro-phenol % R (flux, $\text{l m}^{-2}\text{h}^{-1}$)	4-Chloro-phenol % R (flux, $\text{l m}^{-2}\text{h}^{-1}$)	Phenol % R (flux, $\text{l m}^{-2}\text{h}^{-1}$)
Memb-I	74.18 (710.6)	60.34 (789.6)	48.88 (868.6)	36.88 (809.3)	33.03 (552.7)	21.21 (592.2)	26.42 (592.2)
Memb-II	64.16 (532.9)	52.90 (513.2)	43.92 (908.0)	27.36 (671.2)	27.62 (651.4)	19.63 (532.9)	23.29 (552.7)
Memb-III	58.5 (710.6)	41.64 (789.6)	38.58 (572.5)	32.59 (611.9)	21.59 (552.7)	16.95 (513.2)	20.42 (592.2)
Memb-IV	15.28 (1895.0)	12.17 (2092.4)	13.22 (1934.5)	13.94 (2625.4)	8.32 (1776.6)	2.45 (1677.9)	- (2250.4)

Table IV. Volume and Dipole-moment Results of Phenol Molecules Calculated at Semi-empirical AM1 (A Quantum Chemical Method)

	Pentachloro-phenol	2,4,6-Tri-chlorophenol	2,4-Di-chlorophenol	2,6-Dichloro-phenol	4-Chloro-phenol	2-Chloro-phenol	Phenol
Mol. Wt.	266.5	197.5	163.0	163.0	138.5	138.5	94
Volume, (Å ³)	203.7	170.3	153.0	152.24	135.2	134.5	117.1
Dipole moment, <i>D</i>	1.242	1.072	2.164	1.772	1.477	0.938	1.233
pKa	4.7	7.38	7.87	6.86	9.40	8.48	9.92

**Figure 2.** Variation of removal percentage with the molecular weight of the phenol compounds (inset: with the molecular volume).

have been calculated at semi-empirical AM1 method for the systems shown in (Table IV).^{17,18} To calculate the volume and the dipole moment of these molecules, first the stable conformers have been predicted at AM1 level of theory. AM1 is a semi-empirical Self-consistent Field (SCF) method extensively used in theoretical studies of molecular structure, in which multi-center integrals J_{ij} and K_{ij} are neglected or parameterized, and only valence shell electrons are considered. The Hamiltonian operator takes the form

$$\hat{H}_{val} = \sum_{i=1}^{N_v} \left(-\frac{1}{2} \nabla_i^2 + V(i) \right) + \sum_{i=1}^{N_v-1} \sum_{j=i+1}^{N_v} \frac{1}{r_{ij}}$$

$$= \sum_{i=1}^{N_v} \hat{H}_{val}^{core}(i) + \sum_{i=1}^{N_v-1} \sum_{j=i+1}^{N_v} \frac{1}{r_{ij}}$$

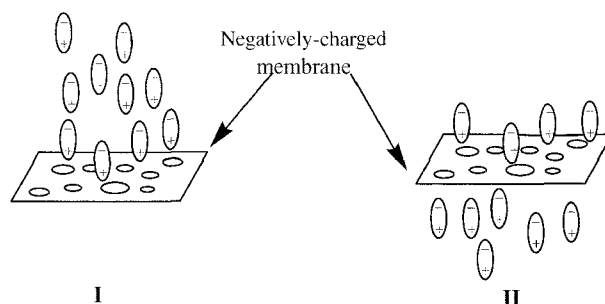
where N_v is the total number of valence electrons in the molecule, $V(i)$ is the potential energy of the i^{th} electron in the field of nuclei and inner-shell electrons. This SCF method neglects the repulsive orthogonalization corrections and the attractive penetration integrals of the one-center core Hamiltonian matrix elements. Semi-empirical methods like AM1 are accurate enough to have useful predictive powers, yet fast enough to allow large systems to be studied.^{19,20}

The rejection data of the membranes and molecular vol-

ume correlation are figured in the inset of Figure 2. The rejection order follows, as molecular volume increase and it is of same trend as molecular weight except in some cases. The anomaly can be explained by considering the polarity of the molecules.

Influence of Polarity of the Solute Molecules. It is usually accepted that the rejection of uncharged (organic molecules) is determined by the size of the feed solutes compared to the size of the membrane pores (considering the pore controlled performance of the membranes). Other physico-chemical effects such as polarity effect also influence the rejection. Since all the membranes are of negative charge due to the residual -COOH group in the polyamide, the permeation of the polar molecules is favored. For the polar molecules, it is due to electrostatic attraction, the dipole is directed towards the membrane charge in such a way that the side of the dipole with the opposite charge is closer to the membrane. This direction is not static, but as a statistical tendency of the fast moving molecules to have this preferential orientation.^{21,22} The dipole is thus directed towards the pores of the membrane and enters more easily into the membrane structure. Because entry into membrane structure is thus facilitated, a higher fraction of polar molecule permeates through the membrane, compared to molecules having relatively low polarity with the same size, thus leading to a lower retention of a polar molecule (Figure 3).

The rejection difference of 2,4 and 2,6-dichlorophenols can be explained by considering the polarity of the mole-

**Figure 3.** Schematic presentation of permeation of polar compounds through charged membrane. **I.** Direction of polar pesticides to the membrane. **II.** Permeation through the charged membrane.

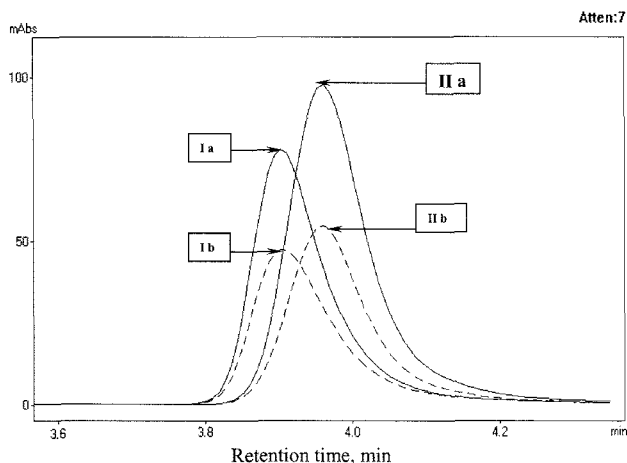


Figure 4. Chromatograms for 2,4-dichlorophenol (I) and 2,6-dichlorophenol (II). (a) and (b) designate for feed and permeate for the Memb-II.

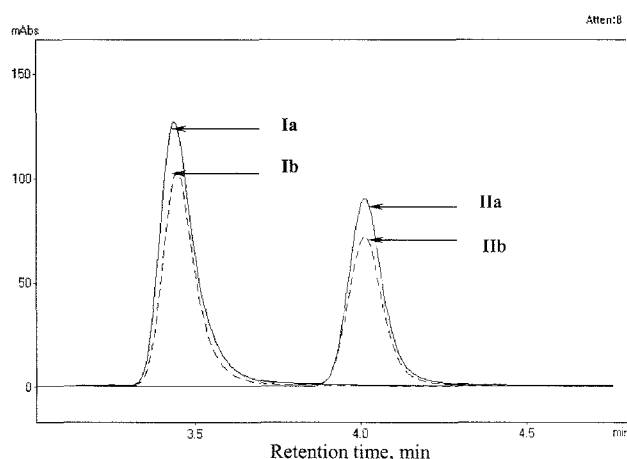


Figure 5. Chromatograms for 4-chlorophenol (I) and 2-chlorophenol (II). (a) and (b) designate for feed and permeate for the Memb-II.

cules. The polarity of the phenol molecules are listed in Table IV. Being the dipole moment is higher for the 2,4-dichloro, the molecule will pass through preferably than 2,6-dichlorophenol. The chromatograms of the corresponding isomers are shown in Figure 4. The lower rejection of 4-chlorophenol with respect to 2-chlorophenol can also be explained in same manner and chromatograms are displayed in Figure 5. Since the dipole moment of 4-chlorophenol is higher, the molecules can pass through the membrane easily.

During the calculation of the dipole moment, the possibility of intramolecular hydrogen bonding between the OH group and the chlorine atom in 2-chlorophenol has been examined. The calculated results indicate that the H-bonded conformation (I) is stable compared to the non H-bonded form (II) (Figure 6). Therefore, the molecular volume and the dipole moment for H-bonded systems have been calculated using the conformation (I). However, the situation is

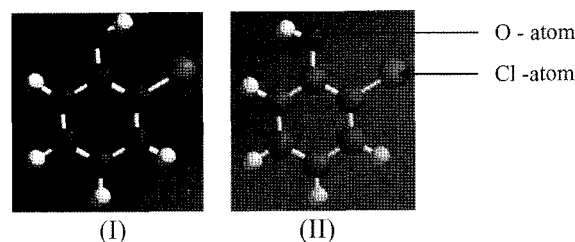


Figure 6. Different conformations of 2-chlorophenol (I) hydrogen bonded conformation and (II) non-hydrogen bonded conformation.

slightly different for 2,4-dichlorophenol. The AM1 computed results suggest that the non H-bonded form (II) is more stable in the aqueous phase.²³ Therefore, in the case of 2,4-dichlorophenol, the molecular volume and the dipole moment have been calculated with the non H-bonded form.

Influence of pKa of the Chlorophenol Compounds.

When hydrogen of the -OH group in the chlorophenol compounds becomes more electron deficient, the -OH group starts to dissociate. The more highly dissociated the phenol, the more highly rejected by the membranes. It can be better interpreted from the pKa values of the chlorophenol compounds (Table III).²⁴⁻²⁶ Lower the pKa value, greater will be the rejection capabilities. Comparing the pKa values of 2,4-dichloro and 2,6-dichlorophenol, the later shows more rejection ability as its dissociation is more. The same situation also occurs for 2 and 4-chlorophenol (i.e. $R_{2\text{-chlorophenol}} > R_{4\text{-chlorophenol}}$).

Influence of Salt Rejection Property of the Membranes.

Four different membranes depending upon their salt rejection ability are used to correlate the performances of the removal of phenol compounds. It is shown that the removal performances of compounds follow the same order of all the four membranes, as the salt rejection. Thus, the removal of phenol compounds follows the order Memb I > Memb II > Memb III > Memb IV.

Conclusions

In this study, the rejection properties of phenol compounds with the low-pressure thin film composite polyamide membranes are examined. Moreover, the rejection properties of NaCl and Na₂SO₄ are also examined. The obtained results are summarized as follows:

1. The removal performance of the phenolics is mostly follows based on size exclusion.
2. The removal performance is also follows on the polarity of the molecules especially for the isomers (2- and 4-chlorophenol and 2,4 and 2,6-dichlorophenol). The molecules having relatively low polarity are of high rejection by the membranes.
3. The separation efficiency of isomers is also explained from their pka values ($R_{2,6\text{-dichlorophenol}} > R_{2,4\text{-dichlorophenol}}$) ($R_{2\text{-chloro}}$

$^{phenol} > R_{4-chlorophenol}$).

4. The NaCl salt rejection order of the membranes is Memb I > Memb II > Memb III > Memb IV. All the membranes are following the rejection trend $Na_2SO_4 > NaCl$.

5. The removal performance of phenol compounds is also of same trend as salt rejection.

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