Membrane Water Treatment, Vol. 2, No. 3 (2011) 137-145
DOI: http://dx.doi.org/10.12989/mwt.2011.2.3.137

Surfactant enhanced filtration performances of mono-chlorophenol isomers through low-pressure membrane

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(Received November 19, 2010, Accepted June 03, 2011)

Abstract. Membrane processes are major breakthrough for the removal of organic pollutants in water remediation. The separations of solutes depend on nature of the membranes and solutes. The separation performance depends on the nature of the solutes (*i.e.*, molecular volume, polarity, and hydrophobicity) for the same membrane. As 4-chlorophenol is of more dipolemoment compared to 2-chlorophenol, the orientation of the molecule enables it pass through the pores of the membrane, which is of negatively charged and thus separation order follows: 2-chlorophenol > 4-chlorophenol. Hydrophobicity factor also supports the order. Addition of sodium dodecyl sulfate (SDS) to chlorophenol solution shows remarkable increase in separation performance of the membrane. The improvement in separation is 1.8 and 1.5 times for 4- and 2- chlorophenol consecutively in case of 0.0082 M SDS (1cmc = 0.0082 M) in the solution. 4-chlorophenol has better attachment tendency with SDS because of its relatively more hydrophobic nature and thus reflects in performance *i.e.* the separation performance of 4-chlorophenol with SDS through the membrane is better compared to 2-chlorophenol.

Keywords: thin film composite; membrane; surfactant; chlorophenol; hydrophobicity

1. Introduction

To resolve the issue of insufficient water for sustainable development, separation processes play an increasingly significant role as the dominant technology in water purification. Wastewater is a potential water source if its quality after treatment satisfies the criteria for reuse. Different potential techniques to treat wastewater (viz. active carbon filtration, ozone treatment, membrane filtration) are reported in the literature (Bhattacharya 2006, Heijman and Hopman 1990, LaGrega *et al*. 1994, Martin-Gullanet and Font 2001).

Membrane processes also have the good potential compared to other conventional methods to reuse the wastewater. The membrane processes are simple, easy to operate and no requirement for a change of phase or state of the solvent (Bhattacharya and Mishra 2004). The key advantages of membrane filtration are – requirement of minimum use of chemicals, produce a purified effluent that can be reused, while the waste stream that requires disposal is concentrated and reduced in volume (Belhateche 1995). The membrane processes are energy intensive processes.

Among membrane processes nanofiltration/ reverse osmosis are the potential techniques to remove small organic compounds from its aqueous solutions. Although steric hindrance, charge are the main control parameters in terms of the separation performances of the membranes, the nature of the solutes

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(viz. hydrophobicity, pKa, polarity) has the key roles also (Arsuaga *et al*. 2006, 2010) (Bhattacharya 2005) (Nghiem and Schafer 2005). The positive combining effects increase the performances where as counter effects result poor performances of the membranes. Scientists have reported qualitative assessment of the rejection of dissolved organic compounds depending upon the nature of membranes and organics (Bellona *et al*. 2004) (Vander Bruggen *et al*. 2006).

To make it more attractive and energy saving, the water-soluble surfactants deserve special attention. Surfactants have the ability to form aggregates itself as well as with the hydrophobic solutes present in water. Dissolved organics tend to be soluble in micelle and usually more hydrophobic the pollutant is, the more it can be dissolved in the surfactant aggregates (Bielska and Szymanowski 2004). Addition of surfactants makes the solute molecules bigger on interaction and thus sieving effect is more effective. Moreover, the adsorption of surfactants results the charged moiety on the membranes, thus it is very helpful in separation of polar organics. History of surfactant based separation has started by Scamehorn et al in 1980's for the remoal of Cu(II) ions from the waste water (Scamehorn and Harwell 1989). Researchers investigate the removal of inorganic pollutants such as metal ions and nutrients such as nitrate and phosphate by this technique (Baek *et al*. 2003, 2004), (Montel *et al*. 1991). Removals of heavy metal ions by micelle enhanced ultrafiltration are extensively studied (Li *et al*. 2004, 2006) (Tung *et al*. 2002). To remediate the water pollutants in terms of some phenolic derivatives, there is the evidence of surfactant addition in feed water (Syamal *et al*. 1995) (Purukait *et al*. 2005a, 2005b) (Yogesh *et al*. 2008) (Yogesh *et al*. 2009).

The use of phenol compounds are in significant quantities through out the world in different usage viz. pharmaceuticals, resins, plastics, disinfectants, paints, antioxidants, perfumes. There is a concern that phenols are harmful ecotoxins and possess carcinogenic, cytotoxic and teratogenic properties (Bukasowska and Kowalska 2003). Living organisms are affected through it (Genononi 1997) as water is one of the paths that often facilitate wandering.

In the present study, our attention is focused on comparative remediation of chloro-phenol (2-chloro and 4-chloro) toxicity from water through membranes. The effect of addition of sodium dodecyl sulfate (anionic surfactant) in the separation performances of chlorophenol through membranes is studied. Moreover, we have carried out the study through laboratory-based polyamide thin film composite membranes. The low pressure driven filtration technique is employed in the particular experiment to show the variation of separation performances of isomers as well as with the addition of SDS.

2. Materials and methods

Polysulfone (Udel, P 3500, Solvey Advanced polymers, USA), Nonwoven polyester fabric was taken for the asymmetric membrane preparation. m-phenylene diamine and trimesoyl chloride (Lancaster) were used to prepare thin film composite membrane. 2-chlorophenol, 4-chlorophenol, Glucose (Glaxo, India), Sodium chloride (Qualigen, India), Magnesium sulfate (Qualigen, India), Sodium dodecyl sulfate (SD fine, India) was used as feed for the experiment. Hexane, Dimethyl formamide (Merck, India) was used as solvents.

Cross-flow filtration mode was used for testing the performance of the membranes. Salt rejection measurement was done based on the conductivity data by using conductivity meters (Eutech Instruments, CON 510 (conductivity-TDS meter, Singapore). The experimental set up used for the filtration mode is sketched in Fig. 1. It was based on four pressure cells, connected in series where membranes were fixed. The pressure was applied and feed passed parallel to the membrane. The

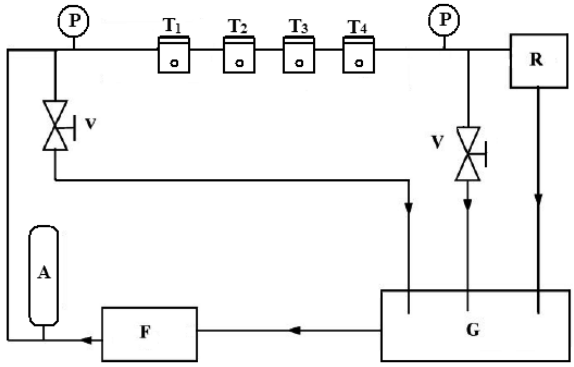


Fig. 1 Schematic diagram of cross-flow filtration mode (P, pressure gauze, T_1, T_2, T_3, T_4, pressure test cell; R, back pressure regulator, V, by pass valve, A, pressure accumulator, F, pump, G, feed solution tank).

recyclability of feed stream is also there in the mode. The permeability was monitored at 1.03 MPa after 1 h. HPLC (waters Alliance model coupled with 2996PDA detector) was used to measure the concentrations of chlorphenol solution. For glucose analysis Waters Alliance model with waters 2414 refractive index detector, was used.

2.1 Preparation of thin film composite membrane

Polysulfone (PS) solution (14% w/v) was prepared in dimethyl formamide solution. The PS membrane casting was done on non-woven polyester fabric in a prototype-casting machine. Diffusion exchange of dimethyl formamide from the interstices of polysulfone aggregates by non-solvent water was taking place during phase inversion. In this phase inversion technique, two phases were formed *i.e.* polymer rich and poor phase. Interfacial polymerization of m–phenylene diamine and trimesoyl chloride was done on PS membrane. The polymerization was occured at hexane-water interface. Curing (85^{o}C) of the polyamide formed from the two resulted cross-linked polyamide as well as thin film composite membranes. The details were described in our previous experiment (Yogesh *et al*. 2010).

2.2 Preparation of chlorophenol solutions

At first, an appropriate amount of methanol solution was taken to dissolve 5 mg/L chlorophenol and dissolved in to RO water (already passed through R.O module). The chlorophenol solutions were taken as feed solutions. Sodium dodecyl sulfate in appropriate amount to maintain the concentration (0.04cmc, 0.2cmc, 1cmc, and 2cmc) (cmc = 0.0082 M) (Musnicki *et al*. 2011) was added to 2.5l chlorophenol solution.

2.3 Analytical tools

The chlorophenol concentrations were analyzed with high performance liquid chromatography (HPLC) using the direct injection method under the following conditions Nucleosil C 18 column (Supelco) 4.6 mm × 25 cm × 5 µl, flow 1.0 ml/min, mobile phase acetonitrile/water 80:20 (containing 0.1% acetic acid), UV-Vis detector (λ_{max} = 280 nm).

The salt rejection (%) was measured by passing NaCl and $MgSO_4$ solution (1 mg/L) through membranes. The glucose estimation was done by liquid chromatography (HPLC) using the direct injection method under the following conditions: Supelco Gel 610-H Column 30 cm × 7.8 mm, mobile phase water contains 0.1% phosphoric acid, column flow 0.5ml/min. The surface tension of the feed as well as with surfactants at room temperature (25°C) was determined. The surface tension measurement was done by DCAT-21 (Dataphysics, Germany) using Wilhelmy Plate technique.

3. Results and discussion

The polysulfone solution is intolerant to water. (Stropmik *et al*. 1996) The diffusion exchange of dimethyl formamide (solvent) and water (nonsolvent) controls the phase inversion (*i.e*., solution to solid). Changes in the composition of polysulfone-dimethyl formamide-water system produced by mass transfer of a nonsolvent into a cast solution and of a solvent into the coagulation bath are the mechanisms of the membrane preparation. The steps can be described as solidification, nucleation and growth of polymer lean phase, spinodal demixing, nucleation and growth of the polymer rich phase. (Kim *et al*. 1997) Thus the heterogeneity in structure with the top thin dense layer and

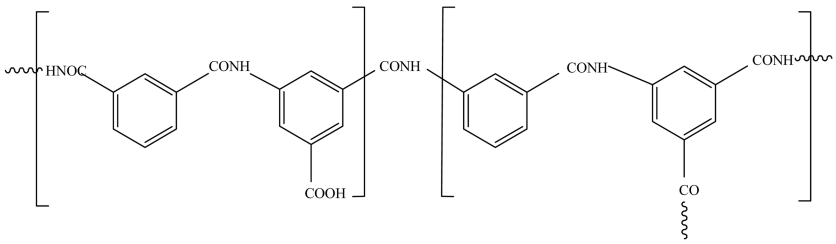


Fig. 2 Chemical structure of crosslinked polyamide from 1, 3 phenylene diamine and 1, 3, 5 trimesoyl chloride.

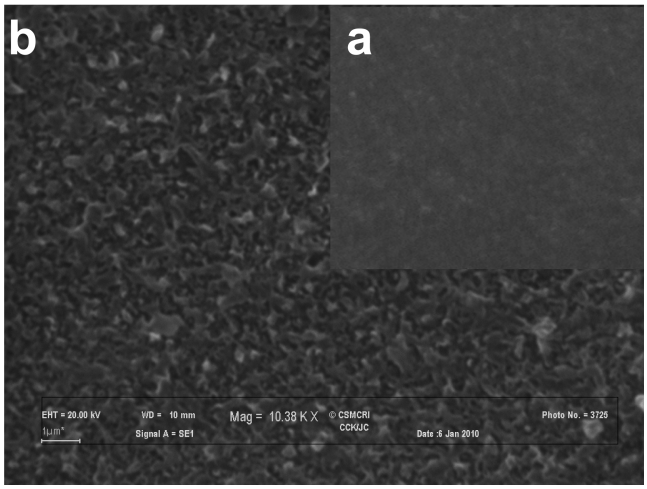


Fig. 3 Scanning electron Micrograph of thin film composite membrane (b) and Polysulfone membrane (a) (in the inset).

Table 1 Performances of membrane in terms of characterization

Membrane	Water flux ($lm^{-2}h^{-1}$)	NaCl %R Flux, ($lm^{-2}h^{-1}$)	$MgSO_4$ %R Flux, ($lm^{-2}h^{-1}$)	Glucose %R Flux, ($lm^{-2}h^{-1}$)
Thin film composite	60.7	28.8 75.1	34.5 69.5	21.3 56.6

macrovoids in the bottom layer is formed.

The interfacial polymerization of m-phenylene diamine and trimesoyl chloride occurs in hexane (organic phase) on the asymmetric polysulfone membrane. Actually reaction does not take place in aqueous phase, because a highly unfavorable partition coefficient for trimesoyl chloride limits its availability in the aqueous phase. (Morgan 1965) It occurs on the polymer rich (*i.e*., thin dense) phase of Polysulfone. The crosslinked polyamide forms through –COCl and $–NH_2$ groups of trimesoyl chloride and m-phenylene diamine respectively and depicted in Fig. 2. Fig. 3 shows the topography of the thin film composite membrane (b) show distinct feature compared to virgin PS membrane, which is presented in the inset (a) of the figure. The particular thin film composite membrane shows its features in terms of characterization and ensemble in Table 1.

The membrane separation process is primarily related to the molecular size of the solutes. (Bhattacharya *et al*. 2006) (Kiso *et al*, 2001) However, molecular weight is the indirect parameter to get the idea of size of the solutes, but for isomer, it is not the parameter to be considered. The separations of the organics depend on the conformation, hydrophobicity, and polarity of the molecules as the membrane pore sizes play the same for both the cases. The separation performance may be the collective influence of the parameters or the major parameters. For 2-chlorophenol and 4- chlorophenol isomer as molecular weight is same steric hindrance effects are same. The physical parameters related to performance are listed in Table 2. The molecular volume and dipole moments are calculated at semiempirical AM1 method for the systems. The detail of the method is described in our earlier experiment (Yogesh *et al*. 2008). In this particular experiment, the polarity factor governs the separation performance. As described earlier, the membrane coating layer is the result of interfacial polymerization of m-phenylene diamine and trimesoyl chloride. The residual –COOH group in the crosslinked polymer results the negative charge in it. It controls the separation of the

Table 2 Chemical structure and physical parameters of 4-chlorophenol and 2-chlorophenols

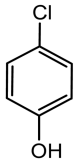
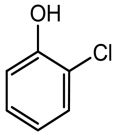
Molecule	Structure	Mol. weight	Volume A^o3	Dipolemoment, (D)	Hydrophobicity (log K_{ow})
4-chlorophenol		128.5	135.2	1.477	2.39
2-chlorophenol		128.5	134.5	0.938	2.15

Table 3 Separation performance of thin film composite membranes for 4-chlorophenol and 2-chlorophenols

Molecule	Volume flux ($lm^{-2}h^{-1}$)	Solute flux ($mMm^{-2}h^{-1}$)	Solute rejection (%)
4-chlorophenol	48.5	1.45	22.99
2-chlorophenol	47.4	1.18	35.93

polar organics. As 4-chlorophenol possesses higher dipolemoment compared to other isomer the dipole is better directed towards the membrane in such a way the side of the dipole with the opposite charge is closer to the membrane. Though direction is not static, but as a statistical tendency of the fast moving molecules to have this preferential orientation. (Bhattacharya 2005, Vander Bruggen *et al*. 1999) This dipole is thus directed towards the pores of the membrane and enters more easily into the membrane structure. Because entry is facilitated, a higher fraction of more polar 4-chlorophenol molecule permeates through the membrane, compared to 2-chlorophenol. Thus, it leads to a lower retention of a polar 4-chlorophenol compared to 2-chlorophenol (Table 3). The volume and solute flux also feature the same. The same phenomenon is also observed for glucose marker. However, glucose is of high molecular weight and molecular size (180 and 158.7 A^{o3} respectively) compared to monochlorophenol, because of the polarity factor (α-glucopyranose 1.99 D, calculated by AM1) the separation is lowered (21.3%) for the same membrane (Table 1). The isomer separation can also be explained by their difference in hydrophobicity. (Van der Bruggen *et al*. 2006) 4-chloro phenol is comparatively more hydrophobic and thus not hydrated and therefore smaller than hydrophilic components with the same molecular weight (2-chlorophenol). Thus 4-chloro phenol has lower hindrance and passes through.

As sodium dodecyl sulfate (SDS) shows its tendency to attach with the hydrophobic organic molecule, the effective size of the aggregated molecule increases. Thus, better separation of the organic pollutant has occurred. As the concentration of SDS increases, separation of chlorophenol through the membranes is also increased. The separation (percentage) of chlorophenols with SDS concentration is featured in Fig. 4. The concentration of SDS are presented in cmc (1 cmc = .0082 M).

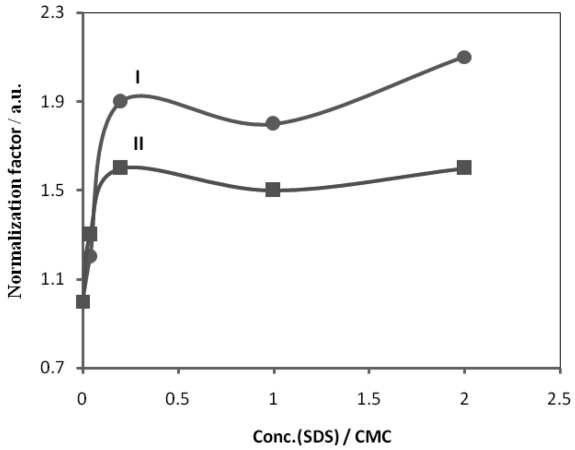


Fig. 4 Normalized rejection performance of thin film composite membrane with different SDS concentration (I: 4-chloro and II: 2-chlorophenol).

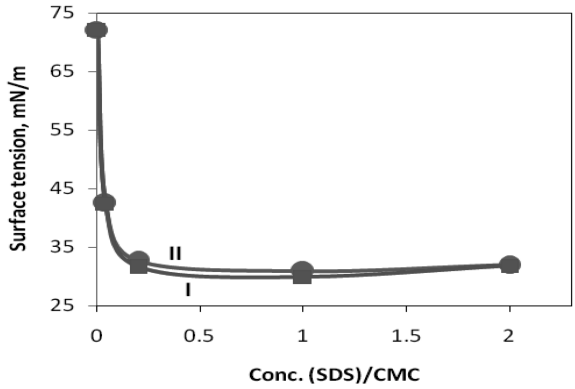


Fig. 5 Surface tension of water with different concentration of SDS (I: 4-chloro and II: 2-chlorophenol).

(Musnicki *et al*. 2011). The separation performances are normalized with respect to the value of separation percentage without SDS. The normalized values show the comparative feature of two chlorophenols. It shows the surfactant enhanced filtration is higher for 4-chlorophenol compared to 2-chlorophenol. The lipophilic tails of the SDS molecules have the tendency to away from the aqueous phase and thus it is of favorable interaction with the hydrophobic moiety. The more hydrophobic nature of 4-chloro phenol (log K_{ow} = 2.39) has better tendency to attach with the SDS compared to 2-chlorophenol (log K_{ow} = 2.15). (Aksu and Yener, 1998) The feature is reflected in the figure. Moreover, at cmc the rejection is little lower in both cases. It may be sometimes surfactant aggregates is favored without phenol moiety. Maximum deterioration of flux (>50%) is observed for the highest concentration of SDS. The decrease in surface tension of the feed solution with the concentration of SDS shows in the Fig. 5. SDS, being a surface active agent tends to adsorb at the interface. Thus it alters the interfacial free energy significantly and as a result significant reduction in the tension results. It shows both (4- and 2-chloro phenol) are similar in pattern. Presence of 4-chlorophenol with SDS results little lower surface tension values. This also supports the earlier fact.

4. Conclusions

In this study the separation performance of monochlorophenol with the low-pressure thin film, composite polyamide membranes are studied. Moreover, additions of SDS with the monochlorophenol are studied. The obtained results are as follows:

1. The separation performance of the monochlorophenol depends on the polarity factor. 2-chlorophenol having relatively low polarity is of high separation by the membranes.
2. Low hydrophobicity of 2-chloro phenol results better attachment of water molecules and effectively bigger molecule compared to 4-chlorophenol results. Thus 2-chloro phenol shows better separation.
3. Addition of sodium dodecyl sulfate (SDS) to chlorophenol solution shows remarkable increase in separation performance of the membranes.
4. The more hydrophobic nature of 4-chlorophenol has better attachment tendency to the SDS and thus reflects in separation performance. The separation performance of 4-chlorophenol with SDS through the membrane is better compared to 2-chlorophenol.

Acknowledgement

Acknowledgement to Ministry of Environment and Forests, India and CSIR, India

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