2.1 Introduction

Surface modification is one of the prior art to modify membranes to get better performance in term of separations and other specific applications viz. biocompatibility, molecular imprinted polymers, immobilization, stimuli response etc [1-8]. Various techniques (viz. chemical, plasma, photo) [9-28] have been used to increase the spectrum of membranes to increase the scope for various applications. It is seen from previous chapter; photo-irradiation is one among them to modify the polymer surface, is quite prevalent and has some advantages over the others. The modification by this technique has resulted in better control over the properties of the membranes e.g. pore size, wettability, surface charge, swellability, response to external stimuli etc while the bulk properties remain intact.

The membranes used for this study are mainly asymmetric polysulfone membranes and thin film composite membranes developed on asymmetric polysulfone membranes from piperazine based polyamide layer. Polysulfone material has been selected to prepare the asymmetric membranes because of its high thermal, chemical and mechanical properties. Moreover, it is intrinsically photo-active and can be easily modified upon photo-irradiation without using photo-initiators. The asymmetric membranes with top dense skin and nodular base are prepared from it by wet phase inversion method. These membranes are expected to show better results in term of surface functionalization/modification and separation of small molecules. These membranes are modified with acrylic acid upon photo-irradiation without initiators. The photo-modified membranes are used mainly for exploration towards the separation of small organic molecules especially water pollutants/pesticides viz. atrazine, simazine, 2,4,6-trichlorophenol (2,4,6-TCP), 2,4,dichlorophenol (2,4-DCP). As pesticides, now days are one of the major polluting constituent sources of our natural resources of water. Moreover, water is one of the major paths that often facilitates easy wandering of these into the food chain and termed as 'vehicle of the pesticides'. The consciousness among the people regarding the intake of pesticides is growing. As a result, attention is getting more focused on the priority toward the supply of safe drinking water. Despite the known fact about these chemicals, there have been almost no clear cut direct methods for cleaning the life-supporting water of such chemicals. So these photo-modified membranes have been worked out for water purification from pesticides.

Besides the removal of the water pollutant through these photo-modified membranes, the effect of pH on the separation of natural pigments from rose petal extract through these membranes has also been exploited. This chapter has been discussed in two sub-sections:

a) Surface functionalization of asymmetric polysulfone membranes with acrylic acid by photo-irradiation

- ❖ For exploitation towards separation of 2,4-dichlorophenol from water
- ❖ For exploitation towards separation of natural pigments from rose petal extract

b) Surface functionalization of thin film composite membrane with acrylic by photo-irradiation

- ❖ For exploitation towards separation of atrazine, simazine, 2,4,6-trichlorophenol, and 2,4,dichlorophenol from water

The first sub section details about the polysulfone membrane preparation by wet phase inversion technique and its modification by acrylic acid upon photo-irradiations without the use of photo-initiator. The second one deals with the preparation of thin film composite membrane and its photo-modification by acrylic acid.

2.2 Materials and methods

2.2.1 Materials

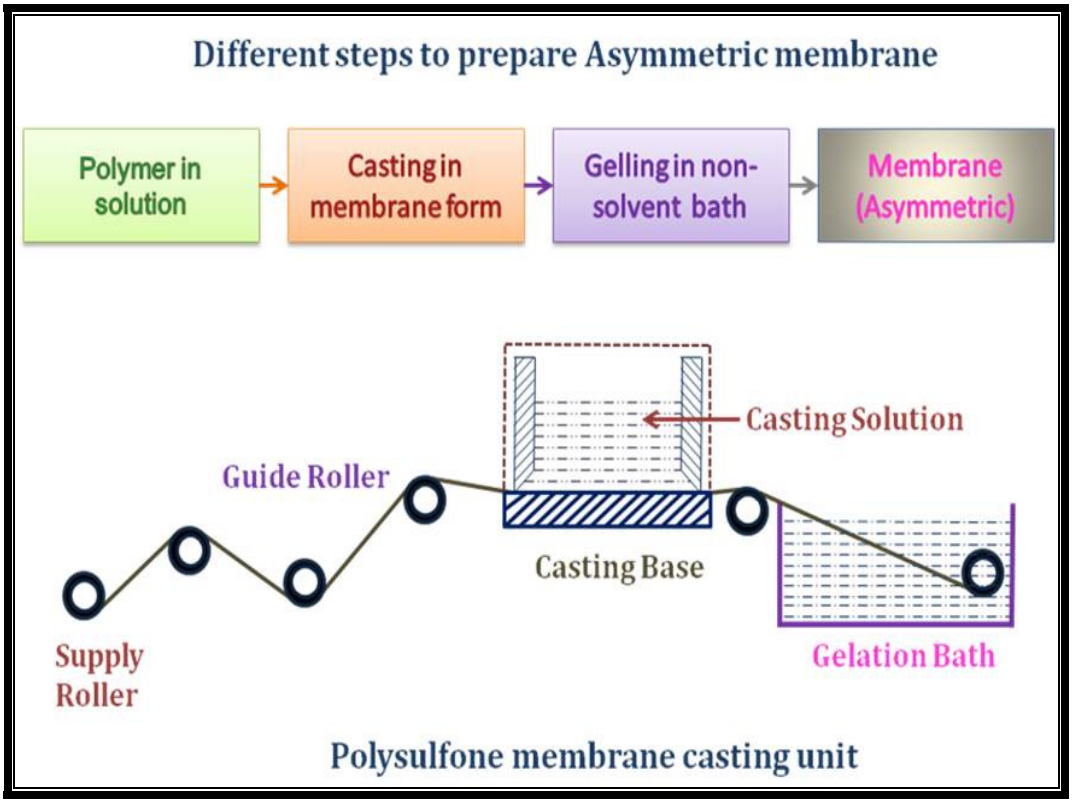
Polysulfone (Udel P-3500; Solvay advanced Polymers, USA), dimethyl-formamide (Merck), Non-woven polyester fabric (Filtration Sciences Corp.,USA), sodium lauryl sulfate (sd fine Chemicals, India) are used to prepare the asymmetric polysulfone membrane. Piperazine (Loba, India) and trimesoyl chloride (Lancaster, USA) are used for the preparation of thin film composite membranes. Acrylic acid (SRL, India) is used as monomer to modify the membrane surface after distillation.

Atrazine, simazine (Sigma, chemicals USA), 2,4,6-trichlorophenol , 2,4-dichlorophenol, (sd fine chemicals, India), glucose (Glaxo, India), sucrose (sd fine Chemicals, India), sodium chloride and sodium sulfate (Qualigens, India) are used for the performance testing of the membranes. Methanol (sd fine chemicals, India) is used to prepare the solution of chlorophenol and other pesticides. Acetone (sd fine chemicals, India) is used to make the extract from rose petals with water. Reverse Osmosis treated water is used in the experiment.

2.2.2 Preparation of asymmetric polysulfone membranes

Polysulfone membranes are prepared from conventional wet-phase inversion technique [29-36]. A homogeneous solution of polysulfone of 15 % (w/w) 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 the non-woven polyester fabric (1m width) by moving the fabric over the guide roller using a proto-type casting machine as shown in figure 2.1 schematically. The polymeric solution casted non-woven fabric is then immersed into the non-solvent gelation bath i.e. water. This results in the demixing of solvent (dimethyl formamide) and non-solvent (here it is water) to phase out the solid asymmetric polysulfone membrane.

Figure 2.1 Schematic presentation of proto-type casting unit of polysulfone membrane.



Sodium lauryl sulfate is used in the gelation bath to control the uniformity of pores in the membrane. The choice of dimethyl formamide solution for dissolving the polysulfone is preferred because of its slow dissolution and it does not lead to fast and

poorly controlled non-homogeneous deformation [37]. The dipping of polysulfone casted fabric is done instantaneously into non-solvent.

2.2.3 General tools and techniques

Membranes prepared and modified for this study have been characterized by various techniques and tools. This includes:

Fourier Transform-Infrared spectrometer:

Infrared spectroscopy is one of the various techniques of spectroscopy which deals with the infrared region of the electromagnetic region. The spectrum of infrared region can be divided into three as near infrared region, mid-infrared region and far-infrared region. Mid-IR region (4000 - 650 cm^{-1}) is the most important region for the analysis of the most of the organic compounds principally with some functional groups. Near IR region (1500 - 400 cm^{-1}) is called as finger print region because of its uniqueness towards any particular compound. Mid-IR region generally causes fundamental vibration, stretching and bending in the molecules which are specific to a particular functional group and these are used to elucidate the structure of the compounds. Attenuated total reflection (ATR) infrared spectroscopy is the allied technique for this where the samples like films, membranes, liquid etc. are analyzed by mounting them on the crystal of very high refractive index like Germanium (Ge), Zinc selenide (ZnSe), Zinc sulfide (ZnS) etc. To confirm the presence of photo-assisted incorporation of acrylic acid on the membranes, attenuated total reflection (ATR) infrared spectroscopy (with a Perkin Elmer Spectrum GX with a resolution $\pm$ 4 cm^{-1}, incident angle 45°) is employed.

Capillary Flow Porometer:

The porometric studies are performed to have an insight about the pore distribution, mean flow pore diameter and mean flow pressure of the membranes. This is done by Capillary Flow Porometer (Porous Materials Inc, USA, Model 1500 AEX), considering the pores as a capillary. The variation in the pore diameter of the acrylic acid modified membrane is studied with respect to polysulfone membrane. In this technique, the membrane samples are soaked in a wetting liquid, Porewick (having $\gamma \Rightarrow$16 dynes/cm) and contact angle is zero i.e. it wets the membranes fully and spontaneously fill all the pores in the sample. Then nitrogen gas is blown through the

membranes and the pressure of the nitrogen gas on one side of the wet membrane samples is then gradually increased. With increasing pressure, the gas removes liquid from smaller pores and the gas flow rate increases. The basic of the porometry can be expressed as

$$D = 4\gamma Cos\theta / p$$

Where D is the diameter of the pore, θ is the contact angle, and p is the differential pressure. As $\theta = 0^\circ$ for wetting liquid (porewick), therefore, $Cos\ \theta = 1$, so the above equation becomes

$$D = 4\gamma / p$$

With this equation diameter of the pores is calculated. Thus mean pore flow and mean pore flow diameter is obtained from the inbuilt software of the porometer. The gas permeation is measured up to 1.38 MPa.

Contact Angle:

The angle at the juncture of liquid / vapour interface and the solid surface is called as contact angle (CA). This is peculiar towards the interaction across the interfaces with the matter. This provides an insight about the hydrophilicity or hydrophobicity of the membrane surface. The Wilhelmy plate method is used to measure the contact angles of the membranes. This involves the measurement of the apparent weight change in the sample when it is immersed in liquid (water) of known surface tension and taken out of it. The following equation satisfy the calculation

$$F = Cos\theta\sigma p - \rho Ahg$$

Where F is the force/weight measured during the immersion and withdrawal of the sample from the liquid (mN), θ is the contact angle, σ is the surface tension of the liquid (mNM^{-1}), p is the wetted perimeter (m), ρ is the liquid density ($Kg\ m^{-3}$), A is the cross-section area of the sample (m^2), h is the immersion dept (m) and g is the gravitational constant.

The contact angle of the polysulfone and acrylic acid modified membranes is measured by Tensiometer (DCAT 21 from Dataphysics, Germany). The motor speed 0.05mm/sec, dipping length 5mm is maintained.

Atomic force microscope:

Atomic force microscopy (AFM) is a very high-resolution type of scanning probe microscopy, with resolution on the order of fractions of a nanometer, more than 1000 times than that of optical diffraction limit. This can be used for imaging, measuring and manipulating matter at nanoscale. This is achieved by "feeling" the surface with accurate and precise movements of a mechanical probe called as cantilevers. This analytical tool is used to get information about the membrane surface. Surface micrographs as well as roughness of the polysulfone and acrylic acid modified polysulfone membranes are obtained by this. The images are obtained from Multimode Scanning Probe Microscope with NanoScope IV controller (M/S Veeco, USA in the tapping mode [38-40]. The scan size is 2 x 2 μm^2 and the scan rate is 1.507 Hz

Scanning electron microscope:

SEM is an imaging / scanning microscope which uses electron beams to get information about the surface of the sample. The primary electron beam interacts with the matter and produces the secondary electrons as signals which contain information about the surface of the sample. This is very much useful in having an insight about the sample's surface topology, morphology composition and other properties such as electrical conductivity. The surface of the sample to be analyzed should be conductive to interact with electrons else it is made conductive by coating a fine layer of gold by sputter coater. The images obtained are black and white as no visible light is employed. The thin film composite membranes along with the acrylic acid modified thin film composite membranes are characterized by Scanning electron microscopy (Leo, 1430UP, Oxford instruments) to have an insight about the surface topology of the membranes.

Thermo-gravimetric analysis:

Thermo-gravimetric analysis is one of the thermal analysis techniques, which 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 technique is used to have an idea about the thermal stability of the compound, to study the kinetic feature of weight loss or weight gain, material characterization as a finger print, for corrosion studies and compositional analysis of the material or mixtures by

controlled parameters. The change in the weight of the virgin polysulfone and modified polysulfone membranes is studied with the help of this technique to confirm the photo-assisted incorporation of the acrylic acid by their decomposition upon heating at a specific rate with time. This is analysed by Mettler Toledo (TGA / SDTA851^e with star^e software) under nitrogen atmosphere by programmed heating at the rate of 10º C/min in the temperature range of 50º - 750º C.

High performance Liquid Chromatography:

HPLC is the advanced technique of chromatography which is based on the principle of adsorption and partitioning. It is a form of column chromatography used frequently to separate, identify, and quantify compounds based on their characteristic polarities and interactions with the stationary phase in the column. It utilizes different types of stationary phases, a pump that moves the mobile phase / eluent (which may be a gas, a liquid or a supercritical fluid) and analyte through the column, and a detector to detect the characteristic retention time for the analyte. The mobile phase is selected such that components of the sample / analyte differ in their interaction/ solubility with it. A component which has more affinity to the stationary phase will take longer to travel through the column than a component with lesser affinity. As a result of these differences in affinity / polarity / solubility / mobility, sample components are separated from each other as they travel through the stationary phase.

The above mentioned tool is used to study the performance of the photo-modified membranes in terms of the rejection of small organics by using different columns and conditions. The pesticide-organics concentrations are analyzed with high performance liquid chromatography (HPLC - GPC Waters, 2695 separation module) (reverse phase), using the direct injection mode under the following conditions: Column, Nucleosil C18 (Supelco) 4.6 x 250 mm x 5 µm, mobile phase acetonitrile / water (80:20), 0.125% acetic acid, flow 1.0 ml/ min, and 2996 photodiode array detector (λ_{max} = 280 nm), temperature 30°C, injection volume: 20 µL. For the glucose and sucrose solution (2414 RI detector HPLC mode) the following conditions are maintained: column Supelcogel C610H, 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.

MWCO of the modified membranes are obtained by size exclusion chromatography by using (HPLC- GPC Waters, 2695 separation module 2414 RI

detector). For PEG - 600 the conditions are maintained in reverse phase and direct injection mode: column ultra-hydrogel 120, 7.8 x 300 mm, mobile phase 0.1 M $NaNO_3$ in water flow 1 ml/min, temperature 25° C.

UV-Visible Spectrophotometer:

Each and every matter has a tendency to interact with electromagnetic radiations and shows some specific transition within it towards a particular range of wavelength. UV-Visible spectrophotometer is one that analyses the interaction of ultraviolet and visible region of electromagnetic radiations with matter. The interaction of these radiations with matter results in the transition in electronic energy level. These are recorded in terms of absorption and emission of the radiations which provide information about the matter. This technique is used to study the rejection of floral pigments and glucose from the acrylic acid modified membranes. UV-visible spectrophotometer (Varian, Carry 500 Scan, USA) is used to analyze the floral pigments at wavelength λ_{max}= 513 nm. 2,4-dichlorophenol and glucose are also analyzed by this technique. Glucose concentrations are measured with phenol-sulfuric acid colorimetric method [41]. The analysis of glucose is based upon a condensation reaction with phenol in an acidic medium, yielding a yellow-orange color [42]. The wave length of detection is 291 nm for 2,4-dichlorophenol and 485 nm for glucose.

Permeability studies

The permeability is measured at room temperature with a laboratory made pressure cell by cross flow filtration method as shown in scheme 2.1. The cross flow method as depicted in figure 2.2 comprises flow through a membrane module in which the fluid on the upstream side of the membrane moves parallel to the membrane surface and the fluid on the downstream side of the membrane moves away from the membrane in the direction normal to the membrane surface.

The effective membrane area is 0.00152 m^2. The water flux and salt rejection experiments are performed with sodium chloride, sodium sulfate. The salt rejection measurement is done by their conductivity relationship, as concentrations follow direct relationship [43-44]. The efficiency of the membranes in removing the studied solutes is determined as follows

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

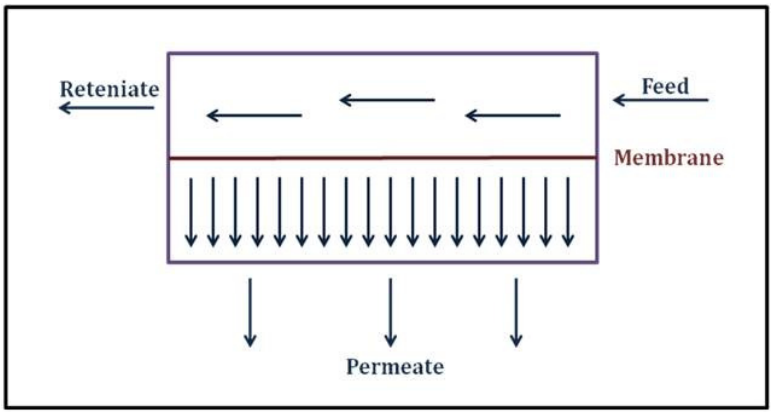
where R is the rejection in percentage, C_p and C_f are the concentration for permeate and the feed solution.

The flux is calculated from the relation:

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

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

Figure 2.2 Schematic representation of cross flow filtration method used in separation performance



Scheme 2.1 Schematic diagram of testing unit for flat membrane (P, pressure gauze; T_1,T_2, T_3, T_4, pressure test cells; R, back pressure regulator; V, bypass valve; A, pressure accumulator; F, pump; G, feed solution Tank)

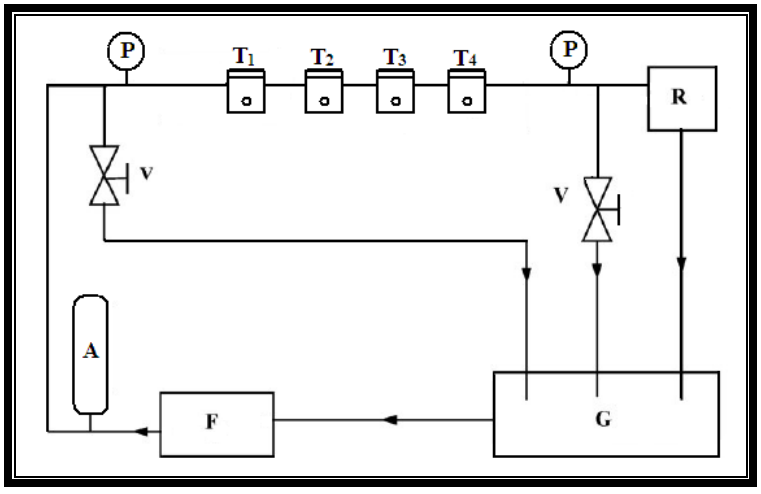


Figure 2.3 Schematic diagram of UV-irradiation set up used for photo-modification of membranes

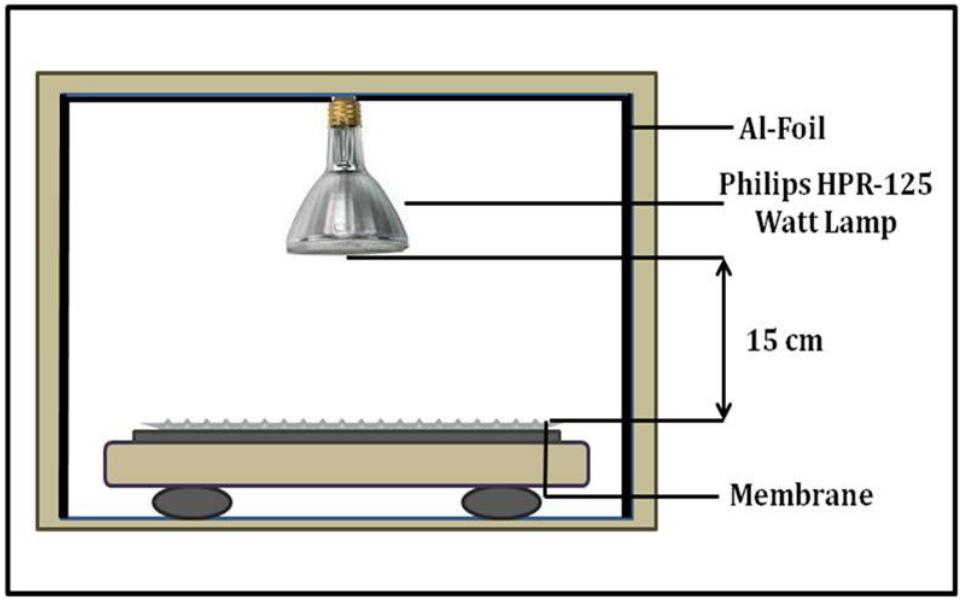


Photo-modification set up/chamber

The modification of polysulfone and piperazine based polyamide thin film composite membranes is achieved in the lab made UV-irradiation chamber as shown in **figure 2.3**. Different types of UV lamps are used to achieve the modification of membranes. The membranes treated with acrylic acid are kept at a specific distance beneath the UV lamp and photo-irradiated for specific time. The so modified membranes are further washed after photo-treatment with plenty of water several times and kept in water for 48 hours prior to further experiment.

2.2.4 Photo-modification of membranes with acrylic acid

Polysulfone is frequently used polymer in the membrane technology now days for preparation of high performance ultrafiltration and microfiltration membranes. This is preferably because of their high mechanical, thermal and chemical stability among others. These membranes are hydrophobic in nature and are basically neutral. This restricts the use of these membranes in different applications. But, the modification of the membrane by various techniques with different monomers has broadened the scope for various applications. In this section polysulfone membranes are modified by incorporating acrylic acid upon photo-irradiation. These modified

membranes show characteristic towards nano-filtration and also show pH response towards separation.

2.2.5 Mechanism for photo-modification of polysulfone membrane

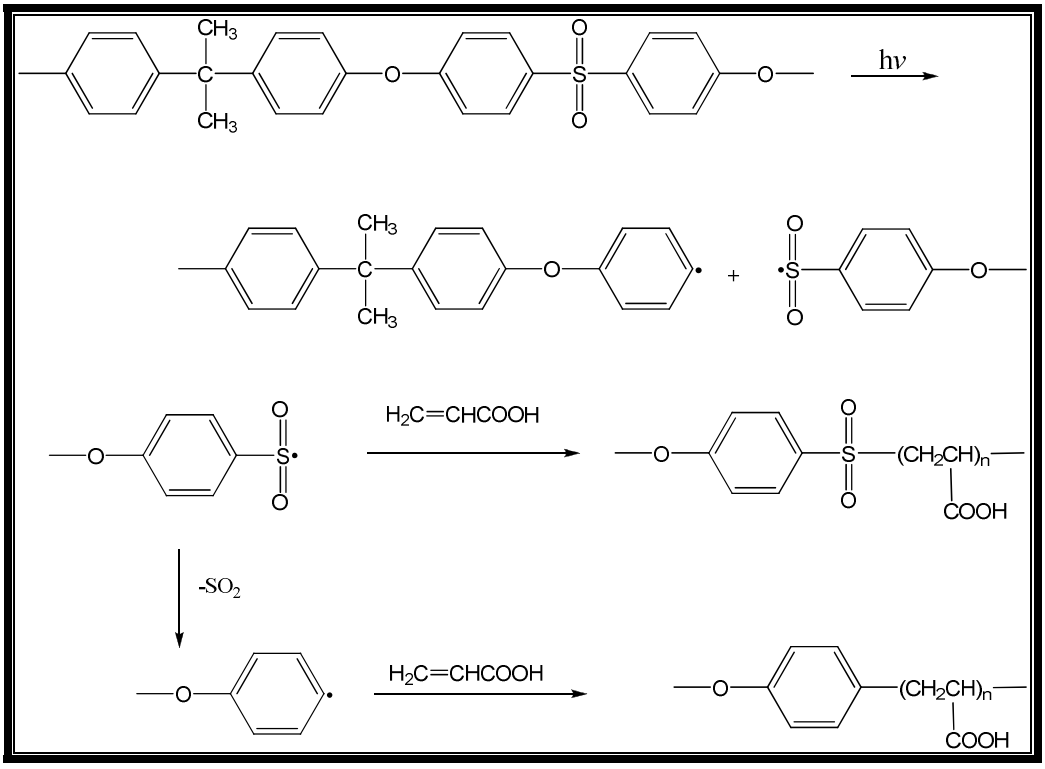
The modification of polysulfone membrane with acrylic acid upon photo-irradiation [45] involves the following steps:

a. Absorption of light by the phenoxyphenyl sulfone chromophores in the polysulfone chain,

b. Photo-excitation which results in the homolytic cleavage of a C-S bond at the sulfone linkage. It also leads to random cleavage of the polymer backbone yielding two radical sites at the ends of the polymer chains and

c. Reaction of acrylic acid with the aryl and sulfonyl radical.

Scheme 2.2 Proposed mechanism for photo-induced modification of polysulfone membrane with acrylic acid.



Alternatively, the sulfonyl radical may lose sulfur dioxide to generate an additional aryl radical which also may initiate polymerization. The probable mechanism of photo-induced modification is shown in scheme 2.2.

2.3 Surface functionalization of asymmetric polysulfone membranes with acrylic acid by photo-irradiation

2.3.1 Exploitation towards separation of 2,4-dichlorophenol from water

Asymmetric polysulfone membranes prepared by wet phase inversion technique are subjected to modification by acrylic acid upon photo-irradiation. Acrylic acid is used to generate the functionality of the membrane, so that the membrane surface can be of some functionality and can show some potential to the ions and low molecular weight compounds from aqueous solution.

2.3.1.1 Photo-modification of polysulfone membranes by acrylic acid

Asymmetric polysulfone membranes are treated with acrylic acid solution for photo-modification. Acrylic acid solution (in water) of different concentrations is spread on the polysulfone membranes (asymmetric side) fitted on glass tray for different time duration. The solution is decanted from the membrane surface and these acrylic acid treated membranes are photo-irradiated for 10 minutes. In this study light induced experiment is done by a UV-lamp (Philips HPR-125 watt) as depicted in figure 2.3. The membrane samples are kept at 15 cm distance from the light source. The lamp generated 300-400 nm and 171 W/m^2 light. All experiments are carried out at ambient temperature and in nitrogen atmosphere. The radiation density flux on all the surface area is assumed to be constant in each run. The experimental details are shown in table 2.1.

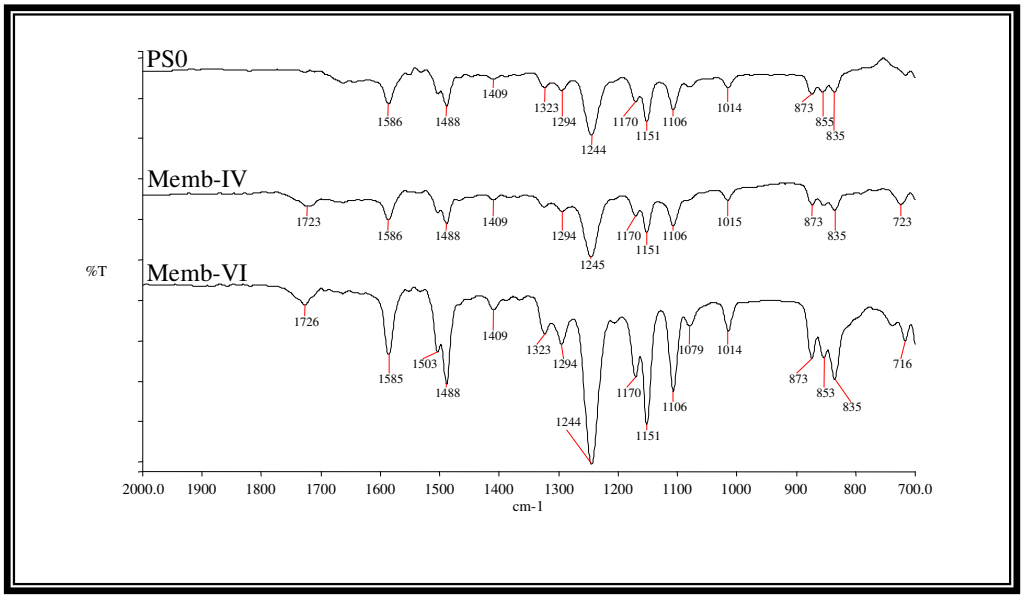
Table 2.1 Experimental conditions and content of acrylic acid on modified membranes

Membrane	**Acrylic acid (%)**	**Dipping time (min)**	**AA content, (mol cm^{-2}) x 10^7**
Polysulfone	--------	--------	--------
Memb-I	1	10	2.9
Memb-II	5	10	3.4
Memb-III	10	10	5.1
Memb-IV	1	30	4.1
Memb-V	5	30	7.2
Memb-VI	10	30	10.2

2.3.1.2 Analysis of photo-modified membrane

The photo-modified polysulfone membranes analyzed by various tools and techniques as mentioned above in general tools and technique used (section 2.2.3). The incorporation of acrylic acid is analysed by FTIR-ATR. Figure 2.4 shows the spectra of (a) polysulfone membrane, and (b) polysulfone-AA membrane with (1% and 10%). The strong reflectance in 1586 - 1488 cm^{-1} is related with the benzene ring stretching mode. The sulfone bands are observed at 1151 cm^{-1}. Asymmetric C-O stretching frequencies occur at 1244 and 1014 cm^{-1}. These observations are similar to earlier reports [46-49] in the literature.

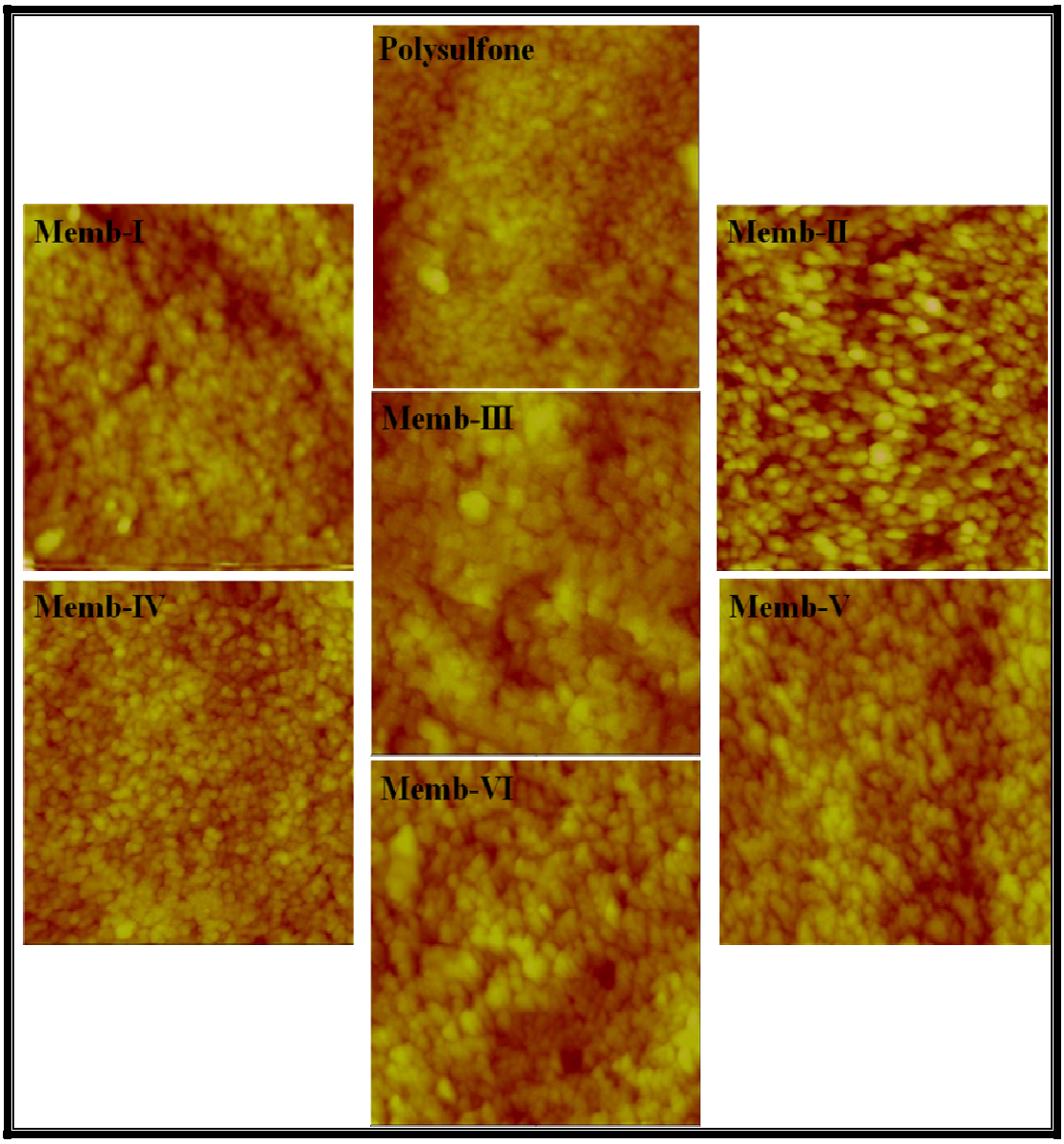
Figure 2.4 FTIR spectra of Polysulfone (PS) and acrylic acid modified Polysulfone membranes (conditions for Memb-IV: dipping time: 30min, AA conc. 1%, photo irradiation time 10 min and Memb-VI: dipping time: 30min, AA conc. 10%, photo irradiation time10 min)



1726 cm^{-1} reflectance of C=O stretching is well observed in the acrylic acid modified membrane. There is a shifting (maximum ~ 6cm^{-1} for Memb-VI) as the molecular environment is different than individual monomer, which exhibits C=O stretching at 1720 cm^{-1}. Absence of 3080 cm^{-1}, 984 cm^{-1}, 927 cm^{-1} frequencies suggest that there is no unsaturation (=C-**H**) on the surface of the polysulfone membrane.

The weight difference of modified membranes is due to the presence of acrylic acid on polysulfone. From table 2.1, it is seen that with the increase in dipping time as well as concentration, increase in weight is reflected systematically and it is in the range of 10^{-6} to 10^{-7} mol/cm^2.

Figure 2.5 AFM micrographs for the polysulfone and acrylic acid modified polysulfone membranes (Memb-I, Memb-II, Memb-III, Memb-IV, Memb-V, and Memb-VI).

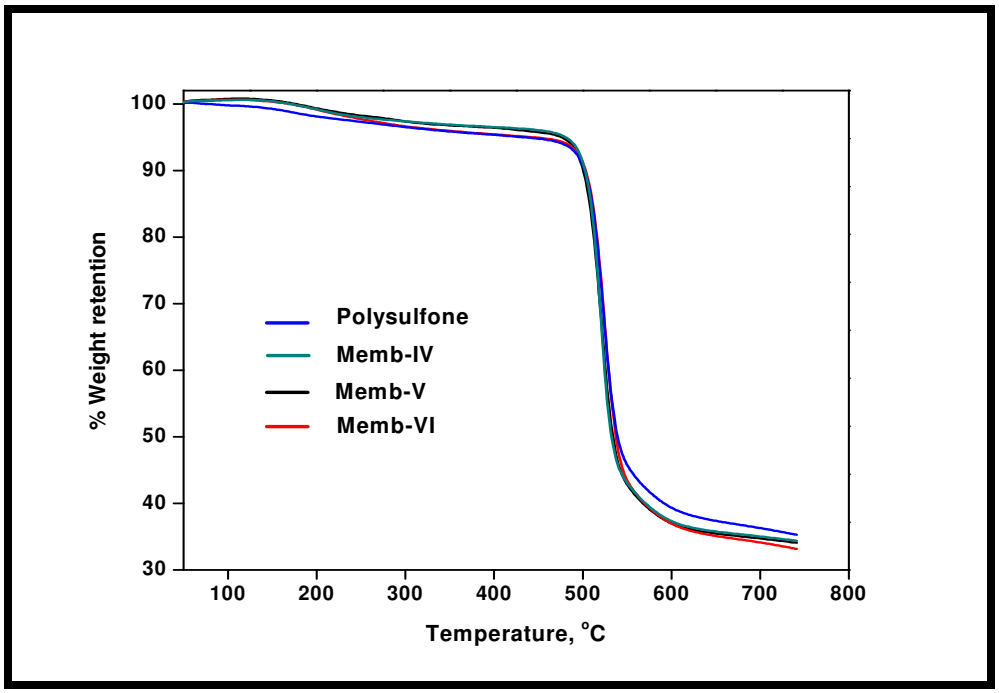


The atomic force micrographs of the virgin polysulfone membrane and acrylic acid modified membranes are shown in figure 2.5. These show the visual evidence of incorporation of acrylic acid on the polysulfone membranes. It is clearly evident from table 2.1 and 2.2 that the roughness is increasing with acrylic acid content on the polysulfone. For Memb-I, the roughness is rather low with respect to polysulfone due to low content of acrylic acid and the incorporation of acrylic acid results in leveling of the rough surface of the asymmetric polysulfone with comparatively low concentration of the monomer.

Table 2.2 Roughness data (nm) of polysulfone and acrylic acid modified polysulfone membranes

Membrane	Unmodified PS membrane	Memb-I	Memb-II	Memb-III	Memb-IV	Memb-V	Memb-VI
Roughness	9.239	7.747	9.268	9.843	8.499	10.603	13.893

Figure 2.6 TGA curves of asymmetric polysulfone and acrylic acid modified membranes



Thermo-gravimetric study of the photo-modified membranes confirms the incorporation of acrylic acid onto the membranes as depicted in figure 2.6. It is observed that for polysulfone and Memb-VI membranes, the weight loss is ~5% at initial decomposition temperature (477° C) and for the other membranes it is ~4%. The weight loss for Memb-VI is more as it reflects the acrylic acid polymerization on polysulfone to the larger extent due to higher concentration of acrylic acid (10%) than the other two membranes. Also the residue left for polysulfone membranes is more (35%) than the others; it is due to incorporation of acrylic acid on other membranes which favors the order.

Figure 2.7 Statistical diagrams for porometric study (a) differential flow rate vs pore diameter and (b) flow rate of the nitrogen gas vs pressure in psi for Memb-IV

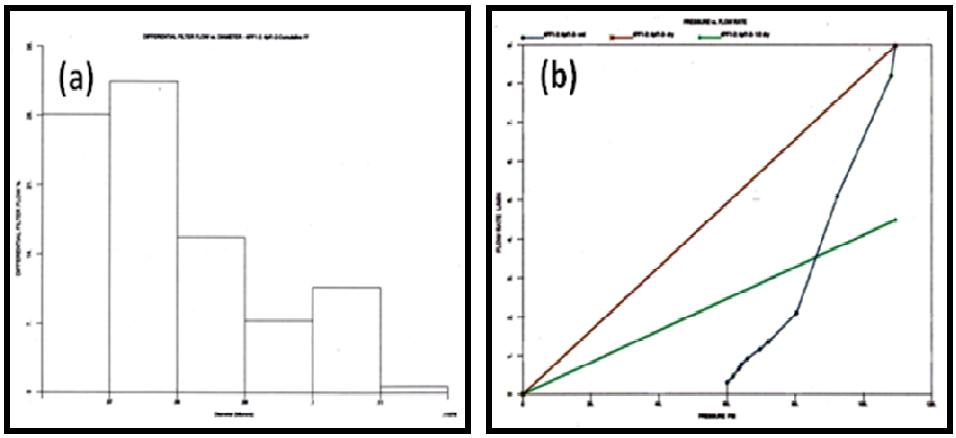


Table 2.3 Porometric data of membranes polysulfone and acrylic acid modified polysulfone membranes

	Unmodified PS membrane	**Memb-I**	**Memb-II**	**Memb-III**	**Memb-IV**	**Memb-V**	**Memb-VI**
Mean flow pore diameter (μm)	0.101	0.080	0.077	0.05	0.047	0.04	0.035
Mean flow pressure (MPa)	0.45	0.57	0.59	0.91	0.97	1.14	1.29

Table 2.3 enlists the porometric data of unmodified as well as modified polysulfone membrane. In case of polysulfone unmodified membranes, the mean flow

pore diameter is 0.101 μm. With the increase in acrylic acid content on the polysulfone, the mean flow pore diameter decreases. The minimum mean flow pore diameter is 0.035 μm for the membrane VI. The mean flow pore pressures for the unmodified and modified membranes are following the reverse trend, as expected. Figure 2.7 depicts the statistical diagrams of porometric studies for membranes Memb-IV for differential flow rate against pore diameter and flow rate at different pressure (psi).

Comparing the contact angles of unmodified and modified membranes, it is seen that with the increase of acrylic acid content, the contact angle decreases. The maximum decrement of contact angle is 2.48° for the modified membrane with respect to unmodified polysulfone membrane. A smaller contact angle indicates more hydrophilic surface [29]. The decrement of contact angle proves the evidence of acrylic acid on the membrane and it also suggests that the hydrophilicity nature is appearing on the modified membrane.

2.3.1.3 Experimental sketch up

The photo-modified membranes are exploited for their performances in terms of their water flux and separation behavior. The modified membranes are well washed with reverse osmosis water and kept for 48 hours in water to remove the unreacted and adsorbed traces of the monomer prior to the further experiment. The permeability is measured at room temperature with a laboratory made pressure cell. The effective membrane area taken for study is 0.00152 m^2. The water flux and salt rejection experiments with sodium chloride, sodium sulfate (2000 ppm) are performed. Permeability of glucose (500 ppm) and 2,4-dichloro phenol (20 ppm) is calculated and are of the short run type, each lasting for about 3h. These are carried out at laboratory temperature and operating pressure of 0.34 MPa. The salt rejection experiments are also performed after 7 days to confirm the leaching out of acrylic acid from the membranes.

2.3.1.4 Analysis of performance behavior

In order to prove the efficiency of the modified membranes for desalination of water, the permeation experiments are performed with synthetic water containing sodium chloride and sodium sulfate (2000 ppm). The membranes are dipped in water for 36 h before the experiment. The performance results of the experiments are shown in table 2.4. The rejection ability of the membranes can be explained by the

functionalized (-COOH) membrane. Different theories are described in the literature to explain the removal of electrolytes [50]. Due to the presence of –COOH group, the salt rejection ability of the membrane could be explained by the well accepted electrical and preferential sorption theoretical models. The rejection order of the ions (SO_4^{2-} > Cl^-) through the membranes can be explained by the relatively greater hydrated size (SO_4^{2-} : 3.79 Å, Cl^- : 3.32 Å) and valency of the sulfate ions. The increase in rejection with the acrylic acid modified membrane can also be explained with the preferential sorption theory suggested by Sourirajan [51].

Table 2.4 Performance of salt rejection of the membranes (Feed concentration 2000 ppm, pressure 0.34 MPa)

Membrane	**Water flux ($lm^{-2}d^{-1}$)**	**NaCl %R (flux, $lm^{-2}d^{-1}$)**	**Na_2SO_4 %R (flux, , $lm^{-2}d^{-1}$)**
Unmodified PS membrane	13644	3.2 (11844)	4.2 (12033)
Memb-I	4169	4.5 (3790)	15.0 (3695)
Memb-II	3032	9.0 (2653)	39.39 (2558)
Memb-III	2464	14.4 (2132)	43.0 (2085)
Memb-IV	3790	5.6 (3506)	24.2 (3222)
Memb-V	2464	13.6 (2132)	45.45 (2085)
Memb-VI	1421	20.4 (1042)	50.0 (1137)

As the acrylic acid content (with increasing the concentration and dipping time) increases on the membrane surface, the preferential layer of water builds up at the membrane solution interface to the greater extent. This preferential layer is enriched in water and is depleted in terms of electrolytes. The higher rejection of divalent anionic salt (Na_2SO_4) compared to monovalent anionic salt (NaCl) clearly suggests the operation of Donnan's ion exclusion phenomena in which electrostatic

interactions plays an important role. The maximum rejections of NaCl and Na_2SO_4 are 20.4% and 50% for Memb-VI. However, the membrane modified by dipping for 1 h in acrylic acid (10%) gives the same performance in terms of salt rejection, as dipping for 30 min in same concentration.

Table 2.5 Performance of membranes in retention of glucose and 2,4-dichloro-phenol

Membrane	**Unmodified PS membrane**	**Memb-I**	**Memb-II**	**Memb-III**	**Memb-IV**	**Memb-V**	**Memb-VI**
	Rejection (%)						
Glucose	9.2	23.0	34.0	42.0	38.0	62.0	78.0
2, 4-DCP	10.5	23.6	25.5	35	36.2	39.3	58.0

The glucose (low molecular weight and neutral) molecule permeability is checked to show the wide variation of the performances of the modified and unmodified membranes. The glucose rejection data of the membranes reflect the trend Memb-III > Memb-II > Memb-I > PS (unmodified) and Memb-VI > Memb-V > Memb IV > PS (unmodified) (table 2.5). This suggests that with the increase in acrylic acid content on the polysulfone, the glucose retention is more. The glucose retention of the membranes shows the pore blocking evidences of the membranes, which is already reflected in porometric data. The glucose rejection of the unmodified polysulfone membrane is 9.2 %, but maximum it is of 78 % for the modified membranes.

The remediation of the water pollutant (2,4-dichlorophenol) is also experimented. The performance data are tabulated in table 2.5. The rejection of 2,4-dichlorophenol by the membranes shows similar trend to glucose rejection data. In comparing with the glucose rejection, the modified membranes show low phenolic rejection, due to relatively low molecular weight and polarity of the molecule with respect to glucose [51, 52].

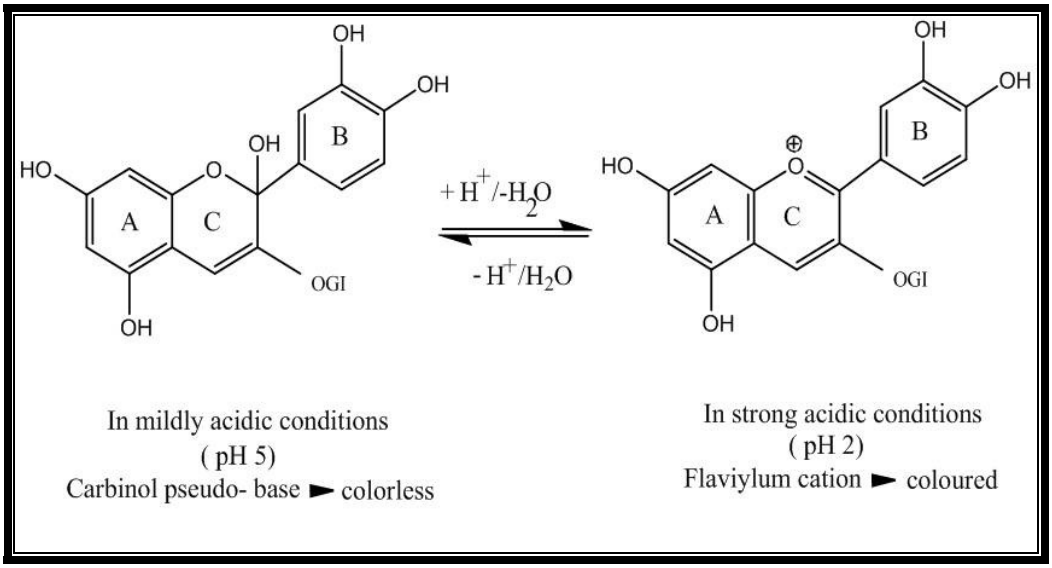
In brief, the acrylic acid modified polysulfone membranes are prepared through light induced technique without using sensitizer. FTIR, AFM, contact angle and porometric study proves the evidence of modified membranes. The salt rejection behavior of the membrane correlates the content of functionality on the membrane.

The rejections of the ions follow the order SO_4^{2-} > Cl^- . The retention of organic molecules (glucose and 2,4-dichlorophenol) also depends on the acrylic acid content on the membrane. The retention of glucose by the modified membrane is higher with respect to 2,4-dichlorophenol is due to higher molecular weight and low polarity of glucose.

2.3.2 Exploitation towards separation of natural pigments from rose petal extract

Color is no doubt most important attributes of the nature. Color speaks and does impart a unique impression in every aspect of human life from clothing to food, luxury to necessity and so more. But, the consciousness of the coloring of the food towards the natural color is increasing as they have the anti-carcinogenic properties [53]. For centuries, rose has been the most important crop in the floriculture industry; its economic importance lies in the use of its petals as a source of natural pigments.

Figure 2.8 pH dependent conformational rearrangements in mildly and strong acidic conditions of the anthocyan molecule

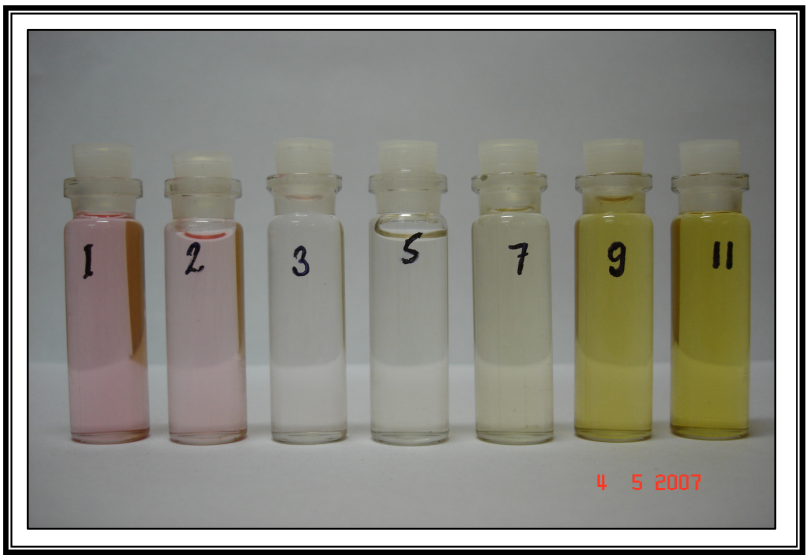


In an examination of the petals of the red rose, it has been shown that the anthocyan pigments contained there and exists in the petals as oxonium salt (i.e. in combination with plant acid) [54]. The antioxidant properties of anthocyans have the apparent lower risk of chronic diseases such as cancer, cardiovascular disease.

Anthocyans are flavanols and their structure represented as in figure 2.8 (Sugar components (glucose, galactose and arabinose) are usually conjugated to the

C-3 hydroxyl group in the ring [53]. Some anthocyanins comprise multiple sugar moieties involving hydroxyl functionalities of the aglycon molecule other than that at C-3 [55]. Anthocyans are water soluble and occur in different pH dependent conformations with varying colors and color intensities (figure 2.9). At pH < 3, the middle ring (ring C) of the predominant anthocyans conformer has a flavylium cation which confers intense color to the molecule. As the pH increases, the intensity of the color decreases and in mildly acidic conditions (viz. pH 5), the solution is colorless. **Figure 2.8** features the different conformers along with their colors of anthocyans at pH 2 and 5.

Figure 2.9 Variation in coloration of anthocyans pigments of rose extract at different pH



In this regard, our objective is to show the performance ability of polysulfone membranes regarding the separation of pigments (anthocyanins) of rose-petals extract from water. Considering the anthocyan pigments, polysulfone membranes have been modified by hydrophilic monomer (i.e. acrylic acid) to low molecular weight cut off. With the distinct advantages viz. low activation energy, high monomer conversion and low monomer residue, forming fast covalent bonds between the monomer and polymeric substrate but doing no perturbation in material's bulk properties, such photo-mediated technique for polymer modification has been employed to achieve this task. Also, there is a unique property of acrylic acid which exhibits significant changes in response to small changes in external stimuli (e.g. pH of the feed solution)

leading towards dissociation/ association of the acidic group. This response of the acidic group of acrylic acid towards the pH offers significant applications in separation orientation. As the modified membranes are pH responsive, the separation performance of the membranes for the rose petal extract at different pH is also compared.

2.3.2.1 Photo-modification of polysulfone

To achieve the target to separate the pigments from rose petal extract, polysulfone membranes are modified with varying concentration (1% and 3%) of acrylic acid. The acrylic acid solution is poured on the polysulfone membrane (skin side) fitted on glass tray (16 x13 cm). The residence time of the solution is kept 30 min. Then, the solution is decanted from the membrane surface and photo-irradiated for 10 min. In this study, the membrane samples are photo-irradiated by UV- light (HPM-13, (Philips) 1000 watt, Lamp voltage 125 volt, current 8.6 amp, Intensity 2000 μwatt/cm^2 (Diazo irradiation, 320 - 440 nm) at a distance 20 cm from the lamp. The photo-irradiation arrangements are similar to the one as shown above in figure 2.3. All experiments are carried out at an ambient temperature. The radiation density flux on whole surface area is assumed to be constant in each run.

2.3.2.2 Analysis of photo-modified membrane

The incorporation of acrylic acid is confirmed by FTIR-ATR studies as discussed in section 2.3.1.2. The stretching mode of C=O from acidic group is well observed at 1728 cm^{-1} in the acrylic acid modified membranes. It is also observed that the peak intensity for acidic carbonyl group (C=O) is more for the membrane PS-AA-3 (grafted with 3% of acrylic acid solution) than to PS-AA-1 (grafted with 1% of acrylic acid solution) as expected.

The weight difference data also shows the evidence of incorporation as well as the trend i.e. 3% AA concentration results higher grafting (table 2.6). From the measurement of contact angles of unmodified and modified membranes, it is observed that the modified membranes are of low contact angle being hydrophilic due to incorporation of acrylic acid on the surface of the membranes. The maximum decrement of the contact angle is ~2° for the modified membranes compared to unmodified membrane.

Table 2.6 Detailed characteristic features of the acrylic acid grafted polysulfone membrane.

Membrane	Grafting conditions	Increase in weight/cm^2 (x10^{-4})	Water flux, lm^{-2}d^{-1}	Sucrose (R %)	PEG-600 (R %)	NaCl, (R %) flux, lm^{-2}d^{-1}
PS-(AA)-1	AA: 1%(v/v) Dipping time: 30 min Photo-irradiation time: 10 min	1.909	4357.9	7.4	27.9	15.0 (3979)
PS-(AA)-3	AA: 3%(v/v) Dipping time: 30 min Photo-irradiation time: 10 min	4.984	388.4	89.2	91.8	24.5 (322)

Table 2.6 features the characteristics of the membranes. The separation ability of the modified membranes was tested by uncharged sucrose (Uni-molecular weight) as well as PEG 600 (distributed molecular weight). The results are showing ~ 89% retention for sucrose and ~ 92% retention of PEG 600 for the PS-(AA)-3 modified membranes. The salt rejection performance is tested and it shows that development of ionic functional groups over the modified Polysulfone membrane. It can be well explained by well accepted electrical and preferential sorption mechanism [50, 51]. The salt rejection performance shows that the rejection ability increases with the increase in acrylic acid content on the polysulfone membrane.

2.3.2.3 Experimental sketch up

The experiments are carried out with anthocyan pigments especially from same type of red rose petals. The roses are plucked off in the same day. The rose petals (250 g) are soaked in 70% acetone/water (v/v) solution at room temperature for two hours. The extract is collected from the soaked rose petals by centrifugation process and filtered. The solution is evaporated to 50% of the original volume in atmosphere and the solution diluted 250 times with water for the permeation experiment. The distilled water is used throughout the experiment to avoid complexation from metal ions. Adjustment of pH of the solutions is done by acidifying it.

The titrable acidity of extract solution is calculated using sodium hydroxide solution (0.1 N) to titrate the filtered extract to pH 8.1. The titrable acidity is calculated as percent citric acid. The pH value of the filtered acidity is calculated using pH meter. The details of the rose extract in this context are summarized in table 2.7.

Table 2.7 The characteristic details (pH and titrable acidity) of the rose extract

Rose Variety	Rose Extract mg/g	pH of the extract solution	Titrable acidity of the extract (% wt, g citric acid)
Red	54.56	4.6	0.418

Laboratory made pressure cell is used for the pressure driven measurement. The effective membrane area is 0.00152 m^2. The temperature is kept at 30° C in all the permeation experiments. The pure water fluxes for the modified and unmodified membranes are performed. They are carried out at laboratory temperature and operating pressure of 0.69 MPa. The salt separation performance (NaCl 1000 ppm) of the membranes is determined from their respective conductivity data using the relationship shown previously in section 2.2.3.

The floral pigment for feed and permeate is analyzed from the UV-Visible absorption spectrophotometer (Varian, Carry 500 Scan, USA) and the separation is calculated from the same relationship, as the concentration data is directly proportional as observed from the calibration curve. The absorption data is taken at 513 nm.

2.3.2.4 Analysis of performance behavior

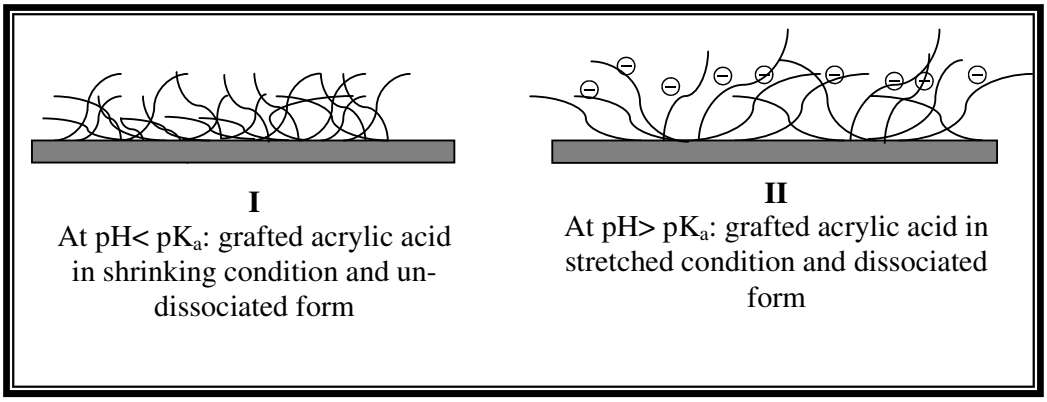
The performance of the membranes is mainly dependent upon the mechanism which operates at membrane / olution interface viz. size exclusion and electrostatic repulsion. For neutral species, size exclusion, and for the charged species electrostatic exclusion is the governing mechanism. It is recognized that the grafted surface is getting charged by coming in contact with the solution. Here, the hydrophilic functional groups (-COOH) for the modified polymeric membrane, the acidic behavior is indeed strongly pH dependent.

When the modified membranes are immersed in solution, the performance is dependent upon the pK_a of the attached acid functional moiety. The charge is related

to the ionization of the chemical functional groups existing on the membrane, which has strongly pH dependent dissociations. At pH < pKa, the –COOH groups will be in neutral form and are mainly in shrinking condition. As a result, the performance is hampered. Of course polarity of the molecule is the factor in this case. At pH > pKa the –COOH will be in ionized form and they are in stretched conditions (figure 2.10). For polar molecules, the rejection performance is better.

The performances of the membranes are featured from the spectra (figure 2.9) of feed and permeate of the rose petal extract for all the membranes at pH 2. It has also been seen visually from the photograph (embedded in figure 2.11). The spectrum clearly shows the absorption of permeates decreases gradually for the membranes modified with the increase in the concentration of acrylic acid. The photograph also features the gradual color to colorless variation for the feed and permeates, passing through different membranes.

Figure 2.10 Grafted acrylic acid in different pH, I. At pH < pKa: grafted acrylic acid in shrinking condition and un-dissociated form and II. At pH > pKa: grafted acrylic acid in stretched condition and dissociated form



The separation performances of the modified and unmodified membranes are showing the order PS-AA(3) > PS-AA(1) > PS. At low pH, the –COOH functionality on the membrane, is un-dissociated as well as un-stretched as already discussed in the general theory as the pKa of acrylic acid is 4.26 and it is 4.7 for the poly (acrylic acid) is [56-57]. The anthocyanin is of ionic character at this pH (figure 2.8); therefore the separation performances by the modified membranes are rather low compared to the performances at pH 5.

With the increase in pH, (as the dissociation is higher above pK_a values) the –COOH functionality will be rather in ionized state. Thus, grafted chain will be stretched and the molecule attains weak negative charge due to the lone pair of electrons on oxygen atom and aromaticity is not developed (figure 2.8). Therefore, rejection performance is more compared to lower pH. The rejection performances of the anthocyanin are varying with the same trend as in low pH. The performances data for the membranes are listed in table 2.8.

Figure 2.11 Different spectral behavior of feed and permeate of rose extract at pH 2, after 1/2h. I feed; II, III, IV permeates through PS, PS-(AA)-1 and PS-(AA)-3 respectively. Coloration of the feed and permeate embedded in the photograph.

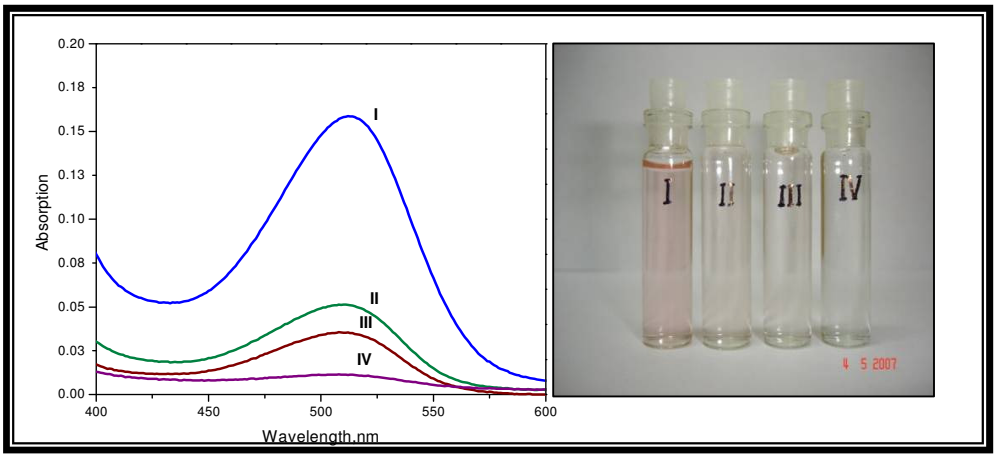
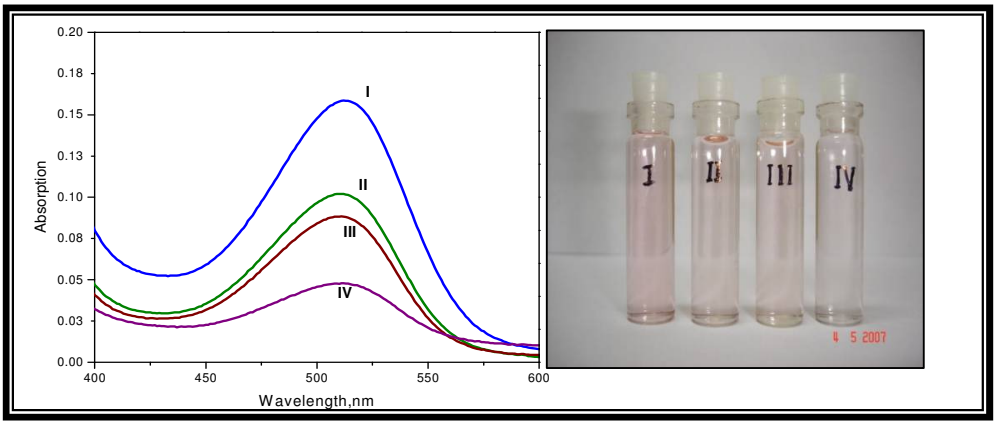


Figure 2.12 Different spectral behavior of feed and permeate of rose extract at pH 2, after 3h. I feed; II, III and IV permeate through PS, PS-(AA)-1 and PS-(AA)-3 respectively. Coloration of the feed and permeate embedded in the photograph.



At low pH, the performance is not steady as depicted from the observation. After 3 h, the separation performances get deteriorated drastically which is also evident from figure 2.12 and table 2.8. The embedded photograph also shows the slight pink color in permeate which can be explained from the chemistry of the molecule. As the addition of H^+ ion to flavanol brings aromaticity as well as positive charge to the moiety and it results an increase in the attractive forces between the ionic parts (flaviylum and chloride). In this condition, the membranes become positively charged (as pH < pKa), initially the permeation of Cl^- is favored and to counter balance the charge, flaviylum cation permeates more with respect to the flavanol at pH 5. Thus, the rejection performance is low in pH 2 with respect to pH 5.

Table 2.8 Comparative performance of membranes for separation of anthocyans at pH 2 and pH 5

Membrane	**After ½ h**		**After 3h**	
	At pH 2 %R (flux, $lm^{-2}d^{-1}$)	**At pH 5 %R (flux, $lm^{-2}d^{-1}$)**	**At pH 2 %R (flux, $lm^{-2}d^{-1}$)**	**At pH 5 %R (flux,$lm^{-2}d^{-1}$)**
PS	62.8 (3979)	69.9 (4168.4)	37.1 (3283.6)	69.9 (3536.5)
PS-AA(1)	77.8 (2179)	79.3 (682)	44.5 (1895)	77.5 (308)
PS-AA(3)	92.8 (322)	94.5 (303)	71.8 (265)	91.2 (284)

With time, as the deposition of flaviylum cation occurs, the membrane positive charge is rather intense and more anionic as well as to counterbalance it the flaviylum ion permeates more. For the PS-(AA)-3, the deposition is rather low, because of its comparatively more hydrophilic nature; the induced positive charge due to deposition of flaviylum ion is rather low compared to Polysulfone. For this, the rejection performance is deteriorated less with respect to PS-(AA)-1 and PS. At pH 5, the nature of the flavanol is neutral or slightly polar in nature and membrane is negatively charged. Thus, with time the performance is quite steady or little deterioration takes place.

In brief, the anthocyanin separation from rose petal extract we have presented from aqueous solution using the photo-modified membranes. Here, photo-modification of polysulfone membranes by AA is proved by FTIR, weight increase as well as contact angle studies. The separation ability of uncharged molecules (sucrose,

PEG 600) is ~90% for the PS-(AA)-3 membranes. The salt separation in little extent also features the ionic character in it. It is found that photo-modified polysulfone membrane is a potential membrane for the separation of anthocyans from rose petal extract. The performance follows the order PS-(AA)-3 > PS-(AA)-1 > PS. The acrylic acid grafted polysulfone membrane being pH responsive; shows different performance behavior at the different pH of the solution. The membrane shows better performance in pH 5 with respect to pH 2. Time dependence study features that the performance is quite steady at pH 5. But, at acidic pH (pH 2), the performance deteriorates. The performance deterioration is also low for PS-(AA)-3 compared to other two membranes.

2.4 Surface functionalization of thin film composite membranes with acrylic acid by photo-irradiation

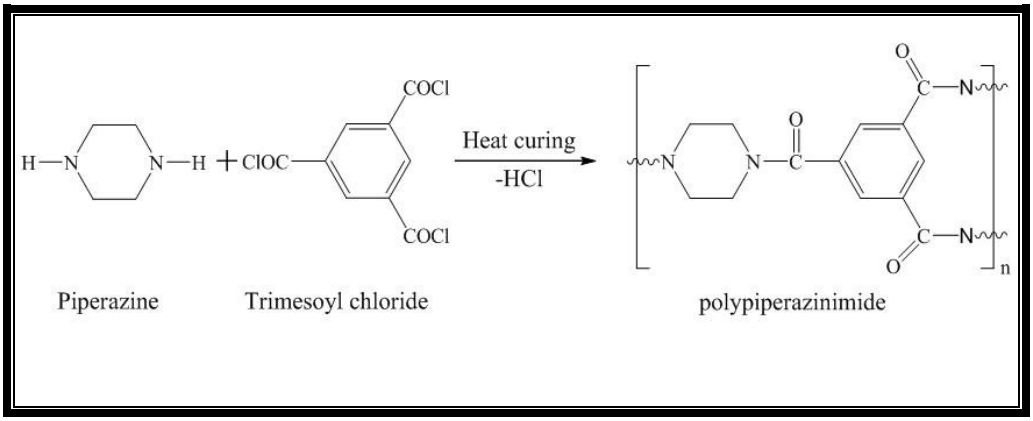
In water processing, the applications of membranes are well understood from the literature. From the last decades, the consciousness regarding the intake of pesticides/water pollutants through water has grown up and removal of these by different techniques has been tested [52, 58]. It has been observed that the membrane filtration technique is one of the potential techniques in removing the pesticides from water. In this area, the recent thrust is thin film composite membranes because of their unique applicability. These membranes are generally made up of porous base membrane (e.g. polysulfone) and an ultra thin fine layer of cross-linked polyamide above it. This ultra thin layer of polyamide acts as a barrier for the separation purposes. They can be used in desalination, water purification and waste water treatment [43, 52, 59-61].

In the present investigation, it has been highlighted the effect of the surface modification to the thin film composite membrane regarding the separation performances of pesticide molecules. The modification is targeted in aiming the improvement of separation performances, is the subject of research. Several techniques are there to impart specific properties of the membranes as discussed earlier. The sequence of the modified acrylic acid and polyamide layer (due to interfacial polymerization of piperazine and trimesoyl chloride) has been altered over the polysulfone membrane and performances regarding the separation of the organics (atrazine, simazine, 2,4,6-trichlorophenol and 2,4-dichlorophenol) is targeted. The schematic presentation of the three different types of membranes is in scheme 2.4.

2.4.1 Preparation of acrylic acid modified thin film composite membranes

Polyamide composite membranes are prepared by the interfacial polymerization [62-64] of piperazine and trimesoyl chloride (TMC) on the surface of the virgin polysulfone membranes and acrylic acid modified polysulfone membranes as depicted in Scheme 2.3.

Scheme 2.3 Schematic presentation of reaction between piperazine and trimesoyl chloride to form polypiperazinimide



The thin film composite membranes prepared from virgin polysulfone membranes are further photo-modified with acrylic acid. The order of sequence of acrylic acid as well as polyamide layer for membrane modification is depicted in table 2.9. First, the polysulfone membranes (virgin/modified) is coated with 2 wt% piperazine solution in water, the excess amount of piperazine solution remaining on its surface is removed and then immersed into 0.1 wt% TMC solution (in hexane) for the interfacial polymerization, after which it is cured at 85°-90° C. The reactivity of the reactants is mainly dependent on the partition coefficient for the two immiscible solvents. As the high unfavorable partition co-efficient for acid chloride limits its availability in the aqueous phase, the interfacial polymerization reaction occurs in the organic (hexane) side, thus the coating follows by dipping in piperazine solution at first and then in trimesoyl chloride.

Thin film composite membranes prepared from virgin polysulfone membranes are modified with acrylic acid of different concentrations (2 and 5%) by dipping the membranes for 15 minutes followed by photo-irradiated for 10 min. In this study light induced experiment is done by a UV-lamp (Philips HPR-125 watt) as depicted in figure 2.3. The polysulfone membranes are also modified by dipping them in acrylic

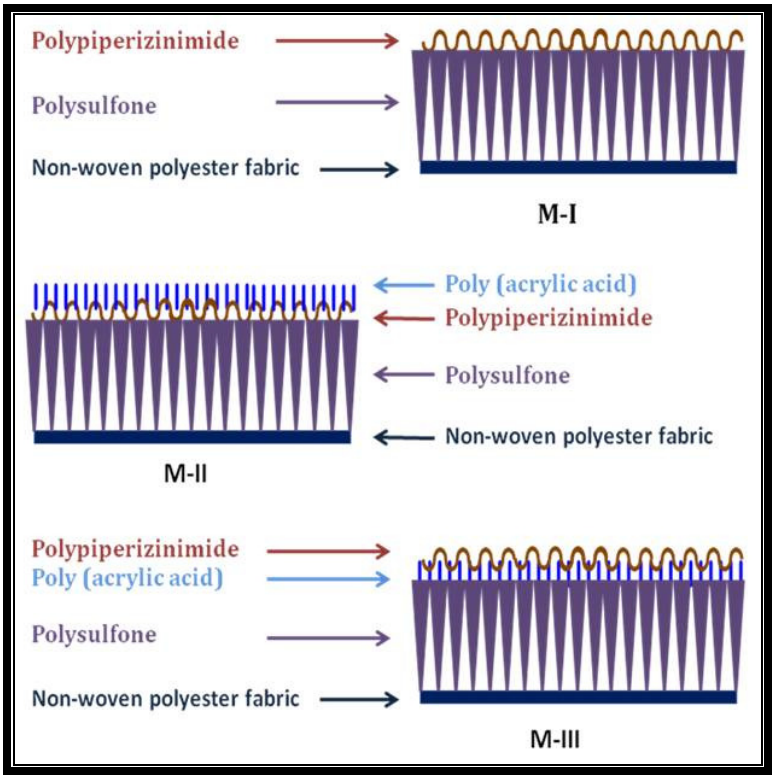
acid of different concentrations (2 and 5%) for 15 minutes and are photo-irradiated for 10 minutes (as explained in section 2.3.1.1). Then, the thin film composite membranes are prepared on the acrylic acid photo-grafted polysulfone membrane as explained before (scheme 2.4).

Table 2.9 Weight difference data and layer composition as in the order in modification of the membranes

Membrane	Composition (order wise)	Weight difference* $(g/cm^2) \times 10^4$
M-I	Polysulfone + polypiperazinimide	-
M-IIa	Polysulfone + polypiperazinimide + acrylic acid (2%)	0.67
M-IIb	Polysulfone + polypiperazinimide + acrylic acid (5%)	1.02
M-IIIa	Polysulfone + acrylic acid (2%) + polypiperazinimide	0.7
M-IIIb	Polysulfone + acrylic acid (5%) + polypiperazinimide	2.04

*Weight difference is taken with respect to M-I

Scheme 2.4 Schematic presentation of the three membranes (M- I, M- II and M-III)



2.4.2 Analysis of modified TFC membranes

FTIR-ATR studies prove the acrylic acid incorporation on asymmetric polysulfone membranes as well as on thin film composite membranes. The peaks at 1725-1729 cm^{-1} are the evidence of acrylic acid incorporated –COOH groups on the membrane by photo-irradiations. The peak intensity of –COOH group is higher for the M-II compared to M-III. The –COOH peak is less intensified (for M-III) due to the polyamide layer over it (figure 2.13). The –CONH- peak intensity (1617 cm^{-1}) is higher for membrane M-III, as the acrylic acid layer is sandwiched between the polysulfone and polyamide layers. The absorption of piperazine is higher on acrylic acid-g-polysulfone than on unmodified polysulfone and this is supported by the increase in wettability which is reflected from decrease in contact angle from 65.8° to 63.5°.

Figure 2.13 FTIR-ATR spectra of unmodified M-I (I) and modified membranes M-IIa (II) and M-IIIa (III)

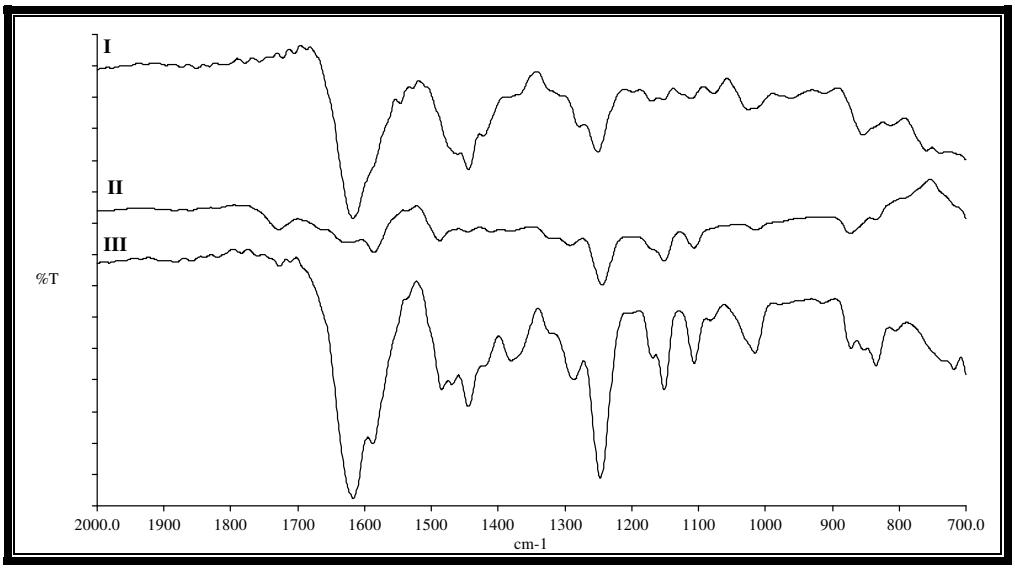
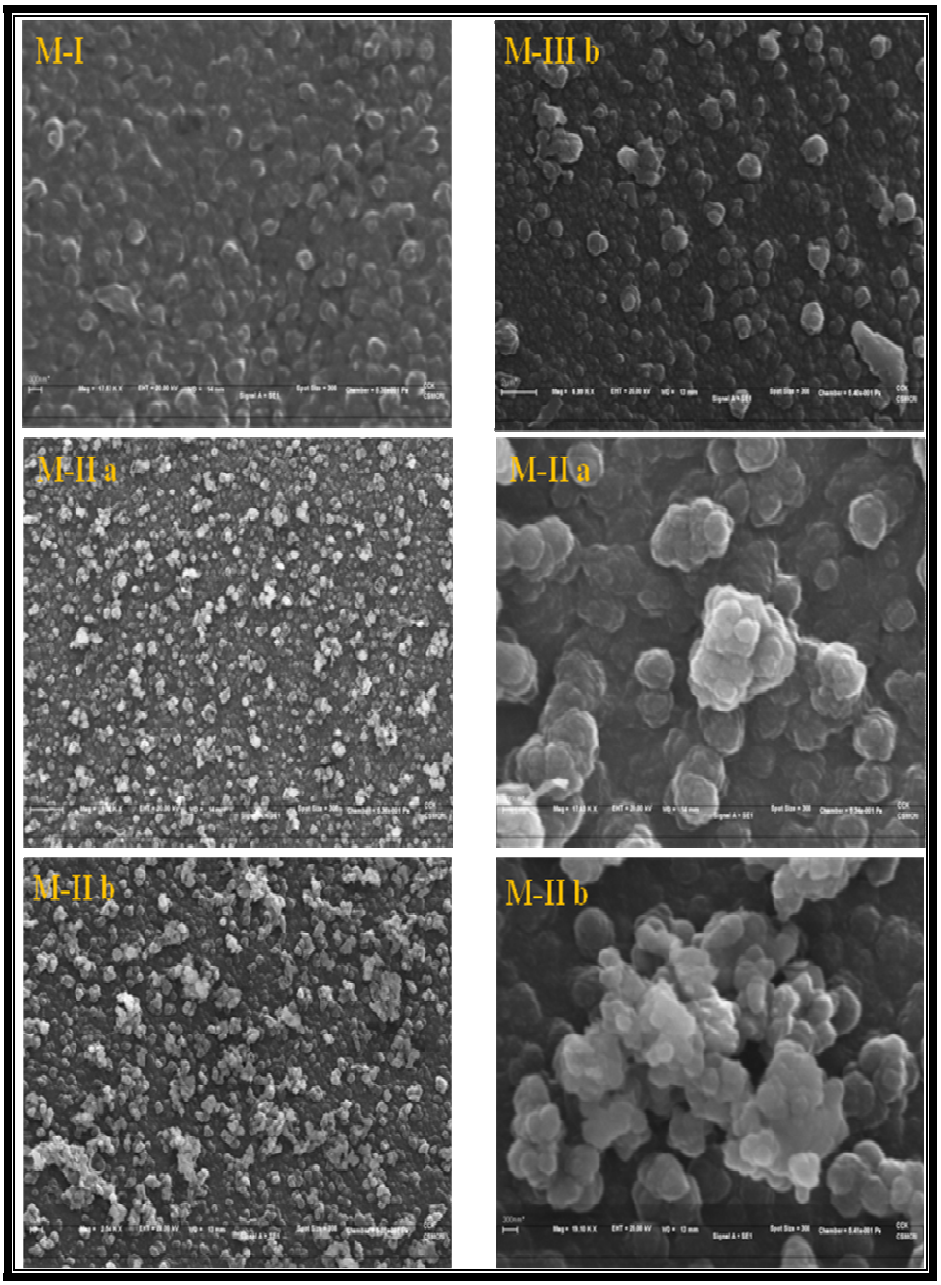


Table 2.9 features the increase in weight of M-II and M-III with respect to M-I, due to incorporation of acrylic acid. It shows that the M-III are of higher weight difference compared to Membrane II as the attachment of acrylic acid is more facile with the polysulfone membrane. The increase in weight also depends upon the acrylic acid concentration in both the cases for M-II and M- III.

Figure 2.14 Scanning electron micrographs of Thin film composite Membranes. M-I (unmodified TFC membrane), M-III b (acrylic acid incorporated below polyamide layer) and M-II a/ b (acrylic acid layer incorporated above polyamide layer) with low (left) and high (right) magnification photograph.



Scanning electron micrographs (figure 2.14) are the evidence of the incorporation of acrylic acid on the thin film composite membrane. The micrograph of M-I shows the surface morphology of the virgin polyamide coating on the

asymmetric polysulfone membrane. The characteristic features of the M-II prove the existence of the incorporation of acrylic acid on the thin film composite membrane. The higher content of acrylic acid incorporation is also clearly reflected for the membranes M-II b than M-II a. However, the surface morphology of M-III, is found similar to membrane M-I.

2.4.3 Experimental sketch up

The photo-modified thin film composite membranes by acrylic acid are subjected to exploit their ability to separate pesticides from water. Also, the solution of glucose and sucrose is passed through them to set as marker. For this solution of various pesticides is prepared. The pesticide-organics are dissolved in methanol solutions (300 mg/L). 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 20 mg/L for the selected pesticides. For permeability measurement laboratory made pressure cell is employed as depicted in scheme 2.1. The permeability is tested at 1.4 MPa. The area of the membrane is $1.52 \text{ X } 10^{-3} \text{ m}^2$.

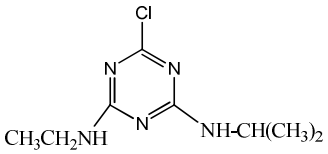
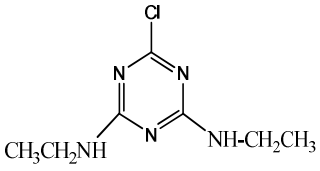
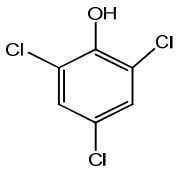
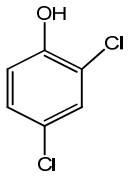
2.4.4 Theoretical calculation of structural parameters

The primary factor which counts for the main rejection mechanism depends on size exclusion, so the first and foremost condition to reject organics by the membrane is their size. This provides an insight about the sieving capability of the membrane. Though membrane molecular weight cut off (MWCO) which refers to the lowest molecular weight of the molecule (in Daltons) that is 90% retained by the membrane, apparently signifies the size of the organics that will be rejected, it is better to consider the volume of experimented organics.

To have an idea about the molecular parameters, semi-empirical AM1 self-consistent field (SCF) method is used in theoretical studies to calculate the molecular volume and dipole-moment [65, 66]. First the stable conformers are predicted at AM1 level of theory, and then the molecular volume and dipole-moment are calculated. The AM1 calculated results along with their simple chemical structures are depicted in table 2.10. Though molecular weight data apparently corresponds to molecular volume order in terms of size exclusion and it has been properly correlated with the volume data. Table 2.10 enlists the molecular volume and molecular weight data along with dipole moment of the pesticides which is calculated from semi quantum

mechanical approach. The interesting point to note that though the molecular weights of simazine and 2,4,6-trichlorophenol are of little difference, but their volumes are of marked difference. The dipole moment data shows that simazine is having the highest dipole-moment among the four.

Table 2.10 Chemical structures and some characteristic data of the solutes used to test the separation performance of the membranes.

Solute Organics (Mol. Formula)	**Chemical structure**	**Mol. wt.**	**Mol. volume (A° ^{3})**	**Dipole moment (D)**	**log P**
Atrazine ($C_8H_{14}ClN_5$)		215.7	212.93	3.44	2.61
Simazine ($C_7H_{12}ClN_5$)		201.7	194.4	3.56	2.18
2,4,6-trichlorophenol ($C_6H_3Cl_3O$)		197.5	170.3	1.072	3.69
2,4-dichlorophenol ($C_6H_4Cl_2O$)		163.0	153.0	2.164	2.92

2.4.5 Separation performances of modified TFC membranes

The separation performance of the modified TFC membranes is analyzed for removal of various pesticides from water and the modified membranes are

characterized by using glucose and sucrose as a marker. Table 2.11 features the remediation performance of pesticides from water. In all the membranes, the rejection order is Atrazine > Simazine > 2,4,6-TCP > 2,4-DCP. This order of remediation proves the size exclusion mechanism and follows the order as depicted in table 2.10 (molecular volume and molecular weight data). The water flux also decreases to less than half for M-III compared to M-I.

The performance of the photo-modified membranes for remediation of pesticides (table 2.11) increases with the increase in acrylic acid content over the membranes. Moreover, the blocking effect is more pronounced for the M-III with respect to M-II as well as M-I. It means that the rejection performances of membranes, in which acrylic acid layer is sandwiched between asymmetric polysulfone and cross-linked polyamide layer, is higher with respect to the membranes where acrylic acid is incorporated at the top. The weight difference data (table 2.9) also shows that M-III has more weight with respect to M-II as acrylic acid grafting of polysulfone is more feasible on polysulfone layer than over the polyamide membrane. This is because of their (polysulfone and acrylic acid) photosensitive nature. The detailed mechanism of acrylic acid attachment is described in section 2.2.5.

Table 2.11 Separation performances of all the three thin film composite membranes with or without acrylic acid layer

Membrane	**Flux ($lm^{-2}d^{-1}$)**	**2,4-DCP**	**2,4,6-TCP**	**Simazine**	**Atrazine**	**Glucose**	**Sucrose**
M-I	1137.0	62.6	67.9	74.81	81.8	71.2	78.5
M-IIa	1191.0	67.3	73.9	76.36	82.7	71.7	87.4
M-IIb	1028.6	69.1	76.9	78.9	88.1	76.2	89.5
M-IIIa	505.0	69.8	89.2	87.4	95.1	87.2	95.3
M-IIIb	473.7	70.5	91.9	87.7	96.08	88.4	95.4

Similar results are also observed in case of permeation study of glucose and sucrose (low molecular weight) through these photo-modified TFC membranes. The molecular volume of glucose and sucrose are 203.7 $Å^3$ and 279 $Å^3$, calculated from quantum mechanical approach. The retention of sucrose is higher than glucose as expected (from the molecular weight as well as molecular volume point of view). Thus, the performance behavior of the photo-modified thin film composite membranes depends on the incorporation/ grafting of acrylic acid.

Apart from the molecular weight and volume, partition coefficient and dipole moment act as synergy in the separation mechanism. The log P is defined as log P = log (C_0/C_w), where C_0 and C_w are the concentrations of solute in *n*-octanol and water layers. The rejection is positively correlated with the log P value. The log P value is listed for all the pesticides in table 2.10 [67, 68]. The higher log P value indicates that pesticides prefer the organic phase to aqueous one. Hence, it tends to remain away from the membrane which is hydrophilic in nature while in operation. Therefore, atrazine rejection is more than that of simazine. Similar results also observed in case of 2,4,6-trichlorophenol and 2,4-dichlorophenol. Though it is seen that 2,4,6-trichlorophenol is having highest log P among the four pesticides experimented, the size exclusion factor is the prime one to consider. Thus, the rejection follows as molecular volume.

Since all the membranes are having some negative charge due to the residual –COOH in the polyamide or added –COOH group from acrylic acid, the permeation of the relatively polar simazine is also favored with respect to atrazine This happens because of electrostatic attraction which operates between membrane and polar molecules [42,43,69]. Results are also explained in case of 2,4-DCP where lower molecular volume and higher polarity favors lower rejection compared to 2,4,6-TCP. However, for all the cases the size exclusion factor is the major factor to be considered for their rejection through the membrane and thus the rejection order follows the trend, though the dipole moment of 2,4-DCP is less than simazine/ atrazine. The blocking effect is more pronounced for the M-III with respect to M-II as well as M-I membrane as for the neutral molecule.

This last section in a pen sketch deals with the preparation and acrylic acid modification of polypiperazinimide based thin film composite membrane. The sequence of the acrylic acid and polypiperazinimide layer is altered. FTIR-ATR, SEM

studies prove that the acrylic acid incorporation on the membrane through photo-irradiation technique. The weight difference also suggests that weight difference of M-III is more than M-II. The weight increase also varies with acrylic acid concentration. The separation of organics follows the order Atrazine > Simazine > 2,4,6-TCP > 2,4-DCP based on preferably size exclusion. Apart from this, the lower log P value and higher polarity factor also favor the decrease in simazine rejection compared to atrazine, as well as 2,4,6-TCP and 2,4-DCP. The rejection performances of the acrylic acid photo-modified thin film composite membrane are higher in comparison to the unmodified membrane. The blocking effect of the M-III membranes is more than M-II as well as unmodified thin film composite membrane (M-I).

2.5 References:

[1]. Ulbricht M. *React Funct Polym*. 31 **(1996)** 165.

[2]. Lee Y M, Ihm S, Shim J, Kim J, Cho C, Sung Y. *Polymer* 36 **(1995)** 81.

[3]. Kinoshita T, Sato M, Takizawa A, Tsujita Y. *J Chem Soc. Chem Comm*.14 **(1984)** 929.

[4]. Sata T, Shimokawa Y. Matsuaski K. *J Memb Sci*. 171 **(2000)** 31.

[5]. Sato M, Kinoshita T, Takizawa A, Tsujita Y, Ito R. *J Polym*. 20 **(1988)** 761.

[6]. Zhang Z B, Zhu X L, Xu F J, Neoh K G, Kang E T. *J Memb Sci*. 342 **(2009)** 300.

[7]. Latulippe D R, Mika A M, Childs R F, Ghosh R, Filipe C D M. *J Memb Sci***.** 342 **(2009)** 227.

[8]. Shi Q, Su Y, Ning X, Chen W, Peng J, Jiang Z. *J Memb Sci*. 347 **(2010)** 62.

[9]. Fang Y, Shi T. *J Memb Sci*. 39 **(1988)** 1.

[10]. Bhattacharya A. *Prog Polym Sci*. 25 **(2000)** 371.

[11]. Good K, Escobar I, Xu X, Coleman M, Pouling M. *Desalination* 146 **(2002)** 259.

[12]. Chennamesetty R, Escobar I, Xu X. *J Memb Sci*. 280 **(2006)** 253.

[13]. Yamaguchi T, Yamahara S, Nakao S, Kimura S. *J Memb Sci*. 95 **(1994)** 39.

[14]. Wang H, Tanaka K, Kita H, Okamoto K. *J Memb Sci*. 154 **(1999)** 221.

[15]. Higuchi A, Koga H, Nakagawa T. *J Appl Polym. Sci*. 46 **(1992)** 449.

[16]. Millesime L, Amiel C, Chanfer B. *J Memb Sci*. 89 **(1994)** 223.

[17]. Kim I C, Choi J G, Tak T M. *J Appl Polym Sci*. 74 **(1999)** 2006.

[18]. Morao A, Escobar I, Pessoa de Amorlm M T, Lopes A, Goncalves I C. *Env Prog*. 24 **(2005)** 365.

[19]. Yamagishi H, Grivello J V, Belfort G. *J Memb Sci*. 105 **(1995)** 237.

[20]. Costamagna V, Wuderlin D, Larranaga M, Mondragaon I, Strumia M. *J Appl Polym Sci*. 102 **(2006)** 2254.

[21]. Kang G, Choee J-H, Rhee J M, Lee H B. *J Appl Polym Sci*. 85 **(2002)** 1253.

[22]. Yamagishi H, Crivello J V, Belfort G. *J Memb Sci*. 105 **(1995)** 237.

[23]. Ulbricht M, Belfort G. *J Appl Polym Sci*. 56 **(1995)** 325.

[24]. Ulbricht M, Belfort G. *J Memb Sci*. 111 **(1995)** 193.

[25]. Chen H, Belfort G. *J Appl Polym Sci*. 13 **(1999)** 1699.

[26]. Cao C, Chung T S, Liu Y, Wang R, Pramoda K P. *J Memb Sci*. 216 **(2003)** 257.

[27]. Kim J H, Park P K, Lee C H, Kwon H H. *J Memb Sci*. 321 **(2008)** 190.

[28]. Kaeselev B, Pieracci J, Belfort G. *J Memb Sci*. 194 **(2001)** 245.

[29]. Boussu K, Vandecasteele C, Vander Bruggen B. *Polymer* 47 **(2006)** 3464.

[30]. Boussu K, Vander Bruggen B, Vandecasteele C. *Desalination* 200 **(2006)** 416.

[31]. Gao L, Tang B, Wu P. *J Memb Sci*. 326 **(2009)** 168.

[32]. Pinnau I, Koros W J. *J Appl Polym Sci*. 31 **(1993)** 419.

[33]. Zhansheng L, Jiang C, Koros WJ. J Polym Sci. 43 (2005) 498.

[34]. Koros W J, Fleming G K. *J Memb Sci*. 83 **(1993)** 1.

[35]. Radovanovic P, Thiel S W, Hwang S T. *J Memb Sci*. 65 **(1992)** 231.

[36]. Wienk I M, Boom R M, Beerlage M A M, Bulte A M W, Smolders C A, Strathmann H. *J Memb Sci*. 113 **(1996)** 361.

[37]. Matsuyama H, Nishiguchi M, Kitamura Y. *J Appl Polym Sci*. 77 **(2000)** 776.

[38]. Boussu K, Vander Bruggen B, Volodin A, Van Haesendonck C, Delcour J A, Vander Meeren P, Vandecasteele C. *Desalination* 191**(2006)** 245.

[39]. Freger, V. *Env Sci Technol*. 38 **(2004)** 3168.

[40]. Freger V, Gilron J, Belfer S. *J Memb Sci*. 209 **(2002)** 283.

[41]. Dubious M, Gilles K A, Hamilton J K, Rebers P A, Smith F. *Anal Chem*. 28 **(1956)** 350.

[42]. Vander Bruggen B, Schaep J, Wilms D, Vandecasteele C. *J Memb Sci*. 156 **(1999)** 29.

[43]. Bhattacharya A, Ray P, Brahmbhatt H, Vyas K N, Joshi S V, Devmurari C V, Trivedi J J. *J Appl Polym Sci*. 102 **(2006)** 3575.

[44]. Bhattacharya A, Mukherjee D C, Gohil J M, Kumar Y, Kundu S. *Desalination* 225 (**2008**) 366.

[45]. Yamagishi H, Grivello J V, Belfort G. *J Memb Sci*. 105 **(1995)** 237.

[46]. Jiang L Y, Chung T S, Kulprathipanja S. *J Memb Sci*. 276 **(2006)** 113.

[47]. Mohr J M, Paul D R, Pinnau I, Koros W J. *J Memb Sci*. 56 (**1991**) 77.

[48]. Kapantaidakis G C, Kaldis SP, Dabou X S, Sakellaropoulos G P. *J Memb Sci*. 110 (**1996**) 239.

[49]. Aitken C L, Koros W J, Paul D R. *Macromolecules* 25 **(1992)** 365.

[50]. Bhattacharya A, Ghosh P. *Rev Chem Eng*. 20 **(2004)** 111.

[51]. Sourirajan S. Reverse Osmosis and Synthetic Membranes: Theory, Technology and Engineering, Sourirajan S. (Ed.), National Research Council, Canada, Ottawa, Canada **(1977)**, Chapter 1.

[52]. Bhattacharya A. *Sep Purif Rev*. **(2006)** 351.

[53]. Cooke D, Steward W P, Gescher A J, Marczylo T. *Eur J Cancer* 41 **(2005)** 1931.

[54]. The colouring matter of Red Roses, Geoffrey Currey Proceedings of the Royal Society of London. Series B, Containing Papers of a Biological Character 93 **(1922)** 194

[55]. Williams C A, Grayer RJ. *Natural Prod Report* 21 **(2004)** 539.

[56]. Shin H S, Kim S Y, Lee Y M, Lee K H, Kim S J, Rogers C E. *J App Polym Sci*. 69 **(1998)** 479.

[57]. Hendri J, Hiroki A, Maekawa Y, Yoshida M, Katakai R. *Rad Phys Chem*. 60 **(2001)** 617.

[58]. Gohil J M, Ray P, Bhattacharya A. *Science and Culture* **(2005)** 348.

[59]. Kiso Y, Nishimura Y, Kitao T, Nishimura K. *J Memb Sci*. 171 **(2000)** 229.

[60]. Boussahel R, Montiel A, Baudu M. *Desalination* 145 **(2002)** 109.

[61]. Vander Bruggen B, Everaert K, Wilms D, Vandecasteele C. *J Memb Sci*. 193 **(2001)** 239.

[62]. Seman M N A, Khayet M, Hilal N. *J Memb Sci*. 348 **(2010)** 109.

[63]. Li L, Zhang S, Zhang X. *J Memb Sci*. 335 **(2009)** 133.

[64]. Ahmad A L, Ooi B S. *J Memb Sci*. 255 **(2005)** 67.

[65]. Dewar M J S, Zoebisch E G, Healy Eamonm F, Stewart J J P. *J Am Chem Soc*. 107 **(1985)** 3902.

[66]. TITAN, Wavefunction, Inc, 18401 Von Karman Avenue, Suite 370, Irvine CA 92612 USA, Schrodinger, Inc., 1500 S W First Avenue, Suite 1180, Portland, OR 97201 USA

[67]. Xing Y, Guanghua Lu, Yuanhui Z. *Chem J Int*. 3 **(2001)**15.

[68]. Kiso Y, Mizuno A, Othman R A A binti, Jung Y-J, Kumano A, Ariji A. *Desalination* 143 **(2002)** 147.

[69]. Gaw L J, Cheng-Nan C, Ren W J. *Water Sci Tech*. 33 **(1996)**75.