4.1 Introduction

Porosity and charge have been the pivotal for the membrane performance study since long time. Different driving forces (viz. conc., pressure, electrical etc.) are used to regulate the performances. The studies done so far in chapter 2 and 3 have also been exploited with the help of photo-irradiations. The second chapter mainly emphasizes the modification of asymmetric polysulfone and polyamide based thin film composite membranes. This involves the attainment of requisite porosity and surface functionalization for betterment towards the remediation of water pollutants by photo-irradiations. While the third chapter details the performance study by addition of surfactants in the solution to remediate water pollutants from photo-treated low pressure thin film composite membranes. But, the development of responsive materials and preparation of membranes from these responsive materials have changed this scenario away from porosity and charge along with various driving forces for the membranes performances for last few decades. Responsive materials / polymers respond with characteristic property changes to small changes in their environment on receiving some signal. They can be classified according to the response/stimuli to which they respond such as: temperature, pH, and light. Hence, preparation of responsive polymer materials are drawing sharp attention as these can adapt to surrounding environments, regulate transport of ions and molecules, change wettability and adhesion of different species on external stimuli, or convert chemical and biochemical signals into optical, electrical, and thermal signals, and vice versa. This stimuli oriented phenomenon has been in use for induction of various kinds of chemical and physical properties in various functional molecules / materials e.g. enzymes, drug delivery, synthetic polymers, polypeptides, artificial lipids and cyclodextrins [1-4].

The developments of the membranes from such responsive materials have opened huge scope in this regard where mass transfer and interfacial properties can be adjusted using external stimuli. Synthesis of the membranes showing response to the external stimuli such as pH, temp., conc. etc. towards the permeability has been well established [5-12]. The study aiming at pH response has been done in section 2.3.2 of second chapter for separation of rose petal extract through acrylic acid grafted polysulfone membranes as rose petal extract and photo-modified membrane (acrylic acid grafted polysulfone), both are pH responsive. Also, the preparation of so called

responsive membranes having propensity towards light has been worked out to some extent in separation processes. These photo-responsive membranes are generally prepared by incorporating some photo-active moiety into the polymer material. This includes azo-compounds, stilbene, spiropyran, viologens etc. When an external stimulus i.e. photon is provided to the membranes incorporated with such responsive moieties, these tend to show some interesting phenomenon like trans / cis isomerization, cyclization / ring opening, development of charge etc [13,14]. This in result brings about changes in dipole moment / structure, the formation of zwitter-ions, or the dissociation into ions of the chromospheres, and as a result of these alteration, the properties of the host matrix i.e. membrane changes. This phenomenon of photo-response may be reflected in the performance behavior of the membranes and it is termed as photo-regulation. Moreover, the development of responsive membranes is at converging sight due to the fact that the reversible changes occur locally at a fast rate and with high selectivity aiming at huge prospect.

The present study is focused on the preparation of such stimuli responsive membranes which are sensitive towards photo-irradiation. The membranes are prepared by incorporating photo-active azo moiety into the membranes. Although most of the work done in this regard involves preparation of responsive membranes either by mixing / blending [15-17] the photo-active moiety while polymer solution preparation or by attaching / fixing [18-22] the photoactive moiety covalently to the base material/polymer as a pendant. But in this study, a novel approach is followed to develop photo-responsive membranes in terms of the way of incorporation of photo-active moiety. The blending/ mixing and covalent attachment of the responsive moiety generally involves the bulk phenomenon rather than surface. Besides this many times one has to compromise regarding the extent of incorporation, homogeneity, compatibility towards the base material and decrease in membrane forming capacity. Here the responsive layer is developed in such a way that membrane surface impart maximum effect toward the performance than the bulk on providing the photons. Such photo-responsive membranes are developed from polysulfone and azo moiety (from aromatic diamine). These are prepared by developing the azo layer on the asymmetric polysulfone membranes by diazotization reaction on polysulfone matrix. These membranes are exploited for their separation behavior upon photo-irradiations. Here, an external stimulus i.e. photo-irradiation is

found to be one of the crucial factors to govern the performances. When these membranes are subjected to photo-irradiation, these has reflected the quite interesting phenomenon of on / off mechanism toward the regulation of permeation of 2-chlorophenol and 4-chlorophenol in the presence / absence of photo-irradiation as azo-moiety is photosensitive. This moiety changes it configuration from cis to trans and vice-versa in response to UV light. Also, it is found that the physical parameters of the 2-chlorophenol and 4-chlorophenol have also the role to contribute towards the performance of membrane. In extension to this study, these azo composite membranes are exploited towards their biocidal activity due to photo-active incorporation. So this study aims towards

- exploitation of azo-composite membranes for the removal of water pollutants viz. 2-chlorophenol and 4-chlorophenol in the presence of photo-irradiations and
- exploitation of the role of azo moiety in the membranes for their biocidal activity

4.2 General materials and methods

4.2.1 Materials

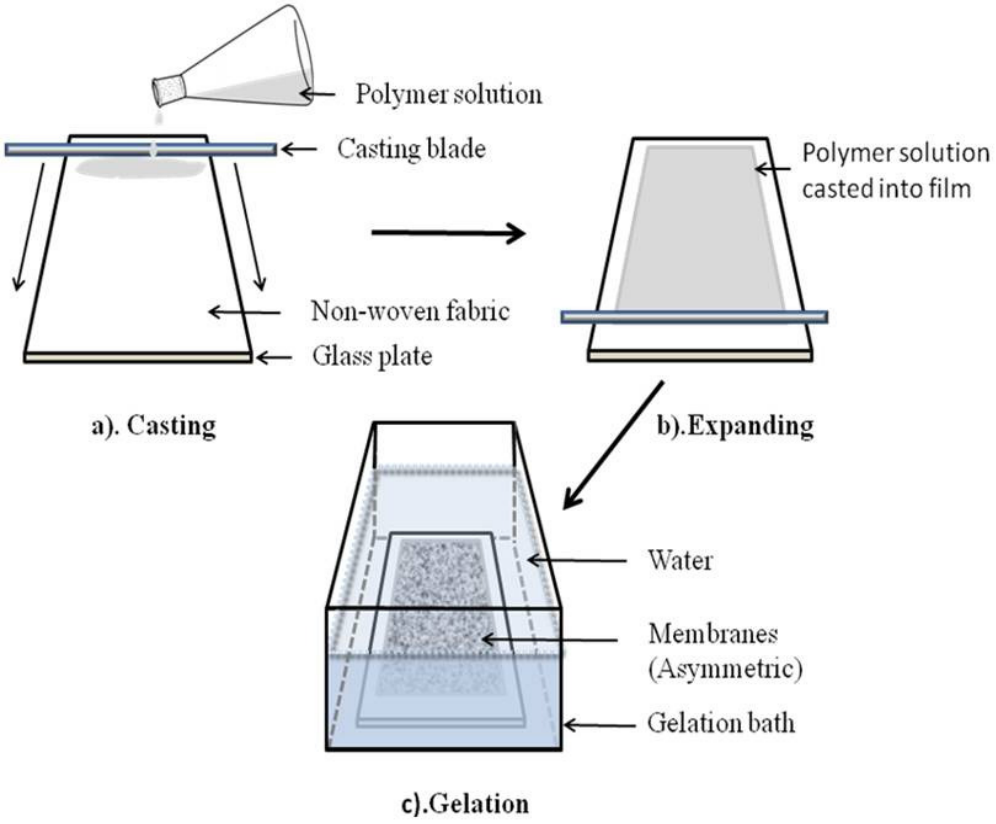
Polysulfone (Udel P-3500; Solvay advanced Polymers, USA), *N,N*-dimethyl-formamide (Merck), Non-woven polyester fabric (Filtration Sciences Corp., USA), sodium lauryl sulfate (sd fine Chemicals, India) are used to prepare the asymmetric polysulfone membrane. *m*-phenylene diamine (Loba, India) and Sodium nitrite (sd fine Chemicals, India) are used for the diazo reaction. All the other reagents used are of laboratory grade for the experiment. *m*-phenylene diamine is distilled before use. 2-chlorophenol and 4-chlorophenol (sd fine Chemicals, India) are used to study the performances behavior of the membrane. Reverse osmosis treated water is used for the experiment. Methanol (sd fine chemicals, India) is used to prepare the solution of pesticides. Reverse Osmosis treated water is used in the experiment. For bio-film formation study, thiosulphate citrate bile salt agar (TCBS), Zobell marine broth, and NaCl; all are procured from Hi media, India. Glycerol (Hi-media, Molecular Biology grade, India) is used for the preparation of the membrane samples for scanning electron microscopic study to confirm bacterial growth. 30% w/v H_2O_2 (sd fine Chemicals, India) is used for peroxide loading.

Methods

4.2.2 Preparation of asymmetric polysulfone membranes

To study the photo-regulation behavior towards the separation of monochlorophenols from water, the photo-responsive membranes are developed from asymmetric polysulfone membranes. The asymmetric polysulfone membranes are prepared form well established conventional wet-phase inversion technique [23-28] as described in section 2.2.2 in the lab by hand casting of the polymer solution on the non-woven polyester fabric as depicted systematically in figure 4.1.

Figure 4.1 Schematic presentation of preparation of asymmetric polysulfone membranes by hand casting

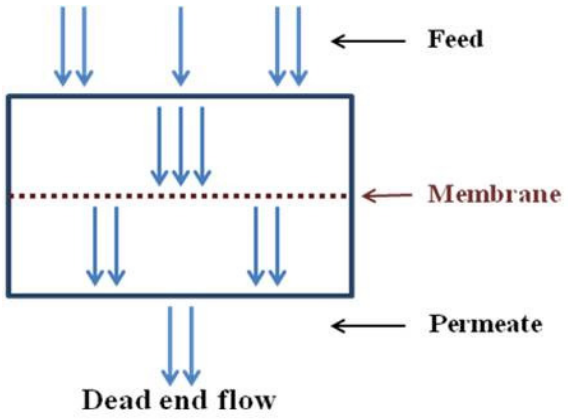


A homogeneous solution of polysulfone 8.5 % (w/w) in N, N-dimethyl formamide is prepared by slow dissolution of polysulfone beads at 45° C by continuous stirring. The thin film of polysulfone solution is casted over the non-woven polyester fabric. The non-woven fabric is fixed on the glass plate (14 x 18 cm). The polymeric solution is poured on one end of the non-woven fabric fixed on the glass plate and is spread into a film by dragging in the doctor's blade towards other

end of the fabric as shown in the figure by maintaining the proper spacing with the help of spacer between the blade and fabric surface. The solution casted non-woven fabric fixed on the glass plate 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. The solidified membrane are kept in reverse-osmosis-treated water for 24 h to remove traces of the remaining solvent and then dried for 48 h at room temperature for further experiment.

In this study, asymmetric polysulfone membranes with concentration more than 8.5 % (w/w) have also been prepared. These membranes are used in dead end filtration cell as depicted schematically in figure 4.2 for permeability studies without any external pressure. Generally, in this method flow is perpendicular to the membrane on applying the pressure. The feed enters at one end of the cell and permeate comes out from another end through the membrane. Hence, their flux is monitored after and prior to incorporation of azo-moiety. The membranes prepared with 8.5 % (w/w) polysulfone are suited best for this study.

Figure 4.2 Schematic presentation of dead end filtration technique



4.2.3 General tools and techniques

The preparation and modification of the membranes along with their performance behavior towards the separation of isomeric monochlorophenol pollutants from water, and their biocidal activity along with the effect of photo-irradiation on azo-moiety have been exploited by using different tool and techniques. These are summarized as:

UV-Visible Spectrophotometer

The effect of UV-irradiation on Bismarck brown has been analyzed by UV-visible spectrophotometer. This analytical tool (Varian, Carry 500 Scan, USA) is used to study the absorption variation for the azo-moiety when it is exposed to UV-irradiation and to dark. This is monitored at wavelength λ_{max} = 460 nm. Also the amount of bismarck brown incorporated on polysulfone membranes is found against the calibration curve plotted for various concentration of this azo moiety.

Mass spectrometer

To confirm the formation of Bismarck brown from diazotization reaction of *m*-phenylene diamine, mass spectroscopy is used. Mass spectrometry is performed using ESI-MS in positive ionization mode. Electrospray ionization (ESI) technique is used in this mass spectrometry to produce ions. It is useful even in producing ions from macromolecules because it overcomes the propensity of these molecules to fragment when ionized as the ionized molecules run through non-potential zone on acquiring energy at a constant potential. These ions are detected further by the detector, detecting the ion with low molecular mass first for having high velocity to reach first. This is done by Micromass, Q-Tof micro^{TM} instrument (from UK).

FT-IR spectrometer

To confirm the incorporation of azo-moiety on the polysulfone membrane, attenuated total reflection (ATR) infrared spectroscopy is employed (with a Perkin Elmer Spectrum GX with a resolution ± 4 cm^{-1}, incident angle 45°).

Thermo-gravimetric analysis

This technique is used to measure the mass of a substance as a function of temperature while the substance is subjected to a controlled program with respect to heating/time. The change in the weight of the polysulfone and azo-modified polysulfone membranes is studied by their decomposition pattern upon heating at a specific rate with time to confirm the incorporation of the azo moiety. This is analyzed by Mettler Toledo (TGA/SDTA851^{e} with star^{e} software) under nitrogen atmosphere and is programmed for heating at the rate of 10º C/min in the temperature range of 30º -700º C.

Contact Angle

Contact angle measurements are done by sessile drop method (DSA 3, KRÜSS, Germany) at room temperature (25° C). The sample membrane is fixed on the glass plate to be analysed. The water drop of 1µl is placed onto the membrane surface by a micro-syringe pointed vertically down onto the sample surface. To avoid the penetration of the water drop into the membrane pores, the drop image is immediately captured, recorded and then analyzed by using image analysis software. The average value is obtained from at least 10 measurements tested for each membrane.

Scanning electron microscope

Scanning electron microscopy (Leo, 1430UP, Oxford instruments) is used to have an insight about the surface topology of the membranes incorporated with azo-moiety. The biocidal effect of the azo-composite membranes is examined by having micrographs of the bacterial colony growth on the membranes with this instrument.

High performance Liquid Chromatography

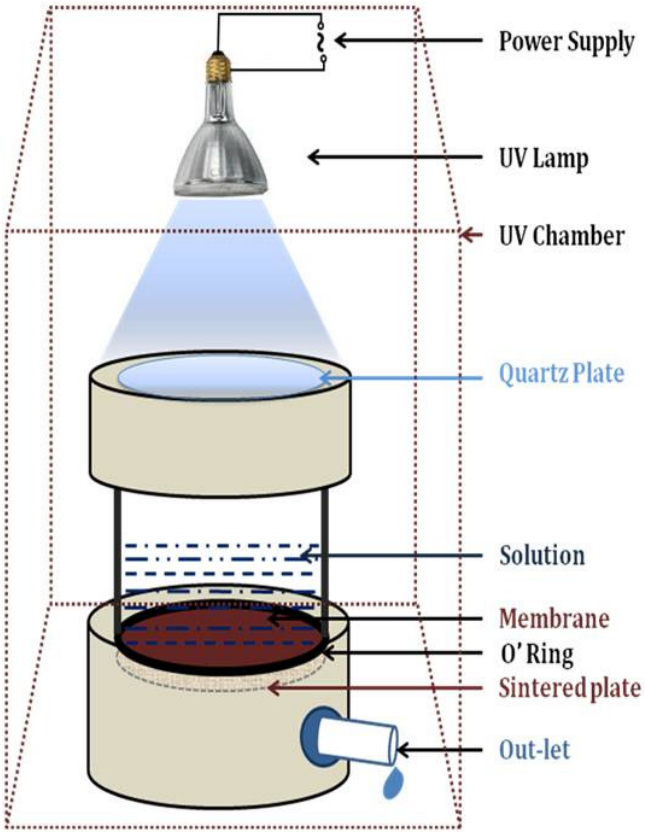
The separation of monochlorophenols is analyzed with high performance liquid chromatography (HPLC-Waters-alliance, 2996 separation module) (reverse phase), using the direct injection mode under the following conditions: Column, Water symmetry C18 (Supelco) 100 mm x 2.1 mm x 3.5 µm. For chlorophenols, the mobile phase is acetonitrile/water (80:20) with 0.125% acetic acid maintaining the flow at 0.3 ml/ min, and 2996 photodiode array detector (λ_{max} = 280 nm) is used at temperature 30° C.

Permeability studies of azo-composite membrane

The membrane permeability is measured at room temperature with a laboratory made permeation cell by dead end filtration method for pollutant removal from water as depicted in figure 4.3. The cell is placed underneath a UV-lamp (Philips HPR-125 watt, light intensity 171 W/m^2) in the UV chamber having aluminum foil wrapped on the inner wall of the chamber. The permeation cell is fitted with a quartz window to allow the UV-irradiation to fall through it on the membrane. The separation condition is maintained without applying any pressure. Permeate is collected rotation wise in dark, visible light and upon UV-irradiation conditions. The

water flux of the membranes is also obtained from cross flow filtration method. This is done to have an insight about the porosity of the membranes.

Figure 4.3 Pictorial diagram of dead end permeation cell used for photo-regulated membrane performance study



The effective area of the membrane taken for permeation study is 0.00283 m^2. The separation efficiency of the membranes in removing the studied solutes is determined by following equation

$$R = (1 - \frac{Cp}{Cf}) \times 100$$

where R is rejection in percentage, C_p and C_f are the concentration of the permeate and the feed solutions.

The flux is calculated from the relation given below:

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

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

4.3 Photo-regulated separation performances of monochlorophenols from water through azo-composite membrane

Membranes having some photo-active moiety when subjected to photo-irradiations, results changes in the physico-chemical properties of the photo-responsive molecule/moiety and in response properties of the host matrix (i.e. membrane) are also changed. This includes change in polarity, charge, color, wettability, and porosity of the membrane depending upon photoactive moiety. As a result, performance behavior of the membrane is also changed. To exploit this photo-induced regulation behavior, the separation performance of bismarck brown based azo-composite polysulfone membranes for monochlorophenol (2-chlorophenol and 4-chlorophenol) pollutants from water is studied.

Mono-chlorophenols are generally used as biocide (fungicides, herbicides) and disinfectant and are also used as an intermediate in the various chemical industries on a large scale. These are used to preserve wood and are used as intermediates in the production of pesticides, dyestuffs, and preservatives [29, 30]. These are toxic for a wide range of organisms, which accounts for their use on wide range as biocides and disinfectants. These are toxic even though these have low aqueous solubility and weak acidic nature. These have quite unpleasant penetrating odour. The toxic nature of these has been well established to plants, fishes and invertebrates [31-33]. The majority of chlorophenols release in the environment is caused by spills and leachate from treated wood. These are also a breakdown product of agricultural pesticides. Significant amounts of chlorophenols are produced during the chlorine bleaching process in pulp and paper-mills, incineration and water chlorination.

Chlorophenols are readily absorbed by the oral, air and dermal routes. Excessive exposure to them can lead to various ill effects [34-37]. These are very hazardous in case of skin and eye contact (irritant) due to their corrosive nature. This may lead to tissue damage which depends on length of contact e.g. eye contact can result in corneal damage or blindness and skin contact can produce inflammation and blistering. Inhalation of dust will produce irritation to gastro-intestinal or respiratory tract, characterized by burning, sneezing and coughing. Severe over-exposure can produce lung damage, choking, unconsciousness or even death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is

characterized by itching, scaling, reddening, or, occasionally blistering. 2-chlorophenol may also affect the unborn child.

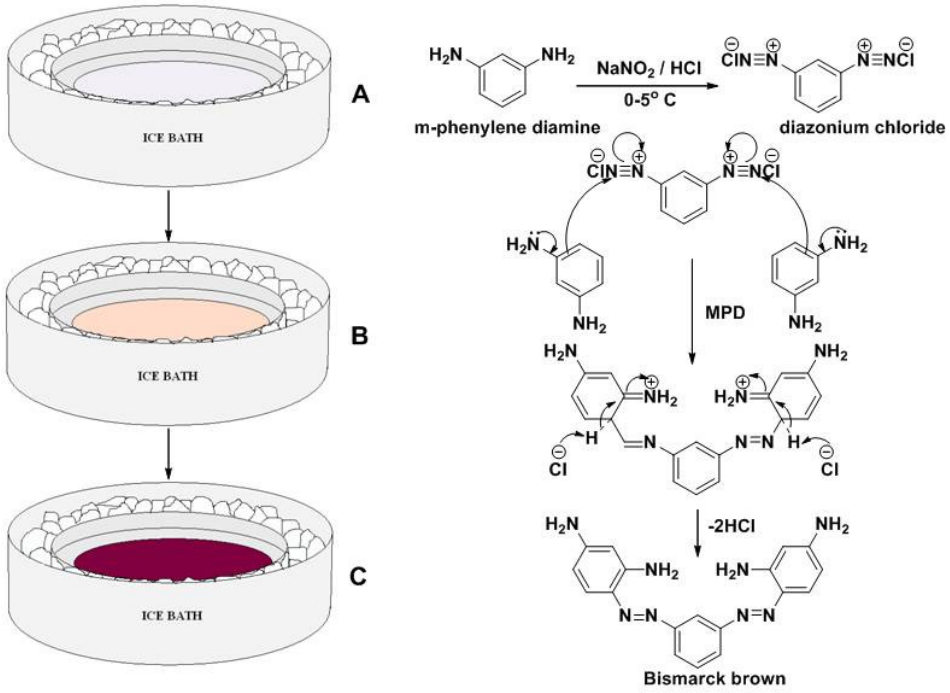
Due to the toxic properties of both of the chlorophenol (2-chlorophenol and 4-chlorophenol) [38, 39], the remediation of these compounds is of great practical significance for environment protection. Keeping in mind the adverse affects of these chlorophenols, it is a must to look for the effective ways to separate them from water. The previous chapters also have emphasized on the removal of these chlorophenols along with other pollutants. The photo-irradiation technique is employed in the preparative steps of the membranes for their removal. This chapter is also focused on the separation of monochlorophenol isomers from water through the photo-responsive membrane while maintaining photo-irradiation in operation

4.3.1 Preparation of azo-composite membranes

The azo-composite membranes are prepared from the method other than blending/ mixing or covalent attachment as is done in most of the membrane preparations. The asymmetric polysulfone membranes prepared as discussed above are used to develop the photo-responsive azo-composite membranes by incorporating azo compound by well known diazotization reaction of *m*-phenylene diamine [40]. This is depicted schematically in figure 4.4.

For this first of all the asymmetric polysulfone membrane is dipped in *m*-phenylene diamine solution (2%) for 30 minutes. *m*-phenylene diamine (MPD) has a strong affinity towards the polysulfone for adsorption compared to other diamines. Then it is dried evaporation. The MPD treated membrane is taken in petridish and is placed in an ice-bath. After 10 minute, when temperature is approximately 4°-5° C, a chilled solution of sodium nitrate mixed with hydrochloric acid is poured in to it. After 10 minutes the solution is decanted and 0.2% *m*-phenylene diamine solution is poured on the membrane. This is followed by dipping the membrane in sodium hydroxide (0.1%) solution to neutralize the excess acid used in diazotization reaction. The azo-modified membranes are washed with plenty of water first, and are followed by washing with 0.1% acidic solution to remove the slackly deposited compound on the membranes. The above reaction is also followed without membrane from MPD to get the same azo compound in powder form for further study.

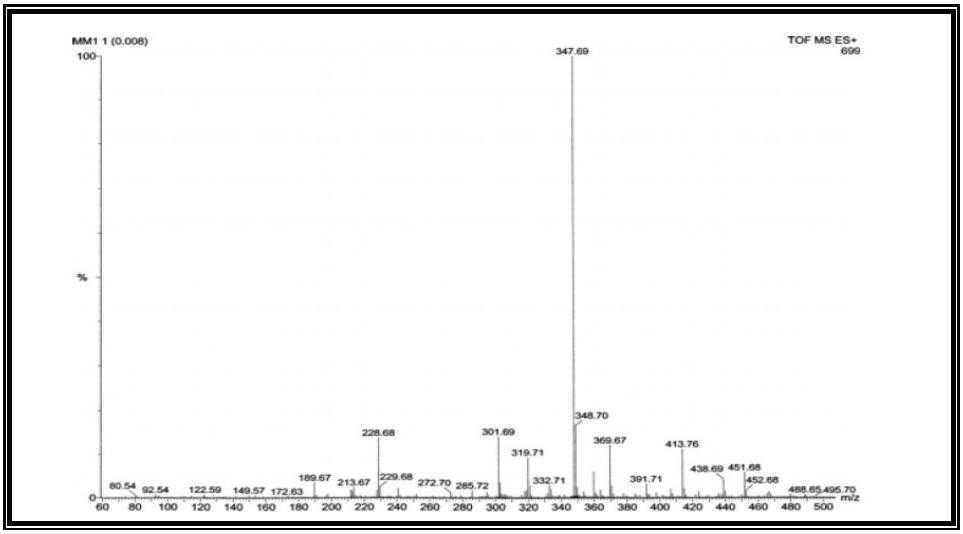
Figure 4.4 Reaction Scheme of formation of Bismarck Brown and its pictorial presentation (a) Polysulfone adsorbed *m*-phenylene diamine, (b) Polysulfone-diazonium chloride, and (c) Polysulfone- azo compound (Bismarck Brown).



4.3.2 Characterization of azo-compound and azo-composite membrane

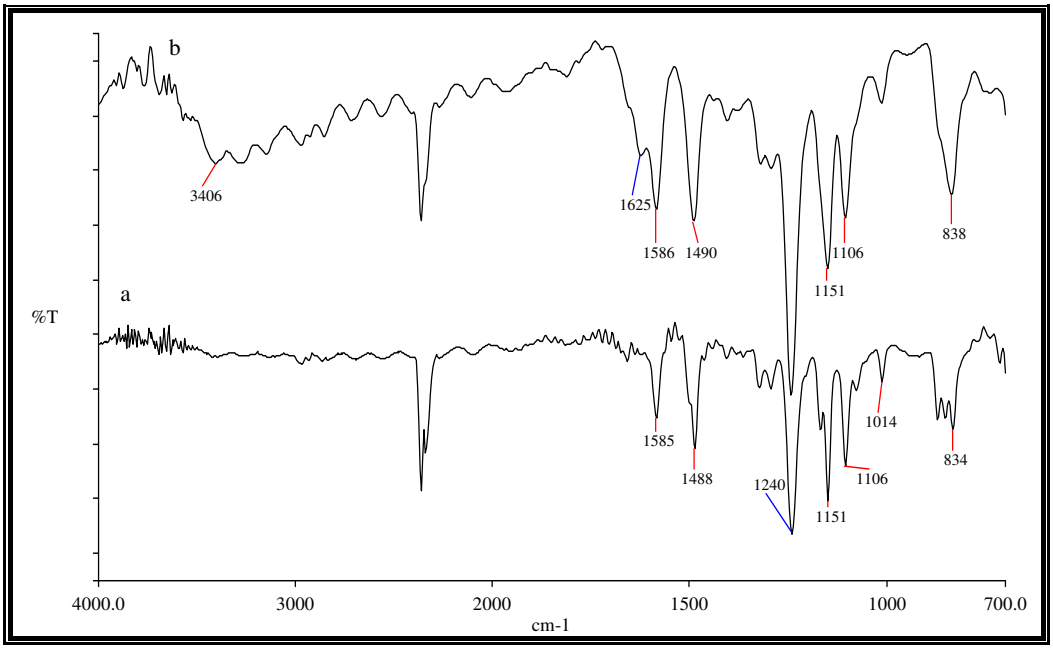
The characterization study of the compound is confirmed by mass spectrophotometer. The m/z peak is observed at 347.69 $[M + H]^+$ for the particular powder in positive ionization mode. The mass spectrum is presented in figure 4.5.

Figure 4.5 ESI-MS spectra of azo compound in powder form.



The calculated molecular mass of Bismarck Brown is 346.17. The compound is also analyzed by UV-visible spectroscopy. An absorption maxima (λ_{max}) is observed at 460 nm for this photoactive moiety.

Figure 4.6 FTIR-ATR spectra of azo-modified (b) and virgin polysulfone (a) membranes.



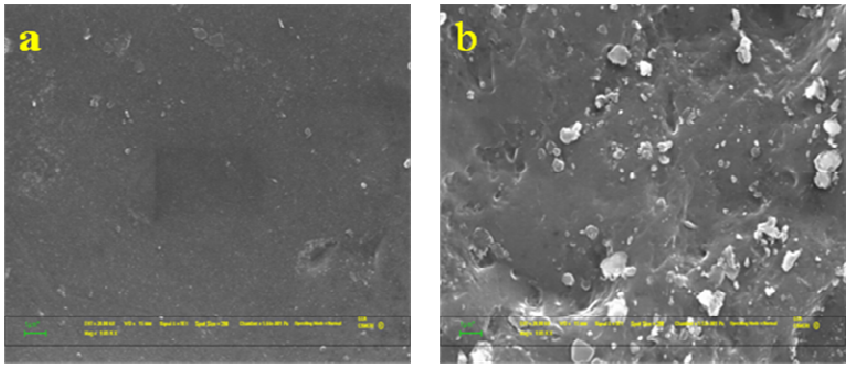
Membranes prepared by diazotization reaction of *m*-phenylene diamine on polysulfone are characterized mainly by FT-IR spectroscopy. Figure 4.6 shows the FTIR-ATR spectra of modified (azo-composite) and virgin (polysulfone) membranes. The development of peak at ~3400 cm^{-1} for modified membranes features the aromatic amine stretching vibrations. The peaks at 1623 cm^{-1} and 1586 cm^{-1} are due to N-H bending vibration studies. These peaks are the characteristic of amine group and prove the presence of amine compound i.e. bismarck brown on the asymmetric polysulfone membrane.

The scanning electron micrograph (figure 4.7) of the membrane samples shows that there is distinct difference between modified membranes and virgin Polysulfone membranes.

Contact angle measurement study reflects the incorporation of azo moiety on the asymmetric polysulfone membrane. There is a decline in the contact angle for azo-composite membrane with respect to virgin polysulfone membranes. It decreases by ~20° from an average of 79.98° (polysulfone membrane) to 59.35° (azo-composite

membrane). The decrease in contact angle shows the development of hydrophilic character on the membrane.

Figure 4.7 Scanning electron micrographs of azo-modified (b) and virgin polysulfone (a) membranes.



The amount of bismarck brown incorporated on polysulfone membrane is also calculated from UV absorption spectroscopy against the calibration curve obtained from the absorbance of Bismarck brown at 460 nm (λ) at different concentrations. The azo modified polymer membrane layer is removed from the non-woven fabric. A fix amount of the removed thin layer is dissolved in dimethyl formamide solvent. In same way a known amount of Bismarck brown compound is dissolved in dimethyl formamide solvent. UV absorption spectra is taken for the compound at different concentration and calibration curve is plotted from the absorbance at 460nm (λ) and thus the amount of the Bismarck brown incorporated per gram of the polysulfone membrane layer is calculated. It is found to be ~0.23 x 10^{-6} mole per gram of the polysulfone membrane film delaminated from non-woven fabric.

Figure 4.8 TGA diagram for the polysulfone and azo-composite membranes

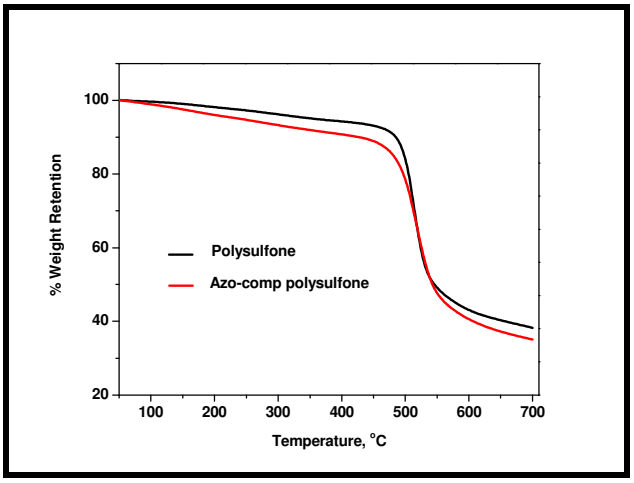


Table 4.1 Weight (%) loss for polysulfone azo-composite membrane at different temperature range during TGA

Membrane	% Weight loss with temperature	
	30°-310° C	310°-700° C
Polysulfone	4.19	57.76
Azo-comp polysulfone	7.36	57.59

To further confirm the incorporation of Bismarck brown compound on the polysulfone membrane, thermo-gravimetric analysis is done for the virgin and azo-composite membranes as depicted in figure 4.8. The decomposition pattern and the percentage weight retention in the TGA graph reflect more weight loss for azo-composite membrane (7.36%) than polysulfone (4.19%) from 30° - 310° C due to decomposition of incorporated Bismarck brown. Table 4.1 depicts the comparative weight loss for the two membranes; reflect the incorporation of azo-moiety into the membrane matrix.

Water flux is calculated from the cross-flow filtration method at 0.14 MPa to have insight about the membranes porosity. It is obtained an average flux of 22400 $lm^{-2}d^{-1}$ for virgin polysulfone and 15200 $lm^{-2}d^{-1}$ for azo-modified composite membrane. The flux data suggests that there is decline in the water permeability for bismarck brown moiety incorporation membrane than the virgin polysulfone. This has led to the decrease in the sieving effect of the polysulfone membrane due to blocking of porous network by azo-moiety.

4.3.3 Experimental Sketch up

The effect of photo-irradiation on the bismarck brown in solution (DMF) is analyzed with the help of UV-visible spectrophotometer. The UV absorption of the solution is taken with and without exposure to photo-irradiations and the change in spectra is recorded to have an insight about the photo-induced changes in the molecular level of the compound in solution.

The membranes with photo-active azo-moiety (bismarck brown) are subjected to study the role of photo-irradiation on the separation performance. For this, the azo-composite membrane is exploited for the separation of monochlorophenol isomers (2-chlorophenol and 4-chlorophenol) in the presence and absence of the UV-irradiations.

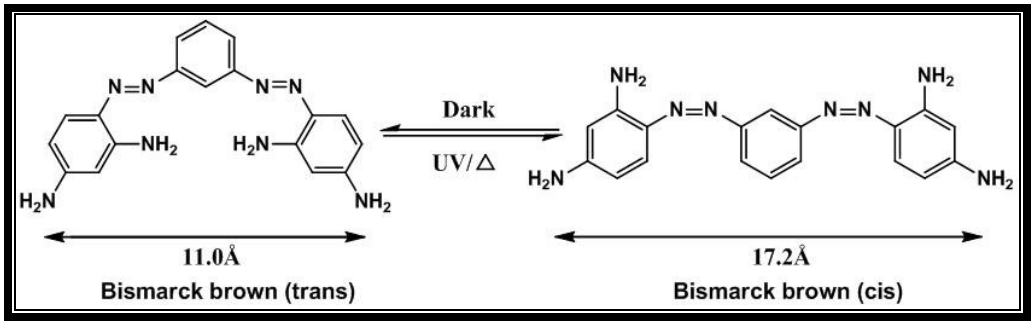
The permeation experiments are performed alternatively by keeping the permeation cell beneath the UV-lamp and in the dark chamber. A fixed volume of the experimental solution (100 ml) is taken in the permeation cell and permeate is collected after half and an hour of equilibration of the membrane during each collection under different condition of irradiations and dark.

To prepare the chlorophenol solution, a fixed amount of the monochlorophenol is taken and dissolved in methanol. An appropriate amount of methanol solution is kept in open condition to evaporate and the residues are dissolved into water (already passed through R.O module). The final concentration is maintained to be 12.5 mg/L.

4.3.4 Effect of UV-irradiation on bismarck brown moiety in solution

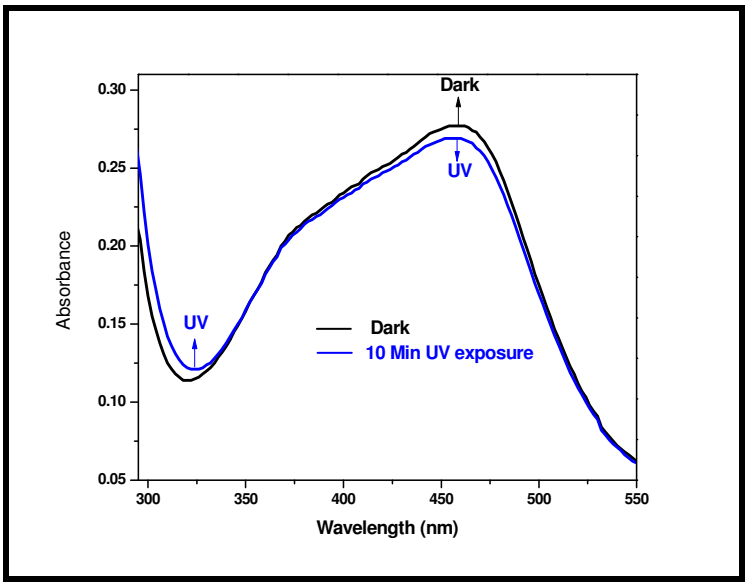
Bismarck brown is basically diazo compound having –N=N– functional group to play with. When such compounds are subjected to photo-irradiation/heat, these alter their conformation along the diazo function group from trans to cis and vice-versa. Same phenomenon happens with Bismarck brown azo compound when photo-irradiated. It attains the cis conformation on photo-irradiation/heating as shown in **figure 4.9.**

Figure 4.9 Structure of reversible conformers of Bismarck brown compound upon photo-irradiation/dark (trans and cis)



This change in confirmation is confirmed by UV-visible spectroscopy as shown in figure 4.10. When the Bismarck brown solution (in dimethyl formamide) is photo-irradiated and it is found that there is decline in the absorbance value at λ_{max} = 460 nm. After some time, it returns back to its original position. As trans form is the most stable in term of the energy and the relative energy difference between the two forms is found is to be very less i.e. 5kJ/mol as depicted in table 4.2.

Figure 4.10 Change in the absorbance of Bismarck brown solution (in DMF) in dark and UV-irradiation condition



4.3.5 Calculation of physical parameters of azo and monochlorophenol conformers

The change in the conformation of the azo-compound upon photo-irradiation is also accompanied by variation in other physical parameters. All calculations have been performed with semi-empirical PM3 method. The geometries are fully optimized at PM3 using SPARTAN [41]. Positive vibrational frequencies have confirmed that the structures are minima as depicted in figure 4.11. Table 4.2 details about the changes in the volume, dipole moment and the distance between N-N amine groups for these conformers.

Figure 4.11 The minima structures of cis (left) and trans (left) conformers of bismarck brown used in semi-empirical PM3 method for physical calculation

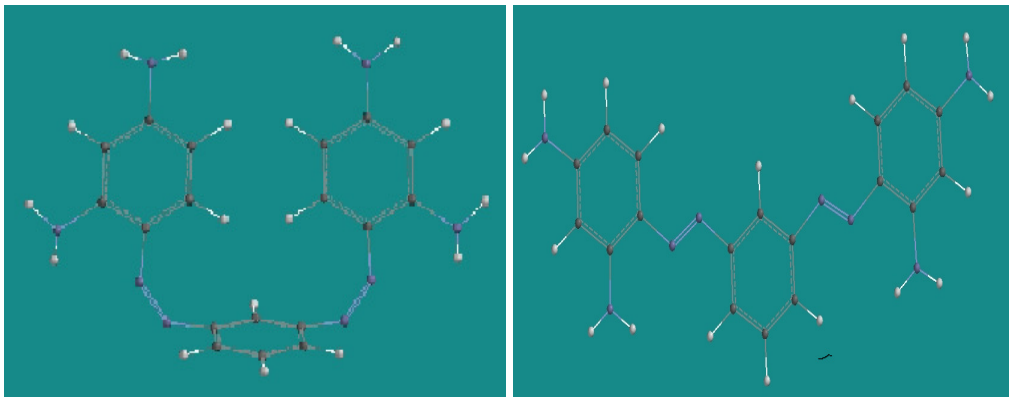


Table 4.2 Values of various physical parameters for trans and cis conformers calculated from semi-empirical PM3 method

Physical parameters	**Bismarck brown**	
	trans- isomer	**cis-isomer**
Energy (kJ/mol)*	0.0	5.0
Volume ($Å^3$)	349.0	344.8
Dipole moment (D)	2.39	5.73
Amine N-N distance (Å)	11.0	17.2

*relative energy

The physical parameters of monochlorophenols are also calculated from the Semi-empirical AM1 self-consistent Field (SCF) method and are depicted in table 4.3. Semi-empirical AM1 self-consistent Field (SCF) method is used in theoretical studies to calculate the molecular volume and dipole-moment data [42, 43] for the two conformers of monochlorophenol. First the stable conformers are predicted at AM1 level of theory, and then the molecular volume and dipole-moment are calculated.

Table 4.3 Volume and Dipole-moment Results of Phenol Molecules Calculated at Semi-empirical AM1 (A Quantum Chemical Method)

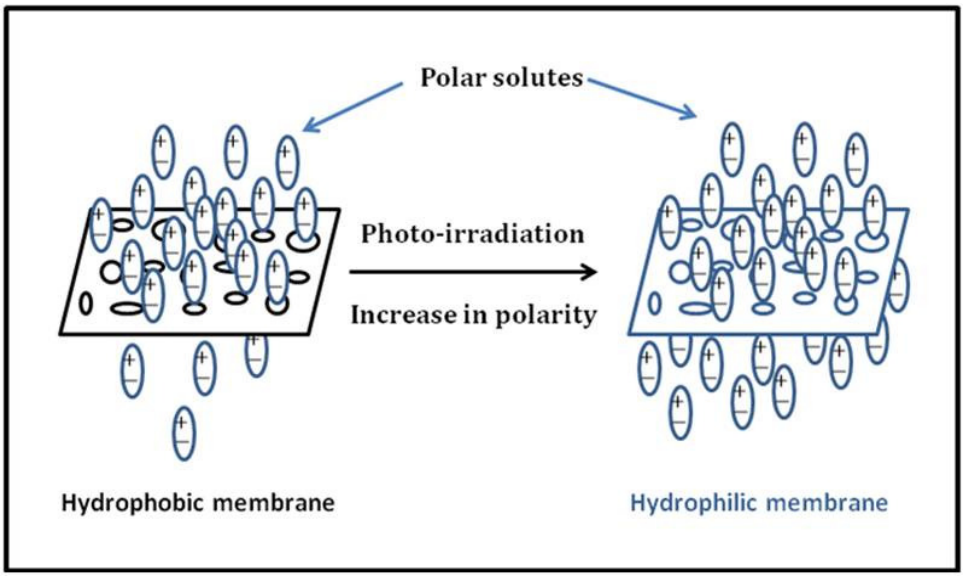
	Mol. Wt.	**Volume, ($A^{\circ 3}$)**	**Dipole moment, D**	**pKa**
2-Chlorophenol	138.5	134.5	0.938	8.48
4-Chlorophenol	138.5	135.2	1.477	9.40

The changes in the values of these physical parameters are very crucial for the membrane performance. The physical parameters of the solutes viz. molecular weight, molecular volume, dipole moment and dissociation constant have a major role as these are helpful in having an idea about the type of interaction they will have with the membrane (in terms of pores, charge) and the solvent.

4.3.6 General theory for separation behavior of photo-responsive membranes

The separation behavior of the membranes is generally governed by its porosity, charge and various driving forces. In addition to these, there are also few parameters which have a vital role to play towards the performance behavior in case of the responsive membranes. Upon photo-irradiation, there occurs trans/cis isomerization, cyclization / ring opening, development of charge etc. mainly in photo-responsive membranes [13, 14]. As a result of these changes, the environment of the photo-responsive moiety is also affected. The change in conformation of particular photo-responsive moiety may lead to change in the dipole moment and contraction or expansion of the moiety. This brings the variation in membranes properties i.e. change in hydrophilicity, opening / closing of the pores. When phenomenon of opening and closing of pores is induced due to contraction /expansion of the photoactive moiety, it will act like responsive gates. As a result more solute particles will pass through when the gate will open and their passage will be hindered if the gate is closed in response to photo-signal.

Figure 4.12 Schematic presentation of the effect of photo-irradiation on the permeation of polar compounds through photo-responsive membrane



In another approach if there is a possibility of induction of change in dipole moment due to conformational change in the responsive-moiety upon photo-irradiation, it will alter the wettability of the membrane surface. The induction of polar nature will result in the increase of hydrophilicity of the membrane while

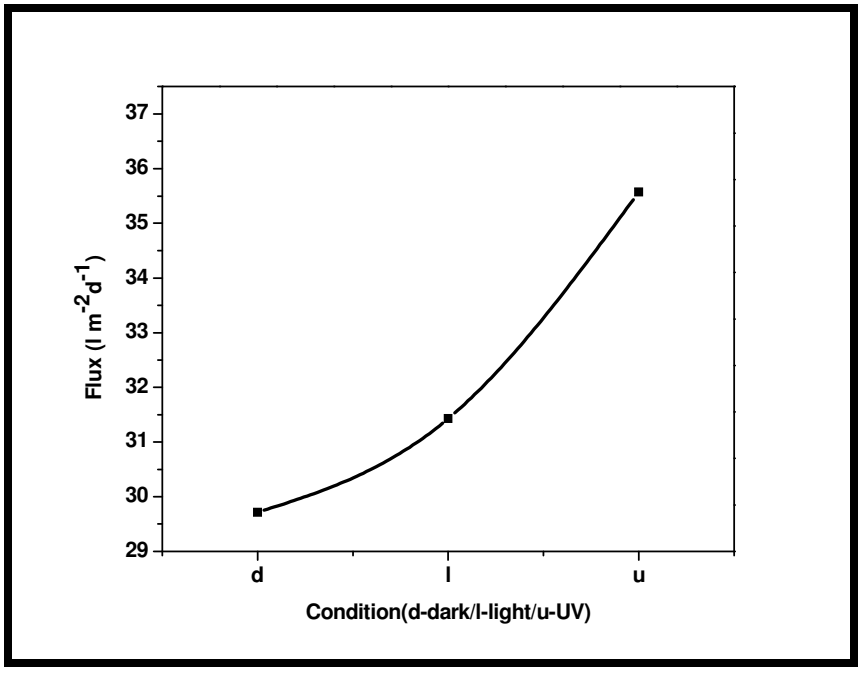
induction of non-polar nature will lead to hydrophobic nature of membrane. This hydrophilic nature of the membrane surface upon photo-irradiation will act as a selective barrier for the hydrophobic/ less polar solute than to hydrophilic/polar one as depicted schematically in figure 4.12.

Moreover, polarity of the solute also contributes to this phenomenon. On photo-irradiation, there is a change in the polarity of the surrounding of the photo-active moiety due to photo-isomerization. This again will favor the permeation of the polar molecule to pass through due to electrostatic interaction between polar solute and polar surface of the membrane.

4.3.7 Performance study of azo-composite membranes for separation of monochlorophenols upon photo-irradiations

The performance of azo-composite membrane in terms of their separation ability towards the separation of monochlorophenol isomers is examined in the presence of photo-irradiation and dark conditions. The membrane is placed in the permeation cell as shown in the figure 4.3 fitted with a quartz window on the top.

Figure 4.13 Variation of water flux in photo-responsive membrane in different conditions (dark/light/UV-irradiation)



Water permeability of the membranes is calculated in the dark and irradiated conditions. It is observed that there is an increase in the water flux upon irradiations

as depicted in the figure 4.13. This is related to the increase in dipole moment of the bismarck brown azo-moiety as depicted in table 4.2. It is due to photo-isomerization of azo-moiety from cis to trans conformer (as depicted in figure 4.9). This change is also reflected in the surrounding (i.e. membrane surface) of azo-moieties. Hence, there is an increase in the polarity of the membrane surface. This in result induces more hydrophilic character for the membrane.

The increase in hydrophilicity is also supported by contact angle measurements. It is observed that there is further decline in the contact angle from 59.35° to 48.55° when samples are irradiated during measurements. The increase in water permeability is also observed at visible light. From table 4.2 it is calculated that the energy difference is only 5 kJ/mol for the two conformer to reversibly isomerizes from trans to cis and it is readily achievable at visible light. Hence, water permeability at visible light also increases but comparatively to small extent than photo-irradiation.

Table 4.4 Variation in the rejection (%) of 2-chlorophenol and 4-chlorophenol during first and second cycle at different conditions through azo-composite membrane

Compound	**% Rejection**					
	First Cycle			**Second cycle**		
	Dark	**Light**	**UV-irradiation**	**Dark**	**Light**	**UV-irradiation**
2-chlorophenol	79.39	69.84	69.33	72.57	60.68	59.51
4-chlorophenol	78.81	65.46	64.31	65.31	46.75	46.58

The separation behavior of the azo-composite membranes is depicted in table 4.4 at different conditions of irradiation. It is observed that there is a decrease in the rejection of the monochlorophenol upon irradiation. It is also observed that there is a decrease in the overall rejection of both of the monochlorophenols upon repetition of the experiment. But the pattern of rejection remains similar to that of first cycle of experimental conditions.

In general, the rejection of the polar/ non-polar molecule is governed by the nature of the membrane surface. If there is inbuilt charge or some polar behavior is induced on the membrane surface, then it influences the separation behavior of such

molecules. For the polar molecules, it is due to electrostatic attraction, the dipole is directed towards the surface of membranes 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 [44-45]. The dipole is thus directed towards the pores of the membrane and enters more easily into the membrane structure. As the entry into membrane structure is facilitated with ease, a higher fraction of polar molecule permeates through the membrane.

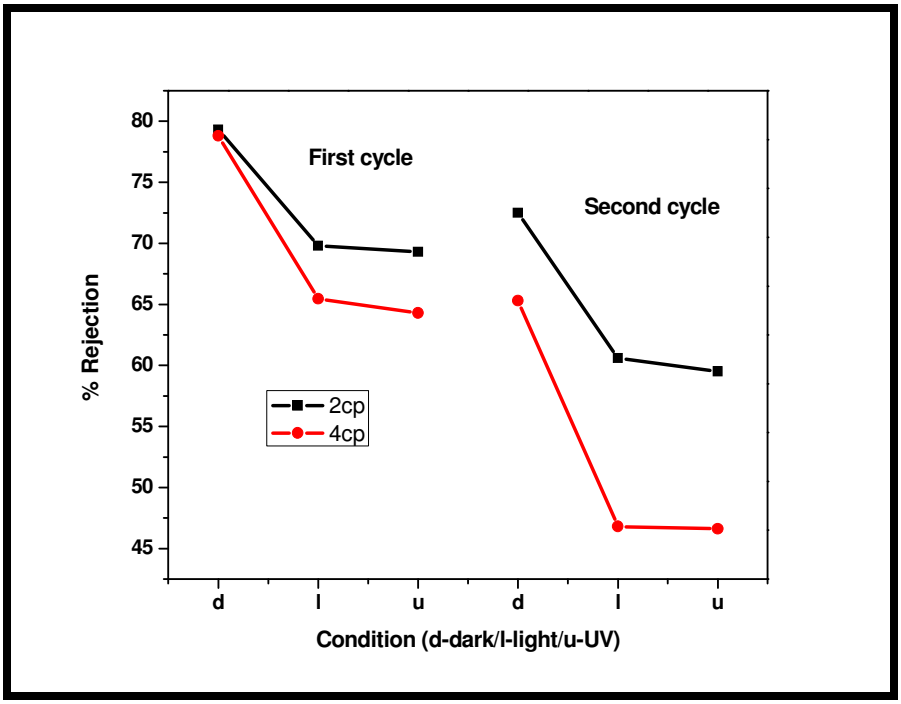
In particular experiment, the conformational change of azo moiety (figure 4.9) occurs due to photo-irradiation and as a result the different polarity results onto the membrane surface. The retention of 2-chlorophenol is found to be maximum in the dark condition. But it decreases upon irradiation with visible and ultra-violet radiations. Although it is observed that the rejection is lowest in the photo-irradiated condition (UV-radiations). Similar separation behavior of the membranes towards 4-chlorophenol is also observed. This may be attributed to the polar nature induced on the membrane surface as a result of photo-isomerization of azo-moiety upon irradiation (refer to table 4.2). As there is change in the polarity of the membrane surface, and monochlorophenols are having some dipole moment (table 4.3), therefore their passage is facilitated with ease upon photo-irradiation to more extent than dark. Beside this, the polar nature of the solute has also a major role to contribute for this behavior in the same way explained above. Therefore, membrane allows the chlorophenol solutes with higher dipole moment to pass through to more extent than the less-polar ones.

It is clearly observed from table 4.4 that 2-chlorophenol is retained more than 4-chlorophenol. This may be due to the difference in the dipole moment of the two chlorophenols. As 4-chlorophenol (1.477 D) is more polar than 2-chlorophenol (0.9388 D), hence it is retained lesser than 2-chlorophenol for the similar condition.

The overall rejection of the monochlorophenols decrease further during second run of experimental solution of isomers for the same conditions as depicted in **figure 4.14**. This is due to the surface polarization of the membranes with each run of the solution with particular monochlorophenol. As the permeation study is carried out in a dead end filtration cell so the membranes is more susceptible towards the

development of more concentrated layer of the solute on the surface. This in turn lowers the rejection of the solute.

Figure 4.14 Variation in the rejection (%) of 2-chlorophenol and 4-chlorophenol during first and second cycle at different conditions



Besides this, there is also an influence of pKa of the chlorophenol compounds on membrane performance. 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 4.3) [46-48]. Lower the pKa value; greater will be the rejection capabilities. Comparing the pKa values of 4-chlorophenol and 2-dichlorophenol, the later shows more rejection ability as its dissociation is more.

4.4 Exploitation towards biocidal effect of the azo-moiety in the membrane

The incorporation of azo–moiety into the membranes has shown photo-responsive behavior upon photo-irradiation and this photo-regulated behavior has been exploited for the removal of monochlorophenol isomers from water. The study is further extended to find out the applicability of these azo-moieties towards the biocidal activity on the membrane surface. Here, the role of azo-moieties is exploited

in this regards if these can inhibit the growth of biofilms and bacterial colony on the membrane surface. A major constraint associates with the use of membrane in water treatment is the deterioration in performances during the course of functioning. It may contain many micro-organisms as well as humic acid and micro-pollutants - all of these species being potential contributors towards membrane fouling. The consequence of the fouling is the deterioration in performance as well as life time of the membranes. The attachment of bacteria to any solid surface from any aquatic environment forms the colonies over which the settlement of macro flora and fauna occurs [49]. This gives the habitat for attachment of that fouling and boring organism (e.g., gastropods, tubeworms, and mussel) [50]. The bacterial attachment results in shortage of lifetime and membrane performances [51]. Sometime bacterial colonization results biofilm formation on the membrane. It is the natural phenomena for bacteria as self-defense against any odds to them. The inhibition of biofilm formation is helpful to expose pathogenic bacteria against any environmental stress (pH, salinity, alkalinity, some heavy metal, nutrient scarcity etc.). The aim of the membrane researchers is to find out the easy solution so that bacterial attachment can be avoided.

To avoid the attachment of undesired organisms, there are many methods. Removal and prevention of biofilms are caused by chemical treatment (chlorine dioxide, sodium hypobromite, mono-/di-/tri-chloroamines, ozone, etc.) as well as UV-disinfection. Apart from these methods, membrane researchers are in a path to find out the possible approaches to inhibit the formation of biofilm. The simplest possible approach is to modify the membranes to inhibit the formation of biofilm i.e., the modification develops the biocidal activity. The art of incorporation of material into the membrane (through blending, grafting, and adsorption techniques) draws attention in the present context. The polymers and materials are mixed and membrane is prepared in the blending method [52]. In the grafting technique, compound is chemically bonded to the polymer through their active sites [53–58] whereas material is adsorbed into the polymeric membrane surface from its solution or vapor state in the adsorption technique. The electrostatic interaction as well as hydrophobicity/ hydrophilicity factor is the possible reason for adsorption. Therefore in the present study, the azo-composite membranes have been exploited for the biocidal activity. The azo-composite membranes have been prepared from the same novel technique.

Some of the marine bacterial groups like Pseudomonas, Bacillus, and Vibrio are generally responsible for biofouling in the marine environment [59]. A presumptive Vibrio sp. isolated from sea water is used as experimental strain in the study. The natural abundance in sea water, biofilm forming capability, and growing ability in nonselective media are the characteristics of the bacteria. This biofouling bacteria generally provides space and facility for other fouling organism like barnacles and many molluscan larvae to settle down in the surface. As bacteria can be diluted to a single cell and studied in liquid culture, this mode of operation has been exploited and used to study the biofilm formation on the abiotic (membrane) surfaces. The bacterial study in liquid culture is advantageous to study by dipping the membrane in to it. Membrane modification is an art to inhibit the biofouling [55, 60, 61]. Literature report is also available that polymeric colored substrate results from functionlization develop biocidal activity [62]. Kobrakov *et al*. [63] has shown that attaching of heteryl containing azo compounds on to textile fibers, results into the development of fungicidal activity. Thus, in the present study, we have tried to test the bactericidal activity as well as biofilm inhibition on the modified membrane and biofilm formation for the unmodified membrane.

4.4.1 Preparation of Azo-composite membranes

To study the biocidal effect of the azo moiety i.e. bismarck brown, the moiety is incorporated on the polysulfone membranes is explained in the section 4.3.1 above. Polysulfone membranes are prepared from the same methods as discussed in section 2.2.2 of chapter 2. A solution of polysulfone (15% w/w) in dimethyl formamide is 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 (1 m) and immediately immersed in non-solvent medium (water), mixed with sodium lauryl sulfate as depicted in scheme 2.1 of section 2.2.2. The membranes are kept in the gelation bath for at least 3 h to complete the wet phase inversion. Then they are washed with water and dried at room temperature.

The azo moiety is incorporated on these membranes by diazotization reaction in the same way as explained in section 4.3.1. The asymmetric polysulfone membrane is dipped in *m*-phenylene diamine (2 %) for 30 minutes. It is dried by evaporation. The membrane is taken in petridish and placed in ice. Sodium nitrate solution mixed with hydrochloric acid is poured in to it. After 10 minutes the solution is decanted and

2 % *m*-phenylene diamine solution is added. This is followed by washing with sodium hydroxide (0.1 %) solution to neutralize the excess acid. Thus, the azo-composite membrane is prepared.

4.4.2 Characterization of azo-composite membranes

To confirm the incorporation of azo-moiety on the polysulfone membrane, FTIR-ATR technique is used. This displays the same peaks at ~ 3400 cm^{-1} for features the aromatic amine stretching vibrations and at 1625 cm^{-1} for N-H bending vibration for azo-moiety as depicted in figure 4.6. Similarly, the scanning electron micrograph shows more or less same surface morphology for incorporation of the azo compound onto the membrane surface as discussed in section 4.3.2.

Contact angle studies show that the mean contact angle of the azo-composite membrane decreases by ~3° (67.26° from 70.21°) with respect to virgin PS membrane (measured by Tensiometer, DCAT 21 from Dataphysics, Germany). The decrease in contact angle reflects the development of hydrophilic character on the membrane. The pure water permeability results show that polysulfone-bismarck brown (PS-BB) membranes are of low water permeability with respect to virgin polysulfone membrane (236.8 to 152.6 lm^{-2} h^{-1} at 0.69 MPa). This is due to the pore blocking of the membranes.

The amount of bismarck brown incorporated on polysulfone membrane is calculated from UV absorption spectroscopy against the calibration curve obtained from the absorbance of bismarck brown at 460 nm (λ) for different concentration. It is found to be 0.28 x 10^{-6} mol/g of the polysulfone membrane film delaminated from 15% (w/w) of polysulfone membrane.

4.4.3 Experimental sketch up

The azo-composite membranes are used to study their biocidal effect. For this the peroxide loading is carried out by dipping the membranes (6 x 2.5 cm) in to 1:1 diluted H_2O_2 (30% w/v) for 18 h. The biofilm forming activities is tested after autoclaving the membranes.

For further study, the *Vibrio* sp. is isolated from coastal water with a salinity of 30 ppt in thiosulphate citrate bile salt agar (TCBS) (Hi media, Mumbai, India) and pure colony is stored at -20°C with 25% glycerol before use.

One single colony of experimental strain is inoculation in zobell broth supplemented with 3% Sodium chloride and is allowed to grow for 12 h. 10 µl of

bacterial inoculums are added to 20 ml of zobell broth in 50 ml test tube. The membranes (PS and PS-BB) with size of 4 x 4 cm^2 are dipped single piece in each tube in sterile condition. The systems are allowed in shaking condition (80 rpm) in water bath at 30° C for 48 h and visible growth of bacterial bio-film over the surface of membranes are checked.

To determine the exact concentration of bacteria attached to the membrane surfaces they are gently washed with sterile distilled water and 1 cm^2 area at the centre of each dipped membrane are swept with sterile cotton swab and mixed with 1 ml of sterile (0.9 %) NaCl. Then suitable dilution mixtures are plated in TCBS agar to estimate the bacterial concentration from each membrane.

The membranes are treated separately for the scanning electron micrograph. It is required to dehydrate the attached bio adhesion without changing the shape. The membranes are dipped in 2% glutaraldehyde for 30 min. They are washed with phosphate buffer (pH 7.2) (two times 5 minutes each). The membranes are transferred to gradually ascending concentration of ethanol 10, 20, 30, 50, 70, 90% and rectified spirit. All the dipping duration is of 30 minutes and it is kept twice in the rectified spirit. Finally the membranes are dried and are ready for scanning electron micrograph study.

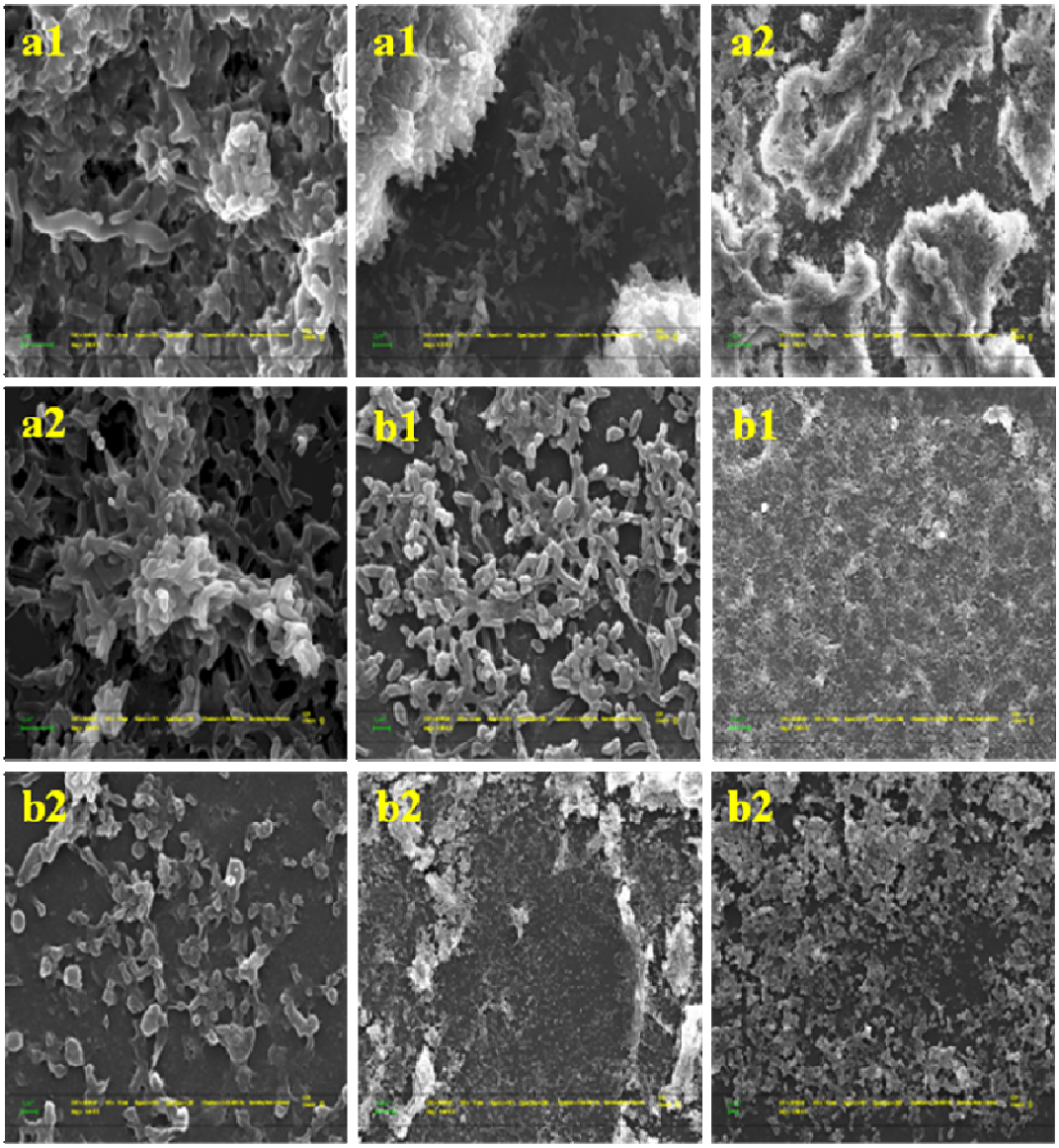
4.4.4 Biocidal effect of the azo-moiety on the membrane

The deterioration of the surface of a material starts with the development of the bacterial colony on the surface which is followed by the bio-film formation. Therefore, biofilm formation is tested for virgin polysulfone and azo-moiety incorporated azo-composite membrane with and without the treatment of peroxide solution.

Table 4.5 Bacterial count on the polysulfone and PS-BB membranes with and without H_2O_2 treatment

Membrane details	Set 1 (CFU mL^{-1})	Set 2 (CFU mL^{-1})
Virgin polysulfone (**a1**)	$3.7x10^6$	$2.9x10^6$
Virgin polysulfone with H_2O_2 (**a2**)	$1.6x10^6$	$2.4x10^6$
PS-BB (**b1**)	$2.4x10^5$	$3.9x10^5$
PS-BB H_2O_2 (**b2**)	$1.1x10^2$	$7.3x10^2$

Figure 4.15 SEM micrographs showing bacterial attachment to polysulfone membranes (a1 and a2) and azo-modified membranes (b1 and b2). Micrographs a1 and b1 shows bacterial growth on the membranes without H_2O_2 treatment and micrographs a 2 and b2 shows bacterial growth on H_2O_2 treated membranes



Formation of a biofilm begins with the attachment of free-floating micro-organisms to a surface. Thus, the hydrophobic interaction between the bacterial cell and membrane should overcome the repulsive forces active within a certain distance from the polymeric surface and irreversibly attached [64]. These first colonists adhere to the surface initially through weak, reversible van der Waals forces. The bacterial

attachment is counted for different membranes and the results are presented in table 4.5. From the results it shows PS-BB membrane has better bio-film inhibition behavior compared to PS membrane. The bacterial attachment of virgin membrane is ~10^4 times more (per sq. cm area) with respect to modified PS-BB membrane. This may be due to the development of hydrophilic character of the modified membrane as it is evidenced from the contact angle studies.

The bio-film is visually observed from the photograph (figure 4.15). The hydrophilicity of the azo-composite membranes show low adhesion of bacterial cell compared to virgin polysulfone membrane. This is also supported by similar results for different substrates in the literature [65, 66].

Scanning micrograph of virgin polysulfone membrane figure 4(a) shows there is multilayer growth of bacterial attachment; whereas for azo-modified membrane figure 4(b) the bacterial count is less compared to virgin membrane

Photo-responsive behavior of the azo-moiety (bismarck brown) has been exploited towards the photo-regulated separation of monochlorophenol isomers from water through azo-composite membranes. The azo-moiety is incorporated in to the asymmetric polysulfone membrane by non-conventional method. It is observed that the separation of monochlorophenol isomer is governed by hydrophilic and polar nature of the membrane induced as a result of photo-isomerization of azo-moiety and with time during second run, it further deteriorates at similar conditions of the irradiation and dark. But overall trend of rejection remains similar for both the isomers. The hindrance of the bio-film formation by *Vibrio* sp. for the modified azo-polysulfone membrane is due to better hydrophilic character. The bacterial count is less than 10^4 for the modified membranes.

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