

# Pentachlorophenol removal from water using surfactant-enhanced filtration through low-pressure thin film composite membranes

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## Abstract

Removal of pentachlorophenol from water is investigated using the surfactant-enhanced cross-flow membrane filtration technique in which anionic surfactant; sodium dodecyl sulfate (SDS) is the carrier of pentachlorophenol. The separation performances are studied by varying SDS concentrations ( $\ll$ critical micelle concentration, CMC). The association between pentachlorophenol and SDS leads to increase their effective size of the feed solutes and thus results the improvement in separation performances of the membrane. The performance is co-related with the separation of markers (glucose and sucrose) as well as salt rejection of the membrane. SDS, in feed induces the charge due to its polar head and thus separation improves due to electrostatic repulsion of membrane and associated molecule. The higher hydrophobicity of pentachlorophenol is also the factor. The study reveals that there is better improvement in pentachlorophenol separation upon addition of SDS for the thin film composite membrane which is of more permeability.

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**Keywords:** Pentachlorophenol; Sodium dodecyl sulfate; Thin film composite membrane; Molecular volume

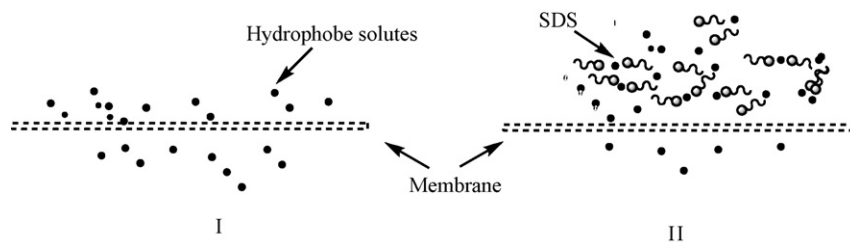
## 1. Introduction

With the success of liquid phase extraction technologies, visionary idea is there to use surfactants in the membrane filtration technique. They are mostly used in the micelle enhanced ultrafiltration technique [1–3]. The basic principle behind this is that the surfactants increase the size and solubilizing power of micellar aggregates (i.e. hydrophobic heads are within the cluster and hydrophilic ones are exposed to solvents) conveys the ability to better perform in the membrane filtration technique. Ordinarily, low molecular weight species ( $<300$  MW) are not removed by ultrafiltration technique. Thus, it is advantageous in terms of pressure requirement. In other words, it is energy saving process.

Pentachlorophenol (PCP) is one of the widespread environmental contaminants of soils, surface and ground water. PCP is probable carcinogen and has been placed on the pollutant priority list [4]. The main use of pentachlorophenol is as pesticides, disinfectant and as well as wood preservatives. With the recent emergence of pentachlorophenol contamination as an important drinking water quality issue, it is targeted to find the proper and useful method to remediate it. In the inspiring study of Baynes et al. [5] it is shown the retarding effect of surfactant addition to pentachlorophenol regarding the diffusive transport through skin. In the present study, the effect of sodium dodecyl sulfate (SDS) coupled with the membrane technology, to remediate the pentachlorophenol from water is exploited. The SDS concentration is employed below its CMC, i.e. concentration in which addition of further surfactants leads to micelle formation. Surface tension measurement is one of the potential techniques to determine it. The CMC is marked as that concentration of surfactants beyond which the surface tension value is not altered. The pictorial diagram of the surfactant-enhanced filtration is

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Scheme 1. Schematic illustration of the concept of surfactant-enhanced filtration: (I) without surfactant and (II) with surfactant.

presented in Scheme 1. In the present study, cross-flow filtration technique is preferred as it inhibits the fouling in better manner due to high shear force operates near the membrane surface. Moreover, the recycling of feed stream is occurred in this technique.

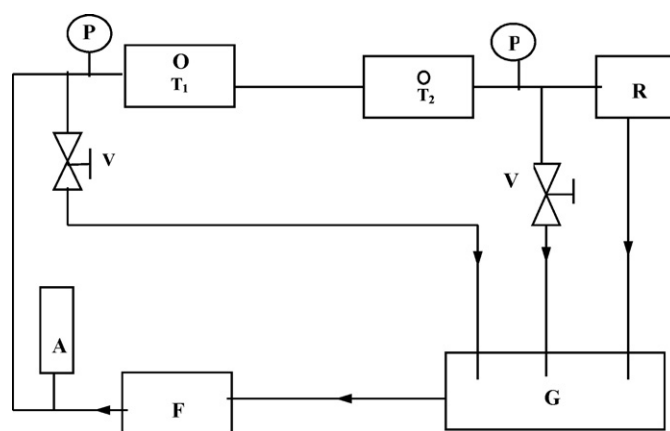
Two thin film composite membranes of different performance behavior in terms of salt rejection and markers (glucose and sucrose) separation were chosen during the study. The polyamide formation from *m*-phenylene diamine and trimesoyl chloride occurred on asymmetric polysulfone membrane and photo-curing was done to form the cross-linked polyamide. The objective of the study is to establish the SDS effect in the remediation of pentachlorophenol from water through these low-pressure photo-cured thin film composite membranes.

## 2. Experimental

### 2.1. Materials

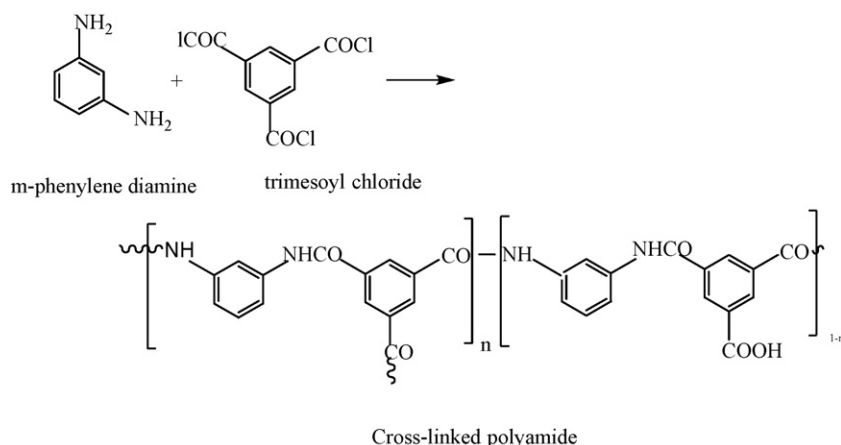
Polysulfone (Udel P-3500; Solvay advanced Polymers, USA), Dimethylformamide (DMF) (Qualigen, India), were used to prepare the asymmetric membrane. *m*-Phenylene diamine (Loba, India) and trimesoyl chloride (Lancaster, USA) were used for the preparation of thin film composite membranes. Pentachlorophenol (National Chemicals, India), sodium lauryl sulfate were used for the performance test of the membranes. Glucose and sucrose (Glaxo, India) were used as the marker of the membranes.

Cross-flow filtration technique is employed for testing the separation of organics through the membrane similar to our ear-



Scheme 2. Schematic diagram of testing unit for flat membrane (P, pressure gauge; T<sub>1</sub> and T<sub>2</sub>, pressure test cell; R, back pressure regulator; V, by pass valve; A, pressure accumulator; F, pump; G, feed solution tank).

lier experiment [6]. The flow rate of the solution is  $48 \text{ l h}^{-1}$  and the size of the membrane is  $0.00152 \text{ m}^2$ . The configuration of testing unit is depicted in Scheme 2. The permeability was monitored at 1.4 MPa. The pH of feed solution (pentachlorophenol) is 6.8. Permeate for the analysis is collected after 1 h. HPLC analysis was done to measure the concentrations of the pentachlorophenol and the carbohydrates (glucose and sucrose). The salt rejection performance was tested by using NaCl solution (2000 mg/l). Considering conductivity shows direct relationship with the sodium chloride concentration, conductivity meter was used to monitor the concentration of NaCl solution and salt rejection performances of the membranes.



Scheme 3. Interfacial polymerization of *m*-phenylene diamine and trimesoyl chloride.

Table 1  
Preparation conditions of membranes

Membrane	Polysulfone (wt.% in DMF)	Preparation conditions
Memb-I	15	Dipping time (in MPD): 7 min, drying time 7 min, dipping time (in TMC) 5 min. Photo-curing time 15 min
Memb-II	16	

## 2.2. Methods

Asymmetric polysulfone membranes were prepared by casting the polymeric solution (in dimethyl formamide) on the non-woven polyester fabric (1 m width) by phase inversion technique [7] using a proto-type casting machine and were dipped into the water (non-solvent for polysulfone).

Interfacial polymerization of *m*-phenylene diamine (2% in water) and trimesoyl chloride (TMC) (0.1% in hexane) was done on the surface of the prepared polysulfone membranes (16 cm × 13 cm) fitted on glass tray. The reaction is depicted in Scheme 3. The environmentally benign photo-curing was done by (Philips HPR-125 watt, generated 300–400 nm light) at an ambient temperature. All the membranes were kept the same distance (10 cm) from UV-lamp so that the radiation density flux on all the surface area of the membranes did not change. The details of the membrane preparation conditions are in ensemble (Table 1).

The molecular volumes of the organic compounds (glucose, sucrose and pentachlorophenol) were calculated using semi-empirical AM1 method [8–10]. The physical parameters of the related organic compounds are displayed in Fig. 1 [11,12].

### 2.2.1. Preparation of pentachlorophenol solution

The pesticides were dissolved in methanol solutions (450 mg/l). The impurities were filtered out and evaporated the solvent to yield pentachlorophenol (pure). An appropriate amount of methanol solution is kept in open condition to evaporate and the residues were dissolved into water (already passed

through reverse osmosis module). The final concentration was 5 mg/l for feed the selected pesticides. Reverse osmosis-treated water is taken to get clear picture of surfactant effects in the remediation of PCP. In the real water matrices, the natural organic matter may have the possibility of binding PCP more and thus separation will improve. The inorganic ion adsorption on the membrane can also influence in narrowing the pores and will marked influence on the rejection of PCP. It is avoided to consider other factors from the real water matrices.

### 2.2.2. Analysis

The pentachlorophenol concentration is analyzed with high-performance liquid chromatography (HPLC-Waters-2996) using the direct injection method under the following conditions: Column: Waters Symmetry C 18 (Supelco) 100 mm × 2.1 mm × 3.5 μm, mobile phase acetonitrile/water (Rankem) (80:20) (containing 0.125% acetic acid), flow = 0.2 ml/min, UV-vis detector ( $\chi_{\max} = 280$  nm). For the carbohydrate analysis HPLC-Waters 2414 was used under the following conditions: Supelco Gel 610H column 300 mm × 7.8 mm, mobile phase water containing 0.5% phosphoric acid, column flow 0.5 m/min.

The salt rejection performance is determined from the conductivity data, considering the direct relationship with the concentration. The rejection performance (%R) is calculated from the usual relationship:

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

where  $C_p$  and  $C_f$  are the concentrations of permeate and feed, respectively.

The surface tension of the feed as well as SDS only was determined. Surface tension measurement was done by DCAT-21 (Dataphysics, Germany), using Wilhelmy plate technique:

$$\gamma \cos \theta = \frac{\Delta w}{P}$$

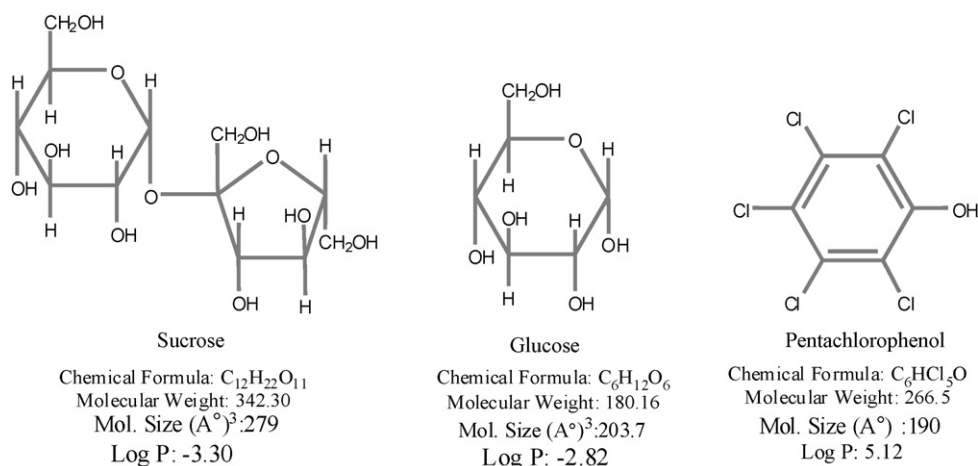


Fig. 1. Physical parameters of solutes.

Table 2

Separation performances of membranes regarding the glucose, sucrose and sodium chloride (pressure: 1.4 MPa,  $C_{\text{glucose}} = C_{\text{sucrose}} = 500 \text{ mg/l}$ ,  $C_{\text{NaCl}} = 2000 \text{ mg/l}$ )

Membranes	Water permeability ( $\text{l m}^{-2} \text{ day}^{-1}$ )	NaCl rejection $R\%$ (flux, $\text{l m}^{-2} \text{ day}^{-1}$ )	Sucrose $R\%$ (flux, $\text{l m}^{-2} \text{ day}^{-1}$ )	Glucose $R\%$ (flux, $\text{l m}^{-2} \text{ day}^{-1}$ )
Membrane I	1705	28.89 (1492)	36.55 (1468.4)	27.57 (1468.4)
Membrane II	806	62.89 (592)	91.54 (786.3)	78.93 (786.3)

where  $\Delta w$  is change in weight of the plate when brought it into contact with the liquid,  $p$  perimeter of the plate,  $\theta$  is the contact angle.

### 3. Results and discussion

#### 3.1. Preparative aspect of thin film composite membranes

The Polysulfone solution in dimethylformamide is immersed in water (non-solvent bath) and dimethylformamide–water exchange leads to phase separation [13] and thus the asymmetric membranes are prepared. The asymmetric membrane is characterized by the polymer rich phase on the top and polymer poor phase in the bottom [14–18]. The polysulfone membranes of different concentrations (15% and 16%) were prepared.

The interfacial polymerization between the *m*-phenylene diamine in water and TMC solution in hexane is occurred on the polysulfone [19,20]. The reaction occurred in hexane phase as highly unfavorable partition co-efficient for acid chloride limits its availability in the aqueous phase [21]. The reaction between *m*-phenylene diamine and trimesoyl chloride formed –CONH– bond and results cross-linked polyamide structure on polysulfone (Scheme 3). The photo-curing was done to form the cross-linked polyamide. Different water permeability as well as separation performances of the markers (glucose and sucrose) having the rejection difference (>50%) was observed.

#### 3.2. Performance of the membranes

Thin film composite membranes have the abilities in removing uncharged components and ionic salts. The removal of

uncharged components may be a result of size exclusion or may be a result from differences in diffusion rates in non-porous structure, which depend also on molecular size. The diffusion rate is smaller for a larger molecule, resulting in an effect similar to size exclusion. On the other hand the charge effect, results the removal of ions. The use of Nernst–Planck model and preferential sorption theory are well known to explain the phenomena [22]. It is accepted that the rejection of uncharged (organic) molecules is determined by the size of the solute molecules compared to the pore size of the membranes [23]. The membranes are characterized in terms of markers (glucose and sucrose) and displayed in Table 2. The separation performances of the pentachlorophenol are showing the same order as in the carbohydrates. It shows similar size exclusion mechanism in all the cases. The performances of the membranes are following the order sucrose > PCP > glucose as their size (Fig. 1). Addition of sodium dodecyl sulfate exerts decisive influence in pentachlorophenol separation. The separation performances are depicted in Figs. 2 and 3. The separation performance is improved up to 50 mg/l and it is saturated beyond that. Here, the saturation in performance is well before the CMC values of sodium dodecyl sulfate (2.1 g/l) [24]. As it is known surfactants have a tendency to reorient them to be isolated from water by adsorption in to an organic matrix, there is the association tendency with the organic molecule, the association of pentachlorophenol with sodium dodecyl sulfate is likely to occur. The association leads to increase the effective molecular size and thus the improvement in rejection results. The association between the two is reflected from the surface tension studies. Fig. 4 shows that the presences of PCP in sodium dodecyl sulfate solution; decrease the surface tension of SDS. This indicates the

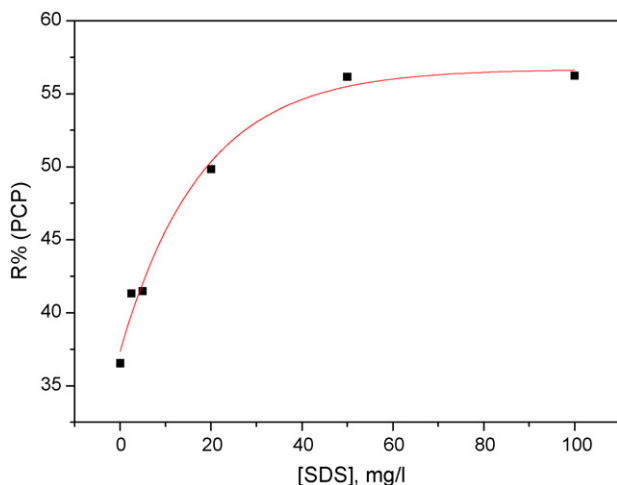


Fig. 2. Separation performances with the variation of SDS concentration for Memb-I ( $C_{\text{PCP}} = 5 \text{ mg/l}$ ), pressure: 1.4 MPa.

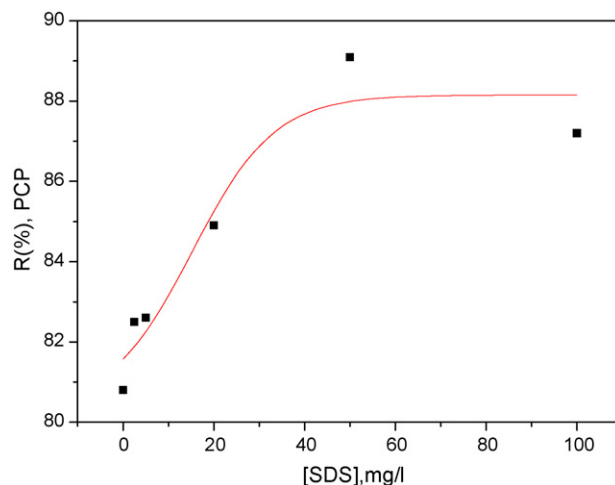


Fig. 3. Separation performances with the variation of SDS concentration for Memb-II ( $C_{\text{PCP}} = 5 \text{ mg/l}$ ), pressure: 1.4 MPa.

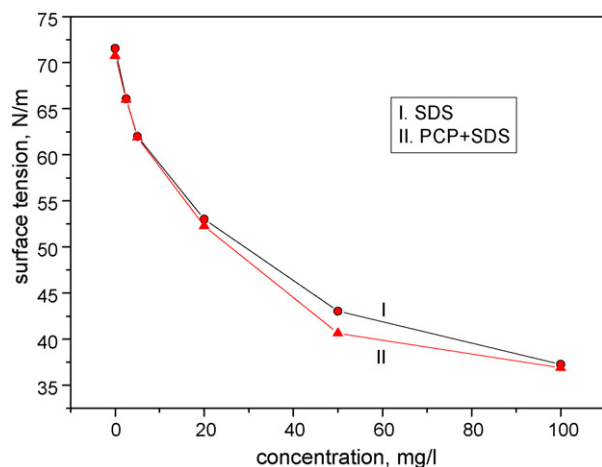


Fig. 4. Surface tension of water mixed with (I) SDS and (II) PCP (5 mg/l) + SDS (SDS concentration up to 100 mg/l).

association of the two molecules, which supports the rejection data with the increase of sodium dodecyl sulfate.

As 'like prefers like' the negatively charged sulfate functional groups of the anionic surfactant molecule cause the membrane to become more negatively charged [25] sulfate polar head. The contact angle of the membranes in SDS solution of different concentration decreases and shows the absorption on the membrane. The maximum decrement in contact angle is  $\sim 8^\circ$  for both the membranes, when it is dipped into the 100 mg/l SDS solution. The interaction of the sodium dodecyl sulfate and PCP molecule results effectively negative charge due to the presence of polar head. The presence of SDS in the feed forms the secondary layer and narrowing the pores and as a result water flux reduction is observed. This fact is also observed by Childress and Elimlech [26] during the study of separation of electrolytes in presence of SDS. Significant flux loss ( $\sim 40\%$ ) is observed for the feed solutions where SDS concentration is higher than 50 mg/l. The electrical repulsion as well as narrowing the pores also acts as synergy in separation.

Apart from the size and charge factor, it can be explained in terms of  $\log P$  (*n*-octanol/water partition co-efficient). The  $\log P$  is defined as  $\log P = \log(C_0/C_w)$ , where  $C_0$  and  $C_w$  are the concentrations of solute in *n*-octanol and water layers [14]. The high  $\log P$  value (5.12) [12] of PCP prefers the organic phase rather than the aqueous one. Hence the general tendency of PCP is away from the membrane, which is relatively hydrophilic in nature, because of SDS on the membrane. In other words, hydrophobicity of the pentachlorophenol acts as synergy to the size exclusion and electrical repulsion.

It is also observed that the surface tension of permeates are similar to all the cases (71 mN/m). It suggests that SDS also removes in maximum extent. The important observation is that the extent in improvement in separation is different for two membranes. The extent of improvement is featured in Figs. 2 and 3 for the two membranes. It is co-related in reverse with the performance of the markers. The less improvement is featured for Memb-II, whereas the higher improvement is reflected for Memb-I. This may be maximum association tendency that is reflected up to membrane II marker cut off.

## 4. Conclusions

The study leads to the following conclusions:

- (1) Surfactant-enhanced cross-flow membrane filtration technique is useful in the remediation of pentachlorophenol.
- (2) The presence of surfactant in PCP contaminated water affects steric (size) exclusion and electrostatic interaction (charge repulsion) and thus the better separation through the membrane results. The pore blocking is due to the presence of SDS in the feed is also another factor for better rejection. The high  $\log P$  factor also treated as a descriptor.
- (3) The better improvement in rejection results for the membrane which is more porous in terms of glucose and sucrose.
- (4) The improvement in PCP separation performances is inversely correlated with the PCP separation performances.

## Acknowledgements

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