Chapter 4

Preparation of MWNT/PSf composite membranes and its effect on metal removal

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4.1 *Introduction*

In present study we report the synthesis of functionalized multi-walled carbon nanotube/polysulfone (MWNT/PSf) composite membranes by the phase inversion method using DMF as solvent and water with isopropanol as coagulant. Carbon nanotubes have proved to be the most promising materials for the design of functional thin films, including those for catalytic membranes, actuation, mechanical thin film applications, and now as nanocomposite membranes with polymer structures.

It has been shown that pristine single walled nanotubes as membranes can be used for efficient gas separation[151].Controlling the architecture of CNT thin films at the nanometer and micrometer-scale is critical to tailoring film properties and functionality; therefore attempts have been made to incorporate the nanotubes into polymer matrices. For example, carbon nanotube/polymer nanocomposite membranes have been fabricated and reported for high flux gas transport[152]. High water vapour permeability has been achieved by using poly(ether urethane) filled with isophorone diisocyanate-grafted carbon nanotubes[153]. It has been reported that enhanced rejection of solutes of brilliant blue R and safranin O from methanol and aqueous solutions can be done using polyamide/functionalized CNT's nanocomposite membranes prepared by interfacial polymerization[154]. Similarly CNT/polycarbonate matrix composite membranes have been found to have good hydrogen separation properties[155]. Unmodified MWCNT/polysulfone microporous conductive membranes have also been prepared by sonication technique[156].

The continued attention of membrane scientists for polysulfone (PSf) is due to its excellent characteristics such as solubility in a large range of aprotic polar solvents (dimethylformamide, dimethylacetamide, dimethylsulfoxide), high thermal resistance (150-170°C), chemical resistance on the entire pH range, resistance in oxidative medium (hypochlorite, hydrogen peroxide) and also due to the high mechanical resistance of the films (fracture, flexure, torsion). They facilitate the formation of interpenetrating networks with blends while preserving the mechanical and thermal properties. As biocompatible and non-degradable materials, these polymers are utilized in bio-applications such as hemodialysis, ultrafiltration, filtration, and bioreactor technology[157,158]. However, applications of the PSf membrane are often limited because of its hydrophobic nature. Because of its hydrophobic properties, performance of PSf membranes results in low water flux and serious membrane fouling. The thermodynamic, rheological and the adsorption properties have been found to significantly change on its surface modification[159,160]. Enhancement of hydrophilicity is one area that is being studied extensively. Carboxylated or sulfonated polysulfone showed increased hydrophilicity. Thus retention towards proteins like sulfhydryl modified bovine serum albumin (cys-BSA) was found to be effected by degree of functionalization[161,162]. Structural segregation and excessive swelling of chitosan/polysulfone composite membranes has been controlled and geometric stability increased by immersing the polysulfone substrate into hydrophilic binding polymer solution like PVA, PAA before casting of chitosan layer[163,164].Various hydrophilic modifications such as UV radiations treatment or additives like emeraldine base polyaniline (PANiEB) could be used to increase pore size without effecting retention and thus improve the performance of polysulfone membranes[165,166]. High performance affinity matrix from epoxy functionalized polysulfone have been reported to show high degree of adsorption and separation of amino acids[167]. Several other methods for polymer modification such as DNA immobilization, oxygen plasma treatment, treatment with aminated derivative could be used to serve various purposes[168-170]. Novel nanocomposite membranes containing single walled carbon nanotubes inside a polysulfone matrix have been reported to show high permeability and diffusiveness for H_2, O_2, CH_4 and CO_2[171,172]. An increase of upto 67% selectivity between polar and non polar gases using oxidized nanotubes/polysulfone composite membranes has been reported[173]. Based on density functional theory calculations, it has been shown that different gas adsorption behaviors are introduced via modification by metals or carboxyl functional groups that further influence the gas permeability. Based on both experimental and theoretical results, it has been suggested that gas diffusion takes place through the interface between polymer chains and carbon nanotubes, rather than the CNT channels. Thus tailoring the modification on the external surface of carbon nanotubes could be an effective method for improving gas separation performance of CNT-based nanocomposite membranes[174].Similarly, modifications on CNT's were also found to enhance the hydrophilicity of the composite membranes of CNT/PSf. However there are conflicting reports on the role of CNTs in the composite membranes. On one hand it is reported that protein fouling behavior of PSf composite membranes by bovine serum albumin and ovalbumin has been drastically reduced due to presence of nanotubes[175] where as on the other hand the modification on the CNT surface with 5-isocyanato-isophthaloyl chloride is reported to enhance protein adsorption on the membrane surface thus resulting in better separation[176].

Heavy metals are among the most prevalent pollutants in the untreated water and are becoming severe public health problem. Industrialization and globalization is the major cause of various kinds of metal pollutants in water. These heavy metal ions are non-degradable and are toxic even at very low concentrations and can cause hypertension, nephritis, abdominal pain, nausea, vomiting, behavioral changes and development defects. Pb^{+2}, Ni^{+2}, Hg^{+2}, Cr^{+6} and Cd^{+2} are hazardous heavy metal ions. A wide variety of techniques to remove heavy metals from water are available, such as, ion exchange reverse osmosis and nanofiltration, precipitation, coagulation/co-precipitation and adsorption. present study concentrates at membrane separation of heavy metal ions from drinking water.

Various studies related to flux improvement, pore structure and size control have made polysulfone/CNT composite membranes an interesting field for desalination[177,178]. However, to our knowledge no studies have been done on the metal ion removal from water using CNT/polysulfone composite membranes. The large surface and the nano size diameters of the CNT's could be effectively used in modifying the polysulfone membrane, a step forward in transforming an ultrafiltration membrane to a nanofiltration membrane. This could then be used for metal ion removal in critical applications. In the present study CNT's were modified to enhance the interaction with the polysulfone matrix and thus expecting it to 'bond' well with the matrix resulting in the modification of the composite membrane in both the porosity and hydrophilicity.

4.2 Materials

Polysulfone(PSf) Udel P-3500 was a gift sample from M/s Solvay Speciality Polymers, Vadodara, India and had the following characteristics: tensile strength-70.3MPa, compressive strength-96MPa, thermal conductivity-0.26W/Mk and specific gravity-1.24. Multiwalled Carbon nanotubes (MWNTs, HiPCO supplied by Iljin Nanotech, Korea) whose purity was greater than 90%, were purchased from Sigma Aldrich and were of diameter 110-170 nm and length 5-9 microns. Ethylenediamine (>99%, Sigma Aldrich), Sodium azide (>99%, Sigma Aldrich), isopropanol, Dimethyl formamide(DMF) were used as it is.

4.3 Experiments

4.3.1 Purification and functionalization of MWNTs

4.3.1.1 Surface cleaning and washing of nanotubes

The >90% pure commercially available MWNTs are still associated with amorphous carbon and traces of metal ions that come to be associated with these nanotubes during preparation and thus were purified. Cleaning the surface of these pristine CNTs with SDS has been previously reported[179]. A modified method for cleaning of surface was adopted and this method helped to remove the amorphous carbon soot and nearly all heavy metals present in the as purchased CNTs. In this process, 2g of these nano tubes were sonicated with 500 ml of 1% Brij 98 (a non-ionic surfactant) for about 2h. The sonicated solution was allowed to stand for about 6h. The sediment was rejected as soot associated with the nanotubes. The nanotubes were collected from the mother liquor by subsequent centrifugation and sedimentation at 3000 rpm for 15 minutes. This process was repeated 2-3 times to obtain clean nanotubes. The surfactant associated with the nanotubes could be easily removed by alternate washing with water and brine solution. Subsequently, some of the heavy metals that may have remained attached to the surface of the CNT's were removed by converting these heavy metals into their soluble metal chlorides using 50% HCl solution. The yield was ~35% of the initial raw CNTs used. The remaining could be considered to be amorphous and other undesired carbonaceous material and heavy metal traces. Significantly, the obtained nanotubes do not get attracted to the magnetic needle unlike the uncleaned pristine CNTs which contain Fe, Co, Ni and other trace metals that get attracted to the magnetic bar. Purification and washing removes the unwanted carbonaceous material and metal ions and these washed and dried nanotubes were used to treat with various functionalizing agents.

4.3.1.2 Oxidation, amide and azide functionalization of carbon nanotubes

The washed and cleaned CNTs were treated with a 3:1 mixture of concentrated nitric and sulfuric acid (40 mL) for 24 h at 33°C. The oxidized nanotubes were washed with double distilled water five times, to obtain oxidized clean surfaces of MWNT's. Carboxylation is the most favored starting point because it can be covalently bonded to form ester or amide linkages easily .The sample was then dried in a vacuum oven at 80 °C for 4 h. The oxidized nanotubes were treated with $SOCl_2$ to introduce the acyl groups. 200 mg of obtained nanotubes were added to 20 mL of thionyl chloride and 2mL of DMF (dimethyl formamide) in 100 mL round bottom flask. The system was refluxed for 36 hrs. at 60°C. The product obtained was washed with toluene .The sample was then dried in a vacuum oven at 80 °C for 4 h.

Twenty milligrams of the acylated nanotubes was dispersed by sonication in 10 mL of Ethylenediamine. The sonication was followed by stirring for 16 h at 33°C. The product was then diluted with 200 mL of methanol. The functionalized MWNTs were then dried in a vacuum oven at 80 °C for 4 h. This helped to introduce the amide groups on the CNT's

For azide functionalization, 60 mg of acylated nanotubes were treated with 5mg of NaN_3 in DMF as solvent for 24h, and precipitated in toluene. The product was dried in an oven at 80°C for 4h. The different functionalization carried out were confirmed from FTIR and shown in Figure 4.1.

4.3.2 Blending of CNT's into polysulfone to form nanocomposite membranes

Polysulfone resin was first dried for at least 24h in a vacuum oven at temperature about 80°C before being used. N,N-dimethylformamide (DMF) was used as solvent and water containing isopropanol was used as coagulation medium during the phase inversion process. An optimized two component dope solution was used, 18% (w/w) polysulfone; 82% (w/w) DMF. To this solution different percentage of various functionalized CNT's were added to form PSf-CNT nanocomposite solution. The functionalized CNT's (oxidized, amide, azide) were used for the purpose. MWNTs in five different weight percentages (0.0%, 0.1%, 0.2%, 0.5%, 1.0%) were added to polysulfone solution, for all three different functionalized CNTs.

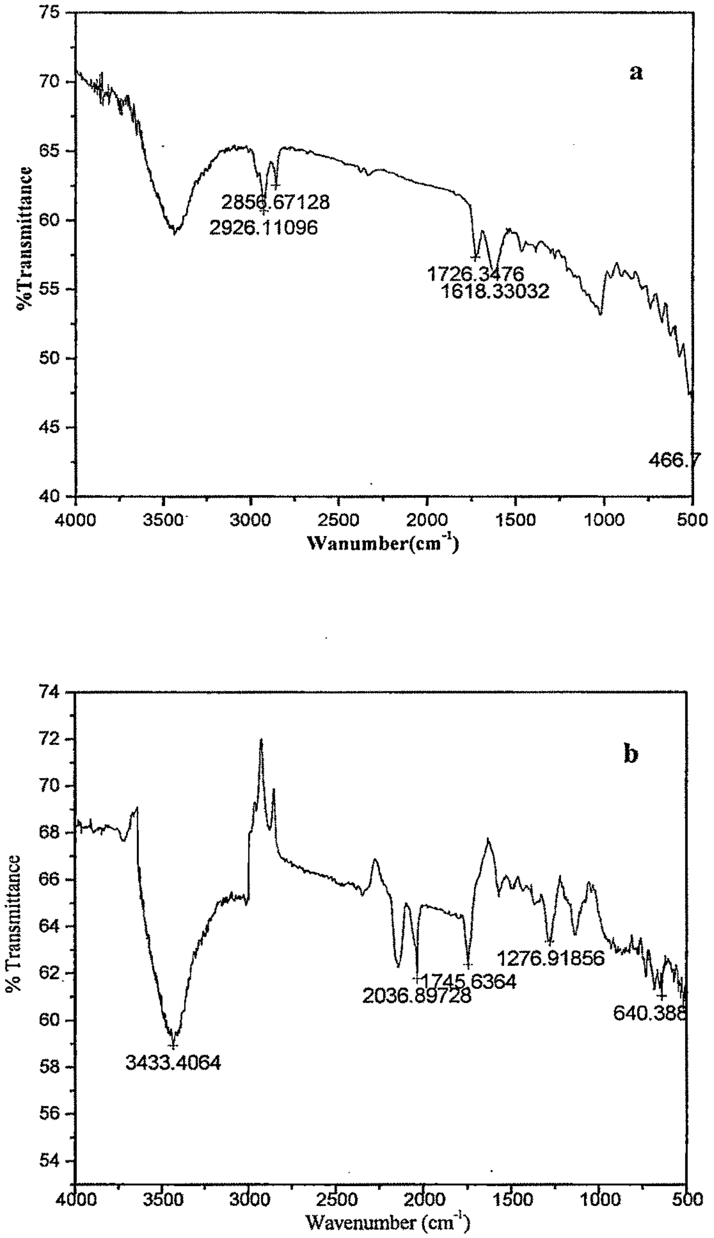

Figure 4.1 FT-IR scans of MWNTs (a) carboxylated MWNT and (b) azide functionalized MWNTs.

These groups were expected to form hydrogen bonds with sulfone groups of PSf (Figure 4.2). The solutions were mixed in a round bottom reaction vessel and stirred using a magnetic bar and sonicated at 60°C for 72h until the polymeric solution became homogeneous. The homogeneous solution was placed in an ultrasonic water bath to remove the gas bubbles that may exist in the casting solution dope prior to the membrane casting process.

4.3.3 Preparation of asymmetric flat sheet membranes

Asymmetric flat sheet membranes were prepared according to the dry/wet phase separation process. The polymer solution was cast on a PET base using glass plate as support. The homogenous polymer solution was stretched into a thin film maintaining the thickness of the film. The casting knife consisted of a steel blade, or a glass rod which rested onto two runners, arranged to form a precise gap of 0.5mm between the rod and glass plate. The cast membranes were immediately soaked in a coagulating water bath containing 1% isopropanol, where the solvent-non solvent exchange takes place and membranes of uniform thickness of 5 mil (125 μm) are prepared. These membranes were then dried at 60°C and kept soaked in deionized water for several days.

4.3.4 Capillary flow porometry

Pore size analysis of membranes was done by Capillary Flow Porometer (Porous Materials Inc, USA, Model 1500 AEX), considering the pore as a capillary. First, the membrane samples were soaked in a wetting liquid, 'Porewick' having low surface tension (γ) of 1.6 N/m^2 and has a contact angle zero with the membrane surface i.e., it wets the membrane samples fully and spontaneously fills all the pores in the sample. Then gas was blown through the membrane and the pressure of the gas was gradually increased until the liquid was removed from the pores, forming gas flow through pores, which increases with further increase in pressure[180,181]. At any given pressure, the largest pore is emptied first and the gas flow starts through the membrane, which gives the bubble point pressure.

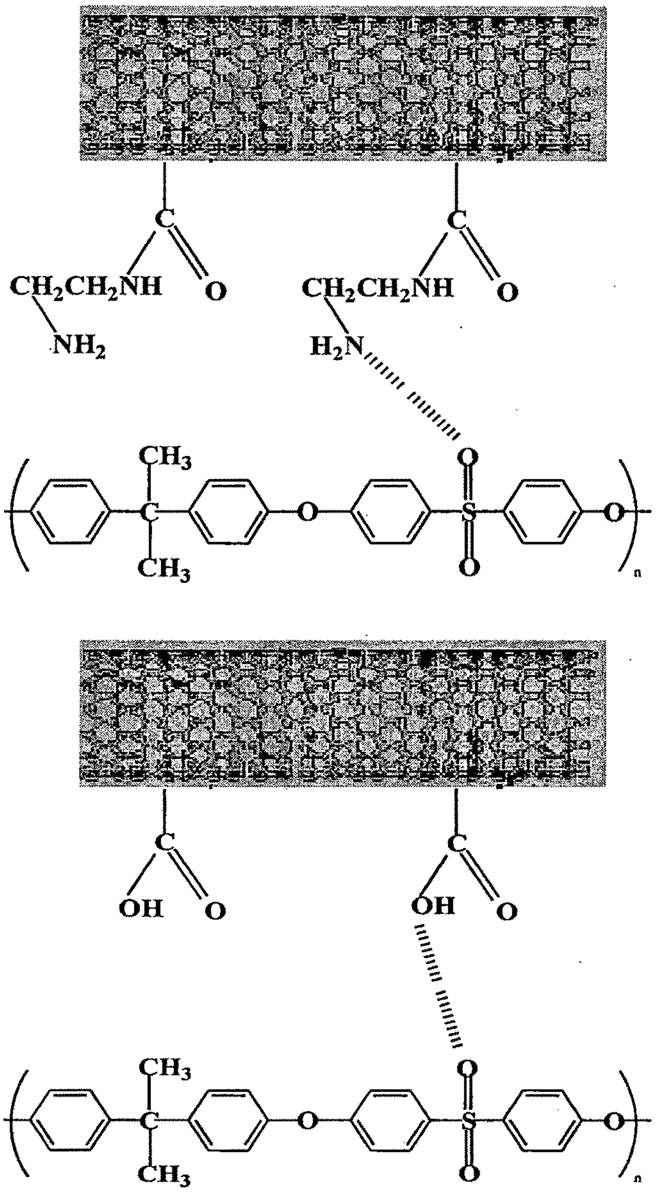

Figure 4.2 Hydrogen bonding between the possible arrangement of functional groups on nanotubes and polysulfone.

On further increase of the pressure, smaller pores are then emptied and gas flow increases. The flow rate was determined as a function of pressure and used to calculate the desired pore characteristics using the Washburn equation.

$D = 4\,\gamma\,\mathrm{Cos}\,\theta/p$

Where D is the diameter of a pore, θ is the contact angle, and p is differential pressure. For wetting liquid Porewick which was used, $\theta = 0^\circ$ and the equation becomes

$D = 4\,\gamma/p$

From this equation the diameter of pores in the membrane were calculated.

4.3.5 Permeation test

The common method to characterize the MWNTs/PSf blend membrane was to measure its performance in terms of pure permeability, flux and solute rejection of different feed solutions, using a general UF test cell set-up. The flux was measured by weighing permeates penetrated through the membrane per unit time and solute rejection was calculated from the concentrations of the feed solution and permeate using the following equation.

Rejection (%) = $(C_f - C_p)/C_f \times 100$

whereC_f and C_p are the concentrations of metal ions in the feed solution and permeate respectively. The C_f and C_p were measured by AAS.The collected filtrate samples were used for quantitative determination of ions using Atomic Absorption Spectrophotometer (Model: Analytikjena Nova-400). The Mercury and Arsenic were measured in graphite furnace mode of AAS and other metal were measured in flame mode of AAS. Control experiments in absence of functionalized CNTs were also carried out in order to correct any adsorption of metal on container surface. These experiments indicated that no adsorption by the container surface were detectable. All atomic absorption spectrometer (AAS) (Analytik-Jena-Nova-400) measurements were carried out on flame mode/graphite furnace mode with single beam. AAS equipped with 100 mm burner, a cross flow nebulizer 5.0 ml/min and 1.2 mm slit were used throughout the experiments. Each experiment was duplicated under identical conditions using this instrument for concentration determination.

4.3.6 Zeta Potential measurement

Zeta potential is a scientific term for electrokinetic potential. It is denoted using the Greek letter zeta (ζ), hence *ζ-potential*. The zeta potential is the electric potential in the interfacial double layer (DL) at the location of the slipping plane versus a point in the bulk fluid away from the interface. In other words, zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle or surface.

Polymeric membranes possess a surface charge due to presence of functional group on their surface. When brought into contact with an aqueous solution, the surface charge is compensated by counter ions in the solution close to the surface, forming the so-called electrical double layer. The vital feature of the electric double layer is that the surface charge is balanced by counter ions, some of which are located very close to the surface, in the so-called Stern layer; the remainder are distributed away from the surface in the diffuse layer (Figure 4.3). An important parameter of the electric double layer is the Stern potential, that is, the potential at the boundary between the Stern and diffuse layers. The Stern potential cannot, however, be measured directly; the electro kinetic (zeta) potential is often considered an adequate substitute. The zeta potential is the potential at the plane of shear between the surface and solution where relative motion occurs between them. Several techniques can be used to determine the zeta potential of surfaces. The streaming potential technique is most suitable for membrane surfaces.

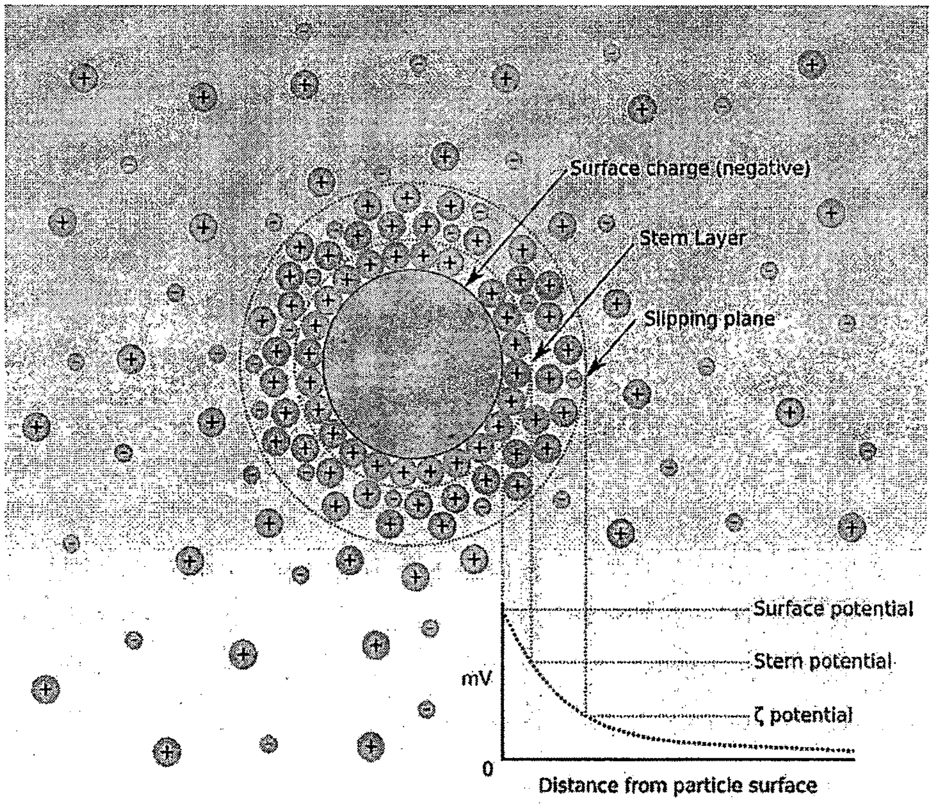

Figure 4.3 Charge development on surface of membrane or dispersed particle in a dispersion medium.

The introduction of Reverse osmosis and nanofiltration membranes have proved a wonderful advancement in water purification technologies The major advantage of membrane treatment is the superior quality of the product water. This quality is attained with the addition of fewer chemicals than conventional water treatment. The major obstacle to further incorporation of membrane processes into water treatment plants is membrane fouling. Fouling causes a decrease in the water flux across the membrane, an increase in salt passage through the membrane, and affects both the performance and longevity-of membranes. Membrane foulants can be broadly classified into four categories (1) sparingly soluble salts, (2) biological growth, (3) dissolved organic compounds, and (4) colloidal or particulate matter. The attack of colloidal matter on membrane surfaces is basically due to charge on polymer surfaces. Thus a complete understanding of charges and particle-membrane and particle-retained particle interactions must be considered for more understanding of colloidal fouling. Thus Zeta potential measurement would help in gaining an idea on the value of charges and potential on the surfaces.

4.4 Characterization

The prepared blend membranes were characterized by FT-IR (Perkin-Elmer spectro photometer at 20 scans using the KBr pellet method) and scanning electron microscopy (SEM) using JEOL JSM-5610 model No. 6587 LV instrument for clean surfaces and attached functional groups. The TGA data were obtained in nitrogen atmosphere with Mettler-Teledo Star SW 7.01 thermo gravimetric analyzer at 10 °C/min.

4.5 Results and Discussion

4.5.1 Membrane casting by phase-inversion process

The MWNTs/PSf blend membranes were prepared by the immersion phase inversion process, using DMF as solvent and water with isopropanol as a coagulant. This involves solvent/non-solvent exchange process. Homogeneous solutions of PSf, DMF and functionalized MWNTs were prepared by sonication, and then used for casting blend membranes. By the phase inversion process it was observed that the membranes were uniform without any variation in the concentration of the solution. If the solutions were not homogeneous then the casting would not be uniform and the resulting membrane would have variations in the thickness as well as the porosity would be non uniform.

4.5.2 Characterization of composite polysulfone membranes

4.5.2.1 FESEM

The prepared composite MWNT/PSf membranes had thickness of 5mil (125µm). It is known that polysulfone blend membranes show porous morphology. Addition of MWNTs could help to reduce the pore size, due to nanosize (110-117nm) diameters of MWNTs and this is what can be seen from the FESEM for the membranes in Figure4.4. The functionalization of the surface of the nanotubes helps in formation of physical bonds between the polysulfone and the functionalized nanotube and so this influences the formation of the porous structure. The decrease in pore size of membranes with gradual increase in amount of carbon nanotubes is not very significant, as the arrangement of carbon nanotubes in the membranes is less manageable and controlled. The increase in carbon nanotube makes the surface of the membrane more smooth (Figure4.4b& Figure4.4c) as the solvent-non solvent exchange process becomes slower, owing to increase in viscosity of blend solution. These results are supported by the porometry results which will be discussed later. The largest visible pore size in unblended polysulfone membrane (Figure 4.4a) is 25µ while in blend membrane containing 1% nanotubes, it is less than 1µ.

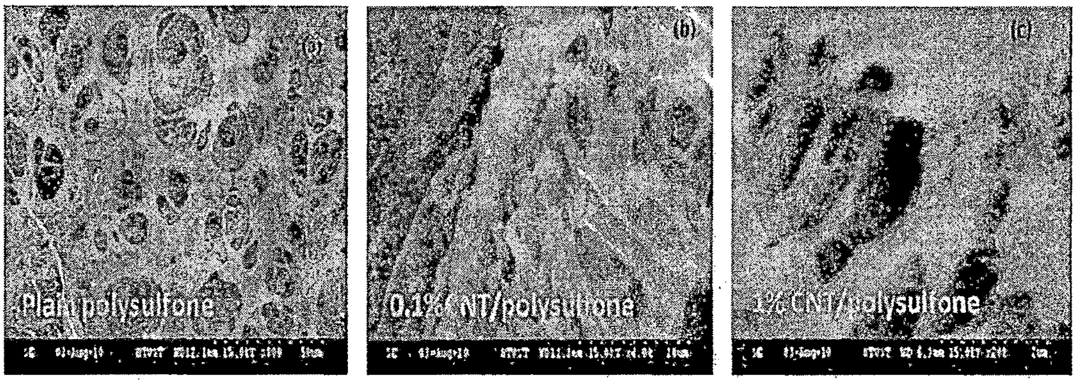

Figure 4.4 FESEM images of CNT/PSf composite membranes (a) 0.0% (b) 0.1% (c) 1% functionalized MWNTs.

4.5.2.2 Infra red spectroscopy

The FTIR spectra of blend membranes containing oxidized and amide functionalized CNTs show presence of bands at 1290cm^{-1} corresponding to S=O asymmetric stretching vibration, 1243.15cm^{-1} corresponding to C-O-C symmetric stretching vibration, 1134.23cm^{-1}corresponding to S=O symmetric stretching vibration for polysulfone. Presence of oxidized nanotubes gives band at 3487.56cm^{-1} (Figure 4.5a) corresponding to -OH stretching vibration, 2850-3000cm^{-1} corresponding to C-H stretching vibration, and at 1720-1730cm^{-1} corresponding to C=O stretching vibration. In Figure 4.5b disappearance of band at 1720cm^{-1} and presence of a weak band at 1623cm^{-1} confirm the presence of amide carbonyl stretch in amide functionalized CNTs. Disappearance of broad band at 3500cm^{-1} and appearance of weak bands at 3250-3400cm^{-1} show the possibility of overlap between N-H stretch of primary amine with O-H stretching in some extent. There is a hydrogen bonding between the nanotubes and the polysulfone,and so the functional peaks of the additional components are seperatly observed.The existense of hydrogen bonding between the carboxylic groups or amide or azide groups of nanotubes and the sulfonic groups of polysulfone membrane has been previously reported[182,183]and is also confirmed from our TEM and FESEM results.

4.5.2.3 Thermo-gravimetric analysis

The TGA data shows the effect of MWNTs in the polysulfone matrix. The blend membranes show a slow and high temperature degradation as compared to polysulfone membrane without MWNTs. MWNTs owing to their high mechanical and heat resistance, offer increased heat tolerance and thus degradation occurs at higher temperatures as the concentration of MWNTs increase from 0-1 wt%. In polysulfone membrane without CNTs, the degradation starts at 312°C, while in blended membranes the degradation temperature increases through 0.1-1.0 wt% MWNT content and is maximum for 1% MWNT /Polysulfone blended membrane i.e. 369°C and 374°C for amide and oxidized MWNTs.

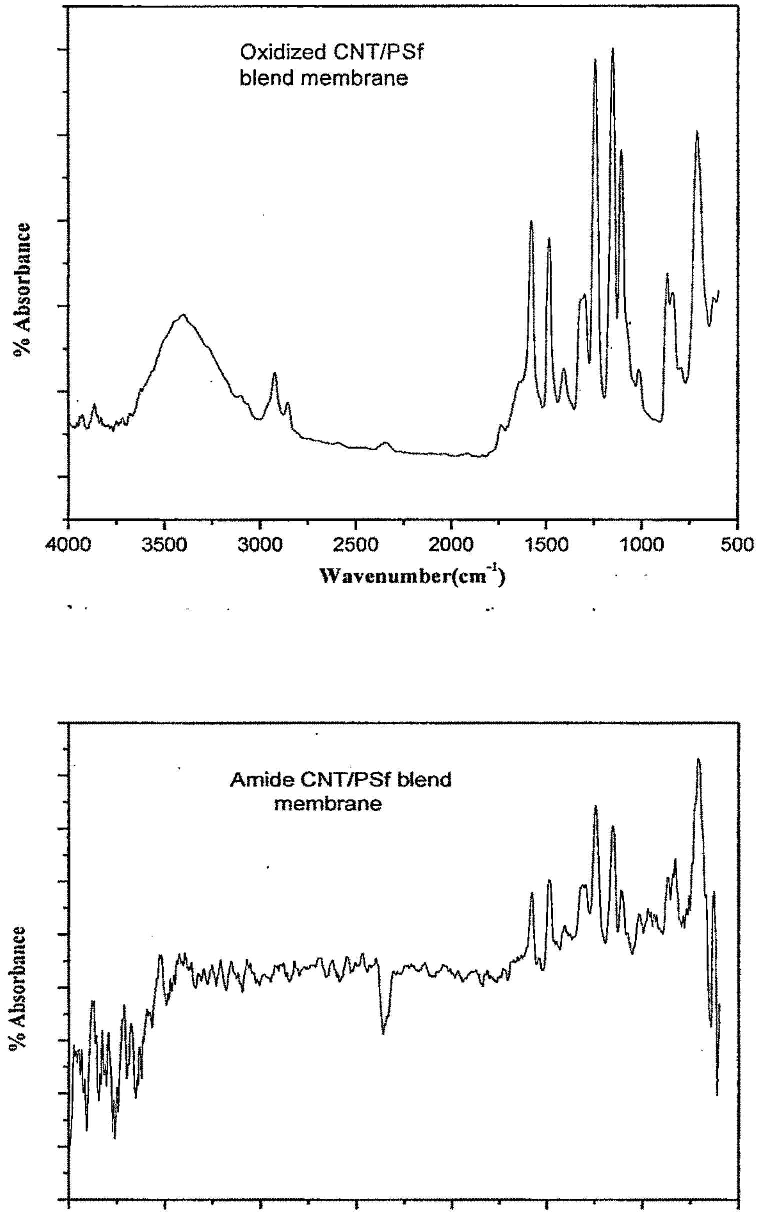

Figure 4.5 FT-IR of (a) oxidized CNT/PSF (b) amide functionalized CNT/PSF blend membranes.

Thus it can be said that carbon nanotubes increase thermal stability of polysulfone membranes as the compatibility between the nanotubes and the polysulfone is enhanced by the functionalization of the nanotubes (Figure 4.6).

4.5.2.4 Capillary flow porometry

The increase in amount is also reflected in form of pore size of membrane and contact angle measurements. When MWNT content is very high (above 1%), the density of MWNTs in membrane is high enough, and steric hindrance and electrostatic interactions between modified MWNTs and aggregate in the membrane during phase-inversion and would make the casting process difficult. Thus composite mixtures containing greater than 1% MWNT were not studied. The high density of MWNTs in the membrane could reduce the porosity. The addition of MWNTs causes an increase in hydrophilicity of the membrane (reduced contact angle) and decrease in pore size. These results can be explained as arising due to the fact that during phase inversion process, hydrophilic MWNTs migrate spontaneously to membrane/liquid interface to reduce interfacial energy. As the amount of MWNTs increases from 0.1-1.0 wt%, the PSf hydrophobic membrane behaves more and more hydrophilic. With increase in MWNTs, there is increase in viscosity of the blend solution and the solvent-non solvent exchange process becomes slower and the surface becomes more smoother, with smaller pore sizes though the pore size variations are not very demarcating on addition of higher percentage of MWNTs.

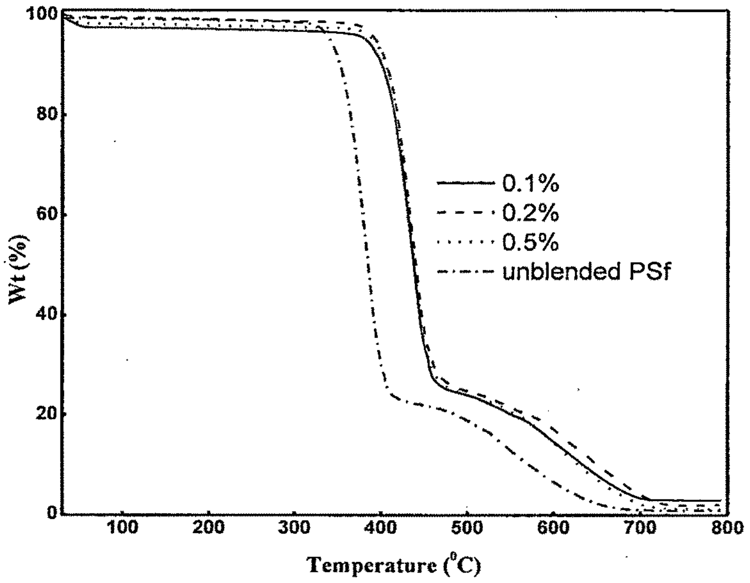

Figure 4.6 TGA data composite polysulfone membranes with different percentages of amide functionalized MWNTs.

These results are in accordance with the flux rate measurements. The smallest pore diameter reduces from 0.1079μ (~100nm) for pure polysulfone to 0.0257μ (~26nm) on addition of nanotubes under similar coagulation bath conditions. This can be seen in Table 4.1.

It is to be noted here that depending on the coagulation bath additives, the pore diameter of the unblended polysulfone can also be controlled. The results are summarized in Table 4.2. In order to determine the pore size distribution of the membrane, the pressure at which the bubble is formed is required. In order to reach bubble point, sufficient gas pressure must be applied to overcome the capillary forces of the pores. Gas pressure is applied on the underside of the membrane, and is gradually increased over time.

A constant flow of rising bubbles on the top side of the membrane indicates that the gas pressure has reached bubble point. It is at this pressure when the largest pore gets emptied first. The smallest pore size can also be calculated by increasing the gas pressure till all pores have been emptied and gas flow through the membrane matches that of a dry membrane. At pressures below the bubble point, gas can only pass through the membrane through diffusion.

4.5.2.5 Zeta Potential studies

Samples were analyzed for the evaluation of zeta potential from streaming current by streaming electrolyte KCl (0.001 M) in contact with PSf/CNT composite membrane samples. The fundamental equation for evaluating zeta potential from streaming current is Helmhotz Smoluschowski i.e.

$$\zeta = \frac{U_s}{\Delta P} \frac{\mu}{\epsilon \epsilon_0} \frac{L}{A} \frac{1}{R}$$

Table 4.1 Variation of the pore size with amount of amide functionalized CNT's.

% MWNT	Pore size(μ)	Contact angle(θ)
0.0	0.1079	77.7
0.1	0.0286	77.6
0.2	0.0262	77.6
0.5	0.0259	77.5
0.7	0.0259	76.3
1.0	0.0257	26.7

Table 4.2 Variation of the smallest pore diameter (micron) and required pressure (MPa) with weight % of CNT's.

	Oxidized CNT's (wt %)					**Amide CNT's (wt %)**				
	0.1	0.2	0.5	0.7	1.0	0.1	0.2	0.5	0.7	1.0
Pore pressure	1.562	1.689	1.740	1.754	262.4	1.600	1.747	1.767	1.767	1.781
Pore diameter	0.029	0.027	0.026	0.026	0.025	0.028	0.026	0.025	0.025	0.025
Mean flow pore pressure	0.465	0.470	0.474	0.479	0.487	0.466	0.471	0.478	0.480	0.489
Mean flow pore diameter	0.098	0.097	0.096	0.095	0.093	0.098	0.097	0.095	0.095	0.093
Bubble point pressure	0.044	0.044	0.045	0.045	0.045	0.044	0.044	0.045	0.045	0.046
Bubble point pore diameter	1.029	1.028	1.027	1.019	1.017	1.029	1.029	1.018	1.014	1.013

Us : streaming potential, ΔP : pressure difference across the channel, μ : viscosity of the solution

$\in$: permittivity of the solution, L, A, and R are the length, cross-sectional area, and electrical .resistance of the channel

Zeta potential was measured with change of pH by adding HCl acid (0.05 M) in the electrolyte. The results obtained for measurement of zeta potential have been summarized in Tables 4.3 and 4.4. All membranes display an i.e.p. (iso-electric point) at an acidic pH; the zeta potential is negatively charged at pH values above the i.e.p. and is positively charged at lower pH. Zeta potential measurements reveals the surface chemistry of the coated membrane samples At lower pH values presence of protonated carboxylic groups in carboxylated CNT /PSf composite membranes give positive zeta potential values .The zeta potential values for carboxylated CNT /PSf composite membranes are more negative at high pH. It is attributed to presence of deprotonated carboxylic groups at surface of composite membranes at high pH. With increase in concentration of carboxylic groups , the potential difference at the interface increase and so zeta potential values increase (more negative).The zeta potential values for amide CNT /PSf composite membranes are comparatively positive due to presence of terminal amine groups which are protonated, and thus gives positive charge to interface. The zeta potential values are negative and move to positive end at low pH values for all types of membranes.

4.5.3 Heavy metal removal

Heavy metal salt solutions were prepared by dissolving the salts in ultrapure water (ElixMillipore) and solutions of 1 ppm concentration were prepared. Stock solutions of chromium and lead of 1000 mg/l concentration were prepared by dissolving, 2.848 g of $K_2Cr_2O_7$, 1.598 g of $Pb(NO_3)_2$, respectively in 1000 ml of ultrapure water (Elix, Millipore), whereas cadmium solution was prepared by dissolving 1 g of cadmium metal in minimum volume of (1 + 1) HCl and then making it up to 1000 ml with ultrapure water. Standard working solutions of copper and arsenic were prepared from 1000 mg/L standard solution (Merck, Germany) and solutions of varying initial concentrations were prepared from a 1000 mg/L by serial dilution using distilled deionized water.

Table 4.3 Values of Zeta potential developed at the surface of PSf/ % carboxylated CNT composite membranes when in contact with an electrolyte solution.

Zeta Potential at different pH					
PSf/ 1% carboxylated CNT composite membrane		PSf/ 0.5% carboxylated CNT composite membrane		PSf/ 0.1% carboxylated CNT composite membrane	
pH	**ZP(mV)**	**pH**	**ZP(mV)**	**pH**	**ZP(mV)**
5.472	-52.49	5.467	-44.87	5.452	-51.63
5.469	-51.89	5.459	-44.92	5.146	-49.37
5.13	-50.97	4.925	-41.55	4.771	-44.92
4.737	-48.2	4.413	-36.35	4.361	-38.5
4.315	-43.54	4.027	-30.53	4.01	-31.84
3.959	-38.17	3.688	-24.19	3.684	-25.01
3.631	-32.55	3.371	-17.96	3.373	-17.69
3.32	-26.31	3.123	-13.05	3.126	-11.67
3.078	-21.44	2.929	-9.271	2.932	-7.323
2.886	-17.42	2.771	-6.453	2.801	-4.613
		2.641	-4.382	2.683	-2.362

Table 4.4 Values of Zeta potential developed at the surface of PSf/ % amide functionalized CNT composite membranes when in contact with an electrolyte solution.

Zeta Potential at different pH					
PSf/ 1% amide functionalized CNT composite membrane		PSf/ 0.5% amide functionalized CNT composite membrane		PSf/ 0.1% amide functionalized CNT composite membrane	
pH	**ZP(mV)**	**pH**	**ZP(mV)**	**pH**	**ZP(mV)**
5.445	-53.5	5.428	-44.52	5.625	-50.93
5.123	-47.14	5.122	-37.04	5.272	-45.6
4.752	-38.53	4.759	-31.54	4.859	-38.82
4.344	-28.54	4.356	-24.37	4.421	-30.59
3.994	-19.77	4.001	-17.14	4.058	-23.45
3.67	-11.37	3.683	-11.18	3.726	-16.49
3.357	-3.608	3.37	-4.897	3.411	-9.581
3.112	2.158	3.123	-0.151	3.163	-4.276
2.918	6.225	2.928	3.086	2.966	0.071
2.761	9			2.807	3.143

The pH of the solutions were set as 2.6 (acidic medium). The pH of Cr^{+6}metal ion solution was further adjusted to 6.8 and 9.5 by the addition of 0.1N solution of NaOH during dilution process. The alkaline and acidic solutions of all other metal ions show hydrolysis and hydroxide formation, and so assumed to be not suitable for metal rejection study by prepared composite membranes. Tests were carried out at different pressures 0.49, 0.686 and 0.882 MPa and at various pH 2.6, 6.8, 9.5 for chromium and at pH 2.6 only for other metal ions. The permeation tests were conducted at 25°C, effective membrane area was 16 cm^2, and feed flow rate 12ml/min. Before measuring the flux, each membrane was subjected at 0.5MPa for about 2h to avoid the compaction effect of the membrane. Studies were also conducted at different pressures.

4.5.3.1 Effect of pressure

Nearly no permeate flow rate was observed below 0.49 MPa and was found to increase with increase in applied pressure (Figure 4.7, Table 4.5). Increased pressure would force the test solution to flow at high rates through the membrane. Permeate flow for 0.2% and 0.5% oxidized CNT/PSf composite membranes at 0.49MPa is 6.2 and 5.7ml/min respectively while 10.5 and 9.8 ml/min respectively at 0.88MPa. Similarly permeate flow for 0.2% and 0.5% amide functionalized CNT/PSf composite membranes at 0.49MPa is 5.9 and 5.8ml/min respectively while 9.9 and 9.9ml/min respectively at 0.88MPa. The results for all other membranes can be seen in Table 4.5. At higher pressures increased flow rates would cause less rejection of unwanted ions. The permeate flow for 1% oxidized CNTs/PSF and 1% amide CNTs/PSF blend membranes at optimum pressure of 0.49MPa was 5.4 and 5.6ml/min. respectively, while it was 6.3ml/min. for plain PSf membrane.

Table 4.5 Permeate flow for different membranes at different pressures.

S.No.	Type of membranes	Feed flow (ml/min)	Permeate flow (ml/min)		
			4.90 bar	6.86 bar	8.82 bar
1.	0.2% Oxidized CNT	12.0	6.2	8.3	10.5
2.	0.5% Oxidized CNT	12.0	5.7	7.6	9.8
3.	1% Oxidized CNT	12.0	5.4	7.3	9.6
4.	0.1% Amide CNT	12.0	6.1	8.3	10.3
5.	0.2% Amide CNT	12.0	5.9	8.0	9.9
6.	0.5% Amide CNT	12.0	5.8	7.9	9.9
7.	0.7% Amide CNT	12.0	5.8	7.9	9.8
8.	1.0 % Amide CNT	12.0	5.6	7.8	9.8
9.	Plain PSf	12.0	6.3	8.7	11.8

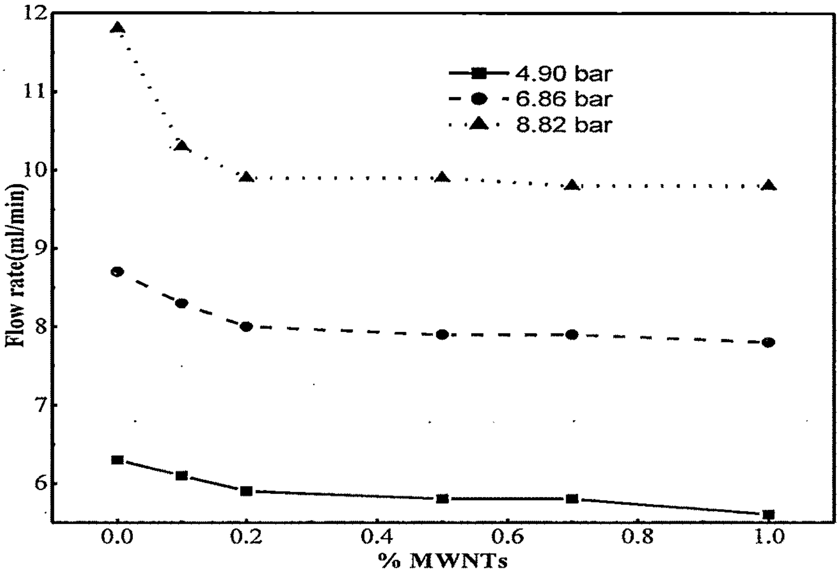

Figure 4.7 Flow rate at different pressures for different amide MWCNT/PSf membranes at acidic pH 2.6.

This decrease in permeate flow accounts for greater hindrance at the surface of membrane due to decreased pore size and thus supports rejection of ions. Percentage rejection of Cr^{+6} at 0.49 MPa and 2.6 pH for composite membranes containing 0.1% and 1% amide functionalized CNT was 80.4 and 94.2 respectively which is reduced to 62.3 and 75.3 respectively, when pressure used is increased to 0.882 MPa and 2.6 pH (Tables4.6 & 4.7). Under similar conditions % rejection of Pb^{+2} at 0.49 MPa for composite membranes containing 0.1% and 1% amide functionalized CNT was 72 and 90.1 respectively which is reduced to 50.2 and 62.0 respectively, when pressure used is increased to 0.882 MPa (Figure 4.8).Percentage rejection of Cr^{+6} at 0.49 MPa and 2.6 pH for composite membranes containing 0.1% and 1% azide functionalized CNT was 80.9 and 94.8 respectively which is reduced to 63.9 and 76.1 respectively, when pressure used is increased to 0.882 MPa and 2.6 pH. Percentage rejection of Cd^{+2}at 0.49 MPa and 2.6 pH for composite membranes containing 0.1% and 1% amide functionalized CNT was 73.1 and 79.1respectively which is reduced to 57.1 and 69.9 respectively, when pressure used is increased to 0.882 MPa and 2.6 pH.

Table 4.6 Removal studies of metal ions at pH 2.6 for amide functionalized MWCNT/PSf. at pressure of 0.49MPa and 0.882MPa.

(%) CNT	Removal Capacity(%) amide					
	Cr (VI)		Pb (II)		Cd (II)	
	0.49	0.882	0.49	0.882	0.49	0.882
0.0	10.2	7.2	10.5	7.4	9.9	9.9
0.1	80.4	62.3	72.0	50.2	72.8	55.3
0.5	90.7	68.6	87.8	54.9	77.4	61.2
0.7	92.8	70.1	88.2	57.6	77.9	61.2
1.0	94.2	75.3	90.1	62.0	78.2	78.2

Table 4.7 Removal studies of metal ions at pH 2.6 for azide functionalized MWCNT/PSf. at pressure of 0.49MPa and 0.882MPa.

(%) CNT	Removal Capacity(%) azide					
	Cr (VI)		Pb (II)		Cd (II)	
	0.49	0.882	0.49	0.882	0.49	0.882
0.0	10.2	7.4	10.5	7.9	9.9	7.3
0.1	80.9	63.9	72.6	52.2	73.1	57.1
0.5	91.6	69.8	88.3	55.8	78.2	62.2
0.7	93.1	72.1	89.1	58.6	78.8	66.8
1.0	94.8	76.1	90.8	65.2	79.1	69.9

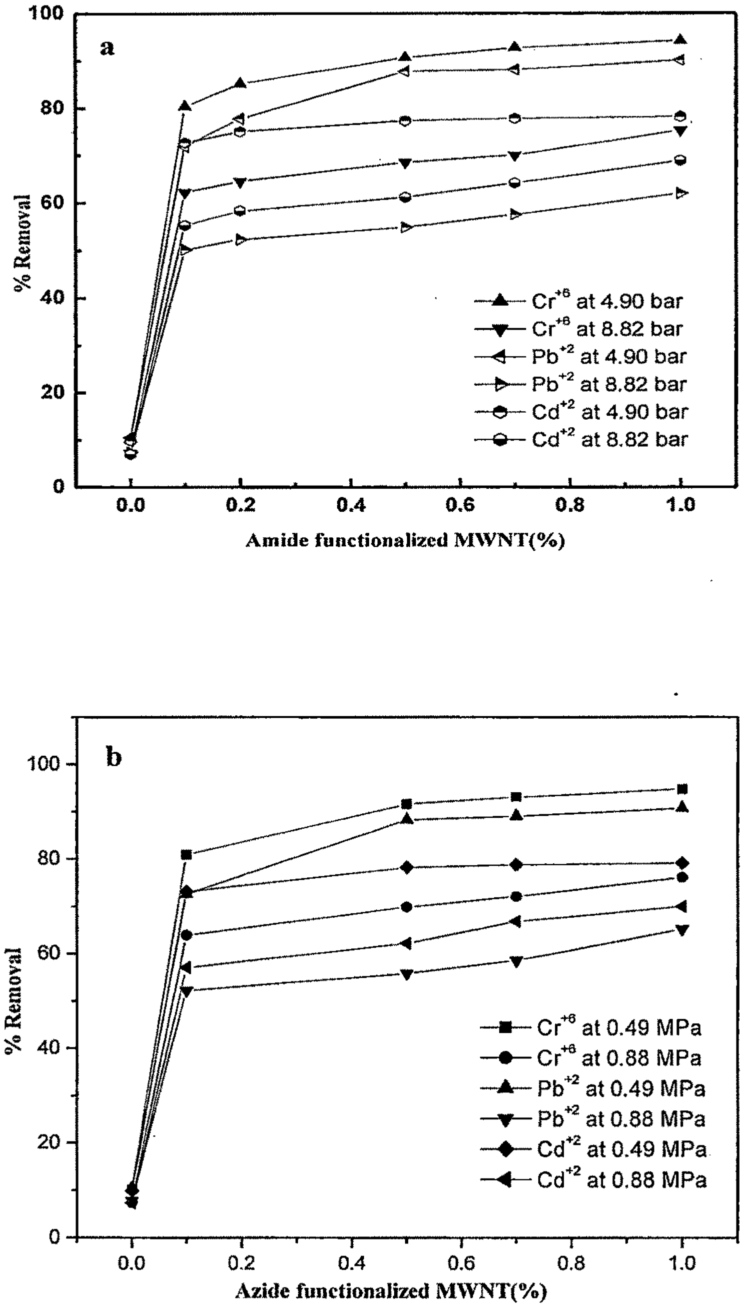

Figure 4.8 %Removal of metal ions at different pressure (a) %amide CNT/PSf (b) %azide CNT/PSf composite membranes at pH 2.6.

4.5.3.2 Effect of pH

Similar rejection experiments confirmed that maximum rejection for $Cr^{+6}$was found at pH 2.6 (acidic), which could be explained as high complexation tendency of surface active sites of the blend membranes. The modified MWNTs provide sites for complexation with metal ions which are absent in plain polysulfone membranes. The –COOH, -OH due to oxidation of membranes surfaces, -CONH- and $-CH_2NH_2$ due to amide functionalization and, $-CON_3$ due to azide functionalization show complex formation with the heavy metal ions. Apart from these at acidic pH, protons also compete with the heavy metal ions, and thus providing maximum rejection or removal at acidic pH. There is decrease in rejection at pH 6.8, which again increases at basic pH (9.5) due to hydroxide formation of Cr^{+6}

(Figure 4.9). These hydroxide salts precipitate out of the solution and thus are removed from the solution. Here hydroxide formation on the membrane surface affects or reduces the membrane activity and so is less desired. Thus pressure of 0.49MPa and pH 2.6 could be considered as optimum condition for metal removal studies.

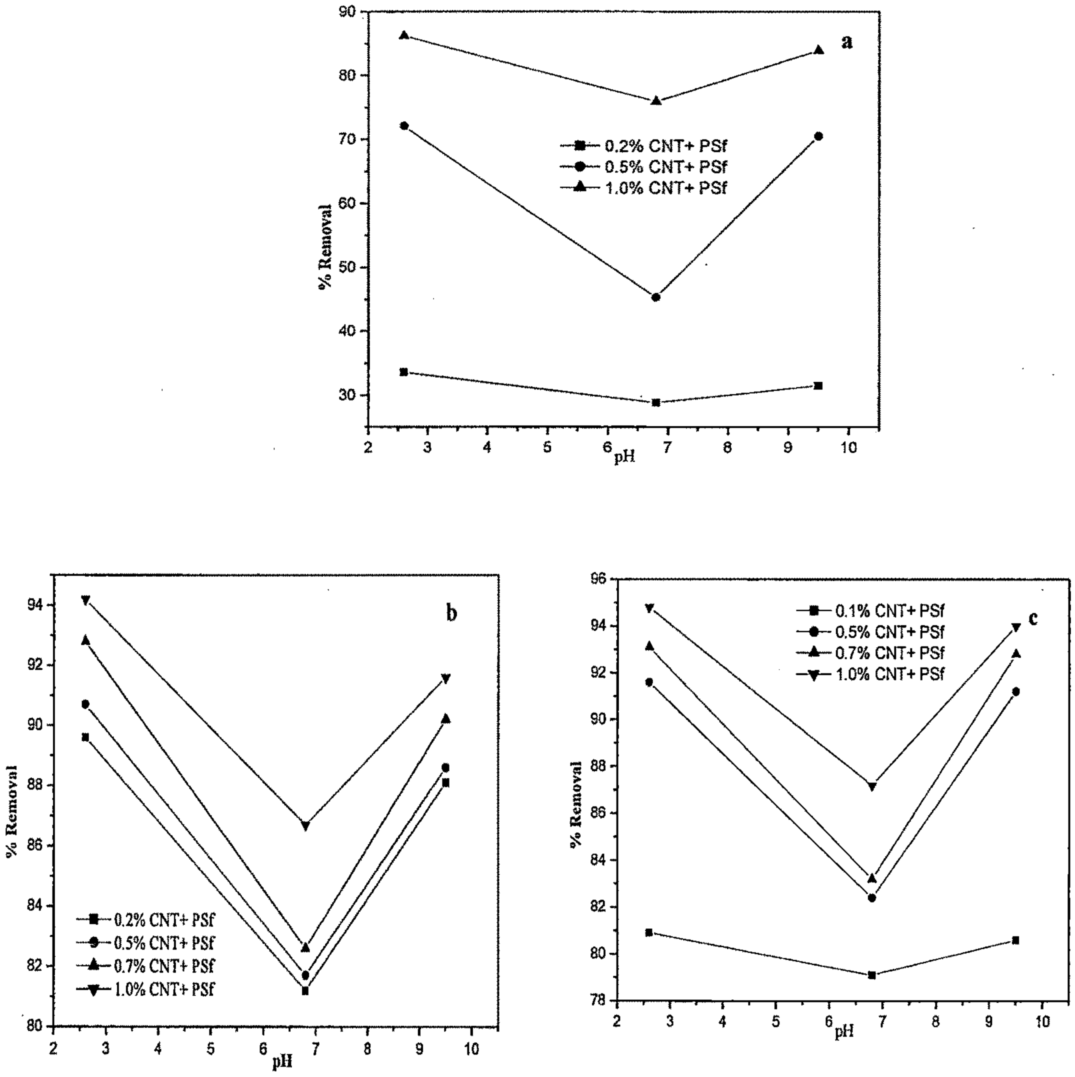

Figure 4.9 Removal studies of Cr^{+6}ions at different pH for (a) oxidized (b) amide (c) azide functionalized MWCNT/PSf. at pressure of 0.49MPa.

Metal removal/rejection studies at set optimum conditions of pH 2.6 and pressure 0.49MPa were done for oxidized, amide functionalized, azide functionalized MWCNT/PSf blend membranes. Metal ions rejection was found to increase with increase in % weight of CNTs added. This may be attributed due to decreased pore size, reduced flow rate and increased number of active sites on CNTs due to functionalization. Appreciable removal was observed for oxidized CNT/PSf composite membranes (Table 4.8). The metal removal was found to be more pronounced in case of membranes containing amide (Table 4.9) and azide (Table 4.10) functionalized CNTs. The presence of amide and azide groups are expected to have better metal binding capacity as compared to carboxylic group, and thus only 33.6% of Cr^{+6} and 41.3% of As^{+3} is rejected using a oxidized CNT/PSf blend while 80.4% of Cr^{+6} and 71.3% of As^{+3} is rejected using amide functionalized CNT/PSf .

In case of amide functionalized CNT/PSf membranes, 0.1% amide gave 80.4% rejection of Cr^{+6} while 1% amide gave 94.2% rejection. On increasing carbon nanotubes, there is decrease in pore size, which gives reduced flow rate and reduced flux, and thus better removal of heavy metal ions on the surface. On the contrary plain polysulfone membranes (without carbon nanotubes) show very less or negligible rejection. Plain polysulfone membranes gave only 10.2% rejection of Cr^{+6}, which is very less as compared to blended membranes.

Table 4.8 Removal studies of toxic metal ions at pH 2.6 for oxidizedMWCNT/PSf at pressure of 0.49MPa.

(%) CNT	Removal capacity (%)				
	Cr (VI)	Cu (II)	Pb (II)	Cd (II)	As (III)
0.0	10.2	10.1	10.5	9.9	10.9
0.2	33.6	44.2	26.8	53.2	41.3
0.5	72.1	68.0	39.7	63.5	51.2
1.0	86.2	79.3	41.3	71.6	83.6

Table 4.9 Removal studies of toxic metal ions at pH 2.6 for amide functionalized MWCNT/PSf at pressure of 0.49MPa.

(%) CNT	Removal capacity (%)				
	Cr (VI)	Cu (II)	Pb (II)	Cd (II)	As (III)
0.0	10.2	10.1	10.5	9.9	10.9
0.1	80.4	85.6	72.0	72.8	71.3
0.2	89.6	88.2	77.6	74.9	75.3
0.5	90.7	90.6	87.8	77.4	77.9
0.7	92.8	90.9	88.2	77.9	79.2
1.0	94.2	93.1	90.1	78.2	79.4

Table 4.10 Removal studies of toxic metal ions at pH 2.6 for azide functionalized MWCNT/PSf at pressure of 0.49MPa.

(%) CNT	Removal capacity (%)				
	Cr (VI)	Cu (II)	Pb (II)	Cd (II)	As (III)
0.0	10.2	10.1	10.5	9.9	10.9
0.1	80.9	85.9	72.6	73.1	71.9
0.5	91.6	91.4	88.3	78.2	78.3
0.7	93.1	91.9	89.1	78.8	80.6
1.0	94.8	93.9	90.8	79.1	80.9

4.6 Conclusions

The polysulfone membranes have an average pore size of 0.05-0.1µ (microns). These membranes show high thermal and chemical resistance, but are highly hydrophobic and susceptible to membrane fouling. The large pore size of 0.1µ and more give less water flux ,and thus only colloids and bacteria are subjected to removal. The MWNTs with clean and active functionalized surfaces, show efficient bonding with the polymeric membrane surfaces. The presence of nanotubes effectively increases the thermal stability of polysulfone, and thermal degradation occurs at comparatively high temperatures. The surface chemistry and charges studied by Zeta potential measurement confirm the presence of active groups and degree of functionalization. The 1%carboxylated CNT /PSf composite membranes have higher value of negative zeta potential, as compared to 0.1%carboxylated CNT /PSf composite membranes. They make the membranes more hydrophilic, impart greater adsorptive nature, and reduced pore size to the range of 20-30nm. The reduced pore sizes and high adsorptivity help the membranes to be efficient enough for metal removal from drinking water. The percent rejection of heavy metal was found to increase with increase in amount of MWNTs. Amide and azide functionalized carbon nanotubes gave better results as compared to oxidized CNTs and best rejection were found at acidic pH 2.6 and pressure 0.49MPa. These encouraging studies can be extended for further investigating the performance of these membranes for more environmentally damaging metal ions.