3.1 Introduction

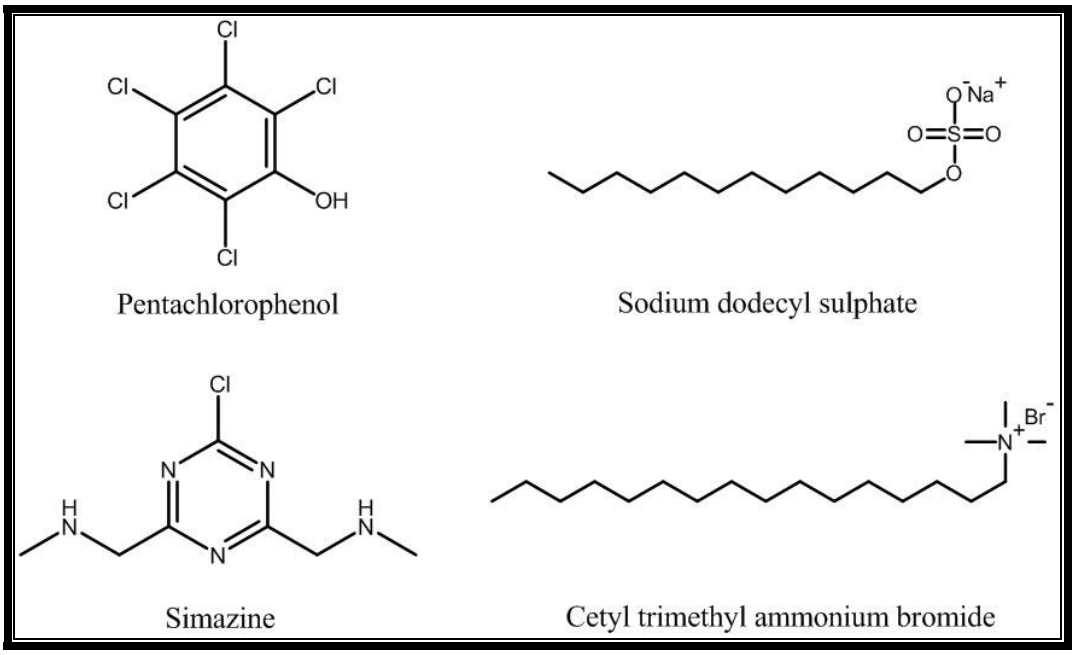
The performances of the membranes in terms of quality separation along with their consistency in behavior are the major challenges and are especially somewhat tricky. Most of the study done so far in this regard to achieve better results generally refers to the modification of the polymeric membranes (viz. surface modification with different monomer involving different techniques and methods, incorporation of different group / moieties in the bulk matrix and like ones [1-13] as a major step. Besides this, there are also some technical approaches regarding filtration which can also bring changes in the performance of the membranes. It may be achieved by adding some additives into the feed solution so that the primary controlling parameters for membrane filtration may change which can result change in size, charge etc. or by altering / bringing technical change in any of the preparative step during membrane preparation.

The previous chapter has mainly dealt with the primary approach of photo-assisted surface modification of the membranes by acrylic acid to get better performance for separation of various water pollutants. The study included in this present chapter involves anchoring of polyamide layer on the polysulfone membrane by giving photo-treatment than conventional thermal-curing. This is also accompanied by visualizing the separation of the two different water pollutants/pesticides through thin film composite membranes by making use of technical approach of addition of the surfactants in the experimental solution. Thus, this chapter deals mainly with the surfactant enhanced filtration of pesticides through photo-treated thin film composite membranes developed from interfacial polymerization of trimesoyl chloride and m-phenylene diamine on polysulfone.

The pesticides are generally low molecular weight (200-400) compounds. Different approaches have been employed to remediate pesticides from water. This involves mainly active carbon filtration, ozone treatment, membrane separation etc [14]. Among these, membranes based separation is getting more prevalent. Moreover, separation of the pesticides by pressure driven filtration techniques along with addition of surfactants in to the feed solution has the potential to excel [15-23]. Over few decades, surfactant mediated separation techniques (viz. micellar liquid chromatography, micellar electro-kinetic chromatography, and cloud point extraction) has grown rapidly [24]. Surfactants are actually amphiphile molecules that comprise a

hydrophobic moiety and a polar or ionic head group. This is because of their unique structural property that these interact with the pesticides which are generally hydrophobic in nature. The interaction occurs through different mechanisms (e.g. surface adsorption, partitioning into the core and co-micellization). The partitioning of pesticides into the hydrophobic core of surfactant micelles results in surfactant-enhanced solublization. This leads to the aggregated surfactant molecules having pesticides in the core. Thus, these aggregated molecules have the possibility towards being retained by the low-pressure-driven membranes. This technique requires low pressure and will reduce the consumption of energy. As the membrane processes are economical and eco-friendly, the preference to adopt the approach to separate pesticides through the membranes is likely to be favored.

Figure 3.1 Chemical structure of surfactants (sodium dodecyl sulphate and cetyl trimethyl ammonium bromide) and pesticides (pentachlorophenol and simazine)



To work out the technical approach of addition of surfactants in the solution to study the separation performance of the membrane, the present work is primarily focused on exploitation towards the separation of

- pentachlorophenol (PCP) and,
- simazine (6-chloro-*N*,*N*′-diethyl-1,3,5-triazine-2,4-diamine)

through thin film composite membrane (TFC) prepared from tricky photo-treatment by addition of different surfactants (viz. sodium dodecyl sulphate (SDS) and cetyl trimethyl ammonium bromide (CTAB),) as depicted in figure 3.1 into the experimental solution of these pesticides.

3.2 Materials and methods

3.2.1 Materials

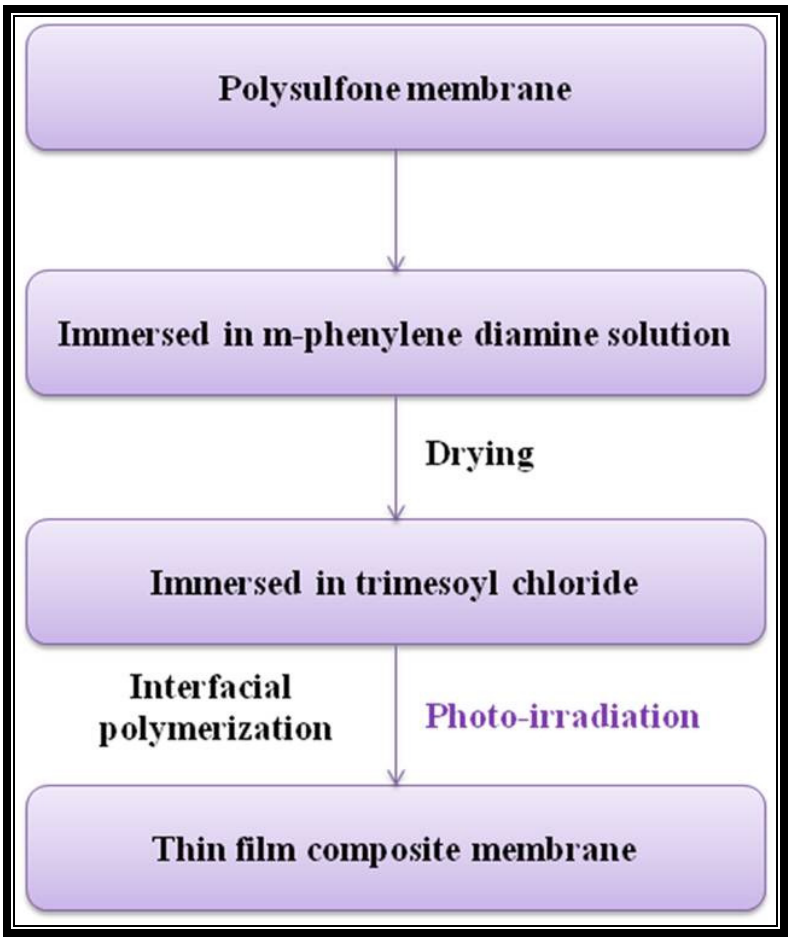
Polysulfone (Udel P-3500; Solvay advanced Polymers, USA), dimethyl-formamide (Merck), Non-woven polyester fabric (Filtration Sciences Corp.,USA), sodium dodecyl sulphate (SD fine Chemicals, India) are used to prepare the asymmetric polysulfone membrane. *m*-phenylene diamine (Loba, India) and trimesoyl chloride (Lancaster, USA) are used for the preparation of thin film composite membranes. Penta-chlorophenol (National Chemicals, India), simazine (technical grade (Sigma, chemicals USA)), sodium chloride, sodium sulphate (Qualigens, India) are used for the performance testing of the membranes. SDS (cationic) and CTAB (cationic) (Sigma Chemicals, USA) are used as surfactants to study the effect of surfactants in the separation ability of the membranes. Glucose and sucrose (Glaxo, India) are used as the marker of the membranes. Methanol (SD fine chemicals, India) is used to prepare the solution of pesticides. Reverse Osmosis treated water is used in the experiment.

3.2.2 Photo-mediated preparation of thin film composite membranes

Polysulfone membranes are prepared from conventional wet-phase inversion technique [25-29] as described earlier in previous chapter (section 2.2.2). A homogeneous solution of polysulfone of various concentrations in dimethyl-formamide is prepared by slow dissolution of polysulfone beads at 45°C by continuous stirring. The thin film of polysulfone solution is casted over non-woven polyester fabric (1m width) by moving the fabric over the guide roller using a proto-type casting machine as depicted in figure 2.1 of chapter 2. The polymeric solution casted non-woven fabric is then immediately immersed into the non-solvent gelation bath i.e. water. This results in the demixing of solvent (dimethyl formamide) and non-solvent (water) to phase out the solid asymmetric polysulfone membrane on non-woven fabric.

The solidified membrane are rinsed with water several times and kept for 18 h in reverse-osmosis-treated to remove solvents and then dried for 48 h at room temperature before thin film composite membrane formation.

Figure 3.2 Schematic presentation of stepwise preparation of thin film composite membrane by photo-treatment

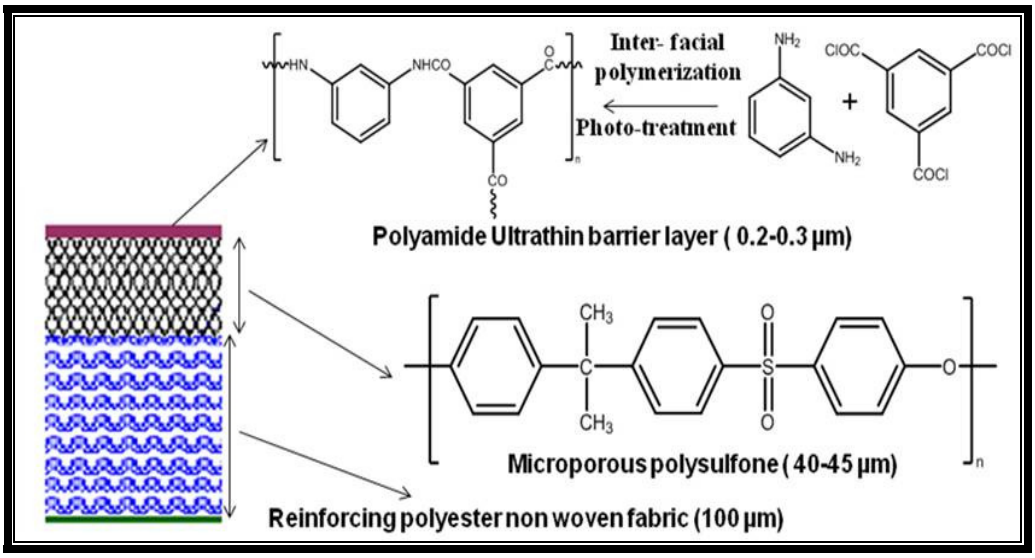


Interfacial polymerization [30-33] of *m*-phenylene diamine (2% in water) and trimesoyl chloride (TMC) (0.1% in hexane) is done on the polysulfone membranes surface (16 x 13 cm) fitted on glass tray as shown schematically in figure 3.2. The reaction occurs in hexane because of highly unfavorable partition coefficient for acid chloride limits its availability in aqueous phase i.e. water [34, 35]. The reaction as well as inbuilt structure is depicted in scheme 3.1.

The membranes are photo-irradiated which otherwise are conventionally subjected to heat curing to form cross-linked polyamide layer in the UV-chamber as

depicted in figure 2.3 of chapter 2 in section 2.2.3. Photo-treatment is preferred because of better cross-linking and consistent performance in terms of salt rejection (~97.2% & 96.8%) than thermally cured membranes (~96.2% & 96%) for sodium sulphate and sodium chloride respectively. The environmentally benign photo-treatment is given by (Philips HPR-125 watt, 300-400 nm wavelength of light) at an ambient temperature. All the membranes are kept at same distance (10 cm) from UV-lamp so that the radiation density flux on all the surface area of the membranes remains uniform.

Scheme 3.1 Symbolic presentation of thin film composite membrane and reaction scheme for interfacial polymerization reaction



3.2.3 General tools and techniques

The characterization of TFC membranes prepared with the assistance of photo-irradiation for incorporation of polyamide layer and their performances in terms of surfactant assisted separation of pesticides are done by various tools and techniques. This includes:

Tools used for surface analysis of the photo-treated TFC membranes

Fourier Transform-Infrared spectrometer:

The incorporation of polyamide layer on the surface of asymmetric polysulfone membrane by condensation reaction between trimesoyl chloride and *m*-phenylene diamine is confirmed with FTIR spectra by analyzing stretching band for

amide (–CONH) functional group. Attenuated total reflection (ATR) infrared spectroscopy is employed for these photo-treated thin film composite membranes (with a Perkin Elmer Spectrum GX with a resolution ± 4 cm^{-1}, incident angle 45°).

Scanning electron microscope:

To ascertain the polyamide layer incorporation further, Scanning electron microscopy (Leo, 1430UP, Oxford instruments) has been used for visual evidences. Thus, scanning electron micrographs of the thin film composite membranes surface are obtained to have an insight about the surface topology of the membranes.

Contact Angle/ Surface tension:

There is a change in the hydrophilicity (i.e. increase) of the membranes when polyamide layer is incorporated on the polysulfone base. This is confirmed by contact angle measurements. This study is done by Tensiometer (DCAT 21 from Dataphysics, Germany) at room temperature (25°C). The motor speed 0.05 mm/sec, dipping length for 5 mm for membrane sample are maintained. The analysis of the surface tension of the pesticide solution with surfactant gives an idea about the interaction of surfactant with the pesticide solution. As the study is based on the surfactant enhanced separation of the pesticides through the photo-treated thin film composite membranes, so the surface tension of the feed and permeate solution is calculated with the same instrument to analyze the performance ability of the membranes with surfactants.

The contact angle is based on an energy balance approach to the three-phase equilibrium, which results in Young's equation [36] Surface tension and contact angle measurement are done by

$$Cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

Where γ represents the surface tension for the particular interface.

The surface tension study of the feed as well as with surfactants is done by using Wilhelmy plate technique using the equation

$$\gamma Cos\theta = \Delta w / p$$

Where Δw is change in weight of the plate when brought it into contact with the liquid, p perimeter of the plate and θ is the contact angle.

Techniques used to analyse the separation performances of the membranes

Basically three major techniques are used to analyse the separation behavior of the photo-treated TFC membranes. It includes conductivity measurement, high performance liquid chromatography (HPLC) and surface tension measurement. The conductivity study is done to confirm the separation abilities of TFC membranes towards the ions. The ionic rejection measurement is calculated by their conductivity relationship, as concentrations follow direct relationship [37, 38]. Surface tension is measured to find out the interaction of the surfactant with the mother liquor and permeate which is done by Tensiometer as explained in the above section.

High performance Liquid Chromatography:

The concentration of the pesticide-organics is analyzed with high performance liquid chromatography. This is achieved by HPLC-Waters-alliance, 2996 separation module (reverse phase), using the direct injection mode under the following conditions: Column, Water symmetry C18 (Supelco) 100 mm x 2.1 mm x 3.5 µm. For pentachlorophenol, the mobile phase is acetonitrile/water (80: 20) with 0.125% acetic acid maintaining the flow at 0.2 ml/ min, and 2996 photodiode array detector (λ_{max} = 280 nm) is used at temperature 30° C whereas for simazine the mobile phase used is acetonitrile / water (80: 20) maintaining the flow at 0.15 ml/ min and UV-Vis detector (λ_{max} = 226 nm) is used. The injection volume is kept 20 µL. Same instrument is used to analyze glucose and sucrose solution as a marker for membrane characterization. For these molecules, 2414 RI detector (HPLC mode) is used and the following conditions are maintained: column Supelcogel C 610H, 30 cm x 7.8 mm, flow 0.5 ml/min 30° C, eluent 0.1% H_3PO_4 in water, injection volume: 60 µL.

Permeability studies

The permeability is measured at room temperature with a laboratory made pressure cell by cross flow filtration method as explained in section 2.2.3 of chapter 2. 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 occurs in this technique.

The effective membrane area is 0.00152 m^2. The water flux and salt rejection experiments with sodium chloride, sodium sulphate are performed. The efficiency of the membranes in removing the studied solutes is determined as follows

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

Where R is the rejection in percentage, C_p and C_f are the concentration for permeate and the feed solution.

The flux is calculated from the relation:

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

Where v indicates the volume of permeate in lit, *t* in days and *A* is effective membrane area (m^2)

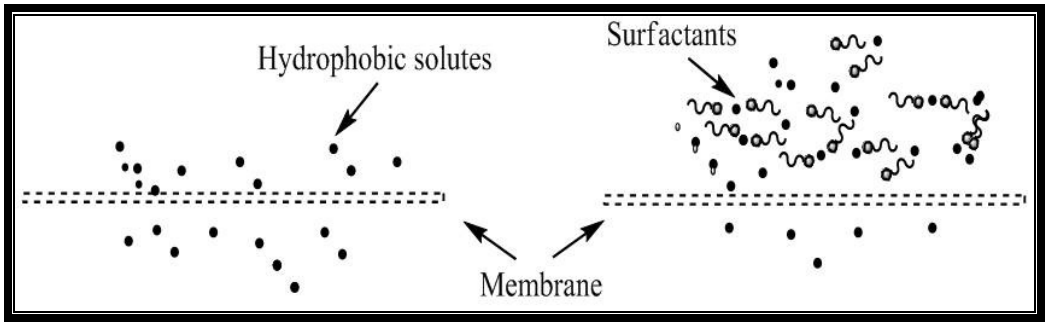
Photo-irradiation chamber

The photo-treatment to thin film composite membranes is achieved in the lab made UV-irradiation chamber as explained in section 2.2.3 of previous chapter. The membranes are kept at a specific distance beneath UV lamp and photo-irradiated for specific time. The photo-treated membranes are further washed with plenty of water and kept for 24 h in water prior to further experiment.

3.3 General theory for surfactant-enhanced filtration through membranes

Surfactants are the compounds with a hydrophilic polar head and hydrophobic non-polar tail. These have the abilities to interact with the pesticides, which are generally hydrophobic in nature. The interaction occurs through different mechanisms (such as surface adsorption, partitioning into the core and co-micellization).

Scheme 3.2 Schematic illustration of the concept of surfactant enhanced filtration I: without surfactant and II with surfactant.



The partitioning of pesticides into the hydrophobic core of surfactant micelles (i.e. hydrophobic heads are within the cluster and hydrophilic ones are exposed to solvents) results in surfactant enhanced solublization. With this, overall size of the pesticide due to micellar aggregates / surface adsorption becomes larger. This overall phenomenon conveys the ability for better performance in the membrane filtration technique as size of the solute is one of the major factor for evaluation of membrane performance because membrane filtration primarily based on sieving mechanism. The aggregated surfactant molecules with the pesticides have better possibility toward being retained by the low pressure driven membranes as depicted in scheme 3.2. Thus, the technique will be of low pressure and energy efficient.

3.4 Exploitation of photo-treated TFC membranes for separation of PCP from water

Pentachlorophenol (PCP) is one of the widespread environmental contaminants of soils, surface and ground water. It is mainly used as pesticide, disinfectant and wood preservative. It is used in consumer items such as boats, furniture, and log homes. Non-wood uses account for no more than 2 % of current consumption. Pentachlorophenol is well acquainted by other names like 2,3,4,5,6-pentachlorophenol; penchlorol; pentachlorofenol; pentachlorophenate; and pentachlorofenolo.

Despite being banned and severely restricted in many countries, PCP remains an important pesticide from a toxicological perspective. It is a stable and persistent compound. It is readily absorbed by ingestion and inhalation in human but is less well absorbed dermally. PCP is probable carcinogen and has been placed on the pollutant priority list [39, 40].

Short term exposure to pentachlorophenol can lead to poisoning that is rapidly fatal. Various studies reveals that exposure to high levels of pentachlorophenol can cause the cells in the body to produce excess heat. This can lead to a very high fever, profuse sweating, and difficulty in breathing. The body temperature can increase to such a level that it may cause injury to various organs and tissues, and even death. There are the reports about pulmonary oedema, intravascular haemolysis, pancreatitis, jaundice and acute renal failure. Chronic occupational exposure to PCP may produce a syndrome similar to acute systemic poisoning, together with conjunctivitis and irritation of the upper respiratory and oral mucosae.

Long-term exposure has also been reported to result in chronic fatigue or neuropsychiatric features in combination with skin infections (including chloracne), chronic respiratory symptoms, neuralgic pains in the legs; and impaired fertility and hypothyroidism secondary to endocrine disruption. Moreover, contact can irritate the eyes, nose, and throat. There is no antidote and adequate data to support the use of repeat-dose oral cholestyramine, forced diuresis or urine alkalinisation as effective methods of enhancing PCP elimination in poisoned humans. Supportive care and vigorous management of hyperthermia are supposed to produce a satisfactory outcome [41, 42].

With the recent emergence of pentachlorophenol contamination as an important drinking water quality issue because of the factors discussed above, it is targeted to find the proper and useful method to remediate it. Surfactant enhanced filtration is one which opens the scope. It has also been found to show some retarding effect of surfactant addition to pentachlorophenol regarding the diffusive transport through skin [42]. In the present study, the effect of Sodium dodecyl sulphate (SDS) coupled with the membrane technology, to remediate the pentachlorophenol from water is exploited.

Table 3.1 Preparation conditions of membranes (M-I and M-II)

Membrane	**Polysulfone (% w in DMF)**	**Preparation conditions**
M-I	15	Dipping time (in MPD): 7min, Drying time: 7min, Dipping time (in TMC): 5min. Photo-treatment time: 15 min
M-II	16	

3.4.1 Development of photo-treated TFC membranes

The thin film composite membranes for the remediation of pentachlorophenol are prepared from polysulfone and interfacial polymerization of *m*-phenylene diamine and trimesoyl chloride as explained above in section 3.2.2. For this the base asymmetric polysulfone membranes are prepared with different concentration (15%

and 16% w/w) of polysulfone in DMF on non-woven polyester fabric by wet phase inversion technique. The asymmetric membranes are then washed well with plenty of water and kept for one day in RO water. These are dried at room temperature and are used to prepare thin film composite membranes. Further detail is given in table 3.1.

3.4.2 Characterization of the photo-treated TFC membranes

The thin film composite membranes prepared by photo-irradiation treatment are analyzed by FTIR spectrophotometer for their functionality. The TFC membranes are characterized with respect to polysulfone as depicted in figure 3.3. It shows the spectra of PS membrane (a) and thin film composite polyamide on polysulfone base membranes (b).

The strong reflectance at 1586-1489 cm^{-1} is due to benzene ring stretching mode of polysulfone material and sulfone (C-SO_2-C) symmetric stretching band is observed at 1150 cm^{-1}[43-45].

In figure 3.3 (b) the 1655 cm^{-1} peak is observed because of C=O stretching due to polyamide structure. This is also supported by the C-N stretching at 1542 cm^{-1} and amide (polyamide) peak at 786 cm^{-1} which confirms the presence of polyamide (cross-linked) structure on the membrane [46]. The two membranes (M-I and M-II) are of similar structure as they involve similar conditions and reactants for interfacial polymerization other than the polysulfone base support and show similar FT-IR spectra.

Figure 3.3 FTIR spectra of (a) polysulfone and (b) photo-treated thin film composite membrane

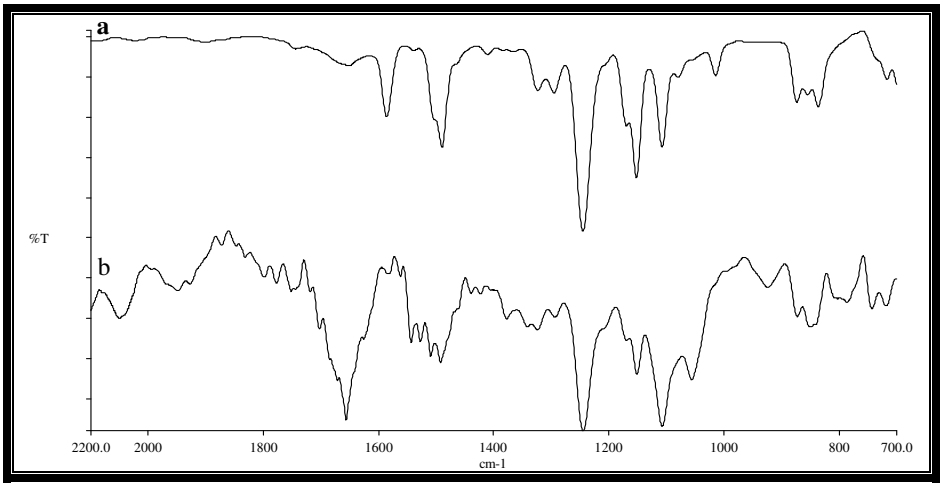
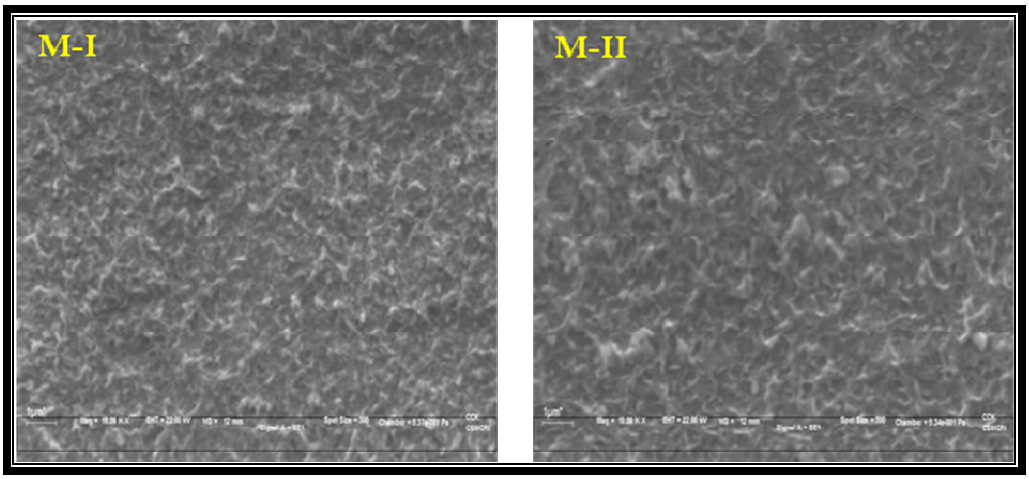


Figure 3.4 Scanning electron micrographs of thin film composite membranes (M-I and M-II)



The scanning electron micrographs are also taken to have visual evidences of the TFC membranes. These are depicted in figure 3.4. These show characteristic morphology of polyamide layer developed on asymmetric polysulfone membranes. The micrographs show more or less similar pattern of formation of cross linked polyamide on the polysulfone for both of the membranes (M-I and M-II).

3.4.3 Preparation of PCP solution

The pesticide is dissolved in methanol (450 mg/L). The impurities are filtered out and evaporated the solvent to yield pure pentachlorophenol. An appropriate amount of methanol solution is kept in open condition to evaporate and the residues are dissolved in water (already passed through reverse osmosis module). The final concentration is maintained 5 mg/L for feed. 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 lead to narrowing of pores which in turn can impart a marked influence on the rejection of PCP. It is avoided to consider other factors from the real water matrices.

3.4.4 Experimental sketch up

The photo-treated thin film composite membranes are exploited for their performances in terms of their water flux and separation behavior towards sodium chloride, glucose, sucrose and PCP. The permeability is measured at room temperature with a laboratory made pressure cell as explained in section 2.2.3 of

chapter 2. The effective membrane area taken for study is 0.00152 m^2. The water flux and salt rejection experiments with sodium chloride (2000 ppm) are performed. The insight of molecular weight cut off of the membranes is obtained by passing the solution of glucose and sucrose (500 ppm each) as a marker through the thin film composite membranes. The solution of pentachlorophenol (5 ppm) is passed through the photo-treated membranes along with the addition of SDS by varying its concentration from 0-100 ppm. The SDS concentration is employed below its CMC, i.e. concentration in which addition of further surfactants leads to micelle formation. The CMC is marked as that concentration of surfactants beyond which the surface tension value is not altered. The permeation studies are carried out at room temperature and operating pressure of 1.4 MPa. Surface tension of the pentachlorophenol solution containing SDS is measured for both the feed and permeates solution.

3.4.5 Analysis of performance behavior of TFC membranes for PCP remediation

Thin film composite membranes have the abilities in removing uncharged components and ionic salts. The removal of uncharged components may be due to size exclusion or differences in diffusion rates in non-porous structure, which depends also on molecular size.

Table 3.2 Separation performances of membranes regarding the glucose, sucrose and sodium chloride (pressure: 1.4 MPa, $C_{glucose} = C_{sucrose} = 500$ mg/L, $C_{NaCl} = 2000$ mg/L)

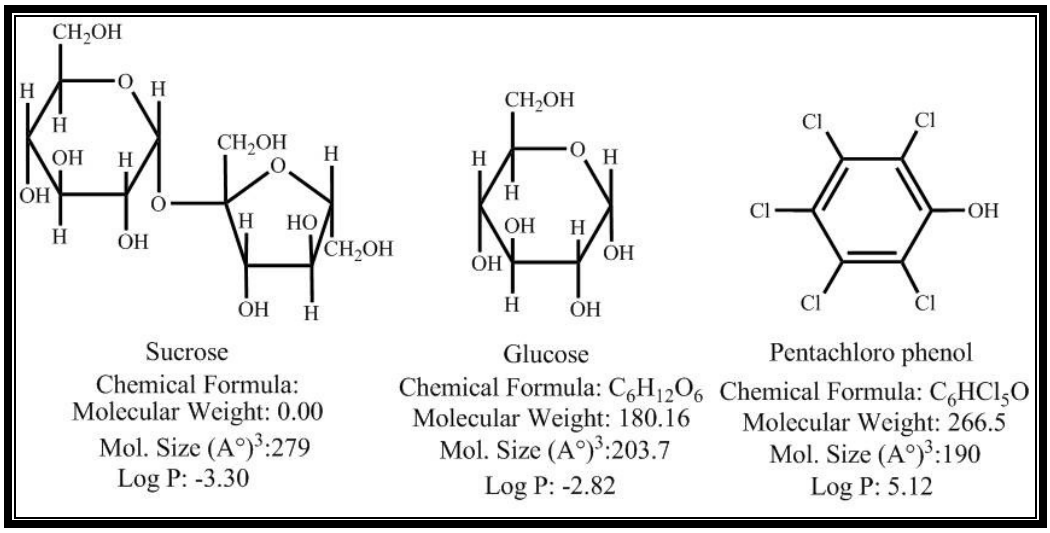
Membranes	**Water permeability ($lm^{-2}d^{-1}$)**	**NaCl rejection (R%) Flux ($lm^{-2}d^{-1}$)**	**Sucrose (R%) Flux ($lm^{-2}d^{-1}$)**	**Glucose (R%) Flux ($lm^{-2}d^{-1}$)**
M-I	1705	28.89 (1492.0)	36.55 (1468.4)	27.57 (1468.4)
M- II	806	62.89 (592.0)	91.54 (786.3)	78.93 (786.3)

The diffusion rate is smaller for a larger molecule, resulting in the effect which is similar to size exclusion phenomenon. On the other hand, the charge effect results

in the removal of ions. The use of Nernst–Planck model and preferential sorption theory are well known to explain the phenomena [47]. 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 [48]. The membranes are characterized in terms of markers (glucose and sucrose) and the results are displayed in table 3.2.

The separation performances of the pentachlorophenol are showing the same order as shown in the carbohydrates separation. 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 does (figure 3.5). Addition of sodium dodecyl sulphate exercises decisive influence in pentachlorophenol separation.

Figure 3.5: Physical parameters of solutes (Sucrose, Glucose, Pentachlorophenol)



The separation performances of photo-treated membranes are depicted in figure 3.6 & 3.7 for membranes M-I and M-II respectively. It is found to improve up to 50 mg/L and t gets saturated beyond this concentration. The saturation in performance is well before the CMC values of sodium dodecyl sulphate (2.1 g/L) [49]. As it is known that the surfactants have a tendency to reorient themselves and these get isolated from water by adsorption into an organic matrix. This happens because of their association tendency with the organic molecules. Same way, the association of pentachlorophenol with sodium dodecyl sulphate is likely to occur. The association between pentachlorophenol and sodium dodecyl sulphate 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. It is depicted in figure 3.8 that the presence of PCP in sodium dodecyl sulphate solution decreases the surface tension of SDS. It indicates the association of the two molecules, which supports the rejection data with the increase in the concentration of sodium dodecyl sulphate.

As 'like prefers like', the negatively charged sulphate functional groups of the anionic surfactant molecule cause the membrane to become more negatively charged [50]. The contact angle of the TFC membranes in SDS solution of different concentration decreases and it favors the absorption of SDS on the membrane. The maximum decrement in contact angle is ~ 8° for both the membranes, when it is dipped into 100 mg/L of SDS solution.

The interaction of the sodium dodecyl sulphate and PCP molecule results effectively into negative charge due to the presence of polar head. The presence of SDS in the feed forms the secondary layer and causes narrowing of the pores and as a result water flux reduction is observed. This fact is also observed by Childress *et al.* [51] during the study of separation of electrolytes in presence of SDS. Significant flux loss (~ 40%) is observed for the feed solutions where SDS concentration is higher than 50 mg/L. The electrical repulsion as well as narrowing of the pores also acts as synergy in separation.

Figure 3.6: Separation performances of M-I for pentachlorophenol remediation with the variation of SDS concentration. (C_{PCP} (5 mg/L), Pressure: 1.4 MPa)

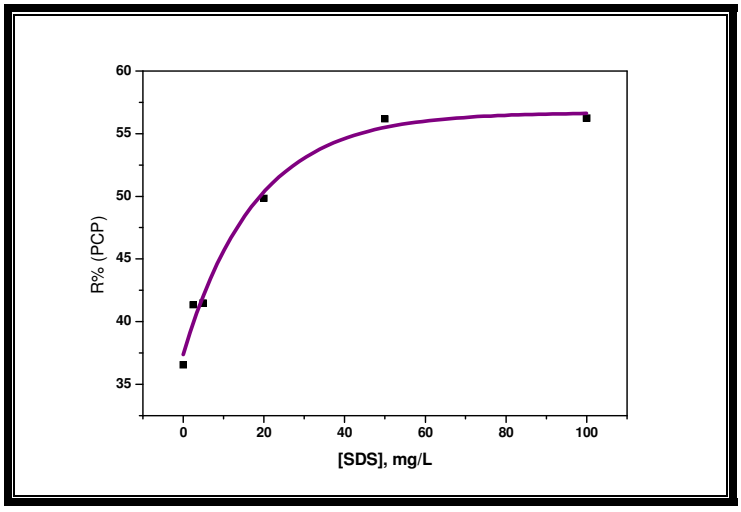


Figure 3.7 Separation performances of M-II for pentachlorophenol remediation with the variation of SDS concentration. (C_{PCP} (5 mg/L), Pressure: 1.4 MPa)

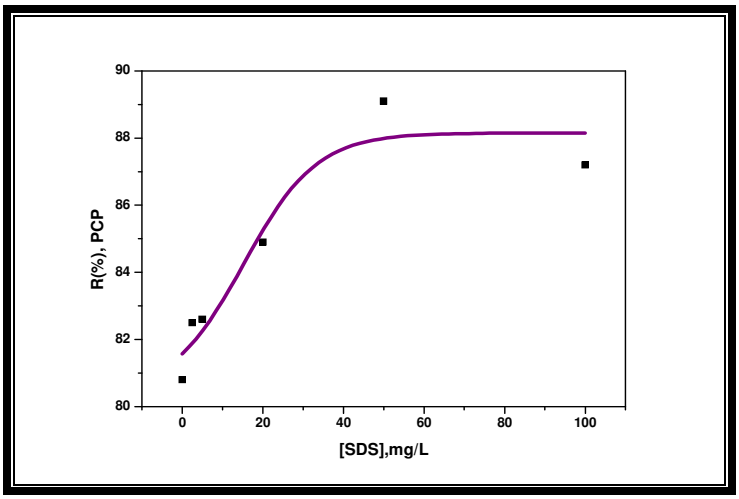
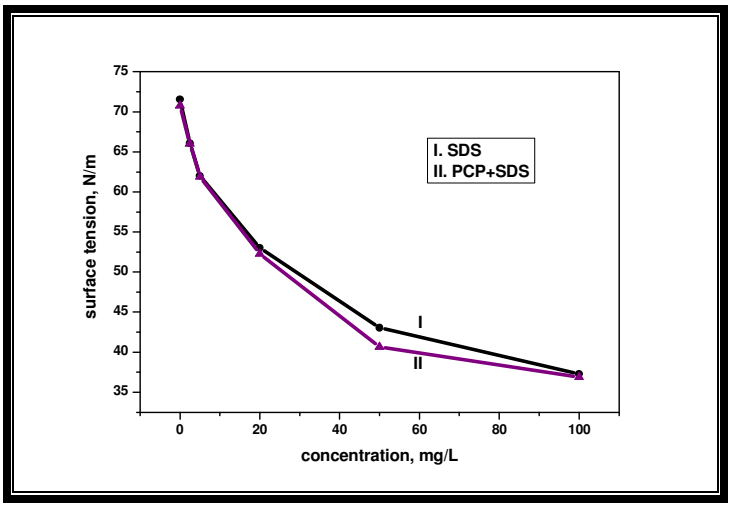


Figure 3.8 Surface tension of water mixed with I. SDS and II. PCP (5mg/L) + SDS (SDS concentration up to 100 mg/L)



Apart from the size and charge factor, it can also be explained in terms of log P (*n*-octanol/water partition co-efficient). The log P is expressed as

$$\log P = \log (C_0 / C_w),$$

Where C_0 and C_w are the concentration of solute in *n*-octanol and water layers [52].

The high log P value (5.12) [53] of PCP prefers the organic phase rather than the aqueous one. Hence, the general tendency of PCP is to remain away from the membrane which is relatively hydrophilic in nature and it is also due to the presence

of SDS on the membrane surface. In other words, hydrophobicity of pentachlorophenol acts as synergy to the size exclusion and electrical repulsion.

It is also observed that the surface tension of permeates are nearly similar in all the cases (71 mN/m). It suggests that SDS is also removed to the maximum extent. The important observation is that the extent of improvement in separation behavior is different for two membranes. The extent of improvement for the two membranes is featured in figure 3.6 and 3.7. It is co-related in reverse with respect to the separation performance toward the markers. The less improvement is featured for M-II (rejection increases from ~ 81% to 88%), where as the higher improvement is reflected for M-I (rejection increases from 36% to 56%). It may be due to maximum association tendency that is reflected in M-II marker cut off.

The study leads to outline the work as surfactant enhanced cross-flow membrane filtration technique is useful in the remediation of pentachlorophenol from photo-treated thin film composite membranes. 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. The better improvement in rejection results for the membrane which is more porous in terms of glucose and sucrose. The improvement in PCP separation performances are inversely correlated with the PCP separation performances.

3.5 Exploitation towards remediation of simazine from water using surfactants

The present work is focused on simazine (6-chloro-*N*,*N'*-diethyl-1,3,5-triazine-2,4-diamine) remediation from water through thin film composite membranes. There are possibilities of water contamination with simazine due to its high persistence in the environment as a result of its intensive use on large areas of agricultural soil and it has given rise to concern about their effects in the environment. It is often used as a 'pre-emergent herbicide' to control weeds before the new seedlings emerge from the soil. Its primary agricultural use is to control broad-leaf and grassy weeds in corn fields, citrus crops, alfalfa and grapes. It is also used to control weeds in strawberries, apples, pears, nuts, olives, pineapples, asparagus, sugar cane, tea and coffee. Its non-agricultural uses have included weed control on vacant lots and right-of-ways, on ornamental trees and shrubs [54].

There is a concern that simazine and other *s*-triazine herbicides may affect the risk of ovarian cancer. It has been implicated as potential endocrine disruptly compounds in humans. In this particular study, the effect of addition of sodium dodecyl sulphate (SDS) (anionic surfactant) and cetyl trimethyl ammonium bromide (CTAB) in the performances of separation of simazine through the membranes are studied. Moreover, we have tried to correlate the performances data of the prepared thin film composite polyamide membranes with their chemistry.

3.5.1 Preparation of photo-assisted TFC membranes simazine remediation

The thin film composite polyamide membranes are prepared same way as explained in section 3.2.2. At first, polysulfone solutions in dimethyl formamide (14 & 15 % w/w) are prepared through slow dissolution in heating condition over the long duration. The viscous polymer solution (in dimethyl formamide) is spread into a thin film on the non-woven polyester fabric, and immediately immersed in non-solvent medium (water). The solidified membrane are rinsed with reverse osmosis treated water for 18 h to remove solvents and then dried for 48h at room temperature before thin film composite membrane formation.

Table 3.3 Preparation conditions for thin film composite membrane (Memb-I and Memb-II)

Membrane	**Polysulfone in DMF (% w/w)**	**Conditions**
Memb-I	14	Coating temp: 15°C , RH%: 85 , Photo-irradiation time : 15 min
Memb-II	15	

Interfacial polymerization of m-phenylene diamine (2% in water) and trimesoyl chloride (TMC) (0.1% in hexane) is performed on the surface of the prepared polysulfone membranes (16 x 13 cm) fitted on glass tray. The reaction as well as inbuilt structure is depicted in scheme 3.1. The environmentally benign photo-curing is carried out by (Philips HPR-125 watt, 300-400 nm wavelength of light) at an ambient temperature. All the membranes are kept the same distance (10 cm) from UV-lamp so that the radiation density flux on all the surface area of the membranes

does not change. The details of the membrane preparation conditions are in ensemble table 3.3.

3.5.2 Analysis of TFC membranes

FTIR spectra by their characteristic stretching and bending band in a molecule can provide information about functional groups and thus chemical structure of the membrane can be revealed. For Memb-1 and Memb-II, there is found to be similar spectra as shown in figure 3.3.

For polysulfone, the strong reflectance at 1586 - 1489 cm^{-1} related to benzene ring stretching mode. The sulfonic ($C-SO_2-C$) symmetric stretching is observed at 1150 cm^{-1} and asymmetric stretching band is observed at 1324 cm^{-1} for ($C-SO_2-C$). Asymmetric C-O stretching frequencies do occur at 1243 cm^{-1} and 1014 cm^{-1}. Similarly, the peak at 1655 cm^{-1} and 1542 cm^{-1} confirms C=O stretching polyamide structure, and C-N stretching respectively for both the membranes (Memb-I and Memb-II) .

Figure 3.9 Scanning electron micrographs of photo-treated TFC membranes (Memb-I and Memb-II)

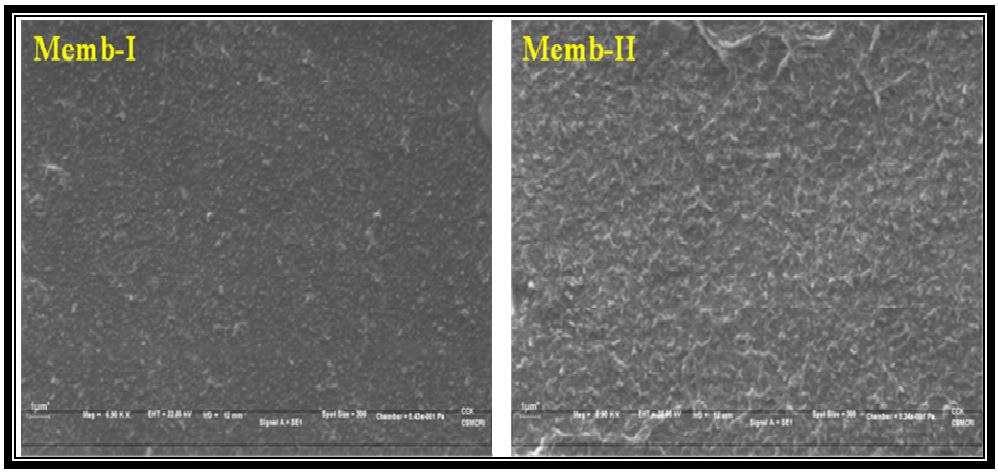


Figure 3.9 shows the topographical scanning electron microscopic view of photo-treated thin film composite membranes. The photograph for Memb-I is showing comparatively smooth structure, as the formation of cross-linked structure occurs on comparatively porous polysulfone base matrix. It is also evidenced from its high transmission. On the other hand, the polyamide (Memb-II) is based on comparatively tight polysulfone (15%) matrix, appears to be dense.

3.5.3 Preparation of simazine solution

For this study, an appropriate amount of methanol is taken to dissolve simazine and the solution is prepared in water (already passed through reverse osmosis module). The final concentration of simazine solution is maintained 0.5 mg/L. The surfactants are added to simazine solution in different concentrations. For each experiment 2.5 L of solution is taken for further analysis along with the surfactant.

3.5.4 Experimental sketch up

The filtration experiments are conducted in cross flow and closed loop mode on filtration arrangements having cells connected in series. The experimental set up used for the treating the solutions are sketched in section 2.2.3 of chapter 2**.** The permeability is monitored at 1.4 MPa. The size of the membrane is 0.00152 m^2. Salt rejection measurement is done on the basis of conductivity data by using conductivity meters after calibration. The water permeability and salt separation as well separation performances of the marker are tested and displayed in table 3.4. The water flux recovery ratio (FRR) [55] is calculated using the following expression

$$FRR(\%) = \left(\frac{PWF_f}{PWF_0} \right) \times 100$$

Where PWF_0 and PWF_f represent pure water fluxes of the membrane before and after filtration respectively.

3.5.5 Separation performances of the photo-treated TFC membranes

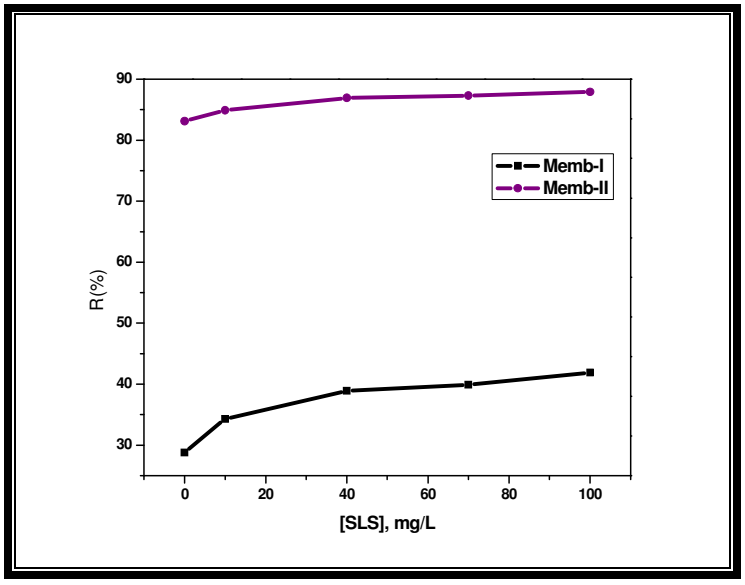
The performance study of the membranes suggests that the two membranes are of difference in characters. The water permeability of Memb-I is recorded to be more than twice with respect to Memb-II, as Memb-I is developed from lower concentration of polysulfone i.e. it is more porous. The salt rejection property of the membrane is found because of the residual –COOH in cross-linked polyamide structure. This rejection behavior of membranes is well explained by different theories (viz. preferential sorption theory, Nernst Planck model) [47]. The salt rejection is also of wide difference for the two membranes, probably because of the difference in base polysulfone membrane matrix. The separation of bi-bivalent $MgSO_4$ is little higher

with respect to uni-univalent NaCl as the uncross-linked –COOH dominates its role. The separation of glucose molecule as a marker is also of wide difference.

Table 3.4 Performances (water permeability and separation of solutes) of membranes

Membranes	**Water permeability ($lm^{-2}d^{-1}$)**	**NaCl R% (Flux, $lm^{-2}d^{-1}$)**	**$MgSO_4$ R% (Flux, $lm^{-2}d^{-1}$)**	**Glucose R% (Flux, $lm^{-2}d^{-1}$)**
Memb-I	1578.94	35.0 (1799.99)	41.7 (1667.37)	22.0 (1357.89)
Memb-II	663.15	81.0 (710.53)	84.8 (757.89)	82.0 (631.57)

Figure 3.10 Separation performances of membranes (Memb-I and Memb-II) for simazine remediation with varying concentrations of SDS



It is well accepted that the rejection of organic molecules is determined by the size of the solute molecules compared to the pore size of the membranes [48]. The pore size of the membrane is characterized by marker. The separation of simazine also shows the same trend as reflected from the separation of glucose and salt i.e. Memb-II shows higher separation compared to Memb-I.

The separation performance of the membranes on addition of sodium dodecyl sulphate to simazine contaminated solution is depicted in figure 3.10. The graph shows that the separation performances of the membranes are found to improve. Since surfactants have a polar and non-polar head and they have a tendency to reorient themselves when these are to be isolated from water by adsorption into an organic matrix. Thus, there is the possibility of the same tendency with the organic molecule i.e. the association of simazine and sodium dodecyl sulphate is likely to occur. The association leads to an increase in the effective molecular size of the simazine and thus the improvement in rejection is resulted through the membranes. The association between the SDS and simazine is also reflected from the surface tension studies (figure 3.11).

The improvement in separation by Memb-I (~12%) is more compared to Memb-II (~ 4%). It shows that better improvement in terms of separation performance is resulted due to more porous structure (in terms of marker and permeability). As the size of the pores (of Memb-II) has reached that limit, the association of simazine and sodium dodecyl sulphate shows little impact compared to other.

Figure 3.11 Variation of surface tension of SDS and the solution of simazine with different concentration of SDS

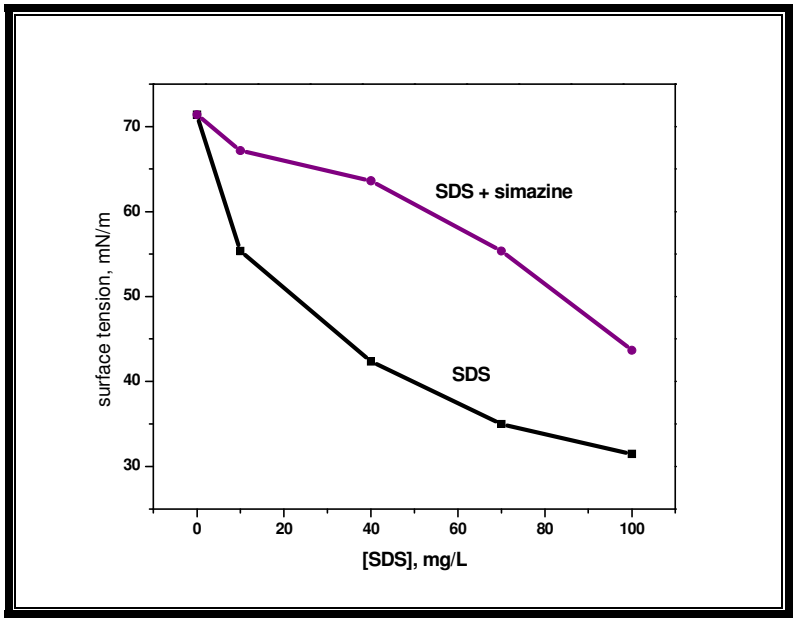
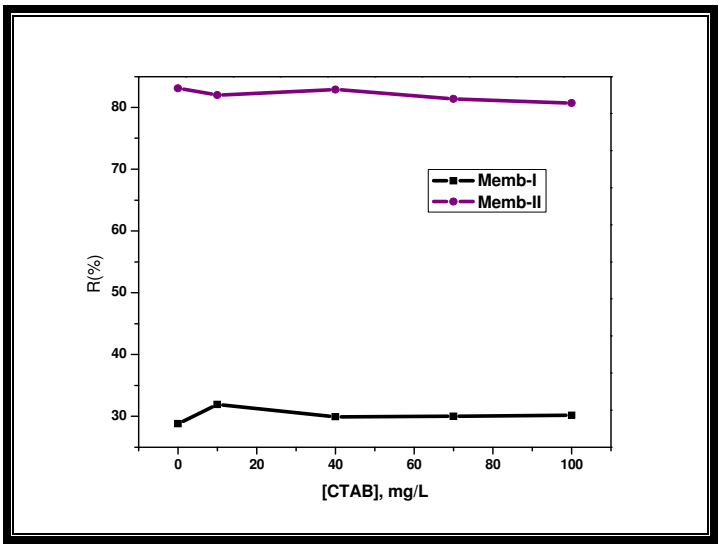
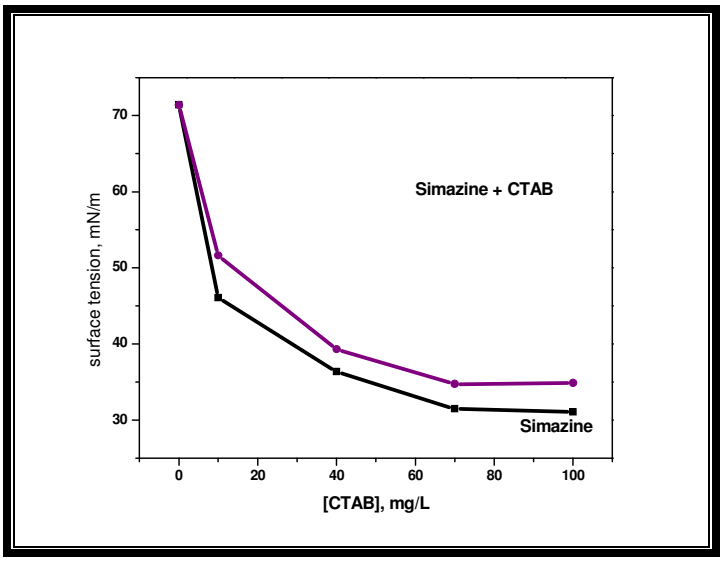


Figure 3.12 Separation performances of membranes (Memb-I and Memb-II) for simazine remediation with varying concentrations of CTAB



The separation performance of simazine with the addition of cetyl trimethyl ammonium bromide (cationic surfactant) is displayed in figure 3.12. It shows that with the addition of CTAB, the separation performances are not improved for the two membranes. The association of simazine with CTAB is little compared to sodium dodecyl sulphate as evidenced from surface tension studies (figure 3.13). In all the case, the surface tension of permeates is more or less similar to 71.4 mN/m. It suggests that the surfactants are removed to maximum extent.

Figure 3.13 Variation of surface tension of CTAB and solution of simazine with different concentration of CTAB



The association of surfactants with the membrane is confirmed by increase in hydrophilic character i.e. decrement in contact angle. The maximum decrement in contact angle is found to be ~4° for both the membranes, when it is dipped into the 100 mg/L sodium dodecyl sulphate solution.

The variation of normalized flux with the sodium dodecyl sulphate concentration is depicted in figure 3.14. The presence of sodium dodecyl sulphate in the feed has resulted in pore narrowing and as a result flux reduction (~38%) is observed for the membranes as observed by Childress and Elimlech *et al* [50]. The negatively charged sulphate functional groups of the sodium dodecyl sulphate molecule cause the membrane to become more negatively charged [51].

On the other hand, the presence of cationic surfactant (CTAB) in the feed has more tendencies to attach with the membrane more as the membrane inbuilt charge is slightly negative because of the presence of residual –COOH functional group. Thus, it shows more solution flux reduction (~ 60%) compared to the simazine- sodium dodecyl sulphate associated one (figure 3.15) and trend is found to be same for both the membranes. Though the flux reduction is higher for the CTAB treated membranes, but the poor association with simazine does not enhance the capability of rejection.

Figure 3.14 Variation of normalized flux with CTAB concentration for Memb-I and Memb-II

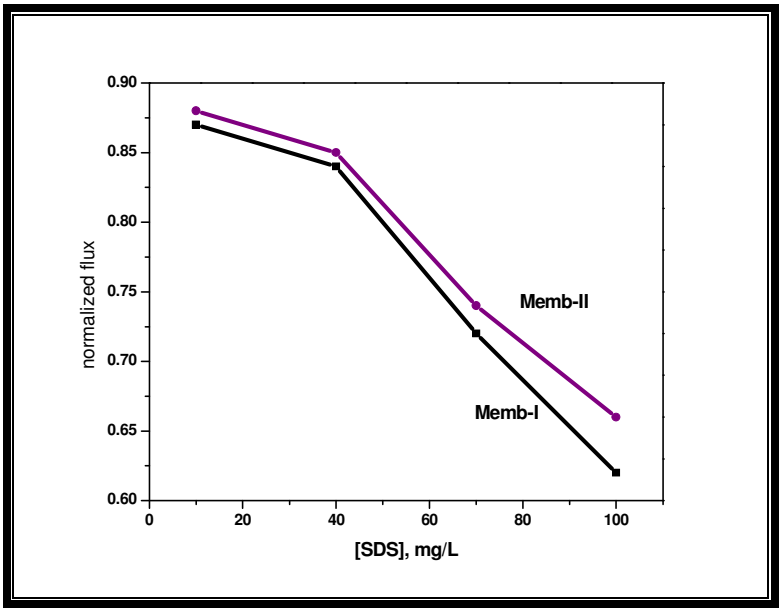


Figure 3.15 Variation of normalized flux with SDS concentration for Memb-I and Memb-II

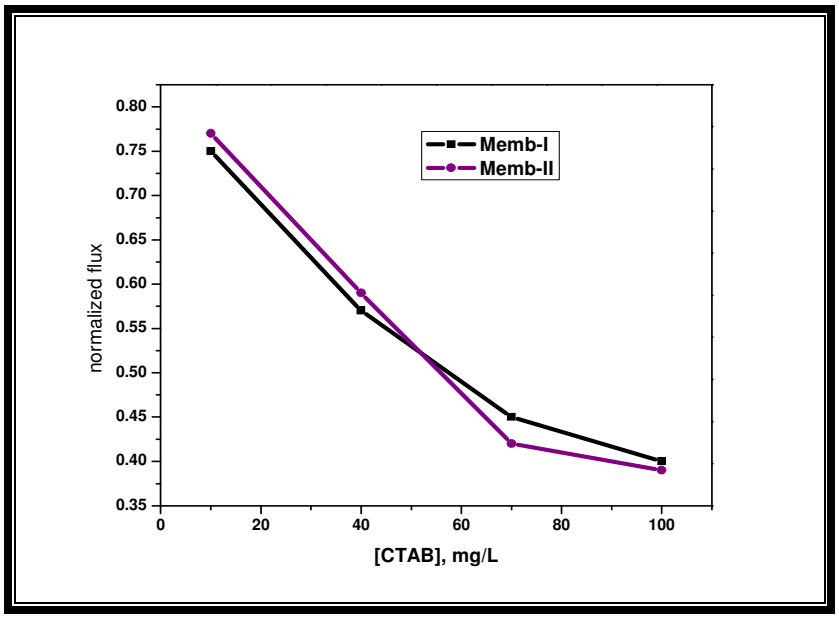
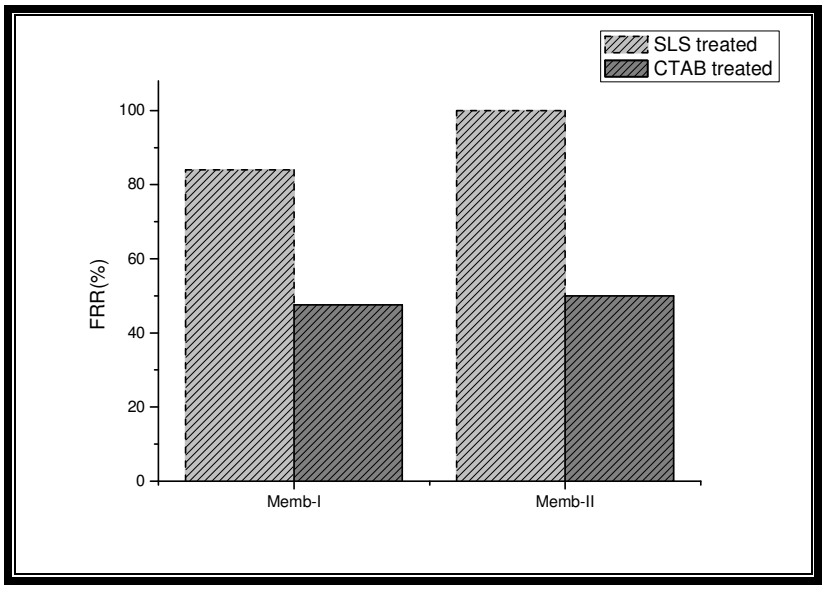


Figure 3.16 Pure water flux recovery ratio of the membranes (Memb-I and Memb-II)



The water flux recovery ratio data also supports the blocking effect in the membrane due to the formation of associated moiety by surfactants and simazine. It shows that water flux recovery ratio for the membranes used for sodium dodecyl sulphate feed is better compared to feed which is CTAB treated. The flux recovery

ratios of the membranes are depicted in figure 3.16. For Memb-II, it is obtained 100% (for sodium dodecyl sulphate treated), as the membranes are of higher porous structure and thus has more tendency to be blocked compared to Memb-I. But, for the CTAB treated membranes as the adsorption of the membrane is higher compared to SLS treated, the flux recovery ratio of both the membranes are found to be similar (~48%).

In brief, the thin film composite membranes based on polysulfone base matrix and photo-induced interfacial polymerization cross-linked polyamide structure on it are marked by organic marker (glucose), salt and water permeability. The present study has been dealt with the effect of addition of surfactants in the membrane permeation and leads to the findings as the rejection behavior of simazine by the membranes is showing similar trend as glucose, salt and water permeability. The addition of surfactant(s) shows different behavior. The addition of sodium dodecyl sulphate to the feed shows more enhancements in rejection for Memb-I, having more porous structure in terms of organic marker. On the other hand, the addition of cetyl tertiary ammonium bromide to the feed shows no improvement in rejection. The pure water flux recovery ratio of both the membranes is studied and it has been found that flux recovery ratio is better when the membranes are dealt with the sodium dodecyl sulphate compared to cetyl tertiary ammonium bromide.

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