DEVELOPMENT OF NANOCOMPOSITE MEMBRANES FOR ENHANCED PERFORMANCES

By

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LIST OF PUBLICATIONS

Journal:

a. Published:

- 1. Carbon nanotube membranes for desalination and water purification: Challenges and opportunities, Soumitra Kar, R.C. Bindal and P.K. Tewari, *Nano Today*, 7, 2012, 385-389.
- Preparation, characterisation and performance evaluation of anti-biofouling property of carbon nanotube-polysulfone nanocomposite membranes", Soumitra Kar, M. Subramanian, Avishek Pal, A. K. Ghosh, R. C. Bindal, S. Prabhakar, J. Nuwad, C. G. S. Pillai, S. Chattopadhyay and P. K. Tewari, *AIP Conference Proceedings*, 1538, 2013, 181-185.
- 3. Reinforcement of nanostructured reduced graphene oxide: a facile approach to develop high performance nanocomposite ultrafiltration membranes minimizing the trade-off between flux and selectivity, Avishek Pal, Soumitra Kar, A. K. Debnath, D. K. Aswal, R. C. Bindal and P. K. Tewari, *RSC Advances*, 5, 2015, 46801-46816.
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Dedicated to Motherhood that has got the Finest, Greatest and Holiest Potential Influence on Mankind

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(Soumitra Kar)

GLOSSARY OF SYMBOLS, ABBREVIATIONS AND TERMS USED

Abbreviations:

Abbreviation	Full form
AFM	Atomic force microscope
ATR	Attenuated Total Reflectance
BSA	Bovine serum albumin
BSE	Back scattered electrons
CCD	Charge coupled device
CFU	Colony forming units
CNT	Carbon nanotube
CRT	Cathode ray tube
DWNT	Double wall nanotube
EDX	Energy dispersive X-ray
EPA	Environment protection agency
FEG	Field emission gun
FRR	Flux recovery ratio
FTIR	Fourier transform infra red
IP	Interfacial polymerisation
LMD	Liter per meter square per day
LMH	Liter per meter square per hour
MMM	Mixed-matrix membrane
MWCO	Molecular weight cut off
MWNT	Multi wall nano tube
NF	Nanofiltration
NMP	N-methyl 2- pyrrolidone
PEG	Polyethylene glycol
PEO	Polyethylene oxide
PES	Polyethersulfone
Psf	Polysulfone
PVDF	Polyvinylidenefluoride
PVP	Polyvinyl pyrrolidone
PWP	Pure water permeability

RO	Reverse osmosis
ROS	Reactive oxygen species
SEM	Scanning electron microscope
SFE	Surface free energy
SR	Solute rejection
SWNT	Single wall nanotube
TFC	Thin film composite
TMP	Trans membrane pressure
TOC	Total organic carbon
UF	Ultrafiltration
UTM	Universal testing machine
WHO	World health organisation
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray diffraction

Nomenclature:

Symbol	Definition of symbol with unit
А	Stokes radius of PEG/PEO, cm
A_k	Ratio of total cross sectional pore area to the effective membrane area
$(C_s)_{\ln}$	Logarithimic solute concentration, kgmole/m ³
C_m	Concentration on membrane surface, kgmole/m ³
C_p	Product concentration, kgmole/m ³
D	Diffusivity, m ² /sec
f(q)	Correction factors for effect of cylindral walls for filtration flow
g(q)	Correction factors for effect of cylindral walls for convection flow
J_{v}	Solvent flux, m/s;
J_{w}	Pure water permeability, m/s
J_s	Solute flux, m/s
L_P	Solvent permeability constant, M/s.Pa
Μ	Molecular wt. of PEG/PEO, kg/kgmole
M_{w}	Molecular wt., Kg/kgmole;
N_A	Avogadro's number
q	Ratio of solute radius and pore radius

r_{s}	Solute radius, m
r_p	Pore radius, m
R _a	Average surface roughness
R _q	Root mean square roughness
R _r	Reversible fouling
R _{ir}	Irreversible fouling
R _t	Overall fouling
R_{10z}	Ten point height
S_D	Steric hindrance factor for diffusive flow
S_F	Steric hindrance factor for filtration flow
\mathbf{V}_{st}	Streaming potential

Greek Symbol:

Symbol	Definition of symbol with unit
Δp	Effective operating pressure, Pa
ΔX	Membrane thickness, m
γ	Gamma radiation, kGy
γ_{LG}	Interfacial tension between the liquid and gas, N/m
γ_{SG}	Interfacial tension between the solid and gas, N/m
γ_{SL}	Interfacial tension between the solid and liquid, N/m
δ	Boundary layer thickness, m
ζ	Zeta potential, mV
θ	contact angle of intrusion liquid, ° (degree)
ø	Porosity
$[\eta]$	Specific viscosity m3/kg
μ	solvent viscosity, Pa.s
μ_{p}	Mean pore size of membranes, nm
σ	Surface tension of liquid, N/m
σ	Reflection coefficient
ω	Solute permeability constant, kgmole/N.s

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Synopsis

SYNOPSIS

Membranes¹ have taken an important place in chemical engineering and technology. They are used in a wide spectrum of applications. The key property that is utilized in membrane based separation technology is the ability to control the permeation rate of chemical species through the membrane; thus, allowing one component of a mixture to permeate the membrane preferentially, while hindering permeation of other components.

Membrane separation process enjoys numerous industrial applications¹ with the following advantages:

- Appreciable energy savings
- Environmentally benign
- Clean technology with operational ease
- Operational simplicity
- High quality products
- Can be used stand alone or in combination with conventional separation processes
- Greater flexibility in designing the systems

However, it offers following challenges:

- Concentration polarization
- Membrane fouling (especially biofouling)
- Trade-off between Flux and Selectivity
- Low radiation resistance behavior

The majority of membranes used commercially are polymeric. The "heart" of a membrane process is the membrane itself. To fully exploit the growing opportunities in the field of liquid phase separation, strong interest exists in the identification of new membrane materials that can offer better selectivity/productivity. Criteria for selecting membrane materials for a given separation are complex. Generally, durability, mechanical integrity at the operating conditions, productivity and separation efficiency are important stipulation. Of these requirements, selectivity, permeation rate, concentration polarisation, compaction and anti-biofouling characteristics are the most basic ones. High selectivity and permeability render the operation parameters more flexible. For pure polymeric material, a general inherent trade-off exists between permeability and selectivity, with an "upper-bound".² Not only the inherent trade-off between flux and selectivity, but also the low (bio)fouling resistance and low radiation resistance properties associated with the polymeric membranes render their applications limited. In view of this situation, a new approach is needed to provide an alternate and efficient membrane with separation properties well above the upper-bound limit between permeability and selectivity, having better biofouling and radiation resistance behaviour. The answer to all these issues comes from mixed matrix membranes.² The mixed matrix membrane essentially calls for the adoption and usage of composite materials for achieving desirable separation. While considering the development of composite system, an unprecedented opportunity is being provided by nanostructured materials with the fact that the building blocks in this dimension makes it possible to design and create unique materials and devices with significant improvements in the physical/ chemical/physico-chemical properties and flexibility.

Nanocomposites can be understood as a solid structure with nanometer-scale repeat distances between the different phases that constitute the structure. They may typically consist of inorganic matrix embedded in organic phase or vice versa. Though the idea of causing improvement and enhancing the properties of a material by fabricating multi-phase composites is not recent, the application of nanocomposite system to membrane science and technology is relatively new and is under rapid evolution. The idea of utilizing the benefits of a nanocomposite as a membrane material is targeted to develop an ideal membrane with improved flux, reasonable selectivity and other desirable characteristics for case specific applications. A wide variety of nanostructured materials have been tested and found as suitable inorganic nanofillers to fabricate nanocomposites membranes with polymer as host matrix. Nanostructured metal oxides³⁻⁶ (e.g., TiO₂, Al₂O₃, SiO₂, MgO, AgO, Fe₃O₄), pure metals (e.g., nanosilver⁷⁻⁹), zeolites¹⁰⁻¹² (e.g., ZSM-5, silicalate-1, zeolite 4A), dendrimers,¹³ carbon nanoparticles (e.g., carbon nanotubes,^{14,15} graphene^{16,17}), that aid in membrane performance, have been extensively studied. Hybrid nanocomposites involving more than one nanomaterials are also being utilized for superior membrane performances.¹⁸⁻²¹

Nanocomposite membranes have got the potential to provide numerous advantages over conventional membranes. Some of the key benefits are mentioned below:

- Over an order of magnitude increase in permeability over native polymer membranes and hence reduced membrane surface area
- Reduced pressure requirements & hence lower energy costs
- Increases mechanical stability
- Increases thermal stability
- Better bio-fouling resistance and hence improvement in membrane life
- Superior radiation resistance behaviour

Motivation for this research work

One of the serious challenges to sustain the modern society is to secure adequate water resources of desirable quality for various designated uses. To address this challenge, membrane water treatment is expected to play an increasingly important role in areas such as drinking water treatment, brackish and seawater desalination, and wastewater treatment and reuse. Existing membranes for water and effluent treatment, typically polymeric in nature, are still restricted by several challenges including the trade-off relationship between permeability and selectivity, low resistance to fouling and radiation. Nanocomposite membranes,²² a new class of membranes fabricated by combining polymeric materials with nanomaterials, are emerging as a promising solution to these challenges. The advanced nanocomposite membranes could be designed to meet specific water treatment applications by tuning their structure and physicochemical properties (e.g. hydrophilicity, porosity, charge density, and thermal and mechanical stability) and introducing unique functionalities (e.g. antibacterial, photocatalytic or adsorptive capabilities).²²

As widely reported in the literature, organic materials are known to undergo degradations under gamma radiations.²³ Particularly for nuclear industry, gamma rays effects on polymeric materials were studied regarding long term behavior and stability.^{24,25} Only a very few studies are available reporting the effect of gamma irradiation on membranes²⁶⁻²⁸ and none of the studies are yet available, to the best of our knowledge, on enhancement of radiation stability of membranes with incorporation of nanostructured materials.

Therefore, facile methods that can be used in making such nanocompositemembranes, and knowledge of structural, morphological, topographical features of a membrane through an in depth investigation of the process parameters and subsequent optimization of the physicochemical

properties, become enormously significant since they exclusively supervise the macroscopicalbehaviors of the membranes, such as minimisation of trade-off existing between flux and selectivity, membranes with improved biofouling and radiation resistance behaviour and charged UF membranes with improved separation efficiencies.

Keeping in to context the necessity of development of enhanced-performance novel membrane materials as a crucial step towards a sustainable societal as well as industrial growth, Membrane Development Section of Bhabha Atomic Research Center adopted a programme of developing indigenous nanocomposite membranes for scale-up applications, particularly for their potential use in water purification, waste water treatment and radioactive effluent treatment. With the awareness about the importance of nanostructured materials that can offer a variety of unusual but interesting properties and having the expertise on processing of polymers, an effort with a strong motivation, thus, was propagated during the tenure of the proposed research work for development of indigenous nanocomposite UF membranes with enhanced performances.

The current thesis entitled "Development of Nanocomposite Membranes for Enhanced **Performances**" has been divided into seven chapters. To appreciate the effect of different nanomaterials, the polymer through-out the research work has been kept same, that is Polysulfone. A brief description of the different chapters is given below.

Chapter 1: In this chapter entitled **"Introduction"**, the background of the rising demand for the membranes as dominant separation devices has been illustrated. The subject of advantageous features of membrane based separation processes have been dealt with to highlight the scientific pursuit of the separation scientists in understanding the importance of membrane material and the various factors affecting the macroscopical behaviors of such membranes. This has been followed

by a discussion on the need for a nanocomposite membrane system and a review of the existing literatures in the field of nanocomposite membranes for water purification/ treatment (including the challenges associated with nanocomposite synthesis) to identify the gap areas for the research work. Towards the end, the chapter discusses the motivation behind and the scope of the research work undertaken.

Chapter 2: This chapter entitled **"Experimental Techniques"**, focuses on the instrumental methods that are used to characterize the nanocomposite membranes. This is important to note that the methods applicable in case of conventional polymeric membranes remain equally applicable for the nanocomposite membranes. Only the micrographic and spectroscopic methods becomes more important in terms of characterising the nanomaterials embedded in the host matrix of polymer.

The characterization methods are discussed under the following categories:

- Conventional physical methods to determine pore size and pore size distribution
- Transport properties like pure water permeability and solute rejection studies
- Micrographic methods to have photographical images
- Spectroscopic methods to know the membrane structure in its molecular level
- Drop shape analysis (contact angle measurements) to ensure hydrophilicity/ hydrophobicity of membrane surface
- Zeta potential measurement to ensure surface charge on membrane surface
- Methods to obtain bulk properties of membranes such as thermal and mechanical properties

Chapter 3: In the present chapter entitled "Development of Nanocomposite Membranes for Minimization of Trade-off between Flux and Selectivity", a polysulfone-reduced grapheme oxide nanocomposite membrane is fabricated and performance evaluation is made. Nanostructured reduced graphene oxide (RGO) is synthesized from graphite powder and characterized. Using non-solvent induced phase inversion technique, a series of nanocomposite ultrafiltration (UF) membranes are developed by in situ impregnation of the as synthesized RGO in polysulfone (Psf) polymer matrix with variation of RGO from 1 to 8 w/w%. The physicochemical features and transport properties offered by the membranes are evaluated. Structural characterization of the Psf-RGO composite UF membranes is done by X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. The variation in porous morphology of the membranes upon impregnation of RGO is evaluated by scanning electron microscopy. Variation in skin surface topography is analyzed by atomic force microscopy. The change in surface hydrophilicity is evaluated by contact angle studies. The thermal and mechanical properties of the membranes are assessed by thermogravimetric analysis and tensile strength measurements, respectively. The studies reveal that an optimum loading of RGO (2 w/w%) in the Psf matrix resulted in membranes with minimization of the trade-off between the flux and selectivity that exists with the conventional UF membranes. The enhanced permeation ability (4200 LMD) of the Psf-RGO composite UF membranes (beyond that of Psf membrane: 3700 LMD) is attributed to the additional and facilitated transport of water caused by the atomically smooth interconnected interlayers (as novel pathways for water permeation) offered by RGO impregnated in the Psf matrices. On the other hand, impregnation of RGO brings synergism in the demixing process, through balancing the inter-diffusion of solvent (N-MehylPyrrolidone) and non-solvent (water) as well as pore former (polyvinyl pyrrolidone) and non-solvent, during phase inversion stage of membrane fabrication, resulting in a pore size distribution of composite membrane that led to better solute rejection compared to pure Psf membrane (Pure Psf: 65 % and Psf-2 wt% RGO: 92 % rejection against polyethylene glycol 35000 Dalton). Hence, the trade-off postulate that a membrane with higher flux should offer low solute rejection is violated, which is an important finding. In addition, the optimum loading of RGO resulted in membranes with improved thermal and mechanical stability. A set of transport equations have been derived from Kedem-Katachalsky's irreversible thermodynamic model, by incorporating pore-size distribution of the membrane and molecular weight distribution (derived from size distribution) of polyethyleneimine. The model is able to explain the experimental findings of Psf-RGO composite membranes with respect to flux and selectivity.

Chapter 4: In this chapter entitled "**Development of Bio-fouling Resistant Nanocomposite Membranes**", two different types of polysulfone (Psf) nanocomposite membranes are developed, one with carbon nanotubes (CNTs) and another with silver (Ag) nanoparticles. Psf-CNT nanocomposites were developed with impregnation of both single walled as well as multi walled CNTs with about 2 % (with respect to polymer weight) loading of CNTs. The performance of the membranes was evaluated in terms of pure water permeability and solute rejection studies. The membranes were characterised using scanning electron microscopy, atomic force microscopy and contact angle studies. The anti-biofouling performance of the membrane surfaces is examined using E. Coli culture and a comparison of antibiofouling tendency obtained with the nanocomposites over the pure polysulfone membranes has been made. It is confirmed that membranes with impregnation of single walled CNTs possess better antibiofoulingbehaviour as compared to pure polysulfone as well as polysulfone membrane embedded with multi walled CNTs. The enhanced bacterial toxicity of single walled CNTs may be attributed to (i) a smaller nanotube diameter that facilitates the partitioning and partial penetration of nanotubes into the cell wall, (ii) a larger surface area for contact and interaction with the cell surface, and/or (iii) unique chemical and electronic properties conveying greater chemical reactivity. On the other hand, attempts have been made to develop nanocompositePsf-Ag UF membranes with loading of silver varying from 0.25 to 6 wt % (with respect to polymer). Membranes were synthesized using phase inversion technique and characterized in terms of the separation performance (water permeability and rejection of single neutral solute). The microstructure and surface properties (like surface hydrophilicity, surface roughness) of the membranes were characterized using scanning electron microscopy, contact angle measurements and atomic force microscopy studies. The microbial decontamination and biofouling studies of the membranes was examined with membranes in candle configuration with an objective of applying these membrane candles for domestic water purification. It is confirmed that incorporation of silver (1 % of polymer weight) not only results in a bio-fouling resistant membrane, but also silver has got a pronounced role to play in bacteria rejection only when the membrane matrix is more porous. It is proposed that in a porous (loose) membrane matrix the exposed surfaces of the silver to cause bacteria killing is more predominant than that in case of relatively nonporous (tighter) membrane matrix. Hence, the biocide property of silver can be best made use of in a porous host matrix with little or no chance of silver leaching out into the product water (as confirmed from silver leaching studies). The experimental output and the idea was utilized to develop a process know-how for a domestic water purification device with about 6 times enhanced flux (compared to conventional UF based domestic water purifier, which offers a flux of 40 liters per day at 1 bar pressure) and 99.99 % bacterial decontamination.

Chapter 5: In this chapter entitled "Development of Radiation Resistant Nanocomposite Membranes", Pyrochlore ($Gd_2Zr_2O_7$) nanoparticle, prepared by gel-combustion method, was

used for development of mixed matrix membrane with polysulfone as host matrix. The concentration of pyrochlore was varied from 0.1 % to 2 % via 0.5 and 1 % of polymer weight. The membranes were prepared using phase inversion technique. The pure water permeability and solute rejection studies (with 200 ppm solutes of 35000 Dalton polyethylene glycol and 100, 000 Dalton polyethylene oxide) of the synthesized membranes were carried out to evaluate the performance of the membrane. To assess the radiation stability of the membranes, γ (gamma) radiation doses of 40, 80, 240, 500 and 1000 kGy were provided to the membranes in aqueous environment. The membranes were characterized using Fourier transform infrared spectroscopy, scanning electron microscopy, energy dispersive X-ray and X-ray photoelectron spectroscopy. The tensile strength and elongation at break for all the samples (both un-irradiated and irradiated) were carried out using Universal Testing Machine. The extent of damage caused due to 1000 kGy irradiation (correlated with the extent of reduction in elongation at break values) is about 90 % for pure polysulfone whereas the membranes with 2 % nanoparticle loading showed only about 57 % reduction in elongation at break, which resulted in a membrane with improved radiation resistance behaviour of all the membrane samples prepared. The enhanced stability of pyrochlore embedded membranes is attributed to the ability of pyrochlore to take up the radiation, which leads to interchanging of the sites occupied by Gd and Zr and in turn dissipation of gamma energy. In this process, polymer host matrix is exposed to gamma radiation to a minimum extent, making the overall composite matrix radiation resistant.

Chapter 6: In this chapter entitled "**Development of Charged Nanocomposite Membranes**", two different types of polysulfone (Psf) nanocomposite membranes are developed, one with carbon nanotubes (CNTs) and another with titanium oxide (TiO₂) nanoparticles. Three different types of CNTs: single walled (SW); double walled (DW); and multi walled (MW) were used for

Psf-CNT membrane development. These CNTs were functionalized with carboxyl group to introduce negative charge on to the CNT as well as the membrane surface. Similarly, TiO₂ was functionalised with sulphonic acid group to introduce negative charge on to TiO₂ as well as the membrane surface. The loading of CNTs in polymer matrix was varied from 0.25 % to 1 % (owing to the difficulty with further loading), whereas the TiO₂ loading was varied from 1 % to 3 %. The membranes were characterized with streaming potential analyser, Drop shape analyser to ascertain the extent of charge and hydrophilicity enhancement caused by charged nanoparticle incorporation on to the polymer host matrix. Pure water permeability and solute rejection studies were carried out to analyse the effect of charge on the enhancement of performance of the membranes. It is observed that though the incorporation of nanomaterials onto polysulfone hardly leads to any improvement in flux and rejection behaviour, the incorporation of charge (carboxyl acid group in case of CNTs and sulphonic acid group in case of TiO₂) leads to a 1.5 to 2 times flux enhancement (Psf membrane: 2880 LMD; NanocompositePsf: 4320 to 5760 LMD) without compromise in the solute rejection abilities (about 90 % solute rejection against polyethylene oxide of 100 kDa) of the membranes. The enhancement in flux is attributed to the charged surface (more hydrophilic) of the membrane brought about by functionalized nanomaterials. It is confirmed that charged nanocomposite UF membranes offer better separation performance compared to nanocomposite as well as pure polymeric membranes.

Chapter 7:In this chapter entitled "**Conclusions & Recommendations**", the results of the entire work carried out in favour of the area of research, as a part of the thesis, have been summarized. The chapter brings out the achievements and the novel scientific understandings emerged out of this work in line with the objectives targeted. The findings can be summarized as below:

- The incorporation of RGO enabled getting a membrane that minimizes the trade-off existing between flux and selectivity in any conventional polymeric membrane.
- The incorporation of CNTs and silver provided bio-fouling resistant membranes which have got the potential to increase the life of a membrane during on-field operation.
- The incorporation of pyrochlore (Gd₂Zr₂O₇) offered a radiation resistant membrane that have got a potential to be used for radioactive effluent treatment.
- The incorporation of negatively charged CNTs and TiO₂ resulted in membranes with improved separation performance.

The chapter also puts forth some recommendations that can be taken up as future scope of studies, like fabrication of hybrid nanocomposite membranes with incorporation of two or more different types of nanomaterials onto same polymer host matrix to result membranes having several enhanced attributes. It is emphasized that the associated challenges need to be addressed in nanocomposite fabrication with respect to scale-up toward technology development.

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CHAPTER - 1

Introduction

1.1. Overview of the separation processes

Separation is a mass transfer process, employed to convert a mixture of substances into two or more distinct product mixtures, at least one of which is enriched in one or more of the mixture's constituents. In some cases, a separation may fully fractionate the mixture into its pure constituents. Separations are carried out based on differences in properties like size, shape, mass, or chemical affinity between the constituents of a mixture, and are often classified according to the particular differences they use to achieve separation. However, when no single difference can be employed to accomplish a desired separation, multiple processes will often be performed in conjunction to achieve the desired output.

The separation, concentration, and purification of molecular mixtures are major problems in the chemical industries. Separation processes need to comply with the requirements of offering high value products in the food and pharmaceutical industries, high quality water in communities and industries, and removal/ recovery of or toxic or valuable components from industrial effluents. For these purposes, multiple conventional separation processes are used industrially, such as:

- Adsorption (adhesion of atoms, ions or molecules from a gas, liquid, or dissolved solid to a surface, which creates a film of the adsorbate on the surface of the adsorbent).
- Centrifugation (separation based on density differences; which involves the use of the centrifugation for the sedimentation of mixtures with a centrifuge).
- Distillation (a method of separating mixtures based on differences in volatilities of components in a boiling liquid mixture).
- Crystallization (process of formation of solid crystals precipitating from a solution, melts or more rarely deposited directly from a gas, or in other way a chemical solid–liquid

separation technique, in which mass transfer of a solute from the liquid solution to a pure solid crystalline phase occurs).

- Drying (a mass transfer process which removes liquid from a solid by vaporization).
- Electrophoresis (separation of organic molecules based on their different interaction with a gel under an electric potential which is the motion of dispersed particles relative to a fluid under the influence of a spatially uniform electric field).
- Evaporation (a type of vaporization of a liquid that occurs only on the surface of a liquid).
- Extraction (leaching or solid extraction is used to dissolve soluble matter from its mixture with an insoluble solid; liquid-liquid extraction is used to separate two miscible liquids by the use of solvent that preferentially dissolves one of them).
- Flocculation (separation of a solid from a liquid in a colloid, by use of a flocculent, which promotes the solid clumping into flocs).
- Filtration (removal of large particulates suspended in fluids by mesh, bag and paper filters).
- Fractional distillation (a process where the compound is heated and, as each of its constituent components comes to a boiling point, its vapors are separated and cooled, so it can be removed in its pure form).
- Ion exchange (a reversible chemical reaction between two substances, usually a relatively insoluble solid and a solution, during which ions of equal charge may be interchanged).
- Magnetic separation (a process in which magnetically susceptible material is extracted from a mixture using a magnetic force).
- Precipitation (the formation of a solid in a solution during a chemical reaction).

• Sedimentation (the tendency for particles in suspension to settle out of the fluid in which they are entrained, and come to rest against a barrier).

1.2. Potential of membrane as a separation device

Membranes¹ have taken an important place in chemical engineering and technology. They are used in a wide spectrum of applications. The key property that is utilized in membrane based separation technology is the ability to control the permeation rate of chemical species through the membrane; thus, allowing one component of a mixture to permeate the membrane preferentially, while hindering permeation of other components. Membrane separation process enjoys numerous industrial applications¹ with the following advantages:

- Appreciable energy savings
- Environmentally benign
- Clean technology with operational ease
- Operational simplicity
- High quality products
- Can be used stand alone or in combination with conventional separation processes
- Greater flexibility in designing the systems

However, it offers following challenges:¹

- Concentration polarization
- Membrane fouling (especially biofouling)
- Trade-off between Flux and Selectivity
- Low radiation resistance behavior

An overview of the different membrane processes, distinguished based on driving forces are enlisted in Table 1. 1.

Driving force	Membrane separation processes
Pressure difference	Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF), Reverse osmosis
	(RO)
Chemical potential	Pervaporation, Dialysis, Gas separation, Vapor permeation, Liquid membranes
difference	
Electrical potential	Electro-dialysis, Membrane electrophoresis, Membrane electrolysis
difference	
Temperature difference	Membrane distillation

Table 1.1: Driving forces and respective membrane separation processes.

The majority of membranes used commercially are polymeric. The "heart" of a membrane process is the membrane itself. To fully exploit the growing opportunities in the field of liquid phase separation, strong interest exists in the identification of new membrane materials that can offer better selectivity/productivity. Criteria for selecting membrane materials for a given separation are complex. Generally, durability, mechanical integrity at the operating conditions, productivity and separation efficiency are important parameters. Of these requirements, selectivity, permeation rate, concentration polarisation, compaction and anti-biofouling characteristics are the most basic but critical ones. High selectivity and permeability render the operation parameters more flexible. For pure polymeric material, a general inherent trade-off exists between permeability and selectivity, with an "upper-bound".² Not only the inherent trade-off between flux and selectivity, but also the low (bio)fouling resistance and low radiation resistance properties associated with the polymeric membranes render their applications limited.

In view of this situation, a new approach is needed to provide an alternate and efficient membrane with separation properties well above the upper-bound limit between permeability and selectivity, having better biofouling and radiation resistance behaviour. The answer to all these issues comes from mixed matrix membranes.² The mixed matrix membrane essentially calls for the adoption and usage of composite materials for achieving desirable separation. While considering the development of composite system, an unprecedented opportunity is being provided by nanostructured materials with the fact that the building blocks in this dimension makes it possible to design and create unique materials and devices with significant improvements in the physical/ chemical/ physico-chemical properties and flexibility.

Nanocomposites can be understood as a solid structure with nanometer-scale repeat distances between the different phases that constitute the structure. They may typically consist of inorganic matrix embedded in organic phase or vice versa. Though the idea of causing improvement and enhancing the properties of a material by fabricating multi-phase composites is not recent, the application of nanocomposite system to membrane science and technology is relatively new and is under rapid evolution. The idea of utilizing the benefits of a nanocomposite as a membrane material is targeted to develop an ideal membrane with improved flux, reasonable selectivity and other desirable characteristics for case specific applications.

Nanocomposite membranes have got the potential to provide numerous advantages over conventional membranes. Some of the key benefits are mentioned below:

- Over an order of magnitude increase in permeability over native polymer membranes and hence reduced membrane surface area
- Reduced pressure requirements & hence lower energy costs

- Increased mechanical stability
- Increased thermal stability
- Better bio-fouling resistance and hence improvement in membrane life
- Superior radiation resistance behaviour

1.3. Perspectives on nanocomposite membranes

According to membrane structure and location of nanomaterials, nanocomposite membranes can be classified³ into four categories: (1) conventional nanocomposite; (2) thin-film nanocomposite (TFN); (3) thin-film composite (TFC) with nanocomposite substrate; (4) surface located nanocomposite. The typical structures of these membranes are illustrated in Fig. 1.1.



Surface Located Nanocomposite

Fig.1.1: Classification of nanocomposite membranes (Adapted with permission from Ref. 3).

1.3.1. Conventional nanocomposites

The idea of fabricating nanocomposite membranes was originally developed to overcome the Robeson upper boundary (Fig. 1.2) in the field of gas separation in 1990s,^{2,4} where highly selective zeolites were incorporated into polymers to improve both permeability and selectivity.^{5,6}



Fig.1.2: Relationship between the O₂/N₂ selectivity and O₂ permeability for polymeric membranes and inorganic membranes (the dots indicates the performance of polymeric materials) (Adapted with permission from Ref. 2.).

It has been shown by the researchers⁴ that polymers having permselectivity values at or near the upper bound are virtually all glassy polymers, which is due to the better diffusivity selectivity of glassy over rubbery polymers. Comparison of the upper-bound plot of log P_i/P_j versus log P_i (where P_i represents the permeability of the more permeable gas) shows that glassy polymers dominate the upper bounds for all 15 gas pairs possible.

Mixed matrix membranes present an opportunity for tunable water treatment membranes, through increased selectivity, targeted functionalities, and improved thermal, chemical and mechanical stability. Fabrication of nanocomposite membranes is mostly based on phase inversions (PI) method in which nanofillers are dispersed in polymer solution prior to the PI process, and can be prepared in either flat sheet or hollow fiber configurations (Fig 1.3³). This type of membrane is usually made for microfiltration (MF) or ultrafiltration (UF) applications that require porous structure.



Fig. 1.3: Schematic of fabrication of nanocomposite membrane by phase inversion method in case of flat sheet and hollow fiber configuration (Adapted with permission from Ref. 3).

Literatures showed that the incorporation of metal oxide nanomaterials (TiO₂, ⁷⁻¹² SiO₂, ¹³⁻¹⁶ Al₂O₃,¹⁷⁻¹⁹ Fe₃O₄,^{20,21} MnO₂,²² ZnO²³) into polymers could not only tune structure and physicochemical properties (hydrophilicity, porosity, charge density, chemical, thermal and mechanical stability) of membranes, but also introduce unique and targeted functionalities (e.g., antifouling, antibiofouling, and photocatalytic characteristics) into the membranes. The importance as well as impact of application of carbon nanotube (CNT) membranes in the area of water technology development is tremendous. A substantial amount of work²⁴⁻²⁹ have been carried out with impregnation of CNTs (simply as one of the reinforcements for incorporation of better properties like antibiofouling and/or better strength, etc.) in polymer host matrix. Zeolites are used as reinforcement materials in polymeric host matrix^{30,31} to increase hydrophilicity, enhance cross-linking property and molecular sieving. Silver is one of the promising and most widely studied biocides that has been successfully introduced into various membrane materials such as polysulfone, polyethersulfone, polyvinylidene fluoride.³²⁻³⁶ The addition of silver nanoparticles into the polymer membranes not only improved the membrane performance in terms of their flux but also fouling resistance. Graphene derivatives on the other hand are gaining significant interest in the field of material research owing to its high surface area and outstanding electrical and mechanical properties.^{37,38}

1.3.2. Thin film nanocomposites

Thin film composite (TFC) membrane consists of an ultra-thin barrier layer (usually made of polyamide on the top of a more porous supporting layer (usually UF). It has been the major type of RO/NF membrane since being first developed by Cadotte in the 1980s,³⁹ and widely used to desalinate seawater/brackish water or remove heavy metals, hardness, organic pollutants such as

pesticides, disinfection by-products (DBPs), endocrine disrupting compounds (EDCs), and pharmaceutically relevant compounds.

With the introduction of novel technologies to fabricate nanocomposite materials, a new approach has been proposed based on dispersing nanomaterials into the ultra-thin barrier to improve membrane performance for filtration applications. Nanomaterials used for mixed matrix membrane preparation have are being explored to fabricate thin film nanocomposite (TFN) membranes, including zeolites, CNTs, silica, Ag, TiO₂. Common fabrication process is through the *in-situ* interfacial polymerization (IP) process between aqueous m-phenylenediamine (MPD) and trimesoyl chloride (TMC) organic solution as presented in Fig. 1.4.³ The nanofillers can be dispersed either in aqueous or in organic phase resulting improvement in performance offered by the TFN membranes.⁴⁰



Fig. 1.4: Schematic of fabrication of Thin Film Nanocomposite membrane by interfacial polymerization. (Adapted with permission from Ref. 3).

Introducing nanomaterials into polyamide top layer provides new opportunities to fabricate chlorine resistant membranes.⁴¹⁻⁴⁴ Researchers^{45,46} found that after incorporating silica nanoparticles (NPs) into the polyamide thin-film layer, the thermal stability of the TFN membranes was improved, which could be due to the stronger electrostatic and steric interactions between silica and polyamide in the modified polymer structures. Kim et al.⁴⁷ demonstrated that after incorporating hydrophilized ordered mesoporous carbons (H-OMCs) into PA thin-film layer, membranes showed an enhanced surface hydrophilicity. Antimicrobial materials are also applied for TFN membrane applications.^{48,49}

1.3.3. Thin Film Composite with nanocomposite substrate

This class of membranes was first fabricated to develop insight into the effects of nanofiller on membrane compaction behavior. In that study by Pendergastet al.⁵⁰ silica or zeolite NPs were embedded into the polysulfone membrane that was used as support for making TFC membranes for RO applications. The prepared membranes showed a higher initial permeability and experienced less flux decline during the compaction when compared with the original TFC membrane. The reasoning behind could be the enhanced mechanical support offered by the porous UF nanocomposite support to mitigate the collapse of porous structure and thickness reduction upon compaction. Membranes with nanocomposite substrate have neen observed to undergo far less physical compaction and played an important role in maintaining high water permeability.⁵¹ Recently, this concept was mainly implemented to mitigate internal concentration polarization having negative impact on the forward osmosis (FO) and pressure-retarded osmosis (PRO) processes.⁵²

1.3.4. Surface located nanocomposite

Most of the properties, especially in case of NF and RO membranes, is dictated by the surface properties, such as hydrophilicity, pore size charge density, and roughness. Modification of surface properties could significantly improve the efficiency of membrane water treatment. Surface located nanocomposite membranes are prepared based on methods such as self-assembly,⁵³⁻⁵⁵ coating/deposition,⁵⁶ and chemical grafting.⁵⁷⁻⁵⁹ Those fabrication methods can be implemented individually or be involved simultaneously. The approach of preparing this type of membranes bears a tremendous potential in bringing out tunable modifications onto commercially available membranes.

1.4. Synthesis of nanocomposite membranes

Nanocomposites are composites in which at least one of the phases possess dimensions in the nanometer range. Though nanocomposite materials have emerged as suitable alternatives to overcome limitations of microcomposites and monoliths however, they pose fabrication challenges related to the control of elemental composition and stoichiometry in the nanocluster phase.⁶⁰ The unique changes in particle properties are observed when the particle size comes down to a particular level, called 'the critical size'. As dimensions reach the nanometer level, interactions at phase interfaces become largely enhanced leading to drastic improvement in material properties. In this context, the surface area/ volume ratio of reinforcement materials employed in the preparation of nanocomposites is crucial to the understanding of their structure– property relationships as well as resultant performance.

Polymer–inorganic hybrid membranes constitute an emerging and interesting research field and have been developing very fast that influences the separation properties of polymer membranes because of the synergy between inorganic material and organic polymer that can result in a membrane with good hydrophilicity, selectivity, permeability, mechanical strength, and thermal and chemical stability. The nanostructure, the degree of organization and the properties that can be obtained from the nanocomposite materials depend on the physical and chemical nature of their individual components and the synergy between them. The applicability of polymer–inorganic nanocomposite membranes in gas separation and the associated separation mechanisms have been reviewed by researchers.^{61,62} The polymeric-inorganic hybrid membranes are classified into two types according to their structure: type (I), polymer and inorganic phases connected by van der Waals force or hydrogen bonds and type (II), polymer and inorganic phases connected by covalent bonds.

According to the researchers,⁶³ type (I) corresponds to all the systems where no covalent or ioniccovalent bonds are present between the organic and inorganic components. In such materials, the various components only undergo weak interactions such as hydrogen bonding, van der Waals contacts, π - π interactions or electrostatic forces. In type (II) materials, at least a fraction of the organic and inorganic components are linked through strong chemical bonds, such as ionic covalent or Lewis acid-base bonds. Thus, a key point for the design of new hybrids is the tuning of the nature, the extent and the accessibility of the inner (polymer-nanoparticle) interfaces. Because of the differences between the polymer and inorganic phase properties and the strong aggregation tendency of the nanofillers, fabricating an ideal nanocomposite membrane without interfacial defect (Fig. 1.5⁶⁴) is a challenging task.⁶⁴

The interfacial defects (Fig. 1.6^{64}) in such hybrids are hypothesized to form as a result of nucleation of non-solvent and/or a polymer lean phase around the inorganic phase during the phase separation process. Aggregation/dispersion behavior control, which is the first step in the

preparation of new functional materials incorporating nanoparticles, is very difficult for nanoparticles less than 100 nm in diameter due to high energy sites and enhanced surface interactions.⁶⁵⁻⁶⁷



Fig. 1.5: Schematic diagram of an ideal mixed matrix membrane (Adapted with permission from Ref. 64).

The factors that enhance or further induce the agglomeration remain unclear and the surface interaction theories are yet to be understood thoroughly. This causes difficulty in dispersing the nanoparticles during membrane fabrication. However, researchers^{68,69} suggested that an increment in concentration of nanoparticles, and ionic strength and pH of the solution also could induce agglomeration between nanoparticles.

Nanocomposites can be prepared by *in-situ* synthesis of inorganic particles or by dispersion of fillers in a polymeric matrix.⁷⁰ A correct selection of the preparation technique is critical to obtain nanomaterials with suitable properties. The synthesis of polymer nanocomposites usually follows

bottom-up or top-down methodologies. In the bottom-up approach, precursors are used to grow well organised structures from the nanometric level,. Also, blocks-assembly or building block approaches can be used, where nano-objects are hierarchically combined to give rise to the desirable material. Chemical processes, such as, sol-gel, chemical vapour deposition (CVD), template synthesis or spray pyrolysis are employed as bottom-up methodologies.^{70,71}



Fig. 1.6: Interface void (a) and rigidified polymer layer (b) in the polymer–particles interface. (Adapted with permission from Ref. 64).

The procedure of the fabrication of mixed matrix membranes is akin to ordinary polymer membrane fabrication. The first step of mixed matrix membrane fabrication is preparing a homogeneous solution of polymer and particles. For this purpose, the following methods⁶⁴ can be used as shown in Fig. 1.7.⁶⁴



Fig. 1.7: Different methods for mixed matrix dope preparation. (Adapted with permission from Ref. 64).

- 1. Particles are dispersed into the solvent and stirred for a predetermined period of time and then the polymer is added (Fig. $1.7a^{64}$).
- 2. The polymer is dissolved in the solvent and stirred; a predetermined mass of inorganic particles is then added to the polymer solution (Fig. $1.7b^{64}$).

3. Particles are dispersed into the solvent and stirred for a predetermined period of time and the polymer is dissolved in a solvent separately. The particle suspension is then added to the polymeric solution (Fig. $1.7c^{64}$).

In the present research work, the first approach (Fig. 1.7a) has been used in all cases of composite membrane development.

1.5. Motivation and need of the present research work

One of the serious challenges to sustain the modern society is to secure adequate water resources of desirable quality for various designated uses. To address this challenge, membrane water treatment is expected to play an increasingly important role in areas such as drinking water treatment, brackish and seawater desalination, and wastewater treatment and reuse. Existing membranes for water and effluent treatment, typically polymeric in nature, are still restricted by several challenges including the trade-off relationship between permeability and selectivity, low resistance to fouling and radiation. Nanocomposite membranes, a new class of membranes fabricated by combining polymeric materials with nanomaterials, are emerging as a promising solution to these challenges. The advanced nanocomposite membranes could be designed to meet specific water treatment applications by tuning their structure and physicochemical properties (e.g. hydrophilicity, porosity, charge density, and thermal and mechanical stability) and introducing unique functionalities (e.g. antibacterial, photocatalytic or adsorptive capabilities).³

As widely reported in the literature, organic materials are known to undergo degradations under gamma radiations.⁷² Particularly for nuclear industry, gamma rays effects on polymeric materials were studied regarding long term behavior and stability.^{73, 74} Only a very few studies are available reporting the effect of gamma irradiation on membranes⁷⁵⁻⁷⁷ and none of the studies are yet

available, to the best of our knowledge, on enhancement of radiation stability of membranes with incorporation of nanostructured materials.

Therefore, facile methods that can be used in making such nanocomposite membranes, and knowledge of structural, morphological, topographical features of a membrane through an in depth investigation of the process parameters and subsequent optimization of the physicochemical properties, become enormously significant since they exclusively supervise the macroscopical behaviors of the membranes, such as minimisation of trade-off existing between flux and selectivity, membranes with improved biofouling and radiation resistance behaviour and charged UF membranes with improved separation efficiencies.

Keeping in to context the necessity of development of novel membrane materials as a crucial step towards a sustainable societal as well as industrial growth, Membrane Development Section of Bhabha Atomic Research Center adopted a programme of developing indigenous nanocomposite membranes for scale-up applications, particularly for their potential use in water purification, waste water treatment and radioactive effluent treatment. With the awareness about the importance of nanostructured materials that can offer a variety of unusual but interesting properties and having the expertise on processing of polymers, an effort with a strong motivation, thus, was propagated during the tenure of the proposed research work for development of indigenous nanocomposite UF membranes with enhanced performances.

1.6. Scope of Thesis

The current thesis entitled "Development of Nanocomposite Membranes for Enhanced **Performances**" has been divided into seven chapters including "Introduction"). To appreciate the effect of different nanomaterials, the polymer through-out the research work has been kept same,

that is "polysulfone" and phase inversion technique has been used through-out for preparation of membranes. The scope each of the chapters (except the "Introduction") is given below.

The second chapter entitled "**Experimental Techniques**" focuses on the instrumental methods that are used to characterize the nanocomposite membranes. This is important to note that the methods applicable in case of conventional polymeric membranes remain equally applicable for the nanocomposite membranes. Only the micrographic and spectroscopic methods become more important in terms of characterising the nanomaterials embedded in the host matrix of polymer.

In the third chapter entitled "Development of Nanocomposite Membranes for Minimization of Trade-off between Flux and Selectivity", polysulfone-reduced grapheme oxide nanocomposite membrane is fabricated and performance evaluation is made. Using non-solvent induced phase inversion technique, a series of nanocomposite UF membranes are developed by in situ impregnation of the as synthesized RGO in polysulfone (Psf) polymer matrix with variation of RGO from 1 to 8 w/w%. The physicochemical features and transport properties offered by the membranes are evaluated. The studies reveal that an optimum loading of RGO (2 w/w%) in the Ps matrix resulted in membranes with elimination of the trade-off between the flux and selectivity that exists with the conventional UF membranes. In addition, the optimum loading of RGO resulted in membranes with improved thermal and mechanical stability. A set of transport equations have been derived from Kedem - Katachalsky's irreversible thermodynamic model, by incorporating pore-size distribution of the membrane and molecular weight distribution (derived from size distribution) of polyethyleneimine. The model is able to explain the experimental findings of Psf-RGO composite membranes w.r.t. flux and selectivity.

In fourth chapter entitled "Development of Bio-fouling Resistant Nanocomposite Membranes", two different types of Psf nanocomposite membranes are developed, one with carbon nanotubes (CNTs) and another with silver (Ag) nanoparticles. The performance of the membranes was evaluated in terms of pure water permeability and solute rejection studies. The anti-biofouling performance of the membrane surfaces is examined using E. Coli culture and a comparison of antibiofouling tendency obtained with the nanocomposites over the pure Psf membranes has been made. It is confirmed that membranes with impregnation of single walled CNTs possess better antibiofouling behaviour as compared to control Psf as well as Psf membrane embedded with multi walled CNTs. On the other hand, attempts have been made to develop nanocomposite Psf-Ag UF membranes with loading of silver varying from 0.25 to 6 wt % (w.r.t. polymer). Membranes were synthesized using phase inversion technique and characterized in terms of the separation performance (water permeability and rejection of single neutral solute). The microbial decontamination and biofouling studies of the membranes were examined with membranes in candle configuration with an objective of applying these membrane candles for domestic water purification. It is confirmed that incorporation of silver (1 % of polymer weight) not only results in a bio-fouling resistant membrane, but also silver has got a pronounced role to play in bacteria rejection only when the membrane matrix is more porous. It is proposed that in a porous (loose) membrane matrix the exposed surfaces of the silver to cause bacteria killing are more predominant than that in case of relatively nonporous (tighter) membrane matrix. Hence, the biocide property of silver can be best made use of in a porous host matrix with little or no chance of silver leaching out into the product water (as confirmed from silver leaching studies). The experimental output and the idea was utilized to develop a process know-how for a domestic water purification device.

In the fifth chapter entitled "**Development of Radiation Resistant Nanocomposite Membranes**", Pyrochlore (Gd₂Zr₂O₇) nanoparticle, prepared by gel-combustion method, was used for development of mixed matrix membrane with Psf as host matrix. The concentration of pyrochlore was varied from 0.1 % to 2 % via 0.5 and 1 % of polymer weight. The membranes were prepared using phase inversion technique. To assess the radiation stability of the membranes, γ (gamma) radiation doses of 40, 80, 240, 500 and 1000 kGy were provided to the membranes in aqueous environment. The tensile strength and elongation at break for all the samples (both un-irradiated and irradiated) were carried out using Universal Testing Machine. The extent of damage caused due to 1000 kGy irradiation (correlated with the extent of reduction in elongation at break values) is about 90 % for control Psf whereas the membranes with 2 % nanoparticle loading showed only about 50 % reduction in elongation at break, which resulted in a membrane with improved radiation resistance behaviour of all the membrane samples prepared.

In the sixth chapter entitled "Development of Charged Nanocomposite Membranes", two different types of Psf nanocomposite membranes are developed, one with carbon nanotubes (CNTs) and another with titanium oxide (TiO₂) nanoparticles. Three different types of CNTs: single walled (SWNT); double walled (DWNT); and multi walled (MWNT) were used for Psf-CNT membrane development. These CNTs were functionalized with carboxyl group to introduce negative charge on to the CNT as well as the membrane surface. Similarly, TiO₂ was functionalised with sulphonic acid group to introduce negative charge on to TiO₂ as well as the membrane surface. Pure water permeability and solute rejection studies were carried out to analyse the effect of charge on the enhancement of performance of the membranes. It is observed that though the incorporation of nanomaterials onto Psf hardly leads to any improvement in flux and rejection behaviour, the incorporation of charge (carboxyl acid group in case of CNTs and sulphonic acid group in case of

 TiO_2) leads to about two times flux enhancement (w.r.t. control Psf membrane) without compromise in the solution rejection abilities of the membranes.

In the seventh and last chapter entitled "Conclusions & Recommendations", the results of the entire work carried out in favour of the area of research, as a part of the thesis, have been summarized. The chapter brings out the achievements and the novel scientific understandings emerged out of this work in line with the objectives targeted. The findings can be summarized as below:

- The incorporation of RGO enabled getting a membrane that minimizes the trade-off existing between flux and selectivity in any conventional polymeric membrane.
- The incorporation of CNTs and silver provided bio-fouling resistant membranes which have got the potential to increase the life of a membrane during on-field operation.
- The incorporation of pyrochlore (Gd₂Zr₂O₇) offered a radiation resistant membrane that have got a potential to be used for radioactive effluent treatment.
- The incorporation of negatively charged CNTs and TiO₂ resulted in membranes with improved separation performance.

CHAPTER - 2

Experimental Techniques

2.1. Introduction

Any membrane developed under a standard set of conditions (like temperature, relative humidity etc.) needs to be characterised to ensure the application area the membrane is best suited for. Any small change in the membrane preparation conditions may lead to a significant change in membrane structure and membrane morphology, which in turn do affect the separation performance achievable from the membrane. Comprehensive characterization of a membrane following different methods, as a subsequent step of membrane preparation stages is of utmost interest, which is required to be carried out in determining the physicochemical features of a given membrane to acquire the appropriate knowledge about the structural and morphological features of the membrane/ polymer material. This further helps in choosing the appropriate membrane for a specific application, controlling the membrane quality and predicting the membranes' separation performance for various substances.

The characterisation methods described in this section apply well both to the porous as well as nonporous membranes. This is important to note that the methods applicable in case of conventional membranes remain equally applicable for the nanocomposite membranes. Only the micrographic and spectroscopic methods become more important in terms of characterising the nanomaterials embedded in the host matrix (polymer/ ceramic).

The membrane characterization methods can in general be classified⁷⁸ into the following categories:

- Conventional physical methods to determine pore size and pore size distribution
- Spectroscopic methods to know the membrane structure in its molecular level
- Micrographic methods to have photographical images

- Zeta potential measurement to ensure surface charge on membrane surface
- Drop shape analysis (contact angle measurements) to ensure hydrophilicity/ hydrophobicity of membrane surface
- Methods to obtain mechanical properties

2.2. Measurement of pore size and pore size distribution

Under this category the following methods are widely used:

- Bubble Gas Transport Method
- Mercury Intrusion Porosimetry
- Adsorption-Desorption Method (Barett-Joyner-Halenda (BJH) Method)
- Liquid Solid Equilibrium Method (Thermoporometry)
- Gas Liquid Equilibrium Method (Permporometry)
- Permeability Method
- Solute Rejection Method

For polymeric and nanocomposite based systems, Bubble gas transport method, permeability method and solute rejection method are extensively used in membrane characterization.

2.2.1. Bubble Gas Transport Method

This method is based on the measurement of the pressure necessary to blow air through a waterfilled porous membrane. The method so developed has been thoroughly used to characterize membranes and also is called the *bubble point* method. This method is only able to discriminate maximum pore size present in the pore distribution, corresponding to the minimum pressure necessary to blow the firstly observed air bubble. The principle of the bubble-point method is depicted schematically in Fig. 2.1,¹ from which it can be seen that the liquid on the top of the membrane wets the latter. The bottom of the membrane is in contact with air and the air pressure is gradually increased until bubbles of air penetrate through the membrane at a certain pressure.



Fig. 2.1: The principle of the bubble-point method.

An air bubble will penetrate through a pore of radius r_p when the transmembrane pressure difference $\Delta P = P1 - P2$ given by the following Laplace equation is reached.

$$r_p = \frac{2\gamma\cos\theta}{\Delta P} \tag{2.1}$$

In Eq. 2.1, γ is the surface tension at the liquid/air interface and θ is the contact angle. Penetration will first occur through the largest pores and since the pressure difference is known, the pore radius can be calculated from Eq. 2.1. It is also possible to obtain pore size distribution by performing this technique by a stepwise increase of pressure. The method has been improved for both liquid-gas interfaces and liquid-liquid ones allowing the evaluation of pore sizes corresponding to a range of porous material, and is very well commercialized. The bubble point method is an easy, fast and inexpensive method to determine the maximum pore size and pore size distribution of membranes.⁷⁹ Though only active pores are measured, the disadvantage is different results are obtained with different liquids. Liquid displacement is similar to that of gas bubble transport method, where a liquid is pressurized to displace the liquid in the pores. The disadvantage is swelling is probable because of stagnant liquid in the pores, which can affect the pore size.

2.2.2. Permeability Method

Assuming the pores to be capillary in nature, the pore size can be determined by measuring the flux through a membrane at a constant pressure using Hagen-Poiseuille equation.

$$J = \frac{\varepsilon r^2 \Delta P}{8\eta \tau \Delta x} \tag{2.2}$$

Here J is the flux through the membrane at a driving force of $\Delta P/\Delta x$, with ΔP being the pressure difference and Δx the membrane thickness. The proportionality factor contains pore radius (r), the liquid viscosity η , the surface porosity of the membrane ε and the tortuosity factor τ . The pore size distribution can be obtained by varying the pressure, i.e., by a combination of bubble point method and permeability method. It is not necessary that the liquid should wet the membrane.

The Hagen-Poiseuille equation assumes the pores to be cylindrical, which may not be the case. In that case, Kozeny-Carman equation can be used instead. It is assumed in this relation that the pores are interstices between close-packed spheres. The flux is given by,

$$J = \frac{\varepsilon^3 \Delta P}{K\eta S^2 (1 - \varepsilon)^2 \Delta x}$$
(2.3)

Where K is the membrane constant, called the Kozeny-Carman constant, which is dependent on the pore shape and tortuosity. E is the porosity and S is the specific surface area. The permeability method is widely used both for microfiltration and ultrafiltration membranes. This method is entirely based upon the assumptions taken toward the pore geometry which is largely unknown and hence the experimental results are difficult to interpret.

2.2.3. Solute Rejection Method

This is the method frequently used for industrial assessment of membranes. Usually membrane manufacturers use the concept of "cut-off" to characterise their ulrafiltration membranes. Cut-off is defined as that molecular weight which is 90 % rejected by the membrane. The membrane has a cut-off value of 40,000 implies that all solutes with a molecular weight greater than 40,000 are rejected by the membrane by more than 90 %. However, it is not possible to define the separation characteristics of a membrane by this single parameter (molecular weight of solute), because the parameters like shape, flexibility of macromolecular solute and its interaction with the membrane material are all important to be taken into account. On the other hand, concentration polarisation and membrane fouling can affect the separation performances of the membrane. Cut-off values are often expressed in different ways under different test conditions (pressure, geometry of test cell, type and concentration of solute, cross-flow velocity and more importantly molecular weight distribution of solute), which makes it difficult to hold a comparison of the results obtained.

2.3. Spectroscopic Method

Under this category the following techniques are widely used:

• Infrared (IR) and Fourier Transform Infrared (FTIR) Spectroscopy

- X-ray Photoelectron Spectroscopy (XPS)
- Energy dispersive X-ray

2.3.1. Attenuated Total Reflectance-Fourier Transform Infrared (ATR – FTIR) spectroscopy

As a reliable technique for the characterization, identification and quantification of structural features of any polymeric system, infrared (IR) spectroscopy has always shown its' usefulness. An important advantage of this spectroscopic technique is its' ability to analyze material under a very wide range of conditions including solids, liquids and gases. The principle of FTIR relies on the fact that the most molecules absorb light in the infra-red region of the electromagnetic spectrum where the absorption corresponds specifically to the bonds present in the molecule. The background emission spectrum of the IR source is first recorded, followed by the emission spectrum of the IR source with the sample in place. The ratio of the sample spectrum. The resultant absorption spectrum, originated from the bonds' natural vibrational frequencies indicates the presence of various chemical bonds and functional groups of the sample under investigation. It is particularly useful for identification of organic molecular groups and compounds due to the range of functional groups, side chains and crosslinks involved, all of which will have characteristic vibrational frequencies in the infra-red range.

The Attenuated Total Reflectance (ATR) is the most widely used FTIR sampling tool. The technique of ATR particularly has become one of the best choices to study the structure and organization of membranes' material-chemistry in different relevant conditions. The ATR mode associated with the spectrometer generally allows qualitative or quantitative analysis of samples with little or no sample preparation which enhances the speed of sample analysis. In transmission
spectroscopy, the IR beam passes through the sample and the effective path length is determined by the thickness of the sample and its orientation to the directional plane of the IR beam. But the benefit of ATR sampling comes from the very thin sampling path length or depth of penetration of the IR beam into the sample. This is in contrast to traditional FTIR sampling by transmission where the sample must be diluted with IR transparent salt, pressed into a pellet or pressed to a thin film, prior to analysis to prevent totally absorbing bands in the infrared spectrum. In ATR mode of sampling, the IR beam incidents into a crystal of relatively higher refractive index (ZnSe crystal, 45° angle of incidence and refractive index of 2.4) and reflects from the internal surface of the crystal and creates an evanescent wave which projects orthogonally into the sample in intimate contact with the ATR crystal. Some of the energy of the evanescent wave is absorbed by the sample and the reflected radiation (some now absorbed by the sample) is returned to the detector. The schematic representation of ATR phenomenon is shown below in Fig.2.2.



Fig. 2.2: Schematic of ATR.

The penetration depth of the light depends on the refractive indices of the internal reflection element (n_1) and sample (n_2) , wavelength (λ) and the angle of incidence (θ) according to Eq. 2.4.

$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{\left(\sin^2 \theta - \frac{n_2^2}{n_1^2}\right)}}$$
(2.4)

From this equation, it can be seen that the penetration depth depends on the wavelength. Consequently, ATR spectra differ from transmission spectra of the same material in the sense that at higher wave numbers (*i.e.*, smaller λ) the intensity in ATR becomes smaller than in transmission mode.

Generally, most spectrometers calculate an ATR-absorbance spectrum normalizing for the penetration depth (which proportional to the wavelength) according to Eq. 2.5.

$$ATR = -\log\left(\frac{I_t}{I_0}\right) \frac{const.}{\lambda}$$
(2.5)

While the analysis of samples by ATR is easy, it is interesting and useful to be aware of each of the experimental factors like refractive indices of the ATR crystal and the sample, angle of incidence of the IR beam, critical angle, depth of penetration, wavelength of the IR beam, effective path length, number of reflections and quality of the sample contact with ATR crystal characteristics, which affect the final spectrum.

2.3.2. X-ray photoelectron spectroscopy

The technique of X-ray photoelectron spectroscopy (pictorially presented in Fig. 2. 3) has now become widely used for surface characterization of membranes through quantitative estimations

of the elements composing the surfaces. In X-ray photoelectron spectroscopy (XPS) electrons emitted after the interaction between primary X-rays or electrons and a sample are detected. The amount of electrons having escaped from the sample without energy loss is typically measured in the range of 20 to 2000 eV. The data is represented as a graph of intensity versus electron binding energy. Due to the impact of the primary beam (X-ray photon, mostly from an Al-K α or Mg-K α primary source), the atoms in the sample are ionized and electrons are liberated from the surface, as a result of the photoemission process. XPS relies on soft X-rays as the source of primary radiation, which is necessary to provoke ionization of the atoms. In XPS low energy electrons are measured, giving rise to comparable depth and sensitivity values and only a lateral resolution of a few to 100 μ m can be reached. This type of measurements is necessarily performed under high vacuum conditions. Thus, the technique of XPS cannot be considered as non-destructive technique although the analyses themselves are not destructive in nature.



Fig. 2.3: Schematic of XPS operation.

2.3.3. Elemental analysis of membrane surfaces – Energy Dispersive X-ray

The technique of EDX makes use of the X-ray spectrum which is emitted by a solid sample after bombardment with a focused beam of electrons to obtain a localized chemical analysis. All elements from atomic number 4 (Be) to 92 (U) can be detected in principle, though not all instruments are equipped for 'light' elements (Z < 10). Qualitative analysis involves the identification of the characteristic lines appeared in the spectrum and is fairly straightforward owing to the simplicity of X-ray spectra. Quantitative analysis (determination of the concentrations of the elements present in the sample) entails measuring line intensities for each element in the sample and for the same elements in calibration standards of known composition. By scanning the beam in a television-like raster and displaying the intensity of a selected X-ray line, element distribution images or 'maps' can also be produced. Also, images produced by electrons collected from the sample reveal surface topography or mean atomic number differences according to the mode selected. Thus, quantitative surface elemental analysis and mapping have been performed by an energy dispersive X-ray spectrometer (EDX) coupled to the SEM and a micro analysis system (INCA Oxford Instruments, UK), employing a certain accelerating voltage at specific magnification, where the instrument is equipped with an ultrathin beryllium window and 20 mm² Si detector.

2.4. Micrographic methods to have photographical images

Under this category the following techniques are widely used. While a nanocomposite membrane is under consideration, where the structure of nanocomposites usually consists of the matrix material containing the nanosized reinforcement components in the form of particles, whiskers, fibres, nanotubes, etc., the importance of these techniques is more pronounced. These characterisation techniques aid to the understanding of the correlation between structure and performance of a particular nanocomposite membrane.

- Atomic Force Microscopy
- Scanning Electron Microscopy

2.4.1. Atomic force microscopy

The surface topography of any membrane material has been characterized using the technique of atomic force microscopy (AFM), which can provide two as well as three-dimensional informations regarding surface features. An important advantageous outcome of AFM operation is thus the study of surface properties of membranes, the ability to quantify the surface topography and then correlation of them to membranes performances.

The AFM can produce topographical images by scanning a microscopic tip, attached at the end of a cantilever over a surface (Fig. 2.4). The cantilever is typically of silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooks law. Depending on the situation, forces that are measured in AFM include mechanical contact force, van der Waals forces, capillary forces, chemical forces, electrostatic forces, magnetic forces, solvation forces etc. If the tip is scanned at a constant height, a risk would exist that the tip collides with the surface, causing damage. Hence, in most cases a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. Traditionally, the sample is mounted on a piezoelectric tube that can move the sample in the *z* direction for maintaining a constant force, and the *x* and *y* directions for scanning the sample. Alternatively a 'tripod' configuration of three piezo crystals

may be employed, with each responsible for scanning in the x, y and z directions. This eliminates some of the distortion effects seen with a tube scanner. In newer designs, the tip is mounted on a vertical piezo scanner while the sample is being scanned in X and Y using another piezo block. The resulting map of the area z = f(x, y) represents the topography of the sample. Typically, the deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. This photodetector measures the difference in light intensities between the upper and lower photodiodes and then converts this signal into a voltage. This method enables a computer to generate a three-dimensional map of the surface topography.



Fig. 2.4: Schematic of AFM operation.

There are three commonly used AFM techniques: contact mode, noncontact mode and tapping mode. In contact mode, the tip scans the sample in close contact with the surface. This means that the inter-atomic force between the sample and the tip is repulsive, with a typical value of

 10^{-7} N. Problems with contact mode are caused by excessive tracking forces applied to the sample by the probe. Therefore, contact mode AFM cannot be applied to soft surfaces, such as polymeric membranes. In situations where tip contact might alter the sample, non-contact mode is used. In this mode the tip moves about 50-150 Å above the sample surface. Attractive interatomic forces between the tip and the sample are detected, and topographic images are constructed by scanning the tip above the surface. The attractive forces from the sample are, however, substantially weaker (10^{-13} N) than the forces used in contact mode. Therefore, the cantilever is driven to vibrate near its' resonant frequency by means of a piezoelectric element and changes in the resonant frequency as a result of tip-surface force interaction are measured (dynamic detection method). Problems with noncontact mode can be caused by a contaminant layer (present on the sample), which interferes with the cantilever oscillation and results in low resolution. Tapping mode of AFM allows high-resolution topographic imaging of sample surfaces by alternately bringing the tip into contact with the surface to provide high resolution and then lifting it off the surface to avoid dragging the tip across the surface. Tapping mode imaging is again implemented by oscillating the cantilever assembly at or near the cantilevers resonant frequency using a piezoelectric crystal. The piezo motion causes the cantilever to oscillate with a large amplitude (typically greater than 20 nm) when the tip is not in contact with the surface. The oscillating tip is then moved toward the surface until it begins to gently touch or tap the surface. During scanning, the vertically oscillating tip alternately contacts the surface and lifts off, generally at a frequency of 50,000-500,000 cycles per second. As the oscillating cantilever begins to intermittently contact the surface, the cantilever oscillation is reduced due to energy loss caused by the tip contacting the surface. The reduction in oscillation amplitude is used to identify and measure surface features.

Three dimensional surface topographic technique provides specific 3D roughness parameters, which are classified in the following categories as: *amplitude parameters* (based on overall height of the surface) like average roughness (R_a), root mean square roughness (R_q), Ten point height (R_{10z}), Skewness (R_{Sk}) and Kurtosis (R_{Ku}); spatial parameters (based on frequencies of occurrence of surface characteristics) like texture direction of a surface (Rtd) and texture direction index (R_{tdi}); hybrid parameter (based on the combination of height of the formations and frequencies of occurrence of the surface) like surface area ratio (Rdr) and functional parameters (based on special functioning properties like bearing, sealing and lubricant retaining capabilities) like peak material volume (V_{mp}), core material volume (V_{mc}), core void volume (V_{vc}), valley void volume (V_{vv}), surface bearing index (R_{bi}), core fluid retention index, (R_{ci}) and valley fluid retention index (Rvi). A brief theoretical overview of the various amplitude parameters, extracted from the 2D and 3D topographic image analysis, are the major indicators in characterizing the surface topography by implying the amplitude related properties of a surface. These are used to measure the vertical characteristics of the membranes' surface by computing the surface deviations from the mean plane. The topographic image extracted through AFM corresponds to a measured height value, z(x,y) for a given surface area, A, in a surface plane, x-y. Each height value is allied to a pair of surface coordinates, (x,y), and the image is depicted by a matrix with N number of rows and M number of columns which corresponds to the surface (x,y) points being the matrix elements the height z(x,y).

The average roughness (R_a) parameter represents the average absolute deviation of the roughness from the mean plane, the plane for which the volumes enclosed by the image above and below are equal and is represented by the mathematical expression of Eq. 2.6.

$$R_{a}(N,M) = \frac{1}{NM} \sum_{x=1}^{N} \sum_{y=1}^{M} \left(z(x,y) - \overline{z}(N,M) \right)$$
(2.6)

The root mean square (rms) roughness (R_q) represents the standard deviation of the distribution of surface heights within a given area and is more sensitive statistically than the average roughness values to describe the variation of a membranes' surface roughness. This is mathematically represented as Eq. 2.7.

$$R_{q}(N,M) = \sqrt{\frac{1}{NM} \sum_{x=1}^{N} \sum_{y=1}^{M} \left(z(x,y) - \overline{z}(N,M) \right)^{2}}$$
(2.7)

The ten point height (R_{10Z}), defined by ISO system as difference in height between the average of the five highest peaks and the five lowest valleys relative to the mean plane is mathematically represented as Eq. 2.8:

$$R_{10z}(ISO) = \frac{1}{n} \left(\sum_{i=1}^{n} p_i - \sum_{i=1}^{n} v_i \right)$$
(2.8)

Where p_i and v_i represent the height of the ith peak and depth of the ith valley respectively. n is the number of samples along the assessment length.

Statistically skewness is defined as a measure of the asymmetry of the probability distribution of a real valued random variable.⁷⁹ It is related to the third moment of a distribution. The skewness of a surface, R_{Sk}, used to measure the symmetry of the profile about the mean plane, is sensitive and responsive to the occasional presence of deep valleys or high peaks in the surface profile. A symmetrical height distribution, *i.e.*, with as many peaks as valleys, provides a surface with zero skewness whereas surface profile with peaks removed or deep valleys provides surface with negative skewness and that with valleys filled in or with high peaks endows a surface with

positive skewness. The evaluation of R_{Sk} for membranes becomes important when two membrane surface profiles with same R_a or R_q are distinguished based on variation of shapes. The mathematical description of surface skewness of a profile is given by Eq. 2.9.

$$R_{Sk} = \frac{1}{NR_q^3} \sum_{i=1}^{N} \left(Z_i - \overline{Z} \right)^3$$
(2.9)

The statistical definition of Kurtosis gives a measure of the shape of the probability distribution of a real valued random variable. It is closely related to the fourth moment of a distribution. Kurtosis coefficient, R_{Ku} of a surface topographic analysis describes the sharpness of the probability density of a surface profile. It characterizes the relative peakedness or flatness of a distribution compared to the normal distribution. A positive R_{Ku} indicates a relatively peaked distribution and a negative R_{Ku} indicates a relatively flat distribution. If $R_{Ku} > 3$, the distribution curve is said to be leptokurtic distribution which is sharper than a normal distribution, with values concentrated around the mean with the occasional high peak or deep valley. This means high probability for extreme values. If, $R_{Ku} < 3$, the distribution curve is said to be platykurtic distribution with a wider distribution of peaks. In such case, the probability for extreme values is less than for a normal distribution, and the values are wider spread around the mean. If $R_{Ku} = 3$, the distribution curve is of Gaussian type and said to be mesokurtic distribution. The mathematical description for coefficient of kurtosis of a profile is given by Eq. 2.10:

$$R_{Ku} = \frac{1}{NR_q^4} \sum_{i=1}^{N} \left(Z_i - \overline{Z} \right)^4$$
(2.10)

2.4.2. Scanning electron microscopy

A scanning electron microscope (SEM) is a type of electron microscope that can acquire images of a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity.

The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathode luminiscence), specimen current and transmitted electrons, shown below pictorially in Fig. 2.5 & 2.6.



Fig. 2.5 & 2.6: Schematic diagram of electronic interaction with sample and generation of signals.

Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful handlens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes. Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays. Since the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal gold immuno-labels of 5 or 10 nm diameter which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

In a typical SEM, an electron beam is thermionically emitted from an electron gun having energy ranging from 0.0 keV to 40 keV and fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapor pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost. Other types of electron emitters include lanthanum hexaboride (LaB₆) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded and field emission guns (FEG), which may be of the cold-cathode type using tungsten single crystal emitters or the thermally-assisted Schottky type, using emitters of zirconium oxide.

The electron beam is typically focused by one or two condenser lenses (as shown in Fig. 2.7) to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the *x* and *y* axes so that it scans in a raster fashion over a rectangular area of the sample surface.



Fig. 2.7: Schematic diagram of SEM.

When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μ m into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of

secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals which are displayed as variations in brightness on a cathode ray tube. The raster scanning of the CRT display is synchronized with that of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image may be captured by photography from a high resolution cathode ray tube, but in modern machines is digitally captured and displayed on a computer monitor and saved to a computer's hard disk.

2.5. Zeta potential measurement to ensure surface charge on membrane surface

The electrokinetic features of the membranes have been evaluated by streaming potential analysis, employing ZetaCAD electrokinetic analyzer (CAD Inst., France). The streaming potential analyzer consisted of a quartz-cell configuration (Fig. 2.8) is capable of holding two flat sheet membranes in such a way that the membranes are remained separated by spacers and the skin layers are faced each other creating a slit channel for tangential flow of electrolytic solution across the membranes.

The electrical potential difference, generated due to the bidirectional flow of electrolyte (KCl) solution under pressure gradient across the membrane was measured by Ag/AgCl electrodes, equipped with the cell. Zeta potentials of the membranes under varying pH environments, ranging from pH 3 to 11 were evaluated utilizing the streaming potential values and the

relationship between the measurable streaming potential (V_{st}) and the zeta potential (ζ), which is expressed by the Helmholtz-Smoluchowski equation (Eq. 2.8).

$$V_{\rm st} = \frac{\varepsilon}{\lambda \eta} \zeta \tag{2.11}$$

Where, ε is the dielectric constant ($\varepsilon = \varepsilon_0 \varepsilon_r$, being ε_r the relative dielectric constant and ε_0 the vacuum permittivity), η and λ are the viscosity and conductivity of the electrolyte medium. An average value of zeta potential from three replicates was reported and the measurement error was found to be ± 0.5 mV.



Fig. 2.8: Schematic diagram of streaming potential analyzer set-up.

The values of ζ of the membranes as determined with respect to the variation of pH can further be employed to calculate electrokinetic surface charge densities (σ_s) at the shear planes of the membranes as a function of the respective pH environments,⁸⁰ using Eq. 2.12.

$$\sigma_s = \frac{\varepsilon \zeta}{\lambda_{Deb}} \tag{2.12}$$

The Debye-length (λ_{Deb}) was derived according to the Eq. 2.13.

$$\lambda_{Deb} = \sqrt{\frac{\varepsilon RT}{2F^2 I}} \tag{2.13}$$

Where, R, T and F denote the gas constant, absolute temperature and Faraday constant, respectively; and I represents the ionic strength of the electrolyte medium, calculated from the molar concentration (C_i in M) of the ith ion of the electrolyte and the charge number (z_i) of that ion, expressed in Eq. 2.14.

$$I = \sum_{i} Z_i^2 C_i \tag{2.14}$$

For electrokinetic measurements under varying pH environments, HCl and NaOH are used to adjust the pH values which led to presence of excess of similar counter-ions (Cl⁻) at acidic pH and additional dissimilar counter-ion (OH⁻) at alkaline pH, respectively.

2.6. Drop shape analysis (contact angle measurements) to ensure hydrophilicity/ hydrophobicity of membrane surface

In surface science, an instrument generally called a Contact Angle Goniometer or Drop Shape Analyzer is used to measure the static contact angle and surface tension of a solid surface with respect to polar or non-polar solvents. Static contact angle measurement has been conducted using sessile drop method at ambient temperature. A contact angle measuring instrument (DSA 100 of KRUSS Gmbh, Germany) with DSA 1 v 1.92 software uses cameras and software to capture and analyze the drop shape. The contact angle (θ) is defined as the angle formed by a liquid at the three phase boundary where the liquid, vapor and solid intersect. The contact angle depends on the interfacial tensions between the vapor & liquid, liquid & solid and vapor & solid. Another perspective that describes contact angles uses cohesion vs. adhesion. Cohesion is the force between the liquid molecules which hold the liquid together. Adhesion is the force between the liquid molecules and the solid molecules. The contact angle is a quantitative measure that tells the user the ratio of cohesion vs. adhesion. If the contact angle is near zero, meaning the liquid droplet spreads completely on the solid surface, adhesive forces are dominating. If the contact angle is very high, meaning the liquid droplet bead up on the solid surface as water does on a freshly waxed car, cohesive forces are dominating. Higher is the contact angle of a surface lower will be the tendency of that surface to get wet which means the surface is hydrophobic in nature. Similarly lower contact angle value reflects the hydrophilic nature of the surface.

Since in equilibrium the chemical potential of the three phases should be equal so if the solid– vapor interfacial energy (*i.e.*, surface free energy) is denoted as γ_{sv} , the solid–liquid interfacial energy as γ_{sl} and the liquid–vapor interfacial energy (*i.e.*, surface tension) as γ_{lv} , then an equation that must be satisfied in equilibrium is known as Youngs equation which is given by Eq. 2.15.

$$\gamma_{sv} - \gamma_{sl} - \gamma_{lv} \cos\theta_c = 0 \tag{2.15}$$

Where, θ_c is the equilibrium contact angle.

While static contact angles give static information about the interfacial tensions between the solid, liquid and gas, advancing and receding contact angles give some information about the dynamic interaction of the liquid, solid and gas. An advancing contact angle is determined by pushing a droplet out of a pipette onto a solid. When the liquid initially meets the solid it will form some contact angle. As the pipette injects more liquid through the pipette, the droplet will increase in volume, the contact angle will increase, but its three phase boundary will remain stationary until it suddenly jumps outward. The contact angle the droplet had immediately before

jumping outward is termed the advancing contact angle. The receding contact angle is however measured by sucking the liquid back out of the droplet. The droplet will decrease in volume, the contact angle will decrease, but its three phase boundary will remain stationary until it suddenly jumps inward. The contact angle the droplet had immediately before jumping inward is termed the receding contact angle.

The following pictorial representation (Fig. 2.9) gives an impression about the difference in behavior between the advancing and receding contact angle measurements:



Fig. 2.9: Pictorial representation of advancing and receding contact angle measurements.

The difference between advancing and receding contact angles is termed contact angle hysteresis which can be used to characterize surface heterogeneity, roughness, and mobility. The contact angle is also employed to assess the hydrophilicity and surface free energy (SFE) with its polar and dispersive components of the active skin layers of the membranes. For this purpose, three different solvents (water, ethylene glycol and diodomethane) with known surface tension values (γ_s , γ_s^p and γ_s^d , Table 2.1) are employed.

Fowkes method⁸¹ is applied to calculate the SFE along with the polar and dispersive components of the membranes' surfaces from the surface tension values of the probe solvents and contact angle values of the membranes with respect to those solvents. Wetting envelopes are also

constructed for the membranes' surfaces by reversing the method applied to determine the polar and dispersive part of SFE. The closed contour or envelope, with coordinate system made from polar and dispersive part of the SFE defines the line where the condition of contact angle 0° (cos $\theta = 1$) is satisfied.

Table 2.1: Polar (γ_s^p) and dispersive (γ_s^d) components of the surface tension (γ_s) values (subscript s stands for solvent; superscript p and d refer to the polar and dispersive components, respectively) of the probe solvents: water, ethylene glycol and diiodomethane.

Solvent	γ s (mN/m)	γ_s^p (mN/m)	γ_s^d (mN/m)
Water	72.8	51.0	21.8
Ethylene glycol	48.0	19.0	29.0
Diiodomethane	50.8	_	50.8

2.7. Tensile strength measurements

A tensile test, also known as tension test, is probably the most fundamental type of mechanical test that can be performed on material using tensile strength measurement unit (popularly known as universal testing mchine). Tensile tests are simple, relatively inexpensive, and fully standardized. By pulling on the material, it can be determined that how the material will react to forces being applied in tension. By continuing to pull on the material until it breaks, a good, complete tensile profile of the material can be obtained. A curve will result showing how it reacted to the forces being applied. The point of failure is of much interest and is typically called its "Ultimate Strength".

For most tensile testing of materials, in the initial portion of the test, when a material deforms elastically, the amount of deformation likewise depends on the size of the material, but the strain for a given stress is always the same and the two are related by Hooke's Law (stress is directly proportional to strain) as shown in Eq. 2.16.

$$E = \frac{\sigma}{\varepsilon} \tag{2.16}$$

where σ is stress, E modulus of elasticity, ε strain. E is the slope of the line in this region where stress (σ) is proportional to strain (ε) and is called the "Modulus of Elasticity" or "Young's Modulus". The modulus of elasticity is a measure of the stiffness of the material, but it only applies in the linear region of the curve. If a specimen is loaded within this linear region, the material will return to its exact same condition if the load is removed. At the point that the curve is no longer linear and deviates from the straight-line relationship, Hooke's Law no longer applies and some permanent deformation occurs in the specimen. This point is called the "elastic, or proportional, limit". From this point on in the tensile test, the material reacts plastically to any further increase in load or stress. It will not return to its original, unstressed condition if the load were removed. A value called "yield strength" of a material is defined as the stress applied to the material at which plastic deformation starts to occur while the material is loaded. The amount of stretch or elongation the specimen undergoes during tensile testing can also be found out. This can be expressed as an absolute measurement in the change in length or as a relative measurement called "strain". Strain itself can be expressed as the ratio of the change in length to the original length as shown in Eq. 2.17.

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{l_1 - l_0}{l_0} \tag{2.17}$$

where Δl is change of the length, l_1 length after elongation, l_0 original (initial) length.

"Ultimate Tensile Strength" (UTS) of a material is the maximum load the specimen sustains during the test. The UTS may or may not equate to the strength at break. This all depends on what type of material is under testing.

Because membranes vary in chemical and material composition, different test methods are prescribed in various standards, which specify different specimen shapes, sizes, grip lengths and loading speeds. It is seen that temperature, speed of loading, gauge length and strain variation within a specimen affect the tensile tests of a membrane sample. Careful consideration should be made while defining test methods and procedures for evaluating material behaviour. Measurement of mechanical stability of the base membranes are carried out with a universal tensile testing machine (Hemetek Techno Instrument, model LRX Plus, India), at 25 °C with a relative humidity of 40-50%. A constant deformation rate of 100 mm/min is controlled during the analysis. For analysis, dumb-bell shaped specimens of the membrane samples with length of 4 cm and width of 0.6 cm are employed. Tensile strength (TS) and percent elongation at break (EB) are calculated for the membranes in duplicates, using the NEXYGEN plus software.

2.8. Performance evaluation of UF membranes

For measurement of porosity of the membranes, gravimetric method has been applied. A circular piece of the Psf membrane with an area -A and thickness -h is weighed after taking it out from storage of distilled water and then carefully removing the superficial water with filter paper. The

wet membrane is dried in a vacuum oven at 75 °C for 24 h before measuring the weight in dry state. From the weights of the membrane sample in wet (W_0) and dry (W_1) states, the porosity (ϕ) of membrane is calculated using Eq. 2.18.

$$\phi(\%) = \frac{W_0 - W_1}{\rho_w A h} \times 100 \tag{2.18}$$

Where, ρ_w is density of pure water at room temperature. In order to minimize the experimental error, measurements are carried out in duplicates and then calculated the average.

Pure water flux measurement of the base membrane with effective membrane area of 14.4 cm² is conducted under a cross-flow filtration mode operated at 1 bar transmembrane pressure. The steady-state pure water flux (PWF, L.m⁻²day⁻¹ or LMD) is determined by direct measurement of the permeate flow *i.e.*, volume (V, in L) collected during a time period (T, in day) through a membrane area (A, in m²) at certain pressure. Prior to the UF test experiment, membrane is initially subjected to undergo hydraulic compaction for 1 hr in water at standard UF test conditions, to achieve stabilized performance of the membrane.

Utilizing the porosity of the membrane, mean pore size (r_m in nm) is determined by employing the Guerout–Elford–Ferry equation⁸² as Eq. 2.19.

$$r_m = \sqrt{\frac{(2.9 - 1.75\,\phi) \times 8\eta\,hv}{\phi \times A \times \Delta P}} \tag{2.19}$$

where, ϕ (%) and h (m) denote the porosity and thickness of the membrane. The viscosity of water (8.9 × 10⁻⁴ Pa s) is represented as η . The volume of water permeated per unit time (v in m³.s⁻¹) is considered to pass through an effective membrane area of A (m²), under 1 bar transmembrane pressure (ΔP).

For measurement of MWCO of the base membrane, analysis of solute rejection behavior is carried out using neutral organic solutes such as PEG with average Mw of 20k, 35k Da and PEO with average Mw of 100k Da. The test solutions are prepared by dissolving pre-weighed amounts of PEG or PEO in ultra-pure water at a concentration of 200 ppm. The solute rejection studies are carried out at a transmembrane pressure of 1 bar at room temperature. The concentration of PEG or PEO in both feed and product were measured by analysing the total organic carbon (TOC) content of the samples using TOC analyzer (ANATOC-II, SGE analytical science, Australia). The MWCO is determined from a plot of solute rejection *vs* molecular weight, generated in order to construct a MWCO curve, which implies a molecular weight of the organic solute that is 90% retained by the membrane.

The evaluation of transport properties of the membranes has been conducted using a cross-flow UF test cell (Fig. 2.10), at 1-2 bar of transmembrane pressure. The actual test set up is shown in Fig. 2.11. Circular membrane samples, with an effective membrane area of 14.4 cm² are properly washed in de-ionized water and then placed in the test cell with the membranes' active skin layers facing the incoming feed solution. To maintain a steady feed concentration, the experiments are carried out in recycle mode *i.e.*, both the concentrate and the permeate streams are recirculated into the feed tank. The feed solution temperature is maintained at 25-30 °C. Prior to the start of data accumulation, steady-state conditions are achieved for all the UF test experiments when the membranes are allowed to get stabilized by operating for long-run. The solute concentrations in the feed and permeate solutions are obtained through the measurement of total organic carbon content of the respective solutions of polyethylene glycol and polyethylene oxide using a TOC analyyer. All membrane samples are prepared and tested in

duplicate for UF performance evaluation, results of which have been averaged. The steady-state readings of all the cases are recorded and reported.



Fig. 2.10: Schematic description of UF membrane performance testing equipment.(A) Feed tank, (B) Valve, (C) diaphragm pump, (D) Feed line, (E) Stand with clamps, (F) Test cell, (G) Permeate line, (H) Permeate collector, (I) Pressure gauge, (J) Pressure relief valve, (K) Rota meter and (L) Reject line.

The percentage of solute rejection (SR) is determined by conductivity measurement of the respective solutions and calculated as Eq. 2.20.

$$SR(\%) = \frac{C_F - C_P}{C_F} \times 100$$
 (2.20)

Where C_P and C_F are the solute concentrations in permeate and feed solutions, respectively.

The steady-state solvent flux (J_w), expressed in terms of L.m⁻²day⁻¹ (LMD) is determined by direct measurement of the permeate flow *i.e.*, volume (V, in L) collected during a time period, (T, in day) through a membrane area, (A, in m²) at certain pressure using the Eq. 2.21.

$$J_w = \frac{V}{AT} \tag{2.21}$$

CHAPTER - 3

Development of Nanocomposite Membranes for Minimization

of Trade-off between Flux and Selectivity

3.1. Introduction

Membranes and membrane based separation processes are extensively used for water treatment applications. Membranes, however, in general suffer from a serious drawback of inherent tradeoff between flux and selectivity. The efforts to increase the flux of a membrane often lead to decline in selectivity and vice versa. The introduction of nanostructured materials as modifier, however, has opened up new and more innovative options for development of membranes with improved properties. Four classes of nanoscale materials are usually being evaluated as functional materials for water purification: (a) metal-containing nanoparticles,⁸³⁻⁸⁸ (b) zeolites, ^{40,89} (c) carbon nanotubes,⁹⁰⁻⁹⁵ and (d) dendrimers.⁹⁶⁻¹⁰¹ The said materials are important with respect to water purification applications because of having high surface area and many high-energy disordered/defect sites suitable for contaminants uptake. Moreover, the particles can be desirably functionalized for specific uptake of contaminants. A significant amount of work on the development and application of nanocomposite membranes for water purification and waste water treatment have been carried out recently.^{88,102-106}

In present scenario, graphene, which consists of a 2D sheet of sp²-bonded carbon atoms in a hexagonal honeycomb lattice,¹⁰⁷ is drawing the attention of membranologists since it can lead to an ultimately thin membrane (one-atom thick) that can be practically possible. Graphene possibly is going to assume a unique and outstanding place in membrane industry because it has got the potential to provide an ideal membrane with better properties like mechanical strength, chemical & thermal stability and significant flux with no compromise in selectivity.^{108,109} Since the flux across a membrane scales inversely with that of thickness of membrane, graphene can possibly outweigh the performance of conventional pressure driven membranes (thousand times

thicker than graphene). Furthermore, incorporation of graphene, as nanofiller, into polymer matrix can also aid in improving the membrane performance. Polymeric nanocomposites of graphene derivatives have been used in the preparation of different membrane materials to be used for fuel cell membrane,^{110,111} ultrafiltration,¹¹²⁻¹¹⁴ nanofiltration,¹¹⁵ pervaporation¹¹⁶ and gas separation¹¹⁷ applications.

In contrast to the earlier works on graphene oxide (GO) impregnated UF membranes^{118,119} the present work aims at evaluation of performance of nanocomposite UF membranes upon incorporation of nanostructured reduced graphene oxide (RGO). The idea of preferring RGO as beneficial reinforcement material is executed with an endeavor to provide the membrane surface a balance of hydrophilicity (due to the oxygen containing functionalities present over graphene network) and hydrophobicity (due to the inherent nature of graphene). Also, it is expected that RGO, in contrary to GO, would enable a delayed demixing during phase inversion process of membrane fabrication resulting in finer pores on the membrane surface (leading to better rejection attributes of the membrane), while having macro-voids beneath the asymmetric top layer (resulting in no compromise in flux). In addition, the thermal stability of RGO is better compared to GO which could lead to a membrane with improved thermal characteristics.¹²⁰ It is important to note that the permeation of water in a hydrophobic, atomically smooth nanoconfinement is enhanced compared to permeation through the similar sized pores available in the virgin membrane (membrane without GO/RGO).¹²¹ Furthermore, the hydrophilic nature of GO is reduced in having RGO as a reinforcement material, which would essentially pose lesser drag on the water molecules while they are finding ways through the numerous nanochannels,¹¹¹ which in turn should lead to better and unhindered water permeation compared to GO based UF membranes.

With these scientific facts in background, the present work is focused on development of polysulfone-nanostructured reduced graphene oxide (Psf-RGO) based nanocomposite UF membranes employing the in-house synthesized RGO as reinforcing material, following phase inversion technique. The performance of the membranes was evaluated in terms of pure water permeability and solute rejection studies. The synthesized RGO was characterized using various instrumental techniques like Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) analysis. Structural characterization of the Psf-RGO composite UF membranes was carried out by XPS and Fourier Transform Infra-red (FTIR) spectroscopy. Variation in skin surface topography was analyzed by atomic force microscopy (AFM).The change in surface hydrophilicity was evaluated by contact angle studies. The thermal and mechanical properties of the membranes were assessed by thermogravimetric (TGA) analysis and tensile strength measurements, respectively. An ideal membrane with optimum throughput, and rejection attributes along with improved thermal and mechanical properties were obtained at 2 w/w % reinforcement of RGO.

3.2. Experimental

3.2.1. Materials

Polysulfone (Psf, Mw: 30 kDa) from Solvay Speciality Polymers (India), N-methyl-2pyrrolidone (NMP) (purity of \geq 99 %, Sigma-Aldrich) and Polyvinyl pyrrolidone (PVP, K-30; M_w: 40 kDa), procured from SRL (India) were used to prepare polysulfone base membrane. Synthetic graphite powder (particle size: $<20 \ \mu$ m) (Aldrich) was used as a raw material to manufacture reduced graphene oxide for modification of a Psf polymer based UF membrane. Concentrated sulphuric acid, sodium nitrate, potassium permanganate, 30% hydrogen peroxide of analytical grades and hydrazine hydrate (GR 99%) were purchased from different manufacturer and used for the oxidation-reduction process to convert graphite into graphene oxide and then reduced graphene oxide.

3.2.2. Synthesis of graphene oxide (GO) from graphite

Conversion of graphite into graphitic/ graphene oxide (GO) through the process of oxidation, following the modified Hummer's method,^{122,123} was accomplished by treating a mixture of graphite flakes (3.0 g, 1 weight equivalent) and NaNO₃ (1.5 g, 0.5 weight equivalent) with concentrated H₂SO₄ (69 ml), followed by cooling the mixture to 0°C using an ice bath. Then, oxidizing agent KMnO₄ (9.0 g, 3 weight equivalent) was slowly added to the suspension in portions to maintain the reaction temperature below 20°C. The reaction mixture was warmed to 35°C and stirred for 7 hours, resulting in a progressive formation of brownish-grey colored thickened mixture, with diminishing in effervescence. Further, addition of KMnO₄ (9.0 g, 3 weight equivalent) was done in one portion, and the reaction mixture was stirred for 12 hours at 35°C. After completion of the reaction the system was allowed to cool down to room temperature and then poured onto ice-water mixture (400 ml) with 30% H₂O₂ (3 ml) to reduce the residual permanganate and manganese dioxide to colorless soluble manganese sulfate. The brown colored suspension was then turned yellowish brown in colour. The mixture was then purified following the filtration steps, where, the filtrate was centrifuged (4000 rpm for 4 hours),

and then the supernatant was decanted away. The remaining solid material was then washed in succession with 500 ml of water, 200 ml of 30% HCl, and 200 ml of ethanol. The solid GO, thus obtained after the purification process was vacuum-dried overnight at room temperature.

3.2.3. Synthesis of RGO from exfoliated GO

Partial de-oxygenation of the GO was achieved by hydrazine-assisted de-epoxidation of GO.¹²⁴ For this purpose, the as synthesized dried GO (400 mg) was suspended in distilled water (400 ml) with vigorous stirring, yielding an inhomogeneous yellowish brown dispersion. Prior to the reduction process, the dispersion was undergone ultrasonic treatment for 1 hour. Reduction process was carried out with hydrazine hydrate (the weight ratio of hydrazine hydrate/GO = 1) at 100°C temperature for 24 hours with continuous stirring. During completion of reduction, the yellowish brown colored dispersion of graphene oxide in water turned black and the reduced sheets aggregated and precipitated. The partially reduced GO, i.e., RGO was collected by sequentially following few steps like isolation via filtration, washing with distilled water for several times and then drying at 60°C for 24 hours under vacuum to remove the residual solvent. The oxidation-reduction process for conversion of graphite in GO and then into RGO is represented through the reaction scheme as shown in Fig. 3.1.

3.2.4. Characterization of the synthesized GO & RGO

The spontaneous Raman spectra of the as synthesized GO &RGO were recorded using a STR-300 micro-Raman spectrometer (SEKI Technotron, Japan) at room temperature. The samples were excited at 532 nm (power ~20 mW at the sample spot, DPSFS) using a 10X objective lens (Olympus). The scattered light was collected by the same objective lens and a fiber-coupled 300 mm spectrograph (Acton series SP 2300i, 1200 gr/mm) and detected by a thermo-electric cooled $(-75^{\circ}C)$ charge-coupled device (CCD).



Fig 3.1: Schematic of oxidation-reduction reaction for conversion of graphite in GO and RGO.

In order to study the structural variation of the membrane surface XPS measurements were carried out. For XPS characterization of the RGO as well as of the control and composite UF membrane surface, a DESA-150 electron analyzer (Staib Instruments, Germany) equipped with Mg-K α X-ray source (1253.6 eV) was employed. The spectrometer binding energy scale was calibrated with Au-4f_{7/2} photopeak at a binding energy of 83.95 eV. The spectrum was recorded as the intensity (number of counts per second) versus binding energy (BE). Curve fitting of the multiplex photo peaks was performed using Gaussian functions employing a least-squares peak

analysis software (XPSPEAK 4.1) and then peak areas as well as full width at half maximum (FWHM) were also determined.

Textural features of the synthesized GO and RGO were characterized by XRD analysis on a Philips X'Pert pro X-ray diffractometer. The XRD patterns with Cu K α radiation ($\lambda = 1.5418$ Å) at 40 kV and 30 mA were recorded in the range of $2\theta = 10-70^{\circ}$ at a scan speed of 0.5° min⁻¹. The average crystallite sizes for the RGO was determined using Debye-Scherrer's equation (t = K λ /B cos θ , where t = average crystallite size in Å, K = Scherrer constant usually taken as 0.9 Å, λ = X-ray wavelength, θ is the Bragg angle, and B = integral breadth of a reflection located at 2 θ).

3.2.5. Preparation of Psf-RGO composite UF membranes

The nanoadditive, RGO at different weight fractions (1, 2, 4 and 8 w/w% of Psf) was exfoliated in NMP solvent by ultrasonication for 30 minutes. Each of the NMP solutions comprising of dispersed RGO at varying weight fractions was then mixed with 10 g of Psf polymer and 30 (w/w)% PVP, as pore forming additive to prepare polymer solutions of concentration 25 (w/v) %. After vigorous stirring for 24 hours, the dope solutions obtained, were kept overnight at room temperature without stirring until no air bubbles appear in the solution. Asymmetric flat sheet type Psf-RGO composite UF membranes with a very thin and dense skin layer were prepared by non-solvent induced phase inversion method. The as-prepared dope solutions were employed to cast membranes onto a nonwoven polyester fabric as a support layer with a nominal thickness of 100 μ m, using a lab developed doctor's knife device. The membranes were then immediately immersed in a gelling bath containing distilled water at room temperature for immersion precipitation. After primary phase separation and formation stage, the resulting RGO embedded Psf membranes were taken out of water bath and kept in another water bath for 24 hours to allow adequate removal of the solvent (NMP) and leachable additive (PVP) from the membrane matrix in water. The entire casting process was carried out in a controlled atmospheric condition by maintaining the temperature of the surrounding enclosed atmosphere between 21-24°C with a relative humidity of 30–35%. The UF membranes made under similar atmospheric conditions, employing 1, 2, 4 and 8 w/w% of RGO are named as Psf-RGO UF-1, Psf-RGO UF-2, Psf-RGO UF-3 and Psf-RGO UF-4, respectively.

3.2.6. Characterisation of the Psf-RGO composite UF membranes

3.2.6.1. Spectral characterization of skin surface of membranes by FTIR

Vibrational spectra of the RGO embedded UF membranes with Psf base matrices were acquired by FTIR technique. For spectral acquisition in the attenuated total reflectance (ATR) mode, Bruker make Vertex 70 spectrometer system equipped with an ATR unit (ZnSe crystal, 45° angle of incidence and refractive index 2.4) was employed. The membranes skin surface was faced down onto the ATR crystal element and lighter pressure was applied using a MIRacle high pressure clamp with torque-limited press. The radiation penetration depth was 2 µm. All infrared spectra were recorded in absorbance mode over two different wave number regions i.e. 800-1550 cm⁻¹ and 2750-3750 cm⁻¹ at an ambient temperature. For evaluation, 200 scans were taken with a spectral resolution of 2 cm⁻¹.

3.2.6.2. Determination of hydrophilic characters of membrane skin surfaces

Static sessile drop contact angle measurement on the skin surfaces of the Psf-RGO composite UF membranes were performed at an ambient temperature with contact angle measuring instrument

DSA 100 of KRUSS, Germany to evaluate the hydrophilic behavior of the membranes with respect to the probe liquid, de-ionized water. The sessile drop was slowly and steadily formed on the membrane surface by depositing 3 μ l of the de-ionized water with a micro syringe for a residence time of 60 seconds. Eight measurements on different locations of each membrane surface were performed to get the contact angles at membrane-water-air inter phase and then the average of left and right contact angles yielded to get the equilibrium contact angles with their standard deviations.

3.2.6.3. Analysis of surface topographical variation of membranes by AFM

Skin surface topographies of the Psf-RGO composite UF membranes were analyzed by using an AFM instrument (NT-MDT SOLVER next, Russia). Quantitative informations were extracted from the AFM three-dimensional topographies as taken in the semi-contact mode. Small squares of the prepared membranes (approximately 1 cm^2) were cut and glued on a metal substrate. The rectangular cantilever NSG 10 (NT-MDT, Russia) employed for scanning purpose was made out of Si₃N₄ with a spring constant of 11.8 N/m, typical resonance frequency of 240 kHz and a nominal tip apex radius of 10 nm with high aspect ratio. The scanning was done on a 20 μ m×20 μ m area of the membranes in air, at an ambient temperature with a scanning frequency of 0.1Hz. The scanned region was flattened using a second order polynomial to remove curvature and slope from the image and then the resulting best fit was subtracted from the image. For image acquisition and evaluation of surface roughness parameters of the membranes NOVA-P9 software was used.

3.2.6.4. Morphological investigation of membranes by SEM

The morphological analyses, through SEM, of the Psf-RGO composite UF membranes were carried out using Camscan–CS3200LV, UK. To make the membranes electrically conducting, the membrane samples (without support polyester fabric) were fractured in liquid nitrogen into smaller sized strips and sputter coated on the cross-sectional layer with gold-palladium alloy for 100 seconds at a current of 15 mA. The acquisition of cross-sectional images of the membranes was done in secondary electron mode at an acceleration voltage of 15 kV and 1000X magnification.

3.2.6.5. Evaluation of thermal stability of Psf-RGO composite UF membranes

The thermal degradation process as monitored through the change of mass as a function of temperature, for the Psf-RGO composite UF membranes were investigated by employing thermogravimetric analyzer (Mettler-Toledo TGA/DSC 1 with STAR software, Switzerland). The analysis was conducted within a temperature range of 30-600°C at a heating rate of 10°C/min. A continuous flow of nitrogen gas was monitored in the test environment for an inert atmosphere.

3.2.6.6. Determination of mechanical stability of Psf-RGO composite UF membranes

Measurement of mechanical stability of the Psf-RGO composite UF membranes were carried out with a universal tensile testing machine (Hemetek Techno Instrument, model LRX Plus, India), at 25°C with a relative humidity of 40-50%. A constant deformation rate of 100 mm/min was controlled during the analysis. For analysis, dumb-bell shaped specimens of the membrane

samples with length of 4 cm and width of 0.6 cm were employed. Tensile strength (TS) and percent elongation at break (EB) were calculated for the membranes in duplicates, using the NEXYGEN plus software.

3.2.6.7. Measurement of pure water permeability of membranes

Pure water permeability measurements of the Psf-RGO composite UF membranes were conducted in a UF test skid at a transmembrane pressure of 1 bar at room temperature. The steady state pure water permeability (PWP) was determined in terms of liter per square meter per day (LMD) by direct measurement of the permeate flow. The PWP ($L.m^{-2}day^{-1}$) through a membrane area (A, in m²) was calculated as the volume (V, in L) collected during a time period (T, in day) and expressed by PWP = V/A×T. Prior to all UF test experiments, membranes were initially subjected to undergo compaction for 1 hour in water at standard UF test conditions, to achieve stabilized performances of the membranes. The hydraulic compaction behavior of the Psf-RGO composite UF membranes were evaluated in terms of compaction factor by comparing the % flux decline results of each membrane.

3.2.6.8. Evaluation of solute rejection behavior of membranes

All Psf-RGO composite UF membranes were employed for cross-flow permeation experiments in a UF test skid, with an effective membrane area of 14.5 cm². Measurements were carried out using polyethylene glycol (PEG) with average molecular weight of 35 kDa and polyethylene oxide (PEO) with average molecular weight of 100 kDa. The test solutions were prepared by dissolving pre-weighed amounts of PEG or PEO in distilled water at a concentration of 200 ppm and solute rejection studies were carried out at a trans membrane pressure of 1 bar at room
temperature. The concentration of PEG/PEO in both feed and product were measured by analysing the total organic carbon (TOC) content of the samples using TOC analyser (ANATOC, SGE analytical science, Australia).

3.3. Results & Discussions

3.3.1. Characterization of the synthesized RGO

3.3.1.1. Raman studies on as-grown GO and RGO

Structural transformations of GO into RGO, through hydrazine induced chemical reduction pathway was analyzed by the Raman spectroscopic technique. In the Raman spectra of GO and RGO (Fig. 3.2), the D band, attributed to the structural defects or disorderness in the lattice structure, appears at 1356.2 cm⁻¹ (FWHM: 181.2 cm⁻¹) and 1343.5 cm⁻¹ (FWHM:95.1 cm⁻¹), respectively and the G band, attributed to the first-order scattering of the E_{2g} vibrational mode in the graphite sheet, appears at 1575.5 cm⁻¹ (FWHM:139.1 cm⁻¹) and 1579.9 cm⁻¹ (FWHM:81.9 cm⁻¹), respectively.^{125,126} A weak 2D band, observed at 2669.7 cm⁻¹ is due to second order phonon process. It is observed that after being reduced, the D band becomes distinctively more intense as compared to the G band. The ratio of the integrated intensity of the D band to the integrated intensity of the G band (I_D/I_G) is markedly increased from 0.91 for GO to 1.18 for RGO. This phenomenon could be explained by the formation of new and smaller sized abundant sp² domains during the reductive transformation process of exfoliated GO into RGO. The restoration of the conjugated graphene network could be attributed to the proposed mechanism of Stankovich et al.,¹²⁷ where the oxirane rings of the GO sheets get preferentially converted into hydrazino alcohols through ring-opening reaction as induced by the reducing agent and then react further to form an aminoaziridine moiety with subsequent thermal elimination of diimide to form the sp² domains.¹²⁸ The reduction in FWHM values in the D band as well as G band for RGO as compared to GO indicate that there is less disordered sites in the structure of the former species. The in-plane crystallite size, La of the RGO is evaluated from a relation given as La = $(2.4 \times 10^{-10}) \lambda_{laser}^4 (I_G/I_D)$,¹²⁹ where the pre-factor derived by employing 532 nm as λ_{laser} is 19.22 (the pre-factor value is in contrast to the commonly used value of 4.4¹³⁰) and I_G/I_D implies the ratio of the intensity of the G band to the D band. The values of La for the synthesized GO and RGO are found as 20.94 and 16.34 nm, respectively.



Fig. 3.2: Raman spectrum of GO and RGO.

3.3.1.2. XPS studies on RGO

The C-1s XPS core-level spectrum of the synthesized RGO is presented in Fig. 3.3a, where curve fitting and deconvolution of the spectrum yields four separated spectra with different BE values (Table 3.1) for C atoms residing in various chemical environments. The intense component peak

of the deconvoluted C-1s spectrum appeared at the lowest BE of 284.6 eV (FWHM: 1.55 eV) is ascribed to the nonoxygenated ring C of C–C or C–H. The broader and less intense peak appearing at BE of 286.5 eV (FWHM: 2.58 eV) refers to the C of C–OH functional groups.¹³¹ Further, a much broader and shoulder peak appearing at the highest BE of 289.2 eV with respective FWHM of 4.39 eV refers to the carboxylate C of HO–C=O functional groups, residing at the edges of GO and remained unaffected during reduction process by hydrazine.¹³² Additionally, a peak with BE of 285.8 eV (FWHM: 1.54) is also found, which implies the existence of some incorporated N in the lattice structures of RGO due to the reaction of hydrazine with carbonyl groups of GO.¹³³ The deconvoluatedO1s XPS spectra (Fig. 3.3b) of the more surface specific element O (the O-1s photoelectron kinetic energies are lower than those of the C-1s and so the sampling depth of O-1s is smaller) reveal that the oxygen in RGO is existed in two different electronic states. The less intense peak at lower BE of 530.1 eV (FWHM: 1.39 eV, peak area: 3.37%) is assigned to the contribution of the O of HO–C=O functional groups and the broad and intense peak at higher BE of 533.2 eV ((FWHM: 3.62 eV, Peak area: 96.63%) is ascribed to the O of C–OH functional groups.¹³

Evaluation of areas (Table 3.1) of constituent peaks for C-1s and O-1s reveal that a significantly larger proportion of different surface oxygenated functional groups of RGO, located at different sites of its edge and basal plane, existed in the form of hydroxyl and carboxylic acid groups.

3.3.1.3. XRD analysis on GO and RGO

Diffraction peaks corresponding to (002) plane of GO and RGO, appeared to be broad and symmetric that centered at 19.54° and 24.24° (Fig. 3.4a and 3.4b), respectively, signify the

formation of stacked few-layers of the reduced graphene oxide. The interlayer spacing (d_{002}) of GO is evaluated as 0.454 nm.

		C-1s		O-1s			
Material	BE FWHM		Peak area	BE	FWHM	Peak area	
	(eV)	(eV)	(%)	(eV)	(eV)	(%)	
	284.6	1.55	28.16	530.1	1.39	3.37	
RGO	285.8	1.54	16.64	533.2	3.62	96.63	
	286.5	2.58	39.16				
	289.2	4.39	16.04				

Table 3.1: Curve fitting summary of different XPS peaks for RGO.



Fig. 3.3: High resolution XPS core level spectra, a) C-1s and b) O-1s of the synthesized RGO (line with bullets: experimental data; solid line: curve fit of the experimental data).

However, the adopted reduction process relevantly lowers the d_{002} of RGO, which is evaluated as 0.367 nm. The shifting of d_{002} to a lower value, resulting in such low basal placing of RGO is attributed to the absence of residual oxygenated functional groups at the basal planes, indicating

intense reduction of the epoxide sites of GO.¹³⁵ This also indicates subsequent presence of different oxygenated functional groups at the edges of the RGO. Thus, it can be assumed that the numerous spatial ways through adjacent basal planes residing in the stacked few-layers of RGO can serve as hydrophobic channels for fluid transport.¹³⁶ The average crystallite sizes for the RGO, determined using Debye-Scherrer's equation range from 4 - 8 nm. A Lorentzian fit of the peak corresponding to the (002) reflection and use of the Scherrer formula provide the estimation of average number of layers as ~ 16, existing in the synthesized RGO.



Fig. 3.4: XRD pattern of the synthesized, a) GO and b) RGO.

3.3.2. Characterization of the Psf-RGO composite UF membranes

3.3.2.1. Investigation of structural features of Psf-RGO composite UF membranes

The FTIR spectral analyses of the Psf-RGO composite UF membranes, acquired in the specified regions of 800-1550 and 2750-3750 cm⁻¹ are shown in Fig. 3.5a and 3.5b, respectively. The most significant absorption bands appeared in the FTIR spectrum of the membranes are: ~1149 and ~1294 cm⁻¹ (symmetric and asymmetric stretching of O=S=O from diarylsulfone groups)

respectively; ~834 cm⁻¹ (C-H stretching from Ar); ~1489 cm⁻¹ (asymmetric vibration attributed to C-H from methyl groups) and ~1170 cm⁻¹ (stretching vibration of etheric bond of Ar-O-Ar of Psf).¹³⁷ The peaks at ~2930 and ~2870 cm⁻¹ refer to the asymmetric and symmetric stretching vibrations of C-H, respectively. The broad absorption band appearing at ~3420 cm⁻¹ refers to the O-H stretching of the hydroxyl groups due to presence of inherent moisture in the membrane matrices. The non-shifting of characteristic absorption bands in Psf-RGO composite UF membranes corroborate the fact that impregnation of RGO at increasing weight fraction from 1 to 8 w/w% of Psf doesn't affect the structural features of the base matrix. Thus, the FTIR analysis reveals that the RGO, due to its structural features exerts only weak chemical affinity to the surrounding polymer network and reside through physical entrapment within the Psf matrix, on their impregnation.



Fig. 3.5: ATR FT IR spectra a) 800-1550 cm⁻¹ and b) 2750-3750 cm⁻¹ of Psf UF and Psf-RGO composite UF membranes.

A further study on surface chemistry of the selective membranes, (Psf UF and Psf-RGO UF-2), was conducted by analyzing the deconvoluated C-1s (Fig. 3.6a and 3.6b, respectively) and O-1s (Fig. 3.7a and 3.7b, respectively) core level XPS spectra.



Fig. 3.6: High resolution C-1s photoelectron spectra obtained from skin layers of (a) Psf UF and (b) Psf-RGO UF-2 (line with bullets: experimental data; solid line: curve fit of the experimental data).



Fig. 3.7: High resolution O-1s photoelectron spectra obtained from skin layers of (a) Psf UF and (b) Psf-RGO UF-2 (line with bullets: experimental data; solid line: curve fit of the experimental data)

The intense and major component peak of the deconvoluated C-1s spectra is attributed to C–C or C–H bonds of the alkyl and aromatic chains of the polymer network of Psf UF and Psf-RGO UF-2 (appearing at BE of 284.7 $eV^{138, 139}$) with an invariable FWHM of about 1.93 eV. But, there is

a percentage decline in the concerned peak area by 4.77%, from Psf UF to Psf-RGO UF-2 (Table 3.2). This decrease is compensated by an increase of 9.54% in the relative peak area for the broader peak, appeared at BE of 286.1 eV, assigned to the carbon in -C-O- structures. It could be the result of reinforcement of RGO in Psf matrix of the Psf-RGO UF-2, which further suggests that RGO with its retained oxygen-containing functionalities contribute in enhancing the extent of polar sites in Psf membrane surface. The deconvoluated O-1s core level XPS spectra of the Psf UF and Psf-RGO UF-2, respectively, indicate the presence of oxygen in two different chemical states. The bigger peaks at lower BE of 531.3 eV with FWHM of 2.20 eV for Psf UF and 2.25 eV for Psf-RGO UF-2 refer to the collective contribution of presence of oxygen in O=S=O linkages of Psf backbone as well as the physiosorbed oxygen.¹⁴⁰ The percentage enhancement in the area under the curve for the peak of 531.3 eV from Psf UF to Psf-RGO UF-2 is 5.01%. Thus it can be affirmed that presence of such enhanced content of polar oxygenated species on impregnation of RGO seems to bring superior hydrophilic nature of the Psf-RGO composite UF membranes over the pure Psf UF membrane. The smaller peak at higher BE of 533 eV, with FWHM of 2.02 eV for Psf UF and 2.18 eV for Psf-RGO UF-2 is assigned to the oxygen in the structure of -C-O-, resulting out of the presence of oxygen-containing functionalities due to impregnation of RGO.¹⁴¹ The percentage decline in the area under the curve for the peak of 533 eV, by 7.35%, from Psf UF to Psf-RGO UF-2 is due to the relative compensation of the earlier enhancement.

		C-1s		O-1s			
Material	BE	FWHM	Peak area	BE	FWHM	Peak area	
	(eV)	(eV)	(%)	(eV)	(eV)	(%)	
Psf UF	284.7	1.93	66.67	531.3	2.20	59.47	
	286.1	2.59	33.33	533.0	2.02	40.53	
Psf-RGO UF-2	284.7	1.91	63.49	531.3	2.25	62.45	
	286.1	2.66	36.51	533.0	2.18	37.55	

Table 3.2: Curve fitting summary of different XPS peaks for Psf UF and Psf-RGO UF-2.

3.3.2.2. Evaluation of hydrophilic characteristics of Psf-RGO composite UF membranes

The extent of hydrophilic nature of the membranes, as represented by the water contact angle values obtained on each of the membrane surface by the sessile drop method, is given in Fig. 3.8. It is observed that RGO embedded Psf membranes exhibit more hydrophilic surface features than the pure Psf UF membrane. It is interesting to note that 1 w/w% loading of RGO brings significant change in hydrophilic behavior of the membrane (Psf-RGO UF-1) with a contact angle value of $70.7 \pm 0.7^{\circ}$ compared to that of pure Psf UF membrane with contact angle value of $76.2 \pm 1.1^{\circ}$. The impregnation of RGO at lower weight fraction influences the direction of migration and consequent dispersion of the nano-additive towards the skin surface of the membrane due to more affinity of them towards the non-solvent, water.³⁸ The presence of oxygenated functionalities in RGO, as confirmed by the XPS analysis also supports the enhancement of hydrophilic behavior of the skin surfaces of the Psf-RGO composite UF membranes. But, with further loading of RGO, the change in water contact angle values (Psf-RGO UF-2: $69.8 \pm 0.8^{\circ}$, Psf-RGO UF-3: $68.1 \pm 0.6^{\circ}$ and Psf-RGO UF-4: $67.2 \pm 0.9^{\circ}$) were not

pronounced. This feature can be attributed to the fact that at higher loading, the uniform distribution of the RGO gets affected with a further impact in their presence within the skin layers of the Psf matrix. An enhanced permeation behavior (discussed later) with modest change in hydrophilic character for these membranes, fabricated by employing RGO at higher weight fractions, can be elucidated by the proposition that the aggregated RGO reside onto the pore walls within the Psf matrix during the formation of the membranes and induce changes in hydrophilic characters of the porous pathways.¹⁴²



Fig. 3.8: Variation in contact angles (water) of Psf UF and Psf-RGO composite UF membranes.

3.3.2.3. Morphological analysis of Psf-RGO composite UF membranes

Ultrafiltration membranes, fabricated following the technique of non-solvent induced phase inversion process, is known to consist of asymmetric porous structure where the pores formed at the skin surface are smaller in size as compared to the pores formed in the interior of the substructure. The porous structures usually vary in size, shape and density throughout the polymer matrix (i.e., from the dense skin surface to the more porous subsurface) of the membrane. Such variations in membrane morphology depend on the phase behavior of the polymer dope solutions as well as the rate of the non-solvent's indiffusion and the solvent's outdiffusion during phase separation process.¹⁴³ Thus, it can be anticipated that presence of a nanostructured additive with hydrophilic or hydrophobic functionalities can influence the mechanism of formation of nanocomposite UF membranes.

In our attempt to investigate the porous structures of the Psf-RGO composite UF membranes, the cross-sectional SEM images, presented in Fig. 3.9, are analyzed. A visual observation of the size, shape and density of the finger-like pores, residing underneath the skin layer, for the membranes Psf UF (Fig. 3.9a), Psf-RGO UF-1 (Fig. 3.9b) and Psf-RGO UF-2 (Fig. 3.9c) reveal that all the membranes maintain a dense skin layer with roughly similar finger-like porous nature associated with fine porous walls. As illustrated in earlier studies,^{144, 145} the formation of membranes with finger-like pores comprise of few consecutive interdependent stages. Initially, a dense polymer layer is formed as a skin layer at the interface between the cast polymer solution and the gelling medium with concurrent existence of a polymer-rich and a polymer-lean phase underneath the nascent skin layer. However, during the process of phase separation, the nascent skin experiences shrinkage and resultant stress, which if not relieved through stress-relaxation, results in rupture of the skin layer and initiation of growth for the finger-like pores. The growth of the finger-like pores are propagated by the movement of the polymer solution through the channel, forming a pear shaped porous confinement. In our investigation, it is observed that the size, shape as well as density of the finger-like pores change when RGO is impregnated at higher weight fraction

(Psf-RGO UF-4). It could be possible that RGO at lower weight fractions (up to 2 w/w%) with considerably better uniformity in distribution within the polymer matrix may reduce the stress generated in the skin layer of the cast polymer during phase inversion stage and delay the initiation process for growth of the finger-like pores. But, at higher weight fraction (beyond 2 w/w%), due to enhanced particle density as well as greater aggregation of the RGO, there may be significant differences in the interfacial tension which could result in comparatively faster initiation of fingering leading to formation of bigger and more macro-voids, as evident in Fig. 3.9e. As seen in Fig. 3.9c, aggregation of the nanofillers is initiated at 2 w/w% loading of RGO and the extent is increasing with further loading up to 4 w/w% (Fig. 8d). Surprisingly, the aggregates are vanished at 8 w/w% (Fig. 3.9e) loading of RGO which can be attributed to formation of defective membrane having more number of bigger macro-voids. It is important to note that though the aggregate formation is just initiated at 2 w/w% (Fig. 3.9a) and Psf-RGO UF-1 (Fig. 3.9b), which can further be attributed to a delayed penetration of the nonsolvent into polymer matrix during gelling of the polymer.

Thus, the impregnation of RGO at varying weight fractions tune the membranes porous morphology profoundly as the mechanism of formation of the pores get influenced by the presence of the nano-additive.



Fig. 3.9: Cross-sectional SEM images of membranes: (a) Psf UF, (b) Psf-RGO UF-1, (c) Psf-RGO UF-2, (d) Psf-RGO UF-3 and (e) Psf-RGO UF-4.

3.3.2.4. Topographical analysis of skin surfaces of Psf-RGO composite UF membranes

Topographical variations in the skin surfaces of Psf-RGO composite UF membranes were evaluated through AFM analysis. The 2D AFM images of all the membrane surfaces with the respective height histograms are shown in Fig. 3.10. It is observed that the surface topographies of the membranes with associated roughness parameters vary significantly from a relatively smooth surface profile for the Psf UF membrane to progressively rough surfaces for membranes with higher impregnation of RGO (Fig. 3.11).





Fig. 3.10: 2D AFM images and height histograms of (a) Psf UF, (b) Psf-RGO UF-1, (c) Psf-RGO UF-2, (d) Psf-RGO UF-3 and (e) Psf-RGO UF-4.



Fig. 3.11: Surface roughness parameters of Psf UF and Psf-RGO composite UF membranes.

The average surface roughness (R_a) and root mean square roughness (R_q) of the pure Psf UF membrane was found to be 9.49 and 11.74 nm, respectively. However, the surface roughness was found to increase with enhanced impregnation of RGO in the polymer matrices with subsequent effect on distribution in the skin surfaces through varying dispersion of RGO. This is obvious from the gradual increase of R_a and R_q values for RGO embedded Psf based UF membranes, namely Psf-RGO UF-1, Psf-RGO UF-2, Psf-RGO UF-3 and Psf-RGO UF-4, which were found to be about 16.08, 18.12, 28.69 and 33.87 nm, respectively and 19.71, 23.21, 35.43 and 45.55 nm, respectively. With such enhanced roughness of the surfaces, the nanocomposite membranes possess higher effective skin surface area for more efficient contact of water. The R_{10z} , which is the difference in height between the average of the five highest peaks and the five lowest valleys relative to the mean plane, signifies the contrast between the heights and depths of extreme peaks and valleys that may occasionally be present on the surface, due to uneven

distribution of nanomaterials in the surface. For fabrication of the membranes, Psf-RGO UF-3 and Psf-RGO UF-4, when the RGO content turns as high as 4 and 8 w/w% of Psf, the particle density of RGO in the polymer dope solution becomes extremely high causing aggregation of the RGO and results in abrupt increase of their surface areas. Such aggregation can also influence the phase separation processes during formation of the nanocomposite membranes and may lead to inhomogeneous distribution of the clusters of RGO with concurrent nonhomogenity in surface as well as in bulk of the membrane matrices. Impregnation of RGO at 4 w/w% (Psf-RGO UF-3) results in larger voids in the membrane matrices due to formation of the clusters, which is reflected through the surface roughness parameters. In spite of having higher roughness values, the R_{10z} becomes lower i.e., 16.53 nm for Psf-RGO UF-3 as compared to 54.69 nm (Psf-RGO UF-1) and 56.29 nm (Psf-RGO UF-2). However, impregnation of RGO at 8 w/w% (Psf-RGO UF-4) results in presence of aggregated RGO within the Psf skin layer of the membrane, where the average heights of the peaks due to such RGO-polymer aggregates enhances the value of R_{10z} (88.96 nm) abruptly.

3.3.2.5. Study of thermal stability of Psf-RGOnanocomposite UF membranes

The results of TGA-investigation for Psf and Psf-RGO composite UF membranes obtained with different RGO contents (1, 2, 4 and 8 w/w %) is reported in Table 3.3 and Fig. 3.12. The onset degradation temperature (T_d) has increased from 507.8°C (Psf UF) to 513.5°C (Psf-RGO UF-1) and 512.9°C (Psf-RGO UF-2), which is attributed to the presence of well dispersed RGO sheets within the Psf matrix. It is assumed that the increase in thermal stability happens by suppressing the flexibility and mobility of the polymer chains due to uniform distribution of the nano-additive within the Psf matrices. However, the onset degradation temperature decreases with

further loading of RGO beyond 2 w/w % for Psf-RGO UF-3 (509.7°C) and Psf-RGO UF-4 (510.4°C), which is expected to happen because of aggregation of RGO at higher loadings leading to relaxation of the restriction in polymer chain mobility.¹⁴⁶ More importantly, the extent of overall mass loss is maximum (57.61 %) in case of Psf membrane without having any RGO in it. The extents of mass loss in all nanocomposite UF membranes are comparatively lower (from 51.56 to 54.01 %) because of existence of more proportion of RGO (which is thermally stable due to absence of labile oxygen containing functionalities) in the membrane matrix.



Fig. 3.12: TGA Thermograms of pure Psf UF and Psf-RGO composite UF membranes.

3.3.2.6. Analysis of mechanical stability of Psf-RGO composite UF membranes

Evaluation of the membranes tensile strength and percentage elongation at break, shown in Fig. 13 and Table 3.3, reveal the effectiveness of the RGO as nanostructured reinforcement material in bringing better mechanical stability for nanocomposite Psf UF membranes. It is observed that

the tensile strength enhances from 2.94 MPa (Psf UF) to 3.33 MPa (Psf-RGO UF-1) and further to 3.42 MPa (Psf-RGO UF-2) with incorporation of 1 and 2 w/w% of RGO in the Psf matrix. The suitability of RGO as potential reinforcement material is attributed to its higher surface area and aspect ratio. Due to absence of the oxygen containing functionalities, as possible interactive bridging sites of RGO, the nanomaterials presumably reside apart from each other during their dispersion in the precursor dopes at lower weight fractions.¹⁴⁷ Further, since RGO experiences a weak interaction with the polymer (as discussed during structural analysis by FTIR), the possibility of the former to act as cross-linker and subsequent formation of higher molecular weight chains also get diminished. The polymeric chains penetrate in between the RGO sheets resulting in a better uniform distribution of the reinforcement material within the polymer network. Thus, the increase of tensile strength can be ascribed to the fact that there is an effective load transfer from the stretched polymeric chains to the well dispersed RGO.¹⁴⁸ However, there is a decline in the tensile strength with further impregnation of RGO in Psf-RGO UF-3 and Psf-RGO UF-4. The decrease in mechanical strength, as noticed beyond 2 w/w% of RGO impregnation in the Psf matrix, is attributed to the aggregation effect of RGO, which could further lead to non-uniform distribution of the material in the membrane matrices resulting in less efficient load transfer from the continuous phase (Psf) to the disperse phase (RGO).

Generally, the addition of filler decreases the ductility of polymers, e.g., elongation at break.¹⁴⁹ Similar observation has also been obtained in our case. The percentage elongation at break for the nanocomposite UF membranes decrease from Psf UF (36.83%) to Psf-RGO UF-1 (32.41%) and further to Psf-RGO UF-2 (30.04%) with increasing the content of RGO. These results imply that the membranes elasticity decline with progressive impregnation of RGO into the Psf

matrices. The reduced elongation at break often means a reduced energy to break. However, surprisingly, the elongation at break in the present case increases on further loading of RGO beyond 2 w/w%. The behavior can be explained by the fact that the increase in stress levels via reinforcement is not dominant over the reduction in deformation at higher loadings, which is in contrary to the usual findings for nanocomposites.¹⁵⁰

Membrane Code	Therma	al features	Mecha	nical features
	$T_d (^{\circ}C)$	Mass loss (%)	TS (MPa)	EB (%)
Psf UF	507.8	57.61	2.94 ± 0.16	36.83
Psf-RGO UF-1	513.5	51.56	3.33 ± 0.11	32.41
Psf-RGO UF-2	512.9	53.61	3.42 ± 0.07	30.04
Psf-RGO UF-3	509.7	54.01	3.12 ± 0.19	34.01
Psf-RGO UF-4	510.4	52.55	2.84 ± 0.24	38.18

Table 3.3: Thermal features and tensile properties of Psf UF and Psf-RGO composite UF membranes.



Fig. 3.13: Variation in mechanical features for Psf UF and Psf-RGO composite UF membranes

3.3.3. Performance studies of Psf-RGO composite UF membranes

Cross-flow water permeation experiments performed with Psf-RGO composite UF membranes reveal that impregnation of RGOwith the increasing weight fraction leads to better PWP compared to the pure Psf UF membrane. The rejection pattern towards the neutral organic solutes like PEG and PEO, carried out using the membrane samples, are presented in Fig. 3.14. It is noticed that with impregnation of RGO at smaller weight fraction (1 to 2 w/w% of Psf) in the Psf polymer matrix, the solute rejection properties of the UF membranes get improved as compared to the pure Psf UF membrane. It is also observed that the membrane with a loading of 2 w/w% of RGO (Psf-RGO UF-2) achieves a promising MWCO of 30 kDa, as the membrane exhibited 92% rejection with a feed containing 200 ppm of PEG of Mw 35 kDa. Interestingly, the PWP obtained from the respective membrane (Fig. 3.15) turn out to be better than that of pure Psf UF membrane of higher MWCO (100 kDa), which reflect the prevailing over of the trade off between flux and selectivity. Both, a higher rejection (> 90%) towards solute of higher Mw, i.e., PEO (100 kDa) and simultaneous progressive increment in solvent fluxes are maintained by all the membranes, even with loading of RGO at higher weight fractions. But, the rejection performances for the low Mw solute, i.e., PEG 35 kDa, deteriorates with an enhancement of RGO content beyond 2 w/w% i.e. from 4 to 8 w/w%, in the membrane matrices. Thus, RGO embedment in Psf host matrix at an optimum proportion leads to a membrane with better flux and improved rejection qualities. This kind of macroscopical variations is attributed to the change in several microstructural and physicochemical features of the nanocomposite UF membranes. Better solute rejections for Psf-RGO UF-1 and Psf-RGO UF-2, over the pure Psf UF, imply that there may be formation of finer pores on the skin surfaces of the former membranes due to controlled phase inversion process, as discussed during morphological analysis of the membranes by SEM. However, the concurrent increase in PWP of the respective nanocomposite UF membranes corroborates the fact that there could be an enhancement in the extent of nanosized permeating channels for faster transport of the solvent in addition to the improvement in their hydrophilic behaviors as discussed earlier.

Thus, it is worthy to substantiate the enhanced permeation ability of the Psf-RGO composite UF membranes by the additional and facilitated transport of water caused by the atomically smooth interconnected inter layers (as novel pathways for water permeation) offered by RGO impregnated in the Psf matrices. Like the case of hydrophobic CNTs,¹⁵¹ it can also be expected that numerous RGO with interlayer spacing of 0.37 nm, may collectively provide such empty regions as nano-confinements for the solvent molecules (kinetic diameter of water 0.26 nm)to enter preferentially¹⁵² and get ordered during hydraulic permeation process, narrowing their interaction energy distribution with concomitant effect in reduction of their free energy.¹⁵³ However, the narrow entrance of the nano-confinements restricts the transport of solute molecules (PEG/PEO) because of size exclusion phenomena. Furthermore, due to the hydrophobic nature of the walls (basal planes) of permeating channels of RGO, serving as electrostatically frictionless pathways, the water molecules experience less dragging force during their transport.^{56,154} Thus, with reference to the concept of slip flow theory,¹⁵⁵ the above fact can be attributed as a cause for unconstrained hydraulic permeability with restoration of momentum, for the Psf-RGO composite UF membranes. On a further note of explanation, the enhanced permeation ability of the membranes is ascribed to the topographical effects on impregnation of RGO with progressive higher weight fraction leading to increase in effective surface area of the membranes, which is evident from the study of surface roughness analysis.

The formation of phase inversion membranes is also known to be controlled by thermodynamic as well as kinetic variations resulting either instantaneous or delayed demixing during precipitation of the casting polymer solutions.¹⁵⁶ It was mentioned in earlier studies¹⁵⁷ that instantaneous demixing generally leads to membrane with a highly porous substructure and a finely porous thin skin layer, whereas in contrast, a delayed demixing results in a membrane comprising porous substructure with a dense skin layer. Recent studies on nanocomposite asymmetric membranes have attempted to explain that impregnation of a novel nanomaterial like GO, having different hydrophilic functionalities facilitates the rate of diffusive mass exchange between solvent and non-solvent during the phase inversion process of the polymer, consequently resulting in increased porosities as well as larger pore channels, further affecting the rejection and flux behavior of the UF membranes.¹⁵⁸ However, in comparison to those studies, here, in our attempt to impregnate RGO as nano-additive in Psf matrices, the former having a reduced extent of oxygen containing functionalities exhibit less interaction ability with the solvent, NMP and also a low affinity towards the non-solvent, water. Such interaction behavior of the nano-additive favors the solvent's outdiffusion from the cast polymer and simultaneously unfavors the non-solvent's indiffusion into the cast polymer during phase inversion stage in the gelling medium. Thus, the thermodynamic stability of the Psf-RGO dope solution remains reasonably uninterrupted, unlike the case with the hydrophilic counterpart of RGO (i.e., GO). This may induce comparatively slower diffusion kinetics during the phase separation process, which in turn affect the membrane morphology by reducing the porosities in the skin surfaces. The hydrophilic additive, PVP is known to reduce the miscibility of casting solutions with non-solvent, which results in thermodynamic enhancement for phase separation of the polymer, Psf and also stimulates the increase in viscosity of the casting solution, which induces kinetic inhibition against the phase separation process.¹⁵⁹ However, a lower degree of chemical affinity of RGO towards the PVP may enhance the rate of outdiffusion of the later in the non-solvent medium, which could generate more number of micro or macro-voids in the substructure of the asymmetric membrane matrices. It can be assumed that impregnation of the nano-additive, RGO brings synergism in the demixing process by balancing the inter-diffusion of solvent and non-solvent as well as pore former and non-solvent, during phase inversion stage of membrane fabrication.



Fig. 3.14: Solute rejection behavior of Psf UF and Psf-RGOnanocomposite UF membranes.

In porous asymmetric membranes, the occurrence of compaction preferentially happens in the macro-void regions over the micro-void regions of the polymer matrix. Thus presence of larger macro-voids irreversibly tailors the membrane morphology to be more compactable under hydraulic pressure.¹⁶⁰Albeit, the cluster formation leads to an abrupt increase of effective surface area of the membranes with resultant enhanced solvent permeation, the extent of flux decline for the membranes (Fig. 3.16) corroborates the above facts. The enhanced free-volume area with formation of larger macro-voids in the membranes and the change in pore structure, presumably due to the increasing segmental gap between the polymer chains through relaxation effect, as induced by the clusters of RGO may simultaneously affect the solute rejection behavior of the membranes in adverse manner.



Fig. 3.15:PWP behavior of Psf UF and Psf-RGOnanocomposite UF membranes.



Fig. 3.16: Variation in flux due to compaction in the matrices of Psf UF and Psf-RGO composite UF membranes.

3.4. Mathematical modelling for prediction of flux and rejection behaviour of mixed matrix membrane

Various models based on different approaches are reported in literature¹⁶¹⁻¹⁶³ to describe and predict the solute passage through the membrane. Kedem-Katchalsky's irreversible thermodynamics approach has been considered in the present paper as the molecular mechanisms of transport processes within the membrane are not fully understood. The basic equations for the solute flux and the solvent flux¹⁶⁹ are given as:

$$J_{\nu} = L_{p}(\Delta p - \sigma \Delta \pi) \tag{3.1}$$

$$J_{s} = (C_{s})_{\ln} (1 - \sigma) J_{\nu} + \omega \Delta \pi$$
(3.2)

$$\left(C_{s}\right)_{\ln} = \frac{C_{m} - C_{p}}{\ln \frac{C_{m}}{C_{p}}}$$
(3.3)

Here J_V , J_S , represent solvent & solute fluxes, L_P is the filtration coefficient, ΔP is pressure drop across the membrane, σ is reflection coefficient, ω is the solute permeability and $\Delta \pi$ is the osmotic pressure difference between the fluid on membrane surface and product stream, $(C_s)_{ln}$ is logarithmic concentration, C_m is the concentration of the solute on the membrane surface and C_P is the concentration of the solute in the product stream.

In essence σ indicates the solute rejection property of the membrane and ω indicates the solute permeability through the membrane. Since σ is dependent on membrane, there is a need to have an appropriate correction factor for σ , reflecting the membrane nature. Similarly ω requires modification as it refers to the permeability of solute species having a size distribution.

3.4.1. Incorporation of pore theory in rejection model

Pappenheimer¹⁶⁴, Verniory¹⁶⁵ incorporated pore theory for transcapillary transport. According to this theory the membrane structure can be estimated by the parameters σ and ω . Nakao and Kimura¹⁶⁶ has described the structural implications of the ultrafiltration membrane using this 'pore theory'. They have assumed that cylindrical membrane pore has a constant radius r_p and length ΔX and that the spherical solutes have a radius r_s.

 σ and ω can be written in terms of pore theory as:

$$\sigma = 1 - g(q)S_F \tag{3.4}$$

$$\omega = D.f(q)S_D \cdot \left(\frac{A_k}{\Delta X}\right)$$
(3.5)

D is the diffusivity of solute. A_k is the ratio of total cross sectional pore area to the effective membrane area.

$$q = \frac{r_s}{r_p} \tag{3.6}$$

 S_D and S_F are the steric hindrance factors for diffusion and filtration flow respectively and are defined as:

$$S_D = (1 - q)^2 \tag{3.7}$$

$$S_F = 2(1-q)^2 - (1-q)^4$$
(3.8)

f(q) and g(q) are the correction factors for the effects of a cylinder wall and are calculated as:

$$f(q) = (1 - 2.1q + 2.1q^3 - 1.7q^5 + 0.73q^6) / (1 - 0.76q^5)$$
(3.9)

$$g(q) = \left(1 - 0.6667q^2 - 0.2q^5\right) / \left(1 - 0.76q^5\right)$$
(3.10)

Eq. 3.2 can be rewritten as:

$$J_{s} = (C_{s})_{\ln} (1 - \sigma) (L_{p} (\Delta P - \sigma \Delta \pi)) + \omega \Delta \pi$$
(3.11)

$$J_{s} = (C_{s})_{\ln} (g(q).S_{F}) (L_{p}(\Delta P - (1 - g(q).S_{F})\Delta \pi)) + D.f(q).S_{D} \frac{A_{k}}{\Delta X} \Delta \pi$$
(3.12)

$$J_{\nu}(C_s)_{\rm ln} = J_s C_{water} \tag{3.13}$$

$$Rejection = \frac{C_m - C_P}{C_m}$$
(3.14)

$$J_{w} = L_{p} \cdot \Delta P = \left(\frac{r_{p}^{2}}{8\mu}\right) \cdot \left(\frac{A_{k}}{\Delta X}\right) \cdot \Delta P$$
(3.15)

$$\frac{A_k}{\Delta X} = \frac{L_{p.} 8\mu}{r_p^2}$$
(3.16)

 A_k is constant for a specific membrane and can be expressed in terms of pure water flux using Hagen Poiseuille equation (Eq. 3.15) and J_w is pure water permeability, μ is solvent viscosity. J_s is the solute flux (free metal as well as free ligand) L_P , C_M and ΔP were measured during the experiments. r_p was estimated based on experimental studies. Solute fluxes for free metal, and free ligand were calculated using Eq.3.12. ΔP is taken as the operating pressure as the pressure drop along the length of the membrane is negligible. As the experiments were conducted at very low concentrations, $\Delta \pi$ is not significant. However, the values could be estimated based on the molar concentrations. D, μ and r_s were obtained from literature.

3.4.2. Estimation of mean pore diameter r_p of membranes

UF membranes are normally characterized^{167,168} by taking different molecular weight of polyethylene glycol (PEG) and polyethylene oxide (PEO). The stokes radii of these species are calculated using the Eq. 3.17 for PEG and Eq. 3.18 for PEO:

$$A = 16.73 \times 10^{-10} M^{0.557}$$
(3.17)

$$A = 10.44 \times 10^{-10} M^{0.587}$$
(3.18)

where, A is Stoke radius of solute in cm, M is molecular wt. in g/mol.

Following Singh et al.¹⁶⁷ and Michaelis et al.¹⁶⁸ the pore size distribution is estimated as described; A plot of experimental values of solute rejection (%) of UF membrane against the solute diameter (as estimated from the Stokes radius) yields a straight line on a log normal probability scale. The solute diameter corresponding to 50% solute rejection is taken as the mean pore diameter of membrane (r_p). The geometric standard deviation is obtained by the ratio of

solute diameters corresponding to 83.14% and 50% solute rejection, with the assumption that there exist no steric or hydrodynamic interactions. The mean pore size μ_p and the geometric standard deviation σ_p of the membrane can be considered to be the same as the solute mean size and solute geometric standard deviation. From these two data points, the pore size distribution of a UF membrane can be expressed by the following probability density function

$$\frac{df(d_p)}{dd_p} = \frac{1}{d_p \ln \sigma_p \sqrt{2\pi}} \exp\left[-\frac{\left(\ln d_p - \ln \mu_p\right)^2}{2\left(\ln \sigma_p\right)^2}\right]$$
(3.19)

From mean pore size data and the geometric standard deviation data cumulative distribution function of membrane pore sizes can be obtained.

3.4.3. Estimation of solute diameter (D_s)

Solute diameter of polyethyleneimine were estimated using Stoke Einstein formula (Eq. 3.20) where M_w is the average molecular wt. (g/mol), [η] is specific viscosity (cc/g), N_Ais the Avogadro's Number.

$$D_{s} = 2x10^{10} \left(\frac{3x10^{-3} M_{w}[\eta]}{10\pi N_{A}} \right)^{1/3}$$
(3.20)

3.4.4. Molecular weight distribution of solute

Solute size of polyethyleneimine evaluated from Stoke Einstein Equation is 39 nm with assumed molecular weight of 50 kD. Size distribution of polyethylene-imine has been obtained from Dynamic Light Scattering (DLS). The instrument through its inbuilt software provides the size distribution and molecular weight distribution of given polymer and also the size vs. weight fraction and number fraction data.



Table 3.4: Weight fraction and the corresponding maximum size of PEI as obtained through DLS measurement.

Wt.fraction	0.107	0.281	0.281	0.166	0.089	0.044	0.02	0.008	0.003	0.001
Diameter(nm)	1.8	2.5	3.3	4.5	6.1	8.2	11.1	14.9	20.2	27.2

Fig.3.17 provides the intensity (arbitrary units) vs molecular weight in kD and Fig. 3.18 provides the plot of intensity vs size in nm. The size distribution of polyethyleneimine along with the weight fraction of each range (represented by maximum size) derived there-from through the inbuilt software is given in Table 3.4. For all our studies we have used the size distribution as given in Table 3.4.

3.4.5. Determination of the pore size distribution of membrane

Following the method described in 3.4.2., the experimental values of solute rejection for all the five membranes were plotted in log-normal scale as shown in Fig.3.19. The solute sizes corresponding to 50% and 83.14 % were interpolated from the trend line. The mean pore size and standard deviations were calculated as shown in Table 3.5.

As seen in the Table 3.5, the mean pore size of the Psf-RGO-UF-1 (3.89 nm) membrane reduces upon incorporation of 1 wt % of RGO onto Psf host matrix (7.1 nm). The mean pore size (3.69 nm) further reduces for 2 wt % loading (Psf-RGO-UF-2) and subsequently it increases upon loading of RGO beyond 4 wt %. The trend in mean pore size obtained is well in accordance with the experimental solute rejection behaviour obtained as shown in Fig. 3.14. However, the pure water permeability, as shown in Fig. 3.15, increases with increase in loading of RGO. This observation is against the usual trend observed in any membrane process, that is the existence of trade-off between flux and selectivity, which has been violated here. The reasoning behind such observation could lie in the enhanced water permeation through the RGO interlayers as explained in section 3.3.3. Whereas, with the defects caused on the membrane surface with increase loading of RGO (beyond 4 wt %), the solute rejection decreases on the account of increase in mean pore size.

3.4.6. Validation of membrane permeability and solute rejection

Attempts were made to validate the model developed in-house with the experimental findings of water permeability and solute rejection attributes offered by the membranes. The plot showing

the validation of permeability and solute rejection are given in Fig. 3.20 and Fig. 3.21, respectively. The associated error (experiment vs modeling) has been shown in Table 3.6.

Membrane	Psf-UF	Psf- RGOUF- 1	Psg-RGO UF-2	Psf-RGO UF-3	Psf-RGO UF-4
Mean pore size(nm)	7.1	3.89	3.69	4.74	6.6
Standard Deviation (σ_{p})	2.33	2.62	2.65	3.16	2.5

Table 3.5: Mean pore size & standard deviation of the membranes.



Fig. 3.19: Solute rejection vs mean solute size of pure Psf and Psf-RGO membranes.



Fig. 3.20: Validation of membrane permeability.



Fig. 3.21: Validation of membrane solute rejection

As evident, the model is well validated with the error lying within 10 % in all cases. The better agreement between the predicted model values and the real experimental data at higher loading is not clear and that needs to be further looked into.

		Experimental	Model					
	Filler	permeability	Permeability	Experimental	Model	Error in	Error in	
Membrane	fraction	(m/s)10^-5	(m/s)10^-5	rejection	rejection	permeability	rejection	
Psf-RGO	0.01	2 (57	2.42	00.4	96.6	0.0(2072	0.042025	
UF-1	0.01	3.03/	3.43	90.4	80.0	0.062073	0.042033	
Psf-RGO								
UF-2	0.02	4.166	3.9	93.8	87.2	0.06385	0.070362	
Psf-RGO								
UF-3	0.04	4.722	4.4	78.3	81.9	0.068191	-0.04598	
Psf-RGO	0.00		5.27	745	72.0	0.022.122	0.000207	
UF-4	0.08	5.55	5.37	74.5	/3.8	0.032432	0.009396	

Table 3.6: Error (experiment vs modeling) in water permeability and solute rejection of membranes.

3.5. Conclusions

Psf-RGO composite UF membranes with varying proportions of RGO were prepared using phase inversion technique and characterized using various instrumental techniques. The flux and solute rejection studies were carried out using solutions of different molecular weight PEG and PEO. It was observed that an optimum loading of RGO (2 w/w% of Psf) resulted in membranes with MWCO of 30 kDa without compromise in flux as compared to the pure polysulfone membranes with MWCO of 100 kDa. In addition, the optimum loading of RGO (2 w/w% of Psf) resulted membranes with better thermal and mechanical stability. The experimental findings wrt flux and selectivity were modeled with an in-house developed model using Kedem-Katchalsky's irreversible thermodynamics approach and validated.

CHAPTER -4

Development of Bio-fouling Resistant Nanocomposite

Membranes
4.1. Introduction

An ideal membrane should provide reasonable flux without compromise in selectivity. The most important shortcoming associated with the membrane based processes is the fouling of membrane surface because of microorganisms. The fouling so caused is known as biofouling, which is responsible for decline in flux and also in the deterioration of membrane material. Recent years have seen the usage of as-grown and composite carbon nanotubes (CNTs) for microbial control¹⁶⁹⁻¹⁷³ because of their unique physical and chemical properties. Ag exerts an important role as a persuasive bactericidal agent in water disinfection. The anti-microbial efficacy of Ag, in zero-valent and ionic form, against bacteria, viruses and other eukaryotic micro-organisms have been studied in great details.^{33,174-176} The present chapter would discuss the work undertaken in the direction of development of anti biofouling membranes by incorporation of silver and CNTs. Also the important development in terms of a point of use (PoU) Psf-silver nanocomposite based water purification device has been highlighted.

4.2. Psf-silver nanocomposite membrane development

In the developing countries, most of the household water treatment technologies include chemical treatment methods like ozonation and chlorination, ultraviolet treatment, distillation etc. These current approaches have a large foot print and are not in a position to comply with the upcoming water quality standards of the developing urbanized and industrialized nations. It has been realized that a well-defined and well-engineered nanoscale material based PoU water purification device for household applications should come into force to take care of safe water needs for all the sections of our society. With this objective in mind, efforts were oriented to develop an antibiofouling membrane with incorporation of Ag onto Psf matrix. Suitable modification in the membrane formulation was carried out to enable it serve as a PoU water purification device.

4.2.1. Experimental

4.2.1.1. Materials

Psf (Psf; M_w: 30k Da) polymer was obtained from M/s. Solvay Specialties India Pvt. Ltd. The solvent, N-methyl-2-pyrrolidone (NMP) with minimum assay of 99.5% and porogen, Polyvinyl pyrrolidone (PVP, K-30; M_w: 40k Da) of AR grade, as used as such without further purification were procured from SRL Pvt. Ltd. (India). Silver nanoparticles (Ag-nps; particle size: < 100 nm) were procured from M/s. Aldrich. For evaluation of rejection behaviors of the membranes towards organic solute, poly(ethylene oxide) (PEO, Mw: 100k Da) was procured from Sigma-Aldrich. SYTO stain was purchased from Invitrogen, Carlsbad, USA. Tryptone, yeast extract and agar were procured from Difco Laboratories, Detroit, MI, USA. Sodium chloride of AR grade was procured from Thomas Baker (Chemicals) Limited, India. Commercially available porous (nominal pore size: 5-10 μ m) polypropylene (PP) candle-cartridges (dimension: 20.32 cm in length and 5.08 cm in diameter, effective surface area: ~ 300 cm²) were employed as mechanical support during preparation of the membranes in candle-configurations.

4.2.1.2. Preparation of polymer dope solutions

For fabrication of Psf:Ag-nps composite UF membranes in sheet-configurations and further selectively in candle-configurations, two different sets of polymer dope solutions (Set-A and Set-B, presented in Table 4.1 and Table 4.2, respectively), each comprising of five varying compositions were prepared by employing different proportions of Ag-nps.

	Membrane Compositions				
Membrane Code	Psf (g)	PVP (g)	NMP (ml)	Ag-nps(g)	
Psf UF-A				-	
Psf:Ag-1 UF-A				1	
Psf:Ag-2 UF-A	100	40	500	2	
Psf:Ag-4 UF-A				4	
Psf:Ag-6 UF-A				6	
1 SI.Ag-0 01 -A				0	

Table 4.1: Compositions of the prepared dope solutions (Set-A).

Table 4.2: Compositions of the prepared dope solutions (Set-B).

	Membrane Compositions			
Membrane Code	Psf (g)	PVP (NMP	Ag-nps (g)
		g)	(ml)	
Psf UF-B				-
Psf:Ag-0.25 UF-B				0.25
Psf:Ag-0.50 UF-B	100	75	500	0.5
Psf:Ag-1 UF-B				1
Psf:Ag-2 UF-B				2
Psf UF-B Psf:Ag-0.25 UF-B Psf:Ag-0.50 UF-B Psf:Ag-1 UF-B Psf:Ag-2 UF-B	100	g) 75	(ml) 500	0.25 0.5 1 2

More specifically, the extent of the nanoadditive, *i.e.*, Ag-nps was varied at 1, 2, 4 and 6 $(w/w_{Psf})\%$ in the dope solutions of Set-A, comprising of 20 $(w/v_{NMP})\%$ of Psf and 40 $(w/w_{Psf})\%$ of the porogen, PVP. On preparation of the dope solutions of Set-B, the extent of Ag-nps was varied at 0.25, 0.5, 1 and 2 $(w/w_{Psf})\%$, but with an enhanced incorporation of the PVP at 75 $(w/w_{Psf})\%$ in the Psf with concentration of 20 $(w/v_{NMP})\%$. Initially, the dispersed Ag-nps in NMP, kept in hermetically sealed glass bottles were undergone ultrasonic treatment for 30 min,

prior to the addition and subsequent mixing of dried Psf beads and PVP, maintaining the specified compositions. The dope solutions were vigorously agitated for several hours to accomplish complete dissolution of Psf and PVP in the solvent with homogeneously dispersed Ag-nps. Then, the resultant viscous dope solutions (Set-A and Set-B) were kept for overnight in an environmentally controlled atmosphere maintaining the temperature and relative humidity at $25(\pm 1)$ °C and 35-40 %, respectively, to eliminate the trapped air bubbles from the solutions.

4.2.1.3. Preparation of mixed-matrix (Psf:Ag-nps) UF membranes

Prior to fabrication of the UF membranes of two different categories, following non-solvent induced phase inversion method, cleaned glass plates (without having any support fabric) were taped onto their parallel ends in such a way that each of the resulting membranes layer could achieve a thickness of 200 μ m. The as-prepared stable dope solutions of Set-A and Set-B were cast onto the taped glass plates at a steady casting shear. The entire assemblies comprising of the cast films were immediately immersed in a precipitation bath containing ultra-pure water as non-solvent, maintained at room temperature, for immersion precipitation. To ensure the adequate exchange between solvent and non-solvent followed by a resultant absolute removal of the porogen as well as the solvent from the membrane matrices, the resulting membranes were taken out of the water bath and rinsed in fresh water for several times. The entire casting process was carried out in a controlled environmental atmosphere, where temperature and relative humidity were maintained at 25(±1) °C and 35-40%, respectively.

Further, with a desire to scale up the development and contribute in domestic water purification, the features of the as prepared membrane were methodically propagated from the sheetconfiguration to a candle-configuration through development of a device comprising of a mixedmatrix UF membrane candle. A schematic of the two-compartment filtration device is shown in Fig. 4.1a and the actual unit comprising of the mixed-matrix UF membrane candles is presented in Fig. 4.1b.



Fig. 4.1: Two-compartment filtration device: (a) Schematic showing flow path of the stream during filtration; (b) actual unit comprising of a mixed-matrix (Psf:Ag-nps) UF membrane candles.

The development was carried out using the optimized composition of the polymeric dope solution of Set-B (the composition as adopted for development of Psf:Ag-1 UF-B). For comparison purpose, the composition of Set-A as adopted for development of Psf UF-A was also employed for development of UF membrane in candle-configuration. Porous PP-candle cartridges with an effective surface area of ~ 300 cm² and nominal pore size of 5-10 μ m (inset of Fig. 4.1) were employed as base matrices to provide mechanical supports. The formation of membranes through the process of non-solvent induced phase-inversion was allowed to occur on these base matrices following a dip-coating technique, for an optimized residence time. During this period, smooth grey colored Psf:Ag-nps composite film (approximate thickness of 200 μ m) was appeared on the candle cartridge surface. The complete removals of the solvent, NMP and porogen, PVP were ensured through a long time exposure of the candle-cartridges in water baths. The entire process of fabrication was conducted under the similar environmentally controlled atmosphere, *i.e.*, with temperature of $25(\pm 1)$ °C and relative humidity of 35-40 %.

4.2.1.4. Physicochemical characterizations of the mixed-matrix (Psf:Ag-nps) UF membranes

The morphological analyses for the Psf UF and the mixed-matrix (Psf:Ag-nps) UF membranes of two different categories were performed using SEM (Model: SERON AIS2100, South Korea). For SEM imaging purposes, membranes having an area of 0.5 cm² were cut and fractured in liquid nitrogen into smaller sized strips. Then the cross-sectional layers were sputter coated with Au/Pd (60/40) using a sputter coater (Model No. K550X Emitech), under the optimized conditions (Sputtering time: 60 s, Sputter current: 30 mA and Tooling factor: 2.3), in order to reduce the effect of charging making them electrically conductive. All the micrographs were recorded employing identical acceleration voltage of 20 keV and 1000X magnifications when operated in secondary electron mode, for better comparison purpose.

Quantitative elemental analysis of the membrane surfaces was performed by an energy dispersive X-ray spectrometer (EDX, INCA Oxford Instruments, UK), coupled to the SEM (SeronTechnologies INC, Korea) and a micro-analysis system. It was equipped with an ultrathin beryllium window and 20 mm² Si detector. For EDX analysis, an accelerating voltage of 20 keV and a magnification of 4000X were employed. The spectra were acquired for the element of interest, *i.e.*, Ag-nps, as impregnated in the membrane matrices at varying concentrations and C, S, O as well.

Topographical characterizations of the membranes (namely Psf UF-A, Psf:Ag-1 UF-A, Psf:Ag-4 UF-A and Psf UF-B, Psf:Ag-0.25 UF-B, Psf:Ag-1 UF-B) skin surfaces were carried out by

extracting quantitative informations in the semi-contact mode by using an AFM instrument (NT-MDT SOLVER next, Russia). Small squares of approximately 1 cm² of the membranes were cut and glued onto a metal substrate. The rectangular cantilever NSG 10 (NT-MDT, Russia) was made out of Si₃N₄ with a spring constant of 11.8 N/m, having a typical resonance frequency of 240 kHz and a nominal tip apex radius of 10 nm with high aspect ratio. The scanning was done on a 10 μ m × 10 μ m area of the membrane, in air, at room temperature, with a scanning frequency of 0.1 Hz. The scanned regions were flattened using a second order polynomial to remove the curvatures and slopes from the image and then the resulting best fit was subtracted from it. For the purpose of image acquisition and evaluation of surface roughness parameters of the membranes NOVA-P9 software was used. Surface roughness parameters of the membranes were calculated from the height profiles of the images in terms of average roughness (R_a).

Static contact angle measurements, at ambient temperature, were conducted using sessile drop method. A contact angle measuring instrument (DSA 100 of KRUSS Gmbh, Germany) with DSA 1v 1.92 software was employed to assess the hydrophilicity of the skin layers of the membranes, namely Psf UF-A, Psf:Ag-1 UF-A, Psf:Ag-4 UF-A and Psf UF-B, Psf:Ag-0.25 UF-B, Psf:Ag-1 UF-B. The sessile drop was allowed to form slowly and steadily on each of the membrane surface by depositing 3 μ l of the probe-solvent (water) with a microsyringe. The measurements at the membrane-solvent-air interface were completed with an equal residence time of 60 s. At least eight such measurements were done at different locations of each membrane surface and then averaged out to calculate the contact angle and their standard deviations.

The electrokinetic features of the similar sets of membranes were evaluated by employing Zeta CAD electrokinetic analyzer (CAD Inst., France). The streaming potential analyzer consisted of a quartz-cell configuration was capable of holding two flat sheet membranes in such a way that the membranes remained separated by spacers and the skin layers faced each other creating a slit channel for tangential flow of electrolytic solution across the membranes. The electrical potential difference, generated due to the bidirectional flow of 10⁻³M KCl as background electrolyte solution, under applied pressure gradient across the membrane was measured by Ag/AgCl electrodes, equipped with the cell. Zeta potentials (ζ) of the membranes were evaluated using the streaming potential values and on the basis of Helmholtz-Smoluchowski equation (Eq. 2.11). An average value of ζ , derived from three replicates was reported and the measurement error was found to be \pm 0.4 mV.

For measurement of porosity of the Psf UF and the mixed-matrix (Psf:Ag-nps) UF membranes, gravimetric method was applied and porosity was found out using Eq. 2.18. In order to minimize the experimental error, measurements were carried out in duplicates and then calculated the average. Utilizing the porosity of the membrane, mean pore radius (r_m in nm) was also determined by employing the Guerout–Elford–Ferry equation¹⁷⁷ (Eq. 2.19).

4.2.1.5. Evaluation of performances of mixed-matrix (Psf:Ag-nps) UF membranes

Pure water permeability measurements of all the membranes with effective membrane area of 14.5 cm^2 , were conducted under a cross-flow filtration mode operated at 1 bar of transmembrane pressure. The steady-state pure water permeability (PWP, L.m⁻².h⁻¹) was determined by direct measurement of the permeate flow, *i.e.*, volume (V, in L) collected during a time period (T, in h), through a membrane area (A, in m²). Prior to all UF test experiments, membranes were initially

subjected to undergo hydraulic compaction for 1 h in water at standard UF test conditions, to achieve stabilized performances of the membranes.

Measurements of rejection behaviors of the membranes were carried out using neutral organic solute, PEO with average Mw of 100 kDa, respectively. The test solution was prepared by dissolving pre-weighed amount of PEO in ultra-pure water at a concentration of 200 ppm. The solute rejection studies were carried out at a transmembrane pressure of 1 bar at room temperature. The concentrations of PEO in both feed and product solutions were measured by analysing the total organic carbon (TOC) content of the samples using TOC analyzer (ANATOC-II, SGE analytical science, Australia).

To evaluate the extent of depletion of the impregnated Ag-nps during cross-flow filtration mode ultra-pure water was subjected to filtration, employing the membrane (with the derived optimized composition) in sheet-configuration at a transmembrane pressure of 1 bar. The study was also applied to evaluate the depletion behavior of the Ag-nps in candle-configuration, when the candle was settled in the said filtration device with water level in the feed adjusted to different heights, 1 to 10 ft, equivalent to a hydrostatic pressure range of 0.03 to 0.3 bar. The experiments were conducted at $25(\pm 1)$ °C. The product samples were collected for about two months on daily basis (24 liters per day) and analyzed for total Ag content using a VG PQ Excell, (UK) Inductively Coupled Plasma-Mass Spectrometer (ICP-MS), with Argon as carrier gas.

4.2.1.6. Membranes bacterial rejection efficiency

To perform the bacterial retention test for the Psf UF and the mixed-matrix (Psf:Ag-nps) UF membranes in sheet-configurations, a strain of *E. coli* (MG 1655) culture was grown overnight at

37 °C. The *E. coli* cells were harvested at mid-exponential growth phase (~ 10^8 cfu/ml) in sterile Luria Bertani (LB) broth upon incubation at 37 °C under shaking conditions (shaker: Lab-line 4631 Maxi Rotator) at 150 rpm. The density was assumed as 5×10^8 cfu/ml. It was then diluted in sterile saline to a density of 8×10^5 cfu/ml and subsequently purged into the experimental setup with the appropriate membranes for 45 min. Feed and product samples were collected at same time. The samples comprising of bacterial suspension at varying concentrations were agitated in a rotor (Sorvall SS-34) at 15,000 rpm for 2 min and then diluted in such a way that the number of colonies formed by next day varied from 30 to 300. Each sample with a volume of 100 ml was plated and incubated overnight. Colonies were counted on next day. For carrying out the procedures for each of the membranes, fresh cultures of concentration 8×10^5 cfu/ml were prepared.

4.2.1.7. Membranes resistivity on static bacterial adherence

The bacterial culture was also used as the feed to flow in the membrane assembly mounted with the different test membranes. After 2 h of continuous flow, the membrane coupons were retrieved from the assembly and rinsed twice with sterile saline. Circular sections (diameter: 0.4 cm) were punched out from different regions of the membranes and subjected to undergo microscopy studies to analyze the extent of adherence of bacteria to each of the membrane surface. For this purpose, the membranes circular sections were stained with nuclear stain SYTO (6.7 μ M final concentration) for 15 min in dark. The membranes sections were rinsed in saline twice and observed under a fluorescent microscope (Carl Zeiss Axioplus, Germany) with blue excitation (488 nm). The adhered bacterial cells glowed green due to SYTO binding to DNA. For every sample membrane, four different circular sections were observed under the microscope and then, for each circular section 10 fields were observed. Representative images were acquired with microscope associated camera and software. For viability studies, the cross-sections from each test membrane were placed on Luria agar plates with a sterile forceps. The plates were incubated at 37 °C for 24 h. At the end of incubation, the presence or absence of growth was observed visually and the images were obtained by scanning the plates.

4.2.1.8. Membranes bacterial inhibition ability

To assess the biofouling behavior of the membranes under dynamic test conditions, the bacterial culture was further used as the feed flowing in the membrane assembly mounted with the different test membranes. After 2 h of flow the membrane coupons were retrieved from the assembly and rinsed twice with sterile saline. Representative circular sections (diameter: 0.4 cm) were punched from each membrane after flushing with bacteria culture, and placed on Luria agar plates and incubated at 37 °C for overnight. After that, the agar plates were visually observed for detection of the growth of bacteria colonies.

4.2.2. Results and discussions

4.2.2.1. Analysis of physicochemical features of the mixed-matrix UF membranes

The mixed-matrix UF membranes, fabricated following the familiar technique of non-solvent induced phase inversion process are found to consist of asymmetric porous structures. Such morphological characteristics get observed, when the porous features of the representative investigated UF membranes (*i.e.*, Psf:Ag-4 UF-A of Set-A and Psf:Ag-1 UF-B of Set-B) are analyzed based on the respective cross-sectional SEM images, presented in Fig. 4.2. The pore structure of the dense skin region differs in size, shape as well as density from the porous feature

of the interior of the substructure *i.e.*, the continuous sublayer of the membrane. The formation of more porous sublayer is pronounced in case of Psf:Ag-1 UF-B, when Psf dope solution comprising of higher amount of hydrophilic porogen (PVP) is employed for casting of the membrane, in view of the fact that such variations in morphology of the membranes are assumed to vary with the phase behaviors of the Psf dope solutions as well as the dynamics of indiffusion-outdiffusion mechanism of the nonsolvent-solvent system, during the occurrence of phase separation of the polymer.¹⁴³ It is an established fact that the formation of phase inversion membranes are regulated by thermodynamic as well as kinetic variations, resulting either instantaneous or delayed demixing during precipitation of the casting polymer solutions.¹⁸⁶Thus, use of PVP in higher amount seems to result in thermodynamic instability and thereby enhances the rate of instantaneous demixing of the Psf with the non-solvent.^{144,145}The resultant change in formation mechanism of the porous feature of base polymer matrix evidently synchronizes the concurrent process of in-situ impregnation of Ag-nps, influencing the distribution pattern as well as extent of exposure of the nanoparticles in the mixed-matrix UF membrane. Visual inspections of the pores structural features, for the membranes Psf:Ag-4 UF-A (Fig. 4.2a) and Psf:Ag-1 UF-B (Fig. 4.2b) reveal that the former mixed-matrix UF membrane maintains a dense skin layer with finger-like porous substructure associated with fine porous walls, however, the latter carries a distinctive substructure comprising elongated finger-like pores associated with high density of pores as well as larger macro-voids in the porous walls, residing underneath a comparatively thin skin layer. The variations significantly indicate that the formation mechanism of latter class tunes the morphology in such a manner that they (representatively, Psf:Ag-1 UF-B) bear more open finger-like porous substructures with higher void volumes, which in turn provide suitable polymeric confinements for a facilitated distribution of the impregnated Ag-nps.



Fig. 4.2: Cross-sectional SEM images of the mixed-matrix UF membranes, (a) Psf:Ag-4 UF-A; (b) Psf:Ag-1 UF-B.

Elemental analyses of the membranes cross-sections, carried out using EDX study ascertain that other than the desired elements, no other elemental impurities are present in the polymer matrices of the mixed-matrix UF membranes. In the EDX spectra of Psf UF-A and Psf UF-B membranes (Fig. 4.3a and 4.3b, respectively), only C, S and O peaks are obtained, whereas distinct elemental peak of Ag gets obtained along with C, S and O peaks in the Psf:Ag-4 UF-A (Fig. 4.3c) and Psf:Ag-1 UF-B (Fig. 4.3d) membranes. The nominal change in intensity of the characteristic peak of Ag substantiates that there remains differential distribution of the element of interest in Psf:Ag-4 UF-A and Psf:Ag-1 UF-B. This is believed to happen because of change in porous feature of the membrane of latter class where the nanoparticles are retained within a more open network of the polymer and subsequently become enable to get exposed, in spite of the fact that there is higher amount of Ag-nps impregnated in the former class of membrane. The Au peaks, as found invariably in all the spectra are due to absence of Au correction.



Fig. 4.3: EDX spectra of membranes, (a) Psf UF-A, (b) Psf UF-B and (c) Psf:Ag-4 UF-A, (d) Psf:Ag-1 UF-B.

Quantitative evaluation of the topographical features of membranes skin surfaces, investigated through AFM, finds a distinctive trend in variation of the roughness parameters *i.e.*, average roughness (R_a) and root mean square roughness (R_q). They vary significantly from a relatively smooth surface profile for the Psf UF membranes to progressively rough surfaces for the mixed-matrix UF membranes, derived employing the polymeric dope solutions of Set-A and Set-B with higher impregnation of Ag-nps. This seems obvious as gradual increase of both, R_a and R_q values (Table 4.3) is observed for the membranes, namely Psf UF-A, Psf:Ag-1 UF-A and Psf:Ag-4 UF-A, which are found to be about 4.59, 16.36, 29.23 nm, respectively and 7.16, 23.26, 39.37 nm, respectively. A similar trend (Table 4.3) is also noticed for the membranes, namely Psf UF-B, Psf:Ag-0.25 UF-B andPsf:Ag-1 UF-B, where R_a and R_q values are found to be 3.28, 6.57, 14.24

nm, respectively and 5.62, 10.21, 21.72 nm, respectively. The observed linear relationship between the enhancement in surface roughness parameters and the concentration of Ag-nps reflects to the variation in extent of non-uniformity in distribution of the Ag-nps, within the polymeric skin layers of the mixed-matrix UF membranes.

Table 4.3: Variations in roughness parameters of membrane surfaces, derived from Set-A and Set-B.

	Membrane Codes					
Parameters	Psf UF-A	Psf:Ag-1 UF-A	Psf:Ag-4 UF-A	Psf UF-B	Psf:Ag-0.25 UF-B	Psf:Ag-1 UF-B
R _a (nm)	4.59	16.36	19.23	3.28	6.57	14.24
$\mathbf{R}_{q}\left(\mathbf{nm}\right)$	7.16	23.26	29.37	5.62	10.21	21.72

However, a comparison of the surface roughnesses of Psf:Ag-1 UF-A and Psf:Ag-1 UF-B reveals that the extent of uneven distribution of the Ag-nps within the skin layers of the membranes is more pronounced for the dense and less porous polymer matrix of the former as compared to the thin and more porous polymer matrix of the latter.

Analysis of contact angle results, presented in Table 4.4, derived for the membranes, *i.e.*, Psf UF-A ($80.4\pm0.1^{\circ}$), Psf:Ag-1 UF-A ($56.2\pm0.4^{\circ}$) and Psf:Ag-4 UF-A ($61.6\pm0.2^{\circ}$) reveals that hydrophilic behaviors of the mixed-matrix UF membranes depend on the extent of Ag-nps and the nanoparticles physicochemical features as well. Such variation also gets observed for the membranes of other categories, *i.e.*, Psf UF-B, Psf:Ag-0.25 UF-B and Psf:Ag-1 UF-B (Table 4.4), where the contact angle values decrease from $76.3\pm0.2^{\circ}$ to $73.6\pm0.5^{\circ}$ and further to $63.9\pm0.8^{\circ}$. The membranes of former category exhibit noticeable decline in contact angle values, which are assumed to happen due to more superficial distributions of the impregnated Ag-nps in the dense skin regions of the membranes. The role of Ag-nps in inducing hydrophilicity, in spite

of having weak affinity to polar medium can be speculated as their ability towards generation of hydrated Ag⁺, when the probe-solvent (water) comes in contact with the Ag-nps residing at the skin regions of the membranes.¹⁷⁸ However, the little enhancement in contact angle value at further impregnation of Ag-nps, as observed in our study for the membranes derived employing Set-A is attributed to the effect of nanoparticles aggregation.¹⁷⁹ On other side, although the membranes of latter category (Set-B) reflect a distinct improvement in hydrophilicity, but it remains less pronounced in comparison to the former category. A comparison of the hydrophilic characters of Psf:Ag-1 UF-A and Psf:Ag-1 UF-B corroborates the fact in a better way. This behavior implies that the Ag-nps experience a better and uniform distribution within the skin region of a mixed-matrix UF membrane, when more porous polymer matrix is employed as a base for impregnation of the nanoparticles.

The electrokinetic features of the membranes, represented in Table 4.4, are determined by tangential streaming potential measurements with respect to 10^{-3} M KCl solution. This study further demonstrates the role of membranes microstructural features on distribution of the nanoparticles within mixed-matrix UF membranes. For all the membranes, the ζ remains negative, however, the magnitude of ζ decreases when it distinctively varies from -9.60 to -8.64 mV through -4.89 mV for Psf UF-A, Psf:Ag-1 UF-A and Psf:Ag-4 UF-A, respectively. Similar incidents of decline in the magnitude of ζ are also observed for the other category of mixed-matrix UF membranes, where the ζ changes from -11.38 to -10.72 mV for Psf UF-B and Psf:Ag-0.25 UF-B, and then to -8.96 mV for Psf:Ag-1 UF-B.Such trend in decline of ζ substantiates the role of the proposed incidence of oxidative transformation of the impregnated Ag-nps, as discussed during analysis of hydrophilic features of the membranes. The variations

also signify the effect of enhanced impregnation of Ag-nps in the mixed-matrix UF membranes, where the impregnated Ag-nps induce dragging of the tangentially driven Cl⁻ to the bulk of the membranes stationary positively charged sites (Ag⁺ of Ag-nps), leading to shielding of the membranes apparent surface negative charge and thus, effective ζ of the membranes. A further exhaustive analysis of the variation in mixed-matrix UF membranes effective surface charge (*i.e.*, -4.89 mV of Psf:Ag-1 UF-A to -8.64 mV of Psf:Ag-4 UF-A and -10.72 mV of Psf:Ag-0.25 UF-B to -8.96 mV of Psf:Ag-1 UF-B) reflects the apparent homogenised presence of the charged sites through better uniformity in distribution of nanoparticles, the feature which exists within the exterior regions of the more porous polymer matrices of the later.

Table 4.4:Variations in hydrophilic and electrokinetic features of membrane surfaces, derived from Set-A and Set-B.

			N 1	C 1		
		Membrane Codes				
Parameters	Psf UF-A	Psf:Ag-1 UF-A	Psf:Ag-4 UF-A	Psf UF-B	Psf:Ag-0.25 UF-B	Psf:Ag-1 UF-B
Contact angle (°)	80.4 ± 0.1	56.2 ± 0.4	61.6 ± 0.2	76.3 ± 0.2	73.6 ± 0.5	63.9 ± 0.8
ζ (mV)	-9.60	-4.89	-8.64	-11.38	-10.72	-8.96

The determination of surface porosities (Fig. 4.4) of the mixed-matrix UF membranes provides quantitative estimation in change of membranes void volume *i.e.*, the porous features on enhanced impregnation of Ag-nps. The mixed-matrix UF membranes show progressive decline in the porosity as it changes from $73(\pm 1)$ % of bare membrane, *i.e.*, Psf UF-A to $69(\pm 2)$ % for Psf:Ag-1 UF-A and then further to $66(\pm 1)$ % for Psf:Ag-4 UF-A. Similar decline in the trend of porosity is also observed when it varies from $82(\pm 2)$ % for Psf UF-B to $73(\pm 2)$ % for Psf:Ag-1 UF-B through $77(\pm 1)$ % for Psf:Ag-0.25 UF-B. Presence of higher amount of Ag-nps and their

consequent aggregation within polymer matrix seem to reduce the void volumes of the membranes. However, a comparison of the porosities of Psf:Ag-1 UF-A and Psf:Ag-1 UF-B provides further in-depth understanding about the variations in porosities, as use of more porous polymer matrices in constructing the microstructure of the mixed-matrix UF membranes resists the notorious effect of diminution of porosity on enhanced impregnation of Ag-nps.

Further estimation of the membranes' mean pore radius, utilizing the results of porosities and Eq. 2.19 indicates that the membranes derived employing large quantity of the porogen and comparatively less quantity of the nanoadditive have got significantly enlarged entrance routes for facilitated permeation of molecular species than the membranes of other category derived employing less amount of PVP and higher amount of Ag-nps. The trend in enlargement of mean pore sizes *i.e.*, approximately from 60 to 63 nm and then to 68 nm for Psf UF-A, Psf:Ag-1 UF-A and Psf:Ag-4 UF-A, respectively and approximately from 132 to 141 nm and further to 148 nm for Psf UF-B, Psf:Ag-0.25 UF-B and Psf:Ag-1 UF-B, respectively corroborates the above discussed fact.



Membrane types (Set-A and Set-B)

Fig. 4.4: Variations in porosities of membranes derived from Set-A and Set-B.

4.2.2.2. Study of membranes solute rejection and solvent throughput behaviors

The macroscopical features analyzed through determination of solute rejection and pure water permeability, presented in Fig. 4.5 (for Set-A) and 4.6 (for Set-B) indicate the physicochemical variations of the membranes, where significant contribution of the porogen in tuning the porous features and subsequent effect in distribution of the nanoadditive within the polymer matrices of mixed-matrix UF membranes are observed. The membranes derived employing the compositions of Set-A show a gradual decrease in the rejection of neutral organic solute like PEO (100k Da). The %SR (Fig. 4.5a) of bare Psf UF-A decreases from 99.5(±0.2) to 98.2(±0.3)% for Psf:Ag-1 UF-A as 1(w/w_{Psf})% of Ag-nps is impregnated in the latter. This further reduces to 97.6(±0.1)% for Psf:Ag-2 UF-A, 96.2(±0.1)% for Psf:Ag-4 UF-A and then 95.1(±0.3)% for Psf:Ag-6 UF-A, on impregnation of 2, 4 and 6(w/w_{Psf})% of Ag-nps, respectively. Such variation is attributed to the effect of nanoparticles aggregation at higher concentration and consequent presence of clusters of Ag-nps in membrane matrices, thereby creating local defects and allowing the enhanced permeation of the solute molecules as further evident from the variations in mean pore sizes.¹⁸⁰ It is supposed to the fact that the compositions of the dope solutions of Set-A comprising of PVP at lower concentration, 40 (w/w_{Psf})% and Ag-nps at higher concentration *i.e.*, 1, 2, 4 and 6 (w/w_{Psf})% apparently remain ineffective to reduce the van der Waals pair interaction energy, which is a measure of interparticle interactions.¹⁸¹ The said energy parameter is known to be proportionally dependent on the Hamaker constant, which inversely depends on the separation distance between the nanoparticles and differs with the concentration and surrounding chemical environment of the nanoparticle. The macroscopical impact of nanoparticles propensity towards enhanced aggregation at higher concentration, as observed through the membranes solute rejection efficiencies is thus owing to higher interparticle attractive force and, hence, making them more prone to come closer and induce flocculation.¹⁹¹The study of PWP of the membranes (Fig. 4.5b) shows that it changes gradually from $414(\pm 2)$ LMH for Psf UF-A to $420(\pm 3)$ LMH for Psf:Ag-1 UF-A and then to $428(\pm 1)$ LMH for Psf:Ag-2 UF-A. However, at higher impregnation of Ag-nps, the PWP varies to a larger extent *i.e.*, from $450(\pm 4)$ LMH for Psf:Ag-4 UF-A to $489(\pm 2)$ LMH for Psf:Ag-6 UF-A. The ascending trend in solvent throughput of the mixed-matrix UF membranes corroborates the facts of enhancement in effective surface areas, improvement of surface hydrophilic behaviors as well as the possible formation of local defects due to entrapment of Ag-nps as clusters in the polymer matrices, resulting enhanced permeation of the solvent in spite of the progressive loss of porosity.



Fig. 4.5: Variations in (a) solute rejection and (b) pure water permeability of membranes in sheet-configurations, developed from Set-A.

In contrary, the favorable approach of impregnation of Ag-nps in a highly porous polymer matrix stands as productive when the macroscopical behaviors of the membranes belonging to the other

category are analyzed based on their solvent throughputs. Because of formation of comparatively thin skin layers with concurrent existence of high density of pores as well as elongated pore structures, as discussed during analysis of morphological features and further substantiated through the determined mean pore sizes, the mixed-matrix UF membranes derived employing the polymeric compositions of Set-B exhibit a lower rejection towards the solute molecules of PEO (Fig. 4.6a). The %SR of Psf UF-B enhances from $20.3(\pm 0.3)$ to $25.8(\pm 0.2)$ % for Psf:Ag-0.25 UF-B, 28.3(±0.1)% for Psf:Ag-0.5 UF-B, 30.1(±0.2)% for Psf:Ag-1 UF-B and then to31.9(±0.3)% for Psf:Ag-2 UF-B; however, their PWP (Fig. 4.6b) changes from 2480(±4) to $2492(\pm 2)$ and further to $2512(\pm 3)$ LMH, respectively on gradual enhancement in impregnation of Ag-nps from 0.25 to 0.5 (w/w_{Psf})%. The impregnations at even higher concentration of 1 and 2(w/w_{Psf})% of Ag-nps lead to a plateau in the increasing trend of PWP *i.e.*, 2508(±2) and 2502(±1) LMH, respectively. The transport characteristics reveal that the compositions of the dope solution of Set-B comprising of PVP at higher concentration, 75 (w/w_{Psf})% and Ag-nps at lower concentration i.e., 0.25, 0.5, 1 and 2 (w/wPsf)% remain comparatively more effective to diminish the localized effect of higher interparticle attractive force. Such occurrence is believed to happen because of the deployment of lower concentration for the Ag-nps and more importantly the favorable surrounding chemical environment arising due to presence of plenty of PVP molecules around the Ag-nps,¹⁸² which might have wrapped the nanoparticles to induce electrostatic repulsive force for a better stable dispersion of the Ag-nps in the dope solution and consequentially propagating the effect in the respective membranes. The noteworthy enhancement (approximately six fold, comparing Psf:Ag-1 UF-A and Psf:Ag-1 UF-B) in solvent throughput, despite the decline of %SR promisingly reflects on the foremost role of the porogen, PVP in creating more open polymeric network as the porous confinements for facilitated transport of the solvent. These resultant porous confinements are thus supposed to provide more space for the Ag-nps to get uniformly distributed within the polymer matrices, which not only enhances the hydrophilic character of the respective membranes surface as well as compensates the diminution of porosity, but also may create conducting channels (due to formation of $\mbox{Ag}^{\mbox{\tiny +}}$ on contact of the solvent, water with Ag-nps) in the porous sublayer of the membrane. The molecular transport through a semipermeable UF membrane is predominantly controlled by hydrodynamic interactions, but there may exist the simultaneous role of electrostatic interactions for the mixed-matrix (Psf:Ag-nps) UF membranes, where the entrapped ionic sites in the porous pathways increase the hydrodynamic drag due to the improved electrostatic interactions.¹⁸³⁻¹⁸⁵ However, the occurrence of severe lower solvent throughputs for the membranes derived employing the polymer dope compositions of Set-A is ascribed to the diminished effectiveness of the nanoparticles in exerting such physicochemical feature, which is predominantly due to their entrapment as clusters within dense polymer network. Furthermore, a possible distribution of the nanoparticle clusters on the skin surfaces of the membranes, derived employing higher concentration of Ag-nps and a less porous base matrix might have played a role to reduce the passage of solvent transport by blocking the entrances of the pores, the possibility of which seems insignificant in other cases.¹⁷⁶

The investigations as carried out to analyze the depletion behaviors of the impregnated Ag-nps, in both sheet- and candle-configurations of the membrane (selectively Psf:Ag-1 UF-B) reveal that the concentrations of Ag in the permeates remain around 1-5 ppb, as presented in Fig. 4.7. It is noticed that the release of Ag from the mixed-matrix UF membrane, in both the cases and thus the concurrent presence of Ag in permeates get decreased with prolonged process of filtration under a steady operating condition.



Fig. 4.6: Variations in (a) solute rejection and (b) pure water permeability of membranes in sheet-configurations, developed from Set-B.



Fig. 4.7: Variation of Ag depletion from mixed-matrix UF membrane of both sheet- and candle-configuration, during filtration process.

In all cases, the Ag concentration in permeates remains 100 times below the EPA standard (100 ppb) for Ag^+ in drinking water.¹⁸⁶⁻¹⁸⁸ The possible reasons of finding Ag-content in product water are thus attributed to the tentative release of Ag^+ from the surface of Ag-nps as well as the depletion of the Ag-nps. However, the extent of Ag as found in the product water, resulted

through a well controlled release of Ag^+ as well as significantly lower depletion of the Ag-nps remains trivial and obviously within a safe limit, which substantiates the effect of uniform distribution and concurrent favorable entrapment of the Ag-nps within the Psf matrix of the membrane.

4.2.2.3. Study of membranes bacterial rejection efficiencies

Bactericidal efficiencies of the membranes are investigated based on their rejection behaviors towards the gram-negative bacteria, E. coli under dynamic test conditions. The trends in bacterial rejections as obtained with the membranes, prepared employing two different sets of compositions *i.e.*, Set-A and Set-B are presented in Fig. 4.8a and 4.8b, respectively. Amongst the membranes derived from Set-A, the bare Psf UF-A without having any Ag-nps in the membrane matrix exhibits very high resistance (99.99%) towards the permeation of the bacteria, which indicates that the dense semipermeable skin layer enables only the surface pores to exclude the bacteria following a sieving mechanism. However, progressive impregnation of Ag-nps within such dense polymer matrix reduces the bacterial rejection efficiencies of the membranes significantly (i.e., from 99.17 to 97.25%), which is visible through the declining trend of bacterial rejection as presented in Fig. 4.6a. This behavior is supported by the fact that, although there remains high population density of bactericidal nanoparticle in the matrix of each mixedmatrix UF membrane, but the adverse effect of nanoparticles tentative aggregation at high concentration interrupts their effective distribution within the dense polymer matrix of the membranes, creating defects and concurrently providing entrance routes for the bacteria. It further seems that, due to lower surface to volume ratio and associated lower rate in release of Ag⁺, the clusters of Ag-nps turn inefficient to generate enough lethal contacts between their bactericidally-active sites and the surfaces of the cell membranes of *E. coli*, during transport of the stream comprising of living bacteria, through the mixed-matrix UF membrane.¹⁸⁹



Fig. 4.8: Variation in dynamic decontamination behaviors of membrane derived employing a) Set-A and b) Set-B.

The study carried out with other set of membranes, derived employing higher amount of porogen and lower loading of Ag-nps (Set-B) delivers that the concerned mixed-matrix UF membranes distinctively retain the bactericidal characteristics of the impregnated nanoparticles. The bare membrane, Psf UF-B shows 97.72% of bacterial rejection, but the membranes derived employing progressively higher amount of Ag-nps exhibit improved rejection efficiencies as the bacterial rejection enhances from 98.17% (Psf:Ag-0.25 UF-B) to 98.93% (Psf:Ag-0.5 UF-B) and then to a maximum of 99.51% for Psf:Ag-1 UF-B. The results thus ascertain that the impregnated Ag-nps being present in a highly porous matrix of the mixed-matrix UF membrane become able to exert the characteristic mechanistic role in rejecting the bacteria, profoundly. The observations also support the fact that favorable distribution of the Ag-nps within a thin skin layer continued with highly porous matrix facilitates enough lethal interactions to happen between the surface of the cell membrane of *E. coli* and the mixed-matrix UF membranes surface, wrapped with a layer of Ag^+ ions.

4.2.2.4. Study on membranes resistivity on static bacterial adherence

A strong resistivity on static bacterial adherence is obtained for the mixed-matrix UF membrane, Psf:Ag-1 UF-B, when the respective membrane section was observed under fluorescent microscope with blue excitation (488 nm) after being flushed through feed containing bacteria culture, followed by staining with nuclear stain SYTO in dark. Since the adhered live bacterial cells glow green due to SYTO binding to DNA, the fluorescent microscopic images of the membrane sections, shown in Fig. 4.9 substantiate that there is a significant contrast in adherence of live bacteria on the Psf:Ag-1 UF-B (Fig. 4.9b) compared to the pure Psf UF-B (Fig. 4.9a) because of presence of the bactericidal effect of Ag-nps in the former.



Fig. 4.9: Variation in static adherence of E. Coli bacteria on membrane surfaces, a) Psf UF-B and b) Psf:Ag-1 UF-B.

The toxicity of the Ag-nps towards *E. coli* and the resultant perturbation of the cell membrane function of the latter may thus be expected to play in tuning the bacterial adherence behaviors of the membranes, where the lethal interaction is attributed to several hypothesized mechanisms.

Most importantly, the damage of cell membrane integrity induced by the Ag^+ ions, where the ions may interact with sulphur-rich intracellular proteins, likely with the higher affinity thiol groups of respiratory chain proteins.⁸⁷ Such interaction is known to cause death of the cells as it brings severe change in membrane permeability, by a progressive release of lipopolysaccharides (LPS) and membrane proteins, ensuing subsequent dissipation of proton motive force and depletion of intracellular ATP levels.^{190,191} This may also result intracellular accumulation of Ag^+ ions and on a further note cause lethal mutation of DNA.¹⁹² Further, the cell damage may also happen through generation and intracellular accumulation of Reactive Oxygen Species (ROS), assisted by the Ag^+ ions.¹⁹³ It is proposed by some researchers that Ag^+ ions associated with the dissolved O₂ molecules may generate excess of ROS, which further leads to oxidative stress within the cell of *E. coli* because of additional generation of free radicals, damaging both lipids and DNA.¹⁹⁴

4.2.2.5. Study of membranes bacterial inhibition ability

The bacterial inhibition property of the mixed-matrix UF membrane *i.e.*, Psf:Ag-1 UF-B having the maximum bacterial rejection behavior is compared with the bare membrane, Psf UF-B following the inhibition zone method, when they get exposed to a gram-negative bacterial strain. Since the productivity of a membrane proportionally depends on its anti-biofouling property, thus it seems meaningful to evaluate the role of mixed-matrix UF membranes surface in inhibiting the approach of the bacteria towards the surface and concurrently resisting the growth of bacterial colonies, which effectively reduces the chances of irreversible fouling as well as filtration resistance. The Fig. 4.10b shows that Psf:Ag-1 UF-B strikingly exhibits anti-biofouling activity towards the *E. coli*, whereas the bare Psf UF-B (Fig. 4.10a) shows a significant growth

of bacterial colonies, which can be attributed to the presence of Ag-nps within the thin skin regions of the former. The reason behind such signified biofouling resistance behavior of the concerned mixed-matrix UF membrane is attributed to a resultant physicochemical interaction occurred between the Ag-nps and the cells of *E. coli*.



Fig. 4.10: Variation in bacterial inhibition abilities of membrane surfaces, a) Psf UF-B and b) Psf:Ag-1 UF-B.

Silver leaching studies were carried out on the membrane surface to assess the mechanism of water disinfection (from bacteria), which is caused by silver coming down into the product water or the nature of the membrane (surface as well as bulk morphology) itself. Since the silver concentration in the product water is less than the 6-7 ppb in all cases, therefore it was concluded that the nature of the membrane (predominantly the membrane surface (as rightly pointed out by the reviewer) and to some extent the porous bulk) is responsible for the observed bacterial rejection behavior. The extent of depletion of the impregnated Ag-nps, from mixed-matrix UF membrane is found to be insignificant as the concentration of Ag found in the permeates remain below the reported values (4–85 ppb) for the lethal concentration of Ag (Ag⁺ or Ag-nps or both) that results in toxicity for *E. Coli*.^{176,186-188} Interestingly, such insignificant release of Ag, as found in our case indicates that a different mechanistic approach behind the probable physicochemical interaction may be responsible in favor of the profound bacterial inhibition. This further substantiates that the conventional mechanisms behind the toxicity of Ag-nps towards the cell membrane of *E. coli* may not be the sole decisive factors to provide such a very

high (99.51%) bacterial rejection, accompanying with a massive solvent throughput for Psf:Ag-1 UF-B (also has enlarged pores with an approximate mean pore radius of 148 nm, being much larger than Psf UF-A with 60 nm, having 99.99% bacterial rejection) under a dynamic test condition *i.e.*, cross-flow UF. It is thus considered that the bacteria in the feed might have exerted negative chemotactic responses under an anisotropic chemical environment, where the toxic Ag-nps play the role of chemorepellent.¹⁹⁵⁻¹⁹⁷ Generally, within an isotropic chemical environment, the cells of E. coli swim due to the Brownian motion as well as the spontaneous tumbling events happened through the alternating episodes of counter-clockwise (CCW) and clockwise (CW) flagellar rotation. However, under the present altered circumstances arising due to the chemical concentration gradient of Ag^+ , the chemotactic cells of E. coli swim in a favorable direction (away from chemical stimulant or chemorepellent) with more numbers of tumbling events and subsequently modulate their net-movement towards a preferred environment.¹⁹⁵ Though, the primary role of the flagellum of *E. coli* is locomotion, but being sensitive to specific chemicals they might have played as a sensory organelle to induce such a biased motility.^{198,199} The proposed mechanism, represented in Fig. 4.11, in the present case of finding more bacterial rejection through inhibition on bacterial approach, by incorporation of Ag-nps is thus found promisingly distinctive from the prevalent mechanisms, where the controlled release of Ag⁺ ions from the Ag-nps is subjected to be responsible for bacteria killing.181-183

Interestingly, in the present case, irrespective of the state of bacteria *i.e.*, dead (killed by Ag^+ or Ag-nps) or alive, the product stream seems to remain devoid of bacteria, because of a modified surface which resists the permeation of the bacteria by restricting their approach to the surface.

The trend in growth of bacterial colonies also substantially implies that a favorable distribution of Ag-nps within a benign polymer matrix may stand promisingly effective to provide the desired long term sustainability for the pores of mixed-matrix UF membrane.



Fig. 4.11:Schematic of the chemotactic behavior of E. coli, under an anisotropic chemical environment.

4.2.3. Study of mixed-matrix UF membranes salient features in candle-configuration

The mixed-matrix UF membrane (Psf:Ag-1 UF-B) in candle-configuration, assembled in a two compartment device, as shown in Fig. 4.1 was also employed to evaluate the bacterial rejection behavior of the membrane under a hydrostatic pressure head. The utmost bacterial rejection of 99.99% (presented in Table 4.5), from an aqueous feed solution of 10^5 cfu/ml substantiates that the discussed proposed mechanism also plays a key role here, in resisting the permeation of bacteria by restricting their random motility. The rejection efficiency of the membrane towards *E. coli*, in the said device is found to be superior than that of membrane in sheet-configuration (bacterial rejection of 99.51%), with the same membrane casting dope formulation, which could

be because of the prolonged interaction between the bacteria in feed stream and the membrane surface, that is quite probable when the pressure (water head) is low.

For the purpose of a better understanding about the functioning of the mechanism during filtration study, carried out in the two-compartment filtration device, the water level in the feed was adjusted to different heights (1 to 10 ft, that is equivalent to a range of 0.03 to 0.3 bar). It was observed that upto a height of 4 ft, a steady and utmost bacterial rejection of 99.99% is obtained, which could be attributed to an enhanced physicochemical interaction between bacteria and membrane surface, resulted by the characteristic stimulated flagellar motion or chemotactic swimming of bacteria that it performs in response to a chemical gradient.

				Variation of ba	acterial rejection
Membrane	Configuration	Solvent throughput	Bacterial	(%) with di	fferent height
composition		(LMH/bar)	rejection	levels	
			(%)	1-4 ft	4 – 10 ft
Psf UF-A		417(±2)	99.99		_
	Candle				
Psf:Ag-1 UF-B		2500(±3)	99.99	99.99	99.82 - 99.62

Table 4.5: Salient features of mixed-matrix UF membrane in candle-configuration.

However, beyond 4 ft and upto 10 ft, the bacterial rejection slightly declines from 99.82 to 99.62%. This indicates that the effect of residence time plays a crucial role in tuning the extent of interaction and thereby resisting the bacteria more effectively at low water head. But, had it been purely the effect of residence time at such height levels, then the bacterial rejection could have

decreased continuously with increase in the water head over the candle. On the other hand, had it been purely the effect of resultant porous membrane network or the released Ag^+ , the bacterial rejection should be the same throughout different water levels of feed. Furthermore, the leaching of Ag into the product water, which in principle could be responsible for bacteria killing and making the product water free of bacteria, is ignored in our case as the extent of leaching remains less than 5 ppb being independent of the feed water level. If Ag leaching was the predominant mechanism of bacteria killing in our case, the extent of leaching should progressively increase with the water head and in turn should have led to a better bacterial rejection at higher water head, which is not the present case. Thus, the rejection behavior observed at such water level is supposed to be the coupled effect of bactericidal activity of the Ag-nps and a predominant contribution of the negative chemotactic responses by the chemotactic cells of *E. coli*.

The outcomes of the present device strongly suggest that the probability of presence of undesired dead or decayed bodies of bacteria in the purified water can be diminished, since it involves a distinct mechanism during physical filtration process, unlike the conventional devices or methods involving ultraviolet radiation or chemical addition stages. A striking six fold enhancement in solvent throughput *i.e.*, 2500(±3) LMH/bar for the mixed-matrix UF membrane candle (Psf:Ag-1 UF-B, with 99.99% of bacterial rejection) over a membrane candle (Psf UF-A, with 99.99% of bacterial rejection) with 417(±2) LMH/bar, also corroborates the beneficial efficiency as well as superior productivity of the former. The compactness of the device may also draw the commercial interest as inexpensive bactericidal portable gadget for domestic water purification, since that can be easily installed and requires no electricity or addition of any chemicals for filtration of contaminated aquatic streams. A high-throughput of solvent associated

with rigorous removal of bacteria, under only a hydrostatic pressure head implies that the operational as well as maintenance cost may turn out to be almost negligible for smooth functioning of the device. Therefore, such sustainable development may provide a way for the sustainable water management and services, effectively addressing the constraints on water resources management and further satisfy the needs of safe drinking water for the peoples in rural sectors of developing countries.

4.3. Psf-carbon nanotube nanocomposite membrane development

One potential candidate among nanostructured materials is the carbon nanotubes (CNTs). With the objective of having improvement over the existing anti-biofouling tendency of Psf membranes, nanocomposites were developed with impregnation of both single walled as well as multi walled CNTs. The performance of the membranes was evaluated in terms of pure water permeability and solute rejection studies. The anti-biofouling performance of the membrane surfaces was examined using E. Coli culture and a comparison of anti-biofouling tendency obtained with the nanocomposites over the pure Psf membranes has been made. It was observed that membranes with impregnation of single walled CNTs possess better anti-biofouling behaviour as compared to pure Psf as well as Psf membrane embedded with multi walled CNTs.

4.3.1. Experimental

4.3.1.1. Membrane preparation

Single walled (Diameter: 1.2-1.5 nm) and two different types of multiwalled carbon nanotubes (7-15 nm and 110-170 nm) were procured from Aldrich. Four different dope solutions were prepared using Psf (M/S Solvay), N-Methyl Pyrrolidone (NMP) (M/S Sisco Research

Laboratories, India) and nanoparticles. The composition of the membrane casting dope is shown in Table 4.6. A homogeneous dope solution was obtained using ultrasonicator. The membranes were prepared using immersion precipitation technique under a relative humidity of 40 % using demineralized water as gelling medium at 25°C without use of any additives. The thickness of all the membranes was controlled using Doctor's knife with a gap of 200 to 250 micron.

Table 4.6: Composition of dope solutions prepared.

Membrane	PS (in gm)	NMP (in gm)	Nanotube (in gm)
Psf	18	82	NIL
Psf + MWNT	14.8	82	3.2 (diamter:110-170 nm)
Psf + SWNT	14.8	82	3.2 (SWNT)
Psf + MWNT	14.8	82	3.2 (diameter: 7-15 nm)

4.3.1.2. Membrane characterisation

The water permeability of all the membranes was determined using cross-flow filtration unit at 2 bar pressure. Neutral uncharged solute of polyethylene glycol (PEG, Fluka) and polyethylene oxide (PEO, Fluka) of different molecular weights were used to determine the average pore size of the membranes. The concentration of PEG/PEO was taken 200 ppm in the feed. The exact concentration in the feed and permeate was calculated using TOC analyzer (Thermo Electron Corporation, Model No. TOC1200). Pure water permeability and solute (PEO: 200 kDa) rejection data of all the membranes are given in Table 4.7. As evident from the above data, the water permeability was found to be more or less same in all the nanocomposite membranes

compared to pure Psf membrane. From solute rejection studies the characteristic pore radius was found close to 20 nm based on correlation reported by Howe and Clark.²⁰⁰

The pore size, shape and surface morphology of the Psf membrane and Psfnanocomposites were characterized using SEM (Model: SERON AIS2100, South Korea). Each membrane having an area of 0.5 cm² was cut and coated with 25 nm of gold using sputter coater in order to make membrane electrically conducive for SEM imaging to reduce the effect of charging. Water contact angle image sequence was taken through a CCD camera of goniometer from GBX instruments, France. Average roughness of the membrane surfaces was measured using NTMDT (Solver) atomic force microscope (AFM).

Membrane	Pure water permeability (LMH)	% solute rejection
Psf	27 ± 5	95 ± 3
Psf + MWNT	30 ± 2	93 (diamter:110-170 nm) ± 2
Psf + SWNT	23 ± 4	91 (SWNT) ± 4
Psf+ MWNT	26 ± 3	92 (diameter: 7-15 nm) ± 4

Table 4.7: Performance analysis of membrane samples.

4.3.1.3. Bio-fouling studies

Tryptone, yeast extract and agar were from Difco Laboratories, Detroit, MI, USA. Sodium chloride was procured from Thomas Baker (Chemicals) Limited, India. Inoculation of E. coli was done from an overnight culture achieving an initial density of $\sim 1 \times 10^5$ cfu/ml. Overnight culture of E. coli strain BW 25113 was diluted to $\sim 10^5$ cfu/ml in sterile Luria broth. This

bacterial culture was used as the feed flow in the membrane assembly mounted with the different test membranes. After 2 h of flow the membrane coupons were retrieved from the assembly and rinsed twice with sterile saline. Circular cross sections (4 mm) were punched out from different regions on the membrane and placed on Luria agar plates. The plates were incubated for 24 h at 37 °C and observed for visible growth around the membrane discs.

4.3.2. Results and discussion

4.3.2.1. SEM studies

The microstructure of Psf and CNT (110-170 nm) embedded membrane surfaces along with cross sectional views are shown in Fig. 4.12 to Fig. 4.15. The pores of all the membrane samples ranged from ~ 10 nm up to ~ 100 nm in diameter. However, more number of pores was found to be around 90 nm size based on the examination of membrane coupons with SEM at different locations without use of any statistical method. These membranes are typically UF (UF) type. Fig. 4.14 shows the asymmetric nature of nanocomposite membrane developed, whereas Fig. 4.15 clearly shows the impregnation of CNTs on to Psf base membrane.



Fig. 4.12: SEM micrograph of Psf membrane surface.



Fig. 4.13: SEM micrograph of Psf-MWNT (110-170 nm) composite membrane surface.


Fig. 4.14: Cross sectional view of Psf-MWNT surface showing asymmetric layers.



Fig. 4.15:. Cross sectional view Psf-MWNT showing CNTs (110-170 nm).

4.3.2.2. Membrane surface roughness studies

The average surface roughness values of all membrane surfaces were measured using AFM. It was observed that the surface roughness values increased with incorporation of CNTs from a value of 6.7 nm in case of control Psf membrane to about 13-16 nm in case CNT embedded membranes. For the sake of clarity and completion, the 3-D views of only control Psf and nanocomposite membrane with 7-15 nm CNTs are shown in Fig. 4.16 and 4.17 respectively.



Fig. 4.16: AFM 3-D picture of Psf membrane surface.

Fig. 4.17: AFM 3-D picture of Psf-MWNT (7-15 nm) membrane surface.

4.3.2.3. Contact angle studies

Surface hydrophilicity of all membranes was evaluated from equilibrium sessile drop contact angles of deionised water on dried membrane surfaces (drop age: 30 seconds). At least five

equilibrium contact angles were obtained from each membrane and average value will define the equilibrium contact angle. The base Psf membrane has water contact value around 42.6°, whereas for CNT based nanocomposite membranes it looks to be little bit more hydrophobic with contact values of around 62.2° (with CNTs of 1.2-1.5 nm), 50.8° (with CNTs of 7-15 nm) and 58.1° (with CNTs of 110-170 nm). Thus, it was observed that with incorporation of CNTs, the hydrophobicity of the membrane surface increases. For the sake of clarity and completion, the images obtained during equilibrium contact angle measurements of only Psf and Psf-CNT (1.2-1.5 nm) membrane surfaces are shown in Fig. 4.18 and 4.19 respectively.



Fig. 4.18: Image of drop shape for Psfmembrane surface. Fig. 4.19: Image of drop shape for Psf-SWNT (1-2 nm) membrane surface.

4.3.2.4. Studies on bio-fouling resistant behaviour of membrane surface

The anti-biofouling property of the membranes was tested by using a bacterial feed in the membrane assembly mounted with the different test membranes. Representative discs were punched out from different areas of each membrane and observed for the bacterial growth attached to it as shown in Fig. 4.20. In this case lesser bacterial growth was observed in Psf incorporated with single walled carbon nano tube (SWNT) and multi walled carbon nanotube (MWNT) of diameter 7-15 nm compared to native Psf membrane. On the other hand, the bacterial growth over the membrane with MWNT (110 -170 nm) was found more than that of pure Psf membrane. The reason for observing more bacterial growth in MWNT (110-170 nm) impregnated membrane compared to pure Psf membrane is not clear. It may be the case that with

such a range of diameter of CNTs, the antibacterial action is not prominent. As the size of CNTs increase, the specific surface area decreases, leading to decreased opportunity for interaction and uptake by living cells and hence mild or lesser cytotoxicity is observed. Another possibility could be the MWNTs (110-170 nm) are well entrapped in the polymer network rather than lying on the membrane surface, which in turn would result in no/lesser interaction with the bacterial cells and no cytotoxicity is observed. SWNTs exhibited much stronger antibacterial activity than MWNTs that is in agreement with the literature data.²⁰¹ The enhanced bacterial toxicity of SWNTs may be attributed to (1) a smaller nanotube diameter that facilitates the partitioning and partial penetration of nanotubes into the cell wall, (2) a larger surface area for contact and interaction with the cell surface, and/or (3) unique chemical and electronic properties conveying greater chemical reactivity.



Fig. 4.20: Biofouling resistant property of membrane surfaces showing reduced bacterial growth in the SWNT and MWNT (7-15 nm) impregnated nanocomposite membranes: (a) Psf; (b), Psf-MWNT (110-170 nm); (c) Psf-MWNT (7-15 nm); (d) Psf-SWNT (1.2-1.5 nm).

4.4. Conclusions

Mixed matrix UF membrane is developed employing an optimized composition of Psf, PVP and Ag-nps. Utilization of porogen, PVP in higher amount provides a favorable approach of *in situ* impregnation of bactericidal Ag-nps in a highly porous polymer matrix, following non-solvent

induced phase inversion technique and thereby explores the characteristic features of Ag-nps in offering extensive bactericidal effect. The idea has been utilized to develop a point-of-use bactericidal portable gadget having substantial solvent throughput of 2500 LMH/bar, suitable for energy-efficient and cost-effective domestic water purification which can serve the drinking water needs of rural sector having no or intermittent supply of electricity. The advantageous efficiency of bacterial rejection with as high as 99.99% of the present device also resides with the probability of absence of undesired dead or decayed bodies of bacteria in the purified water, since the filtration process involves a distinct mechanism, being predominantly controlled by the negative chemotactic responses of the bacteria.

The CNT impregnated polymeric nanocomposite membranes were developed and characterised. The anti-biofouling performance of the membranes was examined and it was found that the membranes impregnated with SWNT have got better anti-biofouling behaviour compared to that of MWNT. Also it was confirmed that as the diameter of the CNT increased, the anti-biofouling performance of the membrane surface declined. It is believed that the homogeneous dispersion and alignment of the CNTs in membrane host matrix do play a significant role in deciding the extent of improvement in anti-biofouling behaviour, which needs to be examined.

CHAPTER -5

Development of Radiation Resistant Nanocomposite

Membranes

5.1. Introduction

Nuclear power industry provides over 11% of the world's energy leading to radioactive waste generation²⁰² that needs proper and thorough management.^{203,204} Nuclear fuel cycle generates radioactive waste at diverse stages, which covers uranium ore mining and milling, fuel fabrication, reactor operation and spent fuel reprocessing.^{205,206} Alongside, these radioactive wastes also comprises of the use of radioisotopes in medicine,^{207,208} industry²⁰⁹ and agriculture.²¹⁰ The management of radioactive waste involves decontamination and decommissioning activities.²¹¹ Separation processes like evaporation, adsorption, distillation, precipitation, ion exchange etc. are used for the treatment of radioactive waste.²¹² However, membrane based processes have tremendous growth opportunities in the field of separation and recovery of radioactive chemical species because of following reasons; (1) Separation can be fetched by continuous process,²¹³ (2) Low energy consumption,²¹⁴ (3) Membrane process can be combined with other processes,^{215,216} (4) Scalability^{217,218} and more importantly, (5) No requirement of additives.

Membrane processes have wide range of applications and studies showed diverse uses of membrane processes in the field of nuclear industries²¹⁹⁻²²¹ such as, removal of nuclear contamination from soil and water to ensure the health and safety of the inhabitants of the region,²²² separation of impurities from liquid radioactive waste to ensure the safe discharge into the environment,²²³ purification of low-level radioactive waste,²²⁴ direct contact membrane distillation for the processing of low and intermediate level radioactive liquid wastes by surface modified flat sheet membranes to produce distilled water and to reduce the volume of the radioactive wastes for the safe storage and disposal²²⁵ etc.

Through, inorganic (ceramic) membranes have got excellent stability against radioactive environment,²²⁶ their application is somewhat limited owing to the difficulty in their fabrication, the inherent brittleness and more importantly the limitation to fine-tune the pore sizes. On the other hand, polymeric membranes captured significant attention due to higher flexibility, processability, simple pore forming mechanism, ability to tailor-make the membranes for specific application by functionalisation, uncomplicated modification in its internal structure (pores/porosity, internal network etc) and moderate stability (thermal, chemical or mechanical stability) etc.³ However, the low radiation stability of polymeric membranes results in the application of such membranes to a limited extent.

Absorption of high-energy radiation by polymers produces excitation and ionization causing homolytic and/or heterolytic bond scission. The molecular changes occurring in polymers as a result of radiation-induced chemical reactions may be classified as: i) chain crosslinking effecting an increase in molecular weight and formation of a macroscopic network (polymer solubility decreases with increased radiation dose); ii) chain scission effecting a decrease in molecular weight and, thus, substantially changing a polymer materials properties(strength, both tensile and flexural, decreases, and the rate of dissolution in a given solvent increases). In addition to these changes, irradiation of polymers will frequently give rise to small molecule products, resulting from bond scission followed by abstraction or combination reactions.²⁰⁴

The effect of radiation on membranes in general^{77,227} and Psf membrane material in particular has been investigated by the researchers.^{228,229} To justify and enhance the application of polymeric membranes in the management of radioactive waste, membrane needs to be made resistant against the gamma radiation. The solution exists in the form of fabrication of a

composite that can bring into newer and improved properties to a conventional membrane system. Nanostructured materials have got tremendous potential in terms of their uniqueness of properties like high surface area, tunability, low density, high porosity etc. Nanomaterials offers unprecedented opportunities to tailor-make membranes with desirable attribute keeping in to account the targeted application areas.²³⁰⁻²³³

Pyrochlores are the radiation resistant materials and have got significant uses in nuclear industry for waste management.²³⁴ Pyrochlore is isometric and the structural formula ideally considered is ^{VIII}A₂^{VI}B₂^{IV}X₆^{IV}Y[Roman numerals refers the coordination number, A and B sites contain metal cations, X (=O²⁻), and Y (=O²⁻, OH⁻, F⁻) represent anions].²³⁵ The specific chemistries of the A and B site cations and anion, constrain the stability of the ordered pyrochlore structure. The typical range for ionic radii of cations A site is $r_A = 0.087-0.151$ nm and B site is $r_B = 0.040$ -0.078 nm and because a number of the A and B cations have suitable size of ionic radii, many pyrochlore oxides, $A_2^{3+}B_2^{4+}O_7$, have been synthesized. The phase stability of pyrochlore is determined by the ionic radius ratio, r_A / r_B , and the oxygen positional parameter x. The structure can transform to an anion-deficient fluorite structure, (A,B)₄O₇, by disordering of A and B site cations as the A site and B site cations become more similar in size.²³⁶ This cation ionic radius ratio for the stable phase of the ordered pyrochlore lies between 1.46 (Gd₂Zr₂O₇) and 1.78 (Sm₂Ti₂O₇) under ambient conditions. At high pressure-high temperature synthesis, the cation radius ratio for the pyrochlore formation may be extended to the range of 1.29–2.30.²³⁴

With an objective of developing a mixed matrix UF membrane, pyrochlore nanoparticles were impregnated onto Psf host matrix. The work includes synthesis of pyrochlore (Gd₂Zr₂O₇), mixed

matrix membrane fabrication, their characterization and evaluation of effect of gamma radiation on membrane properties as well as performances.

5.2. Experimental

5.2.1. Materials

Psf (Psf, Mw: 30 kDa) from Solvay Speciality Polymers (India), N-methyl-2-pyrrolidone (NMP) (purity of \geq 99 %, Sigma-Aldrich) and Polyvinyl pyrrolidone (PVP, K-30; M_w: 40 kDa), procured from SRL (India) were used to prepare Psf base membrane. Pyrochlore (Gd₂Zr₂O₇) was synthesized by gel combustion route as detailed below for modification onto and modification of Psf polymer based UF membrane. For evaluation of membranes rejection behavior towards organic solutes, poly(ethylene glycol) (PEG, Mw: 35 kDa)was procured from Sigma–Aldrich. The conductivity of mili-Q ultra-pure water used in the experiments was below 2µS/cm.

5.2.2. Synthesis of pyrochlore

 $Gd_2Zr_2O_7$ nanoparticle was prepared by gel-combustion method. Gd_2O_3 (Indian Rare Earths Ltd. of purity 99.9%) was kept overnight at 800°C to remove moisture or any other volatile impurity. Gd_2O_3 was dissolved in minimum volume of concentrated HNO₃ till a colorless and transparent solution was obtained. The stoichiometric amount of $ZrO(NO_3)_2$ (Loba Chemie and 44% metal basis) powder were added to this solution. The resulting solution was boiled till a transparent yellow-colour solution was obtained. Finally glycine was added to the boiling solution in a fueldeficient ratio and solution was further heated till a viscous gel was obtained. The temperature of the hot plate was then raised to about 400°C for auto-ignition. At that temperature, the gel undergoes combustion which results formation of yellowish orange colored fine powders. The obtained powder was calcined at 600 °C for 1 h to remove any carbonaceous impurities.

5.2.3. Preparation of polymer dope solutions

For the fabrication of mixed-matrix (Psf-pyrochlore) UF membranes in sheet–configurations, polymer dope solutions were prepared by employing varying proportions of pyrochlore in hermetically sealed glass bottles. More specifically, the extent of the nanoadditive was varied at 0.1 and 2 (w/w_{Psf})% in the dope solutions comprising of 25 gram of Psf, 7.5 gram of the porogen, PVP and 100 mL of NMP. The dispersion of nanoparticles was undergone ultrasonic treatment for 30 min, prior to the addition and subsequent mixing of dried Psf beads and PVP, maintaining the specified compositions. The dope solutions were then vigorously agitated for several hours to accomplish complete dissolution of Psf and PVP in the solvent with homogeneously dispersed pyrochlore. For comparison purpose, one dope solution (Control) devoid of any nanoadditive was further prepared following the aforementioned composition of polymer and porogen as well as the methodology. Then, the resultant viscous dope solutions were kept for overnight in an environmentally controlled atmosphere maintaining the temperature and relative humidity at $25(\pm 1)$ °C and 35-40 %, respectively, to eliminate the trapped air bubbles from the solutions.

5.2.4. Preparation of control and mixed matrix UF membranes

Prior to fabrication of the desired mixed-matrix UF membranes along with the one required for comparison purpose following non-solvent induced phase inversion method, cleaned glass plates (without having any fabric-base) were taped onto their parallel ends in such a way that each

resulting membrane layer could achieve an estimated thickness of 200 μ m. The as-prepared stable dope solutions and the Control were cast manually onto the taped glass plates at a steady casting shear employing a well-dried, ultra-smooth glass-roller. The entire assemblies comprising of the cast films were immediately then immersed in a precipitation bath containing ultra-pure water as non-solvent, maintained at room temperature, for immersion precipitation. To ensure the adequate exchange between solvent and non-solvent followed by a resultant absolute removal of the porogen as well as the solvent from the membrane matrices, the prepared membranes were taken out of the water bath and rinsed in fresh water for several instants. The entire casting process was carried out in a controlled environmental atmosphere, where temperature and relative humidity were maintained at $25(\pm 1)$ °C and 35-40%, respectively. The membranes as developed under invariable casting condition were properly stored in a water-bath. The membranes were categorized based on the difference in the specified compositions and accordingly defined as Psf-Py-1, Psf-Py-2, Psf-Py-3 and Psf-Py-4. The Control is denoted as Psf as presented in Table 5.1.

Membrane	Psf (in gm)	NMP (in ml)	PVP (in gm)	Pyrochlore (in gm)
Psf				
Psf-Py-1				0.025
Psf-Py-2	25	100	7.5	0.125
Psf-Py-3				0.25
Psf-Py-4				0.5

Table 5.1: Composition of membrane casting solutions.

5.2.5. Irradiation of control and mixed matrix UF membranes

All membrane samples packed in zip-lock polyethylene bags in aqueous environment were exposed to gamma radiation for desired absorbed dose (40 kGy, 80 kGy, 240 kGy, 500 kGy and 1000 kGy). Irradiation was carried out under aerated condition using a gamma chamber (GC-5000) having Co-60 gamma source supplied by M/s BRIT, India. The dose rate of gamma chamber was ascertained to be 1.0 kGy/h using Fricke dosimetry prior to irradiation of the membrane samples.

5.2.6. Characterization of the as-synthesized pyrochlore

Textural feature of the synthesized pyrochlore was characterized by XRD analysis on a Philips X'Pert pro X-ray diffractometer. The XRD patterns with Cu K α radiation ($\lambda = 1.5418$ Å) at 40 Kv and 30 mA were recorded in the range of $2\theta = 10^{\circ}-80^{\circ}$ at a scan speed of 0.5° min⁻¹. The average crystallite sizes for the pyrochlore was determined using Debye-Scherrer's equation (t = $K\lambda/B \cos \theta$, where t = average crystallite size in Å, K = Scherrer constant usually taken as 0.9 Å, $\lambda = X$ -ray wavelength, θ is the Bragg angle, and B = integral breadth of a reflection located at 20).

5.2.7. Physicochemical characterizations of the mixed-matrix UF membranes

The structural variation of the membrane surface was observed from XPS (DESA-150 electron analyzer, Staib Instruments, Germany) incorporated with Mg-K α X-ray source (1253.6 eV). The spectrometer binding energy scale was calibrated with Au-4f_{7/2} photo peak (binding energy 83.95 eV). The spectrum was recorded as the intensity(number of counts per second) versus binding energy (BE). Curve fitting of the multiplex photopeaks was performed using Gaussian functions employing a least-squares peak analysis software (XPSPEAK 4.1).

Vibrational spectra of the UF membranes with Psf base matrices were acquired by FTIR technique. For spectral acquisition in the attenuated total reflectance (ATR) mode, Bruker make Vertex 70 spectrometer system equipped with an ATR unit (ZnSe crystal, 45° angle of incidence and refractive index 2.4) was employed. The membranes skin surface was faced down onto the ATR crystal element and lighter pressure was applied using a MIRacle high pressure clamp with torque-limited press. The radiation penetration depth was 2 μ m. All infrared spectra were recorded in absorbance mode over two different wave number regions, i.e., 800-1550 cm⁻¹ and at an ambient temperature. For evaluation 200 scans were taken with a spectral resolution of 2 cm⁻¹.

The morphological analyses, through SEM, of the composite UF membranes were carried out using CamScan–CS3200LV, UK. To make the membranes electrically conducting, the membrane samples (without support polyester fabric) were fractured in liquid nitrogen into smaller sized strips and sputter coated on the cross-sectional layer with gold-palladium alloy using a sputter coater (Model No. K550X Emitech), under the optimized conditions (Sputtering time: 60 s, Sputter current: 30 mA and Tooling factor: 2.3). The acquisition of cross-sectional images of the membranes was done in secondary electron mode at an acceleration voltage of 15 kV and variable magnification (5kX to 10kX). Quantitative elemental analysis of these membranes surfaces was then performed by an energy dispersive X-ray spectrometer (EDX, INCA Oxford Instruments, UK), coupled to a Scanning Electron Microscope (CamScan-CS3200LV, UK) and a micro-analysis system.

Measurement of mechanical stability of the composite UF membranes were carried out with a universal tensile testing machine (Hemetek Techno Instrument, model LRX Plus, India), at 25°C with a relative humidity of 40-50%. A constant deformation rate of 100 mm/min was controlled

during the analysis. For analysis, dumb-bell shaped specimens of the membrane samples with length of 4 cm and width of 0.6 cm were employed. Tensile strength (TS) and percent elongation at break (EB) were calculated for the membranes in duplicates, using the NEXYGEN plus software.

5.2.8. Evaluation of UF performances of the control and mixed matrix UF membranes

For all the membranes, the extent of molecular separation was evaluated by analyzing the rejection behavior of them towards neutral organic solutes such as PEG, with average Mw of 35 kDa. The test solutions were prepared by dissolving pre-weighed amount of PEG in ultra-pure water at a concentration of 200 ppm.The membranes having identical effective membrane area of 14.5 cm² were employed in a cross-flow filtration unit, operatedunder a trans membrane pressure of 1 bar at room temperature; and in view of minimizing the effect of experimental error the measurements were repeated with three different coupons of each membrane to obtain the average values.The concentrations of PEG in both feed and product solutions were measured by analyzing the total organic carbon (TOC) content of the samples using TOC analyzer (ANATOC-II, SGE analytical science, Australia) and employed for estimation of percentage rejection of the probe organic solutes following Eq. 2.20. The steady-state solvent PWP (J in L.m⁻²day⁻¹) was determined by direct as well as replicate measurements of the permeate flow following Eq. 2.21. Prior to all UF test experiments, the membranes were initially subjected to undergo hydraulic compaction for 1 h in water at standard UF test conditions to achieve stabilized performances of the membranes.

5.3. Results and Discussions

5.3.1. Characterization of synthesized pyrochlore

XRD has been recorded on the calcined powder which confirms the phase purity of the material. The XRD pattern is shown in Fig. 5.1. The parent $Gd_2Zr_2O_7$ crystallizes as pyrochlore which is evident by the presence of diffraction peaks at 20: 27°(3 1 1), 37°(3 3 1), 45°(5 1 1) (using CuK α as radiation source). The crystallite size was calculated from Scherrer's equation and it is found to be 63 nm.



Fig. 5.1: XRD pattern of synthesized Gd₂Zr₂O₇.

5.3.2. Analysis of physicochemical features of the mixed-matrix UF membranes

The EDX spectra of the representative membranes, namely Control-Psf UF, Psf-Py-2 UF, are presented in Figs. 5.2a, and 5.2b respectively.

The spectra of Psf exhibit the presence of C, S and O peaks, whereas the distinct elemental peaks of Gd and Zr are obtained along with the C, S and O peaks in the mixed-matrix UF membrane (Psf-Py-2 UF). XPS analysis indicated that membranes comprise with C, O and S, Gd and Zr

(The spectrum of Gd and Zr are not shown owing to no observable changes). The elemental composition of the membranes were estimated by the intensity centered around 285, 532 and 168 eV signify C(1s), O(1s) and S(2p) peaks, respectively as shown in Fig. 5.3 (a) for Control Psf, 5.3 (b) for Psf-Py-1 UF, 5.3 (c) for Psf-Py-2 UF, 5.3 (d) for Psf-Py-3 UF and 5.3 (e) for Psf-Py-4 UF membranes. The variations in atomic composition (C, O and S) are shown in the Table 5.2.



Fig. 5.2: EDX spectra of skin regions of the membranes: (a) Control-Psf UF (b) Psf-Py-2 UF

The less intense peaks of S as compared to C and O peaks imply availability of lesser content of sulfur on membrane surface which is in tune with Psf structure. Atom % of C is decreasing invariably in all the membranes, whereas the atom % of O is increasing in all the cases. On the other hand, the atom% of S is not varying significantly. The value of %S in case of Psf-Py-1 UF seems to be outlier and erroneous. The decrease in C content is because of chain scission that increases with enhancement in the radiation doses. The increase in %O values could be due to formation of bonding between radiolysed products of water (OH and H₂O) with that of membrane surface. It is important to note that the XPS studies do not reflect anything tangible on the effect of pyrochlore impregnation onto the membrane surface. Only observation that could be

made is the increase in %O values in case of pyrochlore impregnated membranes compared to the control Psf membrane, the reason of which needs to be further looked into.



Fig. 5.3 (a): High resolution photoelectron spectra obtained for unirradiated and irradiated Psf UF membranes.



Fig. 5.3 (b): High resolution photoelectron spectra obtained for unirradiated and irradiated Psf-Py-1 UF membranes.



Fig. 5.3 (c): High resolution photoelectron spectra obtained for unirradiated and irradiated Psf-Py-2 UF membranes.



Fig. 5.3 (d): High resolution photoelectron spectra obtained for unirradiated and irradiated Psf-Py-3 UF membranes.



Fig. 5.3 (e): High resolution photoelectron spectra obtained for unirradiated and irradiated Psf-Py-4 UF membranes.

Psf UF	%C	%O	%S
Unirradiated	64.2	26.7	3.2
Irradiated-240 KGy	59.3	30.6	2.0
Irradiated-1000 KGy	56.6	32.8	1.5
Psf-Py-1 UF			
Unirradiated	61.1	25.3	6.3
Irradiated-240 KGy	57.8	30.6	2.8
Irradiated-1000 KGy	53.2	36.7	2.1
Psf-Py-2 UF			
Unirradiated	64.0	26.5	2.3
Irradiated-240 KGy	59.3	29.3	3.0
Irradiated-1000 KGy	56.8	33.4	3.4
Psf-Py-3 UF			
Unirradiated	63.8	25.7	2.7
Irradiated-240 KGy	59.7	29.2	3.7
Irradiated-1000 KGy	53.2	35.6	2.8
Psf-Py4 UF			
Unirradiated	68.3	24.4	2.1
Irradiated-240 KGy	57.0	30.2	4.0
Irradiated-1000 KGy	51.1	36.6	1.5

Table 5.2: Atomic compositions obtained from XPS analysis of the membranes.

The FTIR spectral analyses of the control and pyrochlore based membranes (unirradiated and irradiated), observed in the specified region from 650 to 1650 cm^{-1} are shown in Fig. 5.4 (a) to 5.4 (e): Fig. 5.4 (a) for Control Psf UF, 5.4 (b) for Psf-Py-1 UF, 5.4 (c) for Psf-Py-2 UF, 5.4 (d) for Psf-Py-3 UF and 5.4 (e) for Psf-Py-4 UF membranes. The FTIR spectra of the membranes show that the most significant absorption bands are around: 1149 cm⁻¹ (symmetric stretching of O=S=O from diaryl sulfone groups), 1294 cm⁻¹ (asymmetric stretching of O=S=O from diaryl sulfone groups), 834 cm⁻¹ (C–H stretching from Ar), 1489 cm⁻¹ (asymmetric vibration attributed to C-H from methyl groups) and 1170 cm⁻¹(stretching vibration of etheric bond of Ar-O-Ar of Ps).No shifting in the characteristic absorption bands of pyrochlore impregnated membranes manifests the fact that incorporation of pyrochlore at different composition in the Control-Psf UF membrane matrix does not affect the internal structural of Psf membrane. The FTIR spectra showing the decline in intensity upon irradiation of Control-Psf UF membranes owes to the deformation of the skin layer of the membrane by gamma rays. Similar trend in decrease of peak intensity is also observed for 0.1 and 0.5 % pyrochlore impregnated membranes Psf-Py-1 & Psf-Py-2). On the other hand, FTIR spectrum of membrane with the incorporation of 1% pyrochlore (Psf-Py-3 UF) does not reveal significant change in peak intensity after the irradiation, which depicts the desired stability and resistance of the core polymeric matrix against the deformation in the irradiation environment. The behavior of membrane with the 2% pyrochlore (Psf-Py-4) is comparable to the Control-Psf UF membrane, which could be due to the tendency of aggregation of pyrochlore nanoparticles at high concentration leading to interfacial defects at the polymernanoparticle interface disrupting the internal structure of polymer network.



Fig. 5.4: FTIR spectra of membranes: (a) Control-Psf UF, (b) Psf-Py-1 UF, (c) Psf-Py-2 UF, (d) Psf-Py-3 UF, (e) for Psf-Py-4 UFmembranes

Fig. 5.5 shows the change in the tensile strength of membranes with the different composition of pyrochlore nanoparticles at different doses of irradiation. The tensile strength of the control Psf membrane decreases with increase in radiation dose owing to the structural damage of membrane by absorption of gamma radiation. Whereas, the extent of decline in tensile strength of pyrochlore impregnated membranes is less compared to that of control Psf membrane. The tensile strength of control Psf membrane decreases by 22 %: from 3.05 (unirradiated membrane) to 2.36 (irradiated upto 1000 kGy) whereas the tensile strength value of the Psf-Py-3 decreases

from 3.11 to 2.63 (~ 15 % decline) and that of Psf-Py-4 from 2.91 to 2.71 (~ 6 % decline). It is evident that incorporation of pyrochlore offers stability to membranes against radiation.



Fig. 5.5: Tensile strength values of unirradiated and irradiated membranes.

Pyrochlore upon impregnation on to the polymeric host matrix takes up a fraction of the radiation falling on to the membrane surface and Gd & Zr interchange their positions absorbing the incident energy (Fig. 5.6) as a result of which the radiation is not transmitted to the host matrix.^{234,236} The introduction of pyrochlore (from 1% composition of pyrochlore) in the Psf membrane exhibits less deterioration of tensile strength upon irradiation (compared to Control Psf), which manifests the restoration of stability of membrane during irradiation.

Fig. 5.7 shows the change in the % elongation at break (% EB) values of membranes with the different composition of pyrochlore nanoparticles at different doses of irradiation. The % EB the

control Psf membrane decreases with increase in radiation dose owing to the structural damage of membrane by absorption of gamma radiation.



Fig. 5.6: Change in structure of pyrochlore upon irradiation, Gd and Zr in $Gd_2Zr_2O_7$ are shown as blue and green color balls, respectively; red coloured ball depicts oxygen; the white portion in red balls in Fluorite indicate vacancies.



Fig. 5.7: Elongation at break values of unirradiated and irradiated membranes.

Whereas, the extent of decline in % EB of pyrochlore impregnated membranes is less compared to that of control Psf membrane. The % EB of control Psf membrane decreases by ~ 90 %: from 31.5 (unirradiated membrane) to 3.05 (irradiated upto 1000 kGy) whereas the % EB value of the Psf-Py-3 decreases from 31.7 to 7.36(~ 76 % decline) and that of Psf-Py-4 from 24.8 to 10.6 (~ 57 % decline). The mechanical testing confirmed that 2 % pyrochlore impregnated membrane (Psf-Py-4) offers the best radiation resistant behaviour amongst all the membranes.

The SEM micrograph of control Psf, Psf-Py-3 and Psf-Py-4 membranes are shown in Fig. 5.8, Fig. 5.9 and 5.10, respectively. Fig. 5.8 (a) shows the image of unirradiated Psf and 5.8 (b) shows the image of Psf membrane irradiated up to 1000 kGy. Fig. 5.8 (c) and 5.8 (d) give an interesting finding with regards to control Psf; with irradiation, there is clustering of pores leading to larger cavity, within which a number of smaller sized pores are seen (Fig. 5.8 (d)). Fig. 5.9 (a) and (b) shows the SEM images of unirradiated and 1000 kGy irradiated Psf-Py-3 UF membrane, respectively, the latter showing no clustering of pores. Psf-Py-4 UF membrane (Fig. 5.10a) was seen to have larger pores. At some locations of Psf-Py-4 irradiated with 1000 kGy, defects are found, as shown in Fig. 5.10 (b). The larger sized pores and defects observed in 1000kGy irradiated Psf-Py-4 membranes could be due to tendency of nanoparticles to agglomerate at higher loading. This finding is corroborated with the high PWP and low rejection attributes offered by 1000 kGy irradiated Psf-Py-4 membrane. Unlike control Psf membrane, it shows that the deteriorating effect caused by the radiation on to the control Psf surface is more pronounced than that of nanoparticle embedded system. In case of 0.1 % and 0.5 % loaded

membranes, no tangible findings were obtained to compare with either control Psf membrane or with Psf-Py-3 and Psf-Py-4 membranes.



Fig. 5.8: SEM images of Control-Psf UF membrane: (a) unirradiated Control-Psf UF membrane, (b) 1000 kGy irradiated Psf UF membrane at 10k X maginification, (c) 1000 kGy irradiated Psf UF membrane at 800 X magnification, (d) 1000 kGy irradiated Psf UF membrane at 5kX magnification.



Fig. 5.9: SEM images of Psf-Py-3 membrane: (a) unirradiated (b) 1000 kGy irradiated.



Fig. 5.10: SEM images of Psf-Py-3 membrane: (a) unirradiated (b) 1000 kGy irradiated.

5.3.3. Performance evaluation of control and mixed matrix membranes

Fig. 5.11and 5.12 show the PWP(L.m-2.Day⁻¹) and % solute rejection (toward 35k PEG), respectively, of membranes with varying composition of pyrochlore at different doses of irradiation. PWP of all the membranes is found to increase with increased dose of irradiation. However, some erroneous (against the trend) PWP values were obtained for 500 kGy irradiated Psf, Psf-Py-1 and Psf-Py-2 membranes. It was observed that the PWP of unirradiated membranes increases from about 960 LMD to 1440 LMD upon addition of nanoparticles upto a loading 1 %,

which may be due to increase in hydrophilicity of the membranes because of incorporation of Gd₂Zr₂O₇. While Psf-Py-4 (2% pyrochlore loading) membrane exhibited PWP up to about 1080 LMD till 240 kGy irradiation, upon increasing the dose from 500 to 1000kGy, the PWP become higher (up to about 3792 LMD) compared to 1000 kGy irradiated control Psf membrane (about 3168 LMD) and other mixed matrix membrane systems in context.



Fig. 5.11: PWP of control and mixed matrix membranes (Unirradiated & irradiated).

Looking at the %SR offered by the membranes (as shown in Fig. 5.12), the 2% pyrochlore loaded membrane offered very low rejection of about 56 % toward PEG 35k after being irradiated with 1000 kGy dose. The 1 % loaded membrane (Psf-Py-3) offers a rejection of 83 % even after being irradiated upto a dose of 1000 kGy. The %SR behaviour of all the mixed matrix membranes except Psf-Py-4 remains consistent and not affected significantly with radiation dose upto 1000 kGy. Though from material point of view, 2 % pyrochlore impregnated membrane (Psf-Py-4) offers the best radiation resistant behaviour from mechanical perspective, the PWP

and % SR analysis in combination reveals that the pyrochlore membranes (Psf-Py-3)with 1% loading can offer optimum flux and rejection behaviour under radiation environment.



Fig. 5.12: Solute rejection behaviour of control and mixed matrix membranes (Unirradiated & irradiated).

5.4. Conclusion

Pyrochlore (Gd₂Zr₂O₇) nanoparticle was prepared by gel-combustion route and was used for development of mixed matrix membrane with Psf as host matrix. The concentration of pyrochlore was varied from 0.1 % to 2 % of polymer weight. The membranes were prepared using phase inversion technique. The pure water permeability and solute rejection studies (with 200 ppm solutes of 35 kDa PEG) of the synthesized membranes were carried out to evaluate the performance of the membrane. To assess the radiation stability of the membranes, γ (gamma) radiation doses of 40, 80, 240, 500 and 1000 kGy were provided to the membranes in aqueous environment. The membranes were characterized using FTIR, SEM, EDX and XPS. The tensile

strength and elongation at break for all the samples (both un-irradiated and irradiated) were carried out using Universal Testing Machine. The extent of damage caused due to 1000 kGy irradiation (correlated with the extent of reduction in elongation at break values) is about 90 % for pure Psf whereas the membranes with 2 % nanoparticle loading showed only about 57 % reduction in elongation at break, which resulted in a membrane with improved radiation resistance behaviour of all the membrane samples prepared. However, from membrane performance point of view, 1 % pyrochlore loaded membrane offered optimum flux and rejection behavior without notable compromise in mechanical strength (Tensile strength of 1000 kGy irradiated membrane: 2.63 MPa) compared to 2 % loaded one (Tensile strength of 1000 kGy irradiated membrane: 2.71 MPa). The enhanced stability of pyrochlore embedded membranes is attributed to the ability of pyrochlore to take up the radiation, which leads to interchanging of the sites occupied by Gd and Zr and in turn dissipation of gamma energy. In this process, polymer host matrix is exposed to gamma radiation to a minimum extent, making the overall composite matrix radiation resistant.

CHAPTER - 6

Development of Charged Nanocomposite Membranes

6.1. Introduction

The persistent challenging issues involved in polymeric ultrafiltration (UF) membranes pertain to the progressive deterioration of permeability and selectivity because of the membranes' extensive inclination to fouling during their prolonged exposure in influent raw water streams.^{17,237-238} The fouling in membrane systems is classified as crystalline fouling, organic fouling, microbial fouling, particulate and colloidal fouling.²³⁹ With usage, growth of gelatinous biofilm usually happens on the membranes' upstream side and the effect of such enhances the membranes' hydraulic resistance through pore-blockage as well as formation of an additional cake layer, further resulting either decline in permeate flux or rise in transmembrane pressure (TMP) during the cross-flow permeation driven under steady-TMP or steady-flux conditions, respectively.²⁴⁰ Both, thus adversely enforce to compromise with productivity as well as costeffectiveness of the membranes, for there is always a need of achieving a desired constant production rate by attempting to regain the physicochemical efficacy of the membranes through intense chemical or physical treatments. Therefore, the concerned factor of membrane fouling reduces not only the UF membranes' lifetime, but concurrently incurs the operational cost to a significant extent as well. The ease of exploitation of functional properties of the metal oxide nanoparticles like Al_2O_3 ,²⁴¹ SiO_2 ,²⁴² TiO_2 ,²⁴³ ZrO_2 ,²⁴⁴ Fe_3O_4 ²⁴⁵ etc. as well as tunable carbonaceous nanomaterials like oxidized CNTs²⁴⁶ and GO²⁴⁷ in porous matrices of various suitable organic polymers substantially enhances the opportunity to achieve improved macroscopical features with superior antifouling properties, and consequently enlightens the extensive and progressive demand of mixed-matrix UF membrane as promising contender for water treatment applications. The present chapter would discuss the research work undertaken in the direction of development of charged nanocomposite membranes by incorporation of functionalized (sulfonated) TiO_2 and functionalized (carboxylated) CNTs. The intention of introducing charged nanomaterials onto the membrane surface was to increase the hydrophilicity of the membrane and thereby reducing the fouling tendency of the membranes.

6.2. Polysulfone-TiO₂ nanocomposite membrane development

The nanoparticles of TiO₂ being widely exploited in membranes' modifications have drawn the attention of intense research in several earlier instances, while in most of the cases their striking photocatalytic activity was harvested by different approaches to improve the quality of product water with a better productivity.²⁴⁸ In a recent attempt,²⁴⁹ TiO₂ nanoparticles of different dimensions were impregnated in polyvinylidenefluoride (PVDF) matrix using phase inversion method to substantiate the role of smaller sized nanoparticles in bringing better antifouling activities in the resultant UF membranes. The different studies carried out by Wu et al.,²⁵⁰ and Li et al.²⁵¹ correlated the effect of nanoparticles concentration with physicochemical and macroscopical features of polyethersulfone (PES)-TiO₂ based UF membranes, signifying the limitation of tentative aggregation of the nanoparticles. With progressive efforts in developing high- performance sustainable membrane materials for the treatment of domestically as well as industrially relevant aquatic media, attempts were made to exploit the advantageous property of novel organofunctionalized nano-TiO₂ as persuasive nanoadditive in developing superior mixed-matrix UF membranes. The functionalization of nano-TiO₂wasmade by employing two different organic entities as organoligands, i.e., Tiron and Chromotropic acid.

6.2.1. Experimental

6.2.1.1. Materials

The base polymer, polysulfone (Psf; M_W: 30kDa) was obtained from M/s. Solvay Specialties India Pvt. Ltd. The solvent, N-methyl-2-pyrrolidone (NMP) with minimum assay of 99.5% and porogen, Polyvinyl pyrrolidone (PVP, K-30; M_W: 40kDa) of AR grade, as utilized without further purification were procured from SRL Pvt. Ltd. (India). The nanoparticle, anatase TiO₂, denoted as nano-TiO₂ (particle size: < 25 nm, assay: 99.7% trace metal basis and specific surface area: 45-55 m^2/g) was procured from Aldrich. For surface modification of the nano-TiO₂, two different reagents namely, Tiron (4,5-Dihydroxy-1,3-benzenedisulfonic acid disodium salt monohydrate, complexometric indicator grade) and Chromotropic acid (1, 8-Dihydroxynaphthalene-3,6-disulfonic acid disodium salt dihydrate, technical grade) were acquired from Fluka and Sigma-Aldrich, respectively. For evaluation of membranes' rejection behaviors towards organic solutes, poly(ethylene glycol) (PEG, Mw: 35 kDa) and poly(ethylene oxide) (PEO, Mw: 100kDa) were procured from Sigma-Aldrich. The protein, Bovine Serum Albumin (BSA) was procured from SRL Pvt. Ltd. (India). The conductivity of mili-Q ultra-pure water used in the experiments was below 2μ S/cm.

6.2.1.2. Synthetic routes adopted for surface modification of nano-TiO₂

The surface modifications of the anatase nano-TiO₂were executed by adopting two different synthetic routes. In one such synthetic approach (Fig. 6.1, pathway – a), Tiron comprising of different binary functionalities (two adjacent reactive –OH sites and two $-SO_3^-Na^+$ sites) was used to functionalize the nano-TiO₂ following a chemisorption procedure.²⁵² The nanoparticles
were initially suspended into an aqueous solution with pH of 2 (controlled using HCl) under ultrasonic treatment for 2 h, and then, a freshly prepared aqueous solution of the Tiron (4 mg/ml, pH 2) was poured into it. The suspension was undergone vigorous stirring at room temperature for 30 min to allow complete chemisorption of the catecholic compound onto the peripheral reactive sites of the TiO₂ nanoparticles. The acidic pH was maintained for the reaction medium to delicately prevent the oxidation of the catecholic end groups of Tiron. The sulfonated nanoparticles were then rinsed with milli-Q water until neutral pH was reached and then centrifuged. The as-synthesized organofunctionalized nano-TiO₂, denoted as F_T – nano-TiO₂ was dried at 80 °C for 24 h and stored for further execution of its' relevance in membrane modification.



Fig. 6.1: Schematics of functionalization of anatase nano-TiO₂ by Tiron and Chromotropic acid; with proposed structures for a) dark-orange colored F_T – nano-TiO₂ and b) pale-grey colored F_C – nano-TiO₂, respectively.

In another route of modification (Fig. 6.1, pathway - b), the synthesis of organofunctionalized nano-TiO₂was conducted according to the method described by Ramesh *et al.*²⁵³ In such

approach, the nano-TiO₂ (3 g) was added to 50 ml of aqueous solution containing 0.8 mg/l Chromotropic acid comprising of different binary functionalities (two reactive –OH sites and two $-SO_3^-Na^+$ sites) as well, and the heterogeneous (inorganic-organic) mixture was stirred at room temperature for 2 h. The functionalized nano-TiO₂ was then filtered off, washed with milli-Q water several times, centrifuged and dried at room temperature for 24 h under vacuum, before getting stored for its prospective usage in the membrane modification.

6.2.1.3. Preparation of polymer dope solutions

For the fabrication of mixed-matrix (Psf: $F_T / F_C - nano-TiO_2$) UF membranes in sheet–configurations, two different sets of polymer dope solutions (Set-A and Set-B), each further comprising of two different compositions were prepared by employing varying proportions of $F_T / F_C - nano-TiO_2$ in hermetically sealed glass bottles. More specifically, the extent of the nanoadditive, F_T – nano-TiO₂ was varied at 1 and 3 (w/w_{Psf})% in the dope solutions of Set-A ($F_T/1$ – nano-TiO₂ and $F_T/3$ – nano-TiO₂, respectively), comprising of 20 (w/v_{NMP})% of Psf and 40 (w/w_{Psf})% of the porogen, PVP. The extent of F_C – nano-TiO₂ and $F_C/3$ – nano-TiO₂, respectively), with an equal inclusion of the PVP and Psf as in the case of Set-A. The dispersion of F_T / F_C – nano-TiO₂ in NMP was undergone ultrasonic treatment for 20 min, prior to the addition and subsequent mixing of dried Psf beads and PVP, maintaining the specified compositions. The dope solutions were then vigorously agitated for several hours to accomplish complete dissolution of Psf and PVP in the solvent with homogeneously dispersed F_T / F_C – nano-TiO₂. For comparison purposes, a set of polymer dope solutions, *i.e.*, two dope solutions

(Set-C) comprising of nano-TiO₂ at 1 and 3 (w/w_{Psf})%, and one dope solution (Control) devoid of any nanoadditive was further prepared following the aforementioned composition of polymer and porogen as well as the methodology. Then, the resultant viscous dope solutions (Set-A, Set-B, Set-C and Control, descripted in Table 6.1) were kept for overnight in an environmentally controlled atmosphere maintaining the temperature and relative humidity at $25(\pm 1)$ °C and 35-40 %, respectively, to eliminate the trapped air bubbles from the solutions.

UF Membranes	Dope	Psf in NMP	PVP	F_T – nano-TiO ₂	F_C – nano-TiO ₂	nano-TiO ₂
Codes	Codes	(w/v _{NMP})%	(w/w _{Psf})%	(w/w _{Psf})%	(w/w _{Psf})%	(w/w _{Psf})%
Psf: F _T /1- nano-TiO ₂				1	_	_
	Set-A					
Psf: $F_T/3$ - nano-TiO ₂				3	-	-
Psf: F _C /1– nano-TiO ₂				_	1	_
	Set-B					
Psf: F _C /3– nano-TiO ₂		20	40	_	3	_
Psf:1- nano-TiO ₂				_	_	1
	Set-C					
Psf:3– nano-TiO ₂				_	_	3
Control-Psf	Control			_	_	_

Table 6.1: Specifications of the precursor dope compositions and the respective derived membranes.

6.2.1.4. Preparation of mixed-matrix UF membranes

Prior to fabrication of the desired mixed-matrix UF membranes of two different classes along with the ones required for comparison purposes following non-solvent induced phase inversion

method, cleaned glass plates (without having any fabric-base) were taped onto their parallel ends in such a way that each resulting membrane layer could achieve an estimated thickness of 200 µm. The as-prepared stable dope solutions of Set-A, Set-B, Set-C and the Control were cast manually, onto the taped glass plates at a steady casting shear employing a well-dried, ultrasmooth glass-roller. The entire assemblies comprising of the cast films were immediately then immersed in a precipitation bath containing ultra-pure water as non-solvent, maintained at room temperature, for immersion precipitation. To ensure the adequate exchange between solvent and non-solvent followed by a resultant absolute removal of the porogen as well as the solvent from the membrane matrices, the prepared membranes were taken out of the water bath and rinsed in fresh water for several instants. The entire casting process was carried out in a controlled environmental atmosphere, where temperature and relative humidity were maintained at $25(\pm 1)$ ^oC and 35-40%, respectively. The membranes as developed under invariable casting condition were properly stored in a water-bath. The membranes were categorized based on the difference in the specified compositions and accordingly defined as Psf: $F_T/1$ – nano-TiO₂UF and Psf: $F_T/3$ – nano-TiO₂ UF for the dope solution of Set-A; Psf: F_C/1- nano-TiO₂UF and Psf: F_C/3- nano-TiO₂ UF for the dope solution of Set-B; Psf:1- nano-TiO₂UF and Psf:3- nano-TiO₂ UF for the dope solution of Set-C; and the Control-Psf UF, presented in Table 6.1.

6.2.1.5. Characterization of the as-synthesized organofunctionalized nano-TiO₂

Phase purity and structure of the functionalized derivatives of nano-TiO₂ (F_T / F_C –nano-TiO₂) were determined by X-ray powder diffraction (XRD) analysis, where the data was collected on a Philips X'Pert pro X-ray diffractometer using Cu-K α radiation ($\lambda = 1.5418$ Å) at 40 kV and 30 mA. The average crystallite sizes were estimated using Scherrer's formula ($t = K\lambda/B \cos\theta$, where

t = average crystallite size in Å, K = Scherrer constant usually taken as 0.9 Å, λ = X-ray wavelength, θ is the Bragg angle, and B = integral breadth of a reflection located at 2θ).

The spontaneous Raman spectra of F_T / F_C – nano-TiO₂ were obtained using a STR-300 micro-Raman spectrometer (SEKI Technotron, Japan). The data acquisitions were carried out over a spectral range of 50–1000 cm⁻¹ at room-temperature for an identical acquisition period of 200 s. The samples were excited at 532 nm (power ~20 mW at the sample spot, Diode Pumped Solid State laser) using a 10X objective lens (Olympus). The scattered light was collected by the same objective lens and a fiber-coupled 300 mm spectrograph (Acton series SP 2300i, 1200 gr/mm) and detected by a thermo-electric cooled (-75°C) charge-coupled device (CCD).

The FTIR spectra of the two different classes of F_T/F_C –nano-TiO₂ were recorded in attenuated total reflectance (ATR) mode using a Bruker Vertex 70 FTIR spectrometer, in a range of 400 – 4000 cm⁻¹.

For X-ray Photoelectron Spectroscopic (XPS) technique, a DESA-150 electron analyzer (Staib Instruments, Germany) equipped with Mg-K α X-ray source (1253.6 eV) was employed for characterization purpose. The spectrometer's binding energy scale was calibrated with Au-4f_{7/2}photo-peak at a binding energy (B.E.) of 83.95 eV. The spectra were recorded as the intensity (number of counts per second) versus B.E. The curve fitting of the multiplex photopeaks was performed using Gaussian functions and then peak area as well as full width at half maximum (FWHM) were also determined.

6.2.1.6. Physicochemical characterizations of the mixed-matrix UF membranes

The mixed-matrix (Psf: F_T / F_C -nano-TiO₂) UF membranes of two different classes were cut into smaller sized strips having an area of 0.5 cm² and then coated with Au/Pd (60/40) using a sputter coater (Model No. K550X Emitech), under the optimized conditions (Sputtering time: 60 s, Sputter current: 30 mA and Tooling factor: 2.3), in order to reduce the effect of charging making them electrically conductive. Quantitative elemental analysis of these membranes' surfaces was then performed by an energy dispersive X-ray spectrometer (EDX, INCA Oxford Instruments, UK), coupled to a Scanning Electron Microscope (CamScan-CS3200LV, UK) and a microanalysis system. It was equipped with an ultrathin beryllium window and 20 mm² Si-detector. For EDX analysis, an accelerating voltage of 20 kV and a magnification of 4000X were employed. The spectra were acquired for the element of interest, *i.e.*, Ti of organofunctionalized nano-TiO₂, as impregnated in the membrane matrices at varying concentrations and C, S, O as well.

Static sessile-drop method was adopted to carry out rapid as well as replicate measurements of the contact angles, and thereby analyze the overall surface hydrophilic features of the investigated membranes having physicochemical heterogeneities. A contact angle measuring instrument (DSA 100 of KRUSS Gmbh, Germany) with DSA 1 v 1.92 software was employed for such evaluation purposes. A specific drop volume of 3 μ l of the probe-solvent (water), deposited from a micro-syringe needle was steadily allowed to produce on each of the membrane surface. The acquisition of the equilibrium contact angle values, at the membrane-solvent-air interface was accomplished with an equal residence time of 60 s. After continuous such measurements being carried out at eight different locations of each membrane surface, the

contact angle values were averaged out and by this means reported with their standard deviations for the respective membranes.

The electrokinetic characteristics of the similar sets of membranes were evaluated by employing ZetaCAD electrokinetic analyzer (CAD Inst., France), which consisted of a quartz-cell configuration being capable of holding two flat sheets of each membrane in such a way that the probed membranes remained separated by spacers and their skin layers faced each other creating a slit channel for tangential flow of electrolytic solution across the membranes.The streaming potential, generated due to the bidirectional flow of 10^{-3} M KCl as background electrolyte solution, under applied pressure gradient across the membrane was measured by Ag/AgCl electrodes, equipped with the cell. Zeta potentials (ζ) of the membranes were evaluated using the streaming potential values and on the basis of Helmholtz-Smoluchowski equation(Eq. 2.11). An average value of ζ , derived from three replicates was reported and the measurement error was found to be ± 0.4 mV.

For measurement of porosity of the investigated UF membranes, gravimetric method was applied. There, a circular piece of each of the membrane with an area - A and thickness - h was weighed after taking it out from storage of distilled water and then carefully removing the superficial water with filter paper. The wet membranes were dried in a vacuum oven at 75 °C for 24 h before measuring the weight in dry state. From the weights of the membrane samples in wet (W_0) and dry (W_1) states, the porosity (\emptyset) of each membrane was calculated using Eq.2.18. In order to minimize the experimental error, measurements were carried out in duplicates and then calculated the average. Utilizing the porosity of the membrane, mean pore radius (r_m in nm) was also determined by employing the Guerout–Elford–Ferry equation (Eq. 2.19).

6.2.1.7. Evaluation of ultrafiltration performances of the mixed-matrix UF membranes

For all the membranes, the extents of molecular separationwere evaluated by analyzing the rejection behaviors of them towards neutral organic solutes such as PEG, with average Mw of 35 kDa and PEO, with average Mw of 100kDa. The test solutions were prepared by dissolving preweighed amount of PEG and PEO in ultra-pure water at a concentration of 200 ppm. The membranes having identical effective membrane area of 14.5 cm² were employed in a cross-flow filtration unit, operatedunder a transmembrane pressure of 1 bar at room temperature; and in view of minimizing the effect of experimental error the measurements were repeated with three different coupons of each membrane to obtain the average values. The concentrations of PEG and PEO in both feed and product solutions were measured by analyzing the total organic carbon (TOC) content of the samples using TOC analyzer (ANATOC-II, SGE analytical science, Australia) and employed for estimation of percentage rejection of the probe organic solutes (R_{PEG/PEO}) following Eq. 2.20.

The steady-state solvent flux (J in $L.m^{-2}day^{-1}$) was determined by direct as well as replicate measurements of the permeate flow following Eq. 2.21. Prior to all UF test experiments, the membranes were initially subjected to undergo hydraulic compaction for 1 h in water at standard UF test conditions to achieve stabilized performances of the membranes. The pure water flux (J_o) was measured whilst operated at 1 bar of transmembrane pressure.

Thereafter, a protein solution comprising of BSA (1000 ppm) and phosphate buffer (pH 7.4) was allowed to permeate through the membranes in dead-end filtration mode at the same transmembrane pressure for 30 min and the respective fluxes (J_1) were estimated. The concentrations of BSA in the solutions of measuring feed and permeate were analyzed by the

TOC analyzer, and the respective percentage rejection of BSA (R_{BSA})was calculated by means of Eq. 2.20. After filtration of the protein solution, the membranes were back-washed with ultrapure water for 30min at a similar transmembrane pressure and subsequently the water flux (J_2) of the cleaned membrane was estimated. The antifouling property of the membranes was evaluated by means of determination of the flux recovery ratio(FRR), which was calculated using Eq.6.1 as²⁵⁴:

$$\mathbf{FRR} = \begin{pmatrix} \underline{\mathbf{I}_2} \\ \underline{\mathbf{J}_0} \end{pmatrix} \times \mathbf{100} \%$$
(6.1)

The flux decline caused by the reversible and irreversible protein fouling, designated by R_r and R_{ir} , were defined by Eq. 6.2 and 6.3, respectively as:²⁵⁴

$$R_{\rm r} = \left(\frac{J_2 - J_1}{J_0}\right) \times 100 \%$$
(6.2)

$$R_{ir} = \left(\frac{J_0 - J_2}{J_0}\right) \times 100 \%$$
(6.3)

The occurrence of overall membrane fouling was considered as the collective contribution of reversible and irreversible fouling, thus the degree of flux decline caused by overall protein fouling (\mathbf{R}_t) in the process of UF was defined by Eq. 6.4 as:

$$R_t = R_r + R_{ir} = \left(1 - \frac{J_1}{J_0}\right) \times 100\%$$
 (6.4)

6.2.2. Results and discussions

6.2.2.1. Analysis of physicochemical characteristics of the organofunctionalized nano-TiO₂

The X-ray diffraction patterns of the synthesized functionalized derivatives of nano-TiO₂, *i.e.*, F_T -nano-TiO₂ and F_C -nano-TiO₂ are shown in Figs. 6.2a and 6.2b, respectively. The XRD

pattern of Fig. 6.2a reveals the presence of a strong diffraction peak at 25.3° (FWHM: 0.6561), indexed to (101) plane diffraction and few successive peaks with lower intensities at 37.8°, 48.1°, 54.2°, 55.2°, 62.6°, 68.9°, 70.1° and 75.1°, which are indexed to the corresponding (004), (200), (105), (211), (204), (116), (220) and (215) plane diffractions, respectively and accordingly attributed to the anatase phase of F_T-nano-TiO₂. Likely, in the XRD pattern of Fig. 6.2b, an intense diffraction peak, appeared at 25.3° (FWHM: 0.7071) followed by few peaks of lower intensities, appeared at 37.9°, 48.1°, 54.3°, 55.1°, 62.6°, 68.8°, 70.3° and 75.2° are indexed to the subsequent (101) and (004), (200), (105), (211), (204), (116), (220), (215) plane diffractions, respectively, and thereby attributed to the anatase phase of F_C-nano-TiO₂.²⁵⁵ The most abundant and thermodynamically stable low energy (101) facets of anatase nano-TiO₂ are supposed to be the reactive surfaces, wherein chemisorptions are occurred when each of the organoligands' two potentially labile protons, *i.e.*, in Tiron associated with the catecholic oxygens and in Chromotropic acid that of the hydroxyl groups induce chemical interactions with the chelating surface Ti atoms of the nano-TiO₂.²⁵⁶ In accordance with the Scherrer formula, the average crystallite sizes of F_T-nano-TiO₂ and F_C-nano-TiO₂ are estimated to be 12.97 and 12.03 nm, respectively.



Fig. 6.2: XRD patterns of the functionalized nano-TiO₂, (a) F_T – nano-TiO₂ and (b) F_C – nano-TiO₂.

The Raman spectra of the F_T – nano-TiO₂ and F_C – nano-TiO₂, acquired at room temperature are shown in Figs. 6.3a and 6.3b, respectively. Anatase phase of nano-TiO₂ is known to belong to a space group D^{19}_{4h} , $I4_1$ /amd with two primitive unit cells, each containing two formulae units of the nano-TiO₂.²⁵⁷ Factor group analysis reveals that there are six Raman active vibrations: $A_{1g}+2B_{1g}+3E_g$. The characteristic frequencies of the Raman bands as observed in Figs. 3a and 3b are 145.2, 198.2, 394.2, 515.8, 634.9 cm⁻¹ and 148.3, 197.6, 394.2, 514.4, 637.4 cm⁻¹, respectively. Amongst these, the bands with highest intensities at 145.2, 148.3 cm⁻¹, the bands with comparatively lower intensities at 634.9, 637.4 cm⁻¹, and the bands with very low intensities at 198.2, 197.6 cm⁻¹ are assigned to the E_g modes of F_T – nano-TiO₂ and F_C – nano-TiO₂, respectively. The bands, both appearing at 394.2 cm⁻¹are referred to the B_{1g} mode. The higher frequency bands, at 515.8 and 514.4 cm⁻¹ are doublet of the A_{1g} and B_{1g} modes.



Fig. 6.3: Room-temperature Raman spectra of the organofunctionalized nano-TiO₂, (a) F_T – nano-TiO₂ and (b) F_C – nano-TiO₂.

The FTIR spectra, represented in Figs. 6.4a and 6.4b corroborate the accomplishment of functionalization of nano-TiO₂ by the employed organoligands, resulting formation of F_T – nano-

TiO₂ and F_C – nano-TiO₂, respectively. A high intensity band attributed to the characteristic Ti-O-Ti stretching vibration appears at 638 cm^{-1} for the former and at 634 cm^{-1} for the latter. The bands at 1034 and 1038 cm⁻¹, assigned to the asymmetric stretching vibration of S–O groups, $v_{asym}(S-O)$, and the bands at 1155, 1158 and 1245, 1240 cm⁻¹, corresponded to symmetric and asymmetric stretching vibrations of the S=O groups *i.e.*, v_{sym} (S=O) and v_{asym} (S=O), respectively substantiate the chemisorptions of Tiron and Chromotopic acid onto the reactive facets of nano-TiO₂.²⁵⁸ The bands at 1458 and 1460 cm⁻¹ are ascribed to the characteristic stretching vibration of the aromatic rings, v(C=C) originated from the benzene and naphthalene rings of the F_T – nano-TiO₂ and F_C – nano-TiO₂, respectively. The broad bands at 3200 and 3263 cm⁻¹, and comparatively narrower bands at 1630 and 1632 cm^{-1} are attributed to the stretching and bending vibrations of the O-H groups, v(O-H) and δ (O-H) originated from the adsorbed water molecules and hydroxyl groups on the surface of F_T – nano-TiO₂ and F_C – nano-TiO₂, respectively. Moreover, a close comparison of the intensities of v(O-H) reveals that the extent of hydroxyl groups, reflecting to the surface hydrophilic sites is more in F_T – nano-TiO₂ than F_C – nano-TiO₂, which is supposed to happen by the more chemisorption of Tiron over Chromotropic acid, resulting out from their structural differences.

The detailed mechanisms of chemisorptions of the Tiron and Chromotropic acid onto the surfaces of nano-TiO₂ were further explored by XPS analysis. The variations in B.E. and respective peak areas, presented in Table 6.2, acquired from the deconvoluted core level X-ray photoelectron spectra of O-1s (Figs. 6.5a and 6.6a), Ti-2p (Figs. 6.5b and 6.6b), S-2p (Figs. 6.5c and 6.6c) and C-1s (Figs. 6.5d and 6.6d) reveal that the structural heterogeneities of the organoligands modulate the molecular level interactions in F_T – nano-TiO₂ and F_C – nano-TiO₂.



Fig. 6.4: FTIR spectra of the organofunctionalized nano-TiO₂, (a) F_T – nano-TiO₂ and (b) F_C – nano-TiO₂.

The curve fitting and deconvolution of O-1s core-level spectra exhibit the asymmetric pattern of each spectrum, presented in Fig. 6.5a, corresponding to F_T – nano-TiO₂ whichyields two constituent spectra; whereas the spectrum with more asymmetry, presented in Fig. 6.6a, attributed to F_C – nano-TiO₂ constitutes three distinctive spectra. Thus, herein we propose that different states of chemical fixation happen in the probed organofunctionalized nanoparticles. The peaks located at B.E. of 529.2 (FWHM: 1.65 eV) and 529.5 eV (FWHM: 2.24 eV), presented in Table 6.2 are attributed to the O-atoms (Ti–O–Ti) of F_T – nano-TiO₂ and F_C – nano-TiO₂, respectively. The broad peaks at higher B.E. of 531 eV for both, however associated with higher FWHM for the former (3.63 eV) than the latter (1.68 eV) are assigned to the O-atoms of the precursor complexing ligands, that are bonded to the nano-TiO₂ surface as C–O–Ti. Such route of chemical fixation is attributed to the occurrence of dissociative adsorptions onto the (101) facets, which are further supposed to occur when the covalently bonded labile protons dissociate from both the –OH groups of each of the organoligands, *i.e.*, Tiron and Chromotropic acid, and subsequently bridge with Ti atoms on the surface of nano-TiO₂, resulting bidentate

binuclear bridging during fixation (Figs. 6.1a and 6.1b).²⁵⁹ In case of F_T – nano-TiO₂, there remains another possibility of concurrent but competitive mode of chemisorption, where chelating mononuclear bidentate sites are formed through bonding of the both O-atoms of adjacent -OH groups (catecholate type) to a single Ti atom (Fig. 6.1a).²⁶⁰ The high intensity and relative peak area of the concerned peak, as indicated in Fig. 6.5a and Table 6.2 substantiate the contribution of the proposed geometry in mixed coverage of bridging and chelating structures in F_T – nano-TiO₂. The appearance of a third constituent peak in the deconvoluted spectrum of O-1s in Fig. 6.6a reveals the concurrent presence of an additional geometry along with the aforementioned bridging bidentate one in F_C – nano-TiO₂, which has also been schematically presented in Fig. 6.1b. The peak at B.E. of 532.5 eV with FWHM of 2.54 eV is attributed to the O-atoms of -OH groups which are covalently bonded to the ring C-atoms of Chromotropic acid, and thus it signifies the contribution of monodentate geometry in F_C – nano-TiO₂.²⁵⁶ It happens when one -OH group gets deprotonated and subsequently bonded to Ti atom, however the neighbouring one remains as such. The bulkiness of the organoligand, Chromotropic acid may be ascribed as the reason behind the formation of monodentate geometry, instead of the chelating mononuclear bidentate geometry like in F_T – nano-TiO₂. A comparison of the relative peak areas imply that the monodentate geometric configuration is energetically more preferred than the bridging bidentate geometric configuration and relevantly, the occupancy of the former on the surface of F_{C} - nano-TiO₂ remains greater than the latter.

The Ti-2p spectra, represented in Figs. 6.5b and 6.6b exhibit the presence of strong peaks at 458 and 458.8 eV with FWHM of 1.74 and 1.99 eV, attributed to Ti- $2p_{3/2}$, and weak peaks at 464 and 464.4 eV with FWHM of 2.40 and 2.57 eV, assigned to Ti- $2p_{1/2}$, where the two peaks are

originated from the surface of Ti⁴⁺ atoms in anatase phase of F_T – nano-TiO₂ and F_C – nano-TiO₂, respectively.²⁵⁶ The distinct shifts of B.E. of Ti-2p_{3/2} and Ti-2p_{1/2},by 0.8 and 0.4 eV, respectively with concurrent broadening of the peaks substantiate that the Chromotropic acid seems capable of strongly abstracting electrons from the adjacent Ti⁴⁺ in the bridging structure of F_C – nano-TiO₂ as compared to the Tiron in F_T – nano-TiO₂. The component peaks reside in a 2:1 ratio of Ti-2p_{3/2}:Ti-2p_{1/2} peak intensity, but the ratio is slightly higher in case of the former as compared to the latter. The deconvoluted core level S-2p spectra, presented in Figs. 6.5c and 6.6c exhibit two contributing peaks, wherein the more intense peaks appearing at 168.7 and 169.6 eV, with FWHM of 3.33 and 2.95 eV, respectively are assigned to the sulfur of $-SO_3^-TH^+$ groups attached to the benzene ring of the bridged Tiron and naphthalene ring of the bridged Chromotropic acid, and the less intense peak at 163.8 eV (FWHM: 4.21 and 3.40 eV) for both corresponds to the presence of sulfur in the converted SH groups.

	Ti-2p	3/2 & Ti-	2p1/2		S-2p			C-1s			O-1s	
Codes	BE	FWH	Peak	BE	FWH	Peak	BE	FWH	Peak	BE	FWH	Peak
	(eV)	Μ	area	(eV)	Μ	area	(eV)	Μ	area	(eV)	Μ	area
		(eV)	(%)		(eV)	(%)		(eV)	(%)		(eV)	(%)
o-TiO ₂	458	1.74	67.98	163.8	4.21	43.08	 284.4	2.38	67.50	529.2	1.65	47.19
– nane	464	2.40	32.02	168.7	3.33	56.92	286.8	4.15	32.50	531.0	3.63	52.81
F_{T}												
-TiO ₂	458.8	1.99	70.29	163.8	3.40	34.30	284.8	2.53	75.42	529.5	2.24	17.70
- nano-	464.4	2.57	29.71	169.6	2.95	65.70	287.5	3.84	24.58	531.0	1.68	38.21
F _c –										532.5	2.54	44.09

Table 6.2: Curve fitting summary of different XPS peaks for a) F_T – nano-TiO₂ and b) F_C – nano-TiO₂.

The greater electron withdrawing ability of the naphthalene ring enables more deshielding effect on the sulfur of $-SO_3^-H^+$ groups in F_C – nano-TiO₂ and thereby exerts higher chemical shift than in the case of F_T – nano-TiO₂. An insight of the ratios of relative intensity (Table 6.2) of the component peaks signifies the relative conversion of the $-SO_3^-H^+$ sites into the -SH, and such occurrence is more constrained in F_C – nano-TiO₂ as compared to F_T – nano-TiO₂. However, the conversion happens without any intervention of external reducing or hydrogenating agent, and thus it is attributed to the effect of photoelectron exposure during XPS measurement.²⁶¹



Fig. 6.5: High resolution photoelectron spectra obtained from F_T – nano-TiO₂ (line with bullets: experimental data; solid line: curve fit of the experimental data); a) O-1s, b) Ti-2p, c) S-2p and d) C-1s.

The deconvolution of the C-1s core-level spectra of as-synthesized F_T – nano-TiO₂ and F_C – nano-TiO₂, presented in Figs. 6.5d and 6.6d, respectively exhibits the presence of two distinct peaks

for C atoms residing in different chemical environments. The intense component peaks appeared at the lowest B.E. of 284.4 and 284.8 eV (Table 6.2), with respective FWHM of 2.58 and 2.53 eV are ascribed to the non-oxygenated ring C of C–C or C–H.²⁶² The broader and less intense peaks appearing at B.E. of 286.8 and 287.5 eV, with FWHM of4.15 and 3.84 eV are referred to the C atoms of C–Osegments.^{42, 43} The effect of deshielding in subsequent chemical shift values is found to be more pronounced in F_C – nano-TiO₂ than F_T – nano-TiO₂, which is attributed to the difference in structural attributes of the complexing organoligands.



Fig. 6.6: High resolution photoelectron spectra obtained from F_C- nano-TiO₂ (line with bullets: experimental data; solid line: curve fit of the experimental data); a) O-1s, b) Ti-2p, c) S-2p and d) C-1s.

6.2.2.2. Analysis of physicochemical features of the mixed-matrix UF membranes

The EDX spectra of the representative membranes, namely Control-Psf UF, Psf:3- nano-TiO₂ UF, Psf: F_T/3 – nano-TiO₂ UF and Psf: F_C/3 – nano-TiO₂ UF are presented in Figs. 6.7a, 6.7b, 6.7c and 6.7d, respectively. All the spectra exhibit the presence of C, S and O peaks, whereas the distinct elemental peak of Ti gets obtained along with the C, S and O peaks in the mixed-matrix UF membranes only. The variations in nanoparticle density, examined through the quantitative elemental analysis of the membranes in terms of the given relative weight and atomic percentages are presented in Table 6.3. The variations in elemental presence of C and S indicate that the differential distributions of the specified elements fall sharply from the bare membrane to the mixed-matrix UF membrane derived employing non-functionalized nano-TiO₂, however there are enhancement in enrichment of those elements when organofunctionalized nano-TiO₂ i.e., F_T - nano-TiO₂ and F_C - nano-TiO₂ are impregnated at similar concentrations. A further insight of such variations in the latter two membranes signify the influence of structural heterogenities of the tethered organoligands. Furthermore, a comparison of the relative weight and atomic percentages of O and Ti in the probed membranes infers that, the skin region of Psf:3-nano-TiO₂ UF is significantly populated with the impregnated nano-TiO₂, and subsequently the surface chemistry gets changed in comparison to the skin region of Control-Psf UF. It is also observed that the nanoparticle densities in the skin regions of Psf: $F_T/3$ – nano-TiO₂ UF and Psf: $F_C/3$ – nano-TiO₂ UF are reduced, and the decline is more in case of the latter. Such variations corroborate that the stability of precursor nanoparticle's dispersion as made in the organic medium of NMP plays a dominating role in their effective uniform distribution within the polymer matrices of the membranes. The stability of such dispersion is known to vary with the interparticle interaction, which is measured by the van der Waals pair interaction energy.¹⁸¹ The energy parameter is proportionally related to the Hamaker constant, which is inversely dependent on the interparticle distances and differs with the concentration as well as surrounding chemical environment.¹⁸¹In case of nano-TiO₂, there remains obvious higher interparticle attractive force during their dispersion in NMP, and hence, they tend to come closer and induce flocculation, the resultant effect of which is manifested through the extensive presence of nano-TiO₂ in the skin region of Psf:3 – nano-TiO₂ UF.

	Elemental (C) quantification		Elementa	ul (O)	Elemental (S)		Elemental (Ti)	
UF Membranes Codes			quantification		quantification		quantification	
	Wt (%)	Atomic	Wt (%)	Atomic	Wt (%)	Atomic	Wt (%)	Atomic
		(%)		(%)		(%)		(%)
Control-Psf	79.83 ± 0.12	86.31	13.55 ± 0.11	11.00	6.62 ± 0.09	2.69	-	-
Psf:3- nano-TiO ₂	60.22 ± 0.18	68.75	33.54 ± 0.21	28.75	5.05 ± 0.14	2.16	1.19 ± 0.15	0.34
Psf: F _T /3– nano-TiO ₂	75.31 ± 0.27	82.66	17.77 ± 0.15	14.64	5.81 ± 0.18	2.39	1.11 ± 0.18	0.31
Psf: F _C /3– nano-TiO ₂	79.68 ± 0.22	86.42	13.35 ± 0.17	10.87	6.08 ± 0.23	2.47	0.89±0.26	0.24

Table 6.3: Skin layer elemental analysis of the membranes: (a) Control-Psf UF, (b) Psf:3– nano-TiO₂ UF, (c) Psf: $F_T/3$ – nano-TiO₂ UF and (d) Psf: $F_C/3$ – nano-TiO₂ UF.

However, tethering of the organoligands on the surfaces of nano-TiO₂ restricts their coagulation propensity in the respective dispersion media by inducing steric as well as electrostatic repulsion, and in that way reducing the attractive van der Waals inter-particle potential as well.²⁶³ The

bulkiness of the Chromotropic acid over Tiron obviously plays a decisive role in tuning the extent of such steric repulsion. The measured weight and atomic percentages of Ti and O in Psf: $F_T/3$ – nano-TiO₂ UF and Psf: $F_C/3$ – nano-TiO₂ UF substantiate the aforementioned mitigating features and the pronounced effect of such in case of the latter as well. This ensures a facilitated distribution of the F_T – nano-TiO₂ and F_C – nano-TiO₂, over the nano-TiO₂ in the resultant mixed-matrix UF membranes.



Fig. 6.7: EDX spectra of skin regions of the membranes: (a) Control-Psf UF, (b) Psf:3– nano-TiO₂ UF, (c) Psf: $F_T/3$ – nano-TiO₂ UF and (d) Psf: $F_C/3$ – nano-TiO₂ UF.

The hydrophilic characters of the investigated membranes are assessed with respect to the probe solvent – water to evaluate the role of organofunctionalized nano-TiO₂ in modifying the surface

chemistry of the mixed-matrix UF membranes. The variations in hydrophilic characters, represented in Fig. 6.8 reveal that impregnation of nano-TiO₂ improves the hydrophilicity and such improvement is more pronounced when organofunctionalized nano-TiO₂, *i.e.*, F_T - nano-TiO₂ and F_{C-} nano-TiO₂ are impregnated on progressively higher concentrations. More particularly, impregnations with 1 and 3 (w/w_{Psf})% loading of nano-TiO₂ reduce the contact angle of Control-Psf UF (70.7°) by 2.2° and 4.1° in Psf:1- nano-TiO₂ UF and Psf: 3- nano-TiO₂ UF, respectively. However, the extent of such decline in contact angle turns more pronounced when impregnations of 1 and 3 (w/w_{Psf})% of F_T - nano-TiO₂exhibit sharp drops by 7.9° and 10.2°, respectively. The mixed-matrix UF membranes derived employing 1 and 3 (w/w_{Psf})% of F_{C-} nano-TiO₂ show even further enhancement in hydrophilicity when there occurs decrease in contact angle value by 8.8° and 11.6°, respectively with respect to the Control-Psf UF. The impregnation of organofunctionalized nano-TiO₂ influences the direction of migration and subsequent dispersion of the nanoadditives towards the skin surfaces of the membranes owing to the more affinity of them towards the non-solvent, water.³⁸



Fig. 6.8: Hydrophilic characters of the membranes: Control-Psf UF, Psf:– nano-TiO₂ UF, Psf: F_T – nano-TiO₂ UF and Psf: F_C – nano-TiO₂ UF.

The variations in hydrophilic characters corroborate that the hydrophilic $-SO_3^-H^+$ groups of the tethered organoligands significantly enhance the efficacy of nano-TiO₂ in modifying the intrinsic hydrophobic character of the Control-Psf UF. Furthermore, the facilitated distribution of organofunctionalized nano-TiO₂ within the polymer matrix of Psf implies that the modified nanoadditives not only influence the physicochemical features of the membranes' skin surfaces but also the skin layers' porous pathways,²⁶⁴ which collectively contribute in enhancing the hydrophilicity of the mixed-matrix UF membranes.

Electrokinetic features of the membranes, determined by tangential streaming potential measurements with respect to 10^{-3} M KCl solution are represented in Fig. 6.9. The matrix of Control-Psf UF devoid of any dissociable functionality being capable of creating surface charges, and thus the respective ζ of – 20.38 mV is attributed to the effect of specific adsorptions of Cl⁻ions from the electrolyte solution on the hydrophobic membrane surface.²⁶⁵ However, the investigated mixed-matrix UF membranes provide different weak or strong sources of charges, which arise due to the non-covalently fixed –OH groups on the surface of nano-TiO₂ or the $-SO_3^-H^+$ groups of the organoligands being attached to the nano-TiO₂. Therefore, the mixed-matrix UF membranes' surfaces exhibit predominant contributions of the tethered functionalities in surpassing the tentative ionic adsorptions by the intrinsic character of the core Psf matrix. The charge carrying sites of the mixed-matrix UF membranes induce surface conductivity in the membranes, and relevantly the extent and exposure of the charge carrying organoligands through their variant distributions alter the electrokinetic features of the membranes as well.²⁶⁶ The influence of such gets reflected through the variations in ζ of the mixed-matrix UF membranes, as the ζ changes from –15.87 to –12.47 mV for Psf: nano-TiO₂

UF, -13.74 to -11.44 mV for Psf: F_T- nano-TiO₂ UF and -13.48 to -10.96 mV for Psf: F_Cnano-TiO₂ UF on impregnation of 1 and 3 (w/w_{Psf})% of nano-TiO₂, F_T- nano-TiO₂ and F_Cnano-TiO₂, respectively. The decline in negative ζ values of the mixed-matrix UF membranes as compared to the Control-Psf UF indicates that the occurrence of severe ionic adsorption on the core Psf matrix of the latter gets overcompensated by the occurred electrokinetic events influenced through the modified compositions of electrochemical double layers in the formers. Such influence is also observed to be progressively pronounced on moving from Psf: nano-TiO₂ UF to Psf: F_T- nano-TiO₂ UF and then to Psf: F_C- nano-TiO₂ UF. The enhanced impregnations of F_T- nano-TiO₂ and F_C- nano-TiO₂ seem to markedly elevate the skin layer conductivities of the respective membranes; however, in spite of such elevation the ζ values decrease to some extent.



Fig. 6.9:Electrokinetic features of the membranes: Control-Psf UF, Psf:– nano-TiO₂ UF, Psf: F_T – nano-TiO₂ UF and Psf: F_C – nano-TiO₂ UF.

This variance can be demonstrated as the result of dragging of the tangentially driven counterions from the hydrodynamic slipping plane or plane of shear to the bulk of the membranes charged layer, through the hydrodynamically stagnant layer of counter-ions. The effective streaming currents of the membranes are thus supposed to get reduced because of such diffusive back flow of the streaming current,²⁶⁷ the phenomenon which is substantiated by the observed electrokinetic features, as manifested through the decline of ζ of the respective membranes.

The variation in porosities of the mixed-matrix UF membranes as a function of the extent of nanoadditives is represented in Fig. 6.10a. Distinctive improvement in the porosities of the mixed-matrix UF membranes get substantiated by the following observed changes, *i.e.*, 40(±0.5)% of the Control-Psf UF to 48(±1)% for Psf:1- nano-TiO₂ UF,55(±0.4)% for Psf: $F_T/1$ nano-TiO₂ UF, and then further to $66(\pm 0.5)\%$ for Psf: F_C/1– nano-TiO₂ UF. The enhancement in porosity is found to be more pronounced while all the employed nanoadditives are impregnated at higher concentration. The organofunctionalized nanoadditives exert their superior effectiveness in modifying the porous morphology of the membranes. The variations in porosities of the mixed-matrix UF membranes *i.e.*, $78(\pm 0.6)\%$ for Psf:3– nano-TiO₂ UF,81(±0.5)% for Psf: F_T/3- nano-TiO₂ UF and 87(±0.8)% for Psf: F_C/3- nano-TiO₂ UF further corroborate the aforesaid fact. The trends also imply that the sheaths of the organoligand -Chromotropic acid seem to remain more effective as compared to that of the Tiron in tuning the electrostatic stabilization of the nano-TiO₂ within the precursor dope solutions, and resultantly providing more porous mixed-matrices in comparison to the former. Further evaluation of the membranes' mean pore radii, represented in Fig. 6.10b indicates that the membranes derived employing higher quantity of the nano-TiO₂ or the organofunctionalized nano-TiO₂consist of significantly finer pores than the membranes derived employing comparatively less quantity of the nanoadditives. The obtained mean pore radii are found to vary accordingly *i.e.*, about 49 to 43 nm for Psf: nano-TiO₂ UF, 83 to 57 nm for Psf: F_T – nano-TiO₂ UF and 74 to 55 nm for Psf: F_C – nano-TiO₂ UF on impregnation of 1 and 3 (w/w_{Psf})% of nano-TiO₂, F_T – nano-TiO₂ and F_C – nano-TiO₂, respectively. It is also noteworthy to mention that the obtained porosities and the respective mean pore radii of the mixed-matrix UF membranes always carry an inverse relationship since the membranes with more porous features encompass with finer, *i.e.*, smaller sized pores and *vice versa*. The said characteristics of the investigated membranes are supposed to be the contributory effect of the hydrophilic nanoadditives in affecting the mechanism of the phase inversion process.²⁶⁴ The formation of phase inversion membranes is known to be controlled by thermodynamic as well as kinetic variations ensuing either instantaneous or delayed demixing during precipitation of the casting polymer solutions.^{156,268}



Fig. 6.10: Variations in (a) porosities and (b) mean pore radii of the membranes: Control-Psf UF, Psf:– nano-TiO₂ UF, Psf: F_T – nano-TiO₂ UF and Psf: F_C – nano-TiO₂ UF.

The instantaneous demixing generally leads to membrane with a highly porous substructure and a finely porous thin skin layer, however, in a contrast manner, the delayed demixing results in a membrane comprising porous substructure with a dense skin layer. In accordance with the aforementioned variations, we thus assume that the organofunctionalized nano-TiO₂ noticeably facilitates the rate of instantaneous demixing, *i.e.*, the diffusive mass exchange between the solvent and the non-solvent.

6.2.2.3. Study of mixed-matrix UF membranes solute rejection and solvent flux behaviors

The %SR and PWP, measured under a steady operating condition, reflecting the variations in macroscopical features of the mixed-matrix UF membranes are presented in Figs. 6.11a and 6.11b, respectively. The representations signify that the organofunctionalized nano-TiO₂, as persuasive nanoadditives induce noteworthy physicochemical variations in the projected mixed-matrix UF membranes. The %SR towards the probed solutes, PEG and PEO are found to be89.2and91.6%, respectively for Control-Psf UF. They increase to 91.2, 93.4 and 92.4, 94.8% for Psf:1– nano-TiO₂ UF and Psf:3– nano-TiO₂ UF, respectively. However, the rejections of the solutes get slightly reduced to 88.6, 92.1 and 89.7, 92.8% for Psf: $F_T/1$ – nano-TiO₂ UF and Psf: $F_T/3$ – nano-TiO₂ UF, respectively. For Psf: $F_C/1$ – nano-TiO₂ UF and Psf: $F_C/3$ – nano-TiO₂ UF, the rejections of the solutes are found to be 90.7, 93.5 and 91.5, 94.9%, respectively. The analyses of steady state PWP of the membranes indicate gradual change from 1750 LMD for Control-Psf UF to 1920 LMD for Psf:1– nano-TiO₂ UF and then to 2000 LMD for Psf:3– nano-TiO₂ UF. The impregnations of organofunctionalized nano-TiO₂, *i.e.*, F_T – nano-TiO₂ and F_C – nano-TiO₂ within the Psf matrices of the mixed-matrix UF membranes also give rise to obvious improvement in PWP. The enhancements are manifested through the obtained PWP as 3500,

4000 and 3400, 4300 LMD for Psf: F_T/1- nano-TiO₂ UF, Psf: F_T/3- nano-TiO₂ UF and Psf: $F_C/1-$ nano-TiO₂ UF, Psf: $F_C/3-$ nano-TiO₂ UF, respectively. The trends obtained for the macroscopical features are in well accordance with the discussed variations in porosities and mean pore radii of the investigated membranes. The non-solvent induced phase inversion process is known to form asymmetric porous structures wherein the discriminating pores formed at the dense skin regions remain smaller in size as compared to the pores formed at the interior regions.¹⁴³ Since impregnation of nano-TiO₂ as well as organofunctionalized nano-TiO₂ influences the mechanism of such pore-formation during phase inversion process by altering the rate of both, *i.e.*, non-solvent's indiffusion and the solvent's outdiffusion, the resultant formation of finer pores evidently leads to the enhancement in %SR for the respective mixed-matrix UF membranes. The concurrent increase in PWP of the membranes also corroborates the above fact in addition to the contributing factor of enhancement in the surface hydrophilicity as discussed earlier. However, the extent of increase in PWP on impregnation of nano-TiO₂ at higher weight fraction seems to be not pronounced as in the case of loading at lower weight fraction, which can be attributed to the notorious effect of tentative aggregation at higher concentration of nano-TiO₂ and the consequent presence of clusters of nano-TiO₂ in the dense skin region of the membrane matrix. It can be anticipated that the modified nanoadditives play superior role in controlling the formation of finer pores in the skin region of the membranes in association with better uniformity in distribution of them within the polymer matrices. The variations in PWP as exhibited by the aforesaid mixed-matrix UF membranes comprising F_{T-} nano-TiO₂ and F_{C-} nano-TiO₂ substantiate that the effect of nanoparticles' aggregation tendency at higher concentration and consequent effect of such in membranes' macroscopical features are restricted to a great extent through deployment of the nanoparticles fabricated with sheath of organoligands. Furthermore, although the molecular transport through a semipermeable UF membrane gets predominantly controlled by hydrodynamic interactions, but there may also exist the simultaneous contribution of electrostatic interactions for the mixed-matrix UF membranes, wherein the implanted charged sites $(-SO_3'H^+)$ being part of the entrapped organofunctionalized nano-TiO₂ exert substantial electrostatic interactions with the diffusing solvent molecules, and thereby improve the hydrodynamic dragging efficiencies of the porous pathways.²⁶⁸ The mixed-matrix UF membranes having high porosities with finer pore sizes may thus carry immense importance because of their potential in providing facilitated transport feature, *i.e.*, better retention ability at high productivity towards permeating molecular species.



Fig. 6.11:Macroscopical features, a) % SR and b) PWP of the membranes: Control-Psf UF, Psf:– nano-TiO₂ UF, Psf: F_T – nano-TiO₂ UF and Psf: F_C – nano-TiO₂ UF.

6.2.2.4. Investigation of mixed-matrix UF membranes antifouling properties

In elucidating the persuasive contributions of the synthesized organofunctionalized nano- TiO_2in modulation of the investigated mixed-matrix UF membranes' antifouling property, the two-steps cyclic UF tests were performed with the membranes using BSA as model protein. Membrane

fouling gets influenced by both, hydrodynamic factors like permeation drag as well as back transport and interfacial interactions between the foulants and membranes, thus all the membranes' different fouling behaviors were evaluated under similar hydrodynamic condition. The time-dependent flux variations and the determined flux recovery ratios are represented in Fig. 6.12 and Table 6.4, respectively.

It is obvious from Fig. 6.12 that, for all the investigated membranes, the stabilized solvent fluxes decline on exposure of the membranes to the protein solution in comparison to that of pure water permeation. This is predominantly attributed to the notorious effect of membrane fouling caused by the interfacial secondary noncovalent (hydrophobic) interactions between the membrane's vulnerable polymeric surface and the penetrating foulants, *i.e.*, molecules of BSA; furthermore the latter progressively coalesce at the surface pore regions leading to pore-blockage as well as formation of cake layers, and thereby resist the solvent permeation.^{237, 240} During the first cycle (Cycle-I), FRR of the membranes as summarized in Table 6.4 indicates that it increases from 57.1% for Control-Psf UF to 57.9 and 60% for Psf:1- nano-TiO₂ UF and Psf:3- nano-TiO₂ UF; 65.7 and 75% for Psf: F_T/1- nano-TiO₂ UF and Psf: F_T/3- nano-TiO₂ UF; and 64.7 and 72.1% for Psf: F_C/1- nano-TiO₂ UF and Psf: F_C/3- nano-TiO₂ UF, respectively. The trends reveal that the investigated membranes comprising of the nanoadditive - nano-TiO₂ at variant concentrations exhibit slightly better antifouling characters as compared to the Control-Psf UF. This is owing to the improved hydrophilicity of the resultant mixed-matrix UF membranes wherein the hydration layers hinder the accumulation of the hydrophobic BSA molecules to some extent.²⁷⁰ However, the impact of the nanoadditives in functional characteristics of the membrane becomes distinctively more pronounced when the F_{T} - nano-TiO₂ and F_{C} - nano-TiO₂are employed at variant concentrations in customizing the membrane surfaces. Peripheral presence of the $-SO_3^-$ H⁺ groups, being tethered via the organoligands at the surface of nano-TiO₂ and the resultant uniformity in distributions of the modified nanoadditives within the Psf matrices impart strong long-range repulsive forces, and also lead to formation of more stable and dense foulant resistive superior hydration layers. The variations noticed in FRR of second cycle (Cycle-II) *i.e.*, 45.7% for Control-Psf UF to 47.4 and 50% for Psf:1– nano-TiO₂UF and Psf:3– nano-TiO₂ UF; 57.1 and 70% for Psf: $F_T/1$ – nano-TiO₂ UF and Psf: $F_T/3$ – nano-TiO₂ UF; and 55.9 and 65.1% for Psf: $F_C/1$ – nano-TiO₂ UF and Psf: $F_C/3$ – nano-TiO₂ UF, respectively substantiate the role of aforementioned facts in altering the protein-affinity feature of the Psf based membrane surfaces.

Table 6.4: Variations in antifouling properties of the investigated membranes in terms of flux recovery ratios (FRR) and resistances towards solvent fluxes caused by total fouling (R_t), reversible fouling (R_r) and irreversible fouling (R_t).

UF Membranes Codes		Cycl	e-I		Cycle-II				
	FRR (%)	R _r (%)	R _{ir} (%)	$R_{t}(\%)$	FRR (%)	$R_r(\%)$	R _{ir} (%)	$R_{t}(\%)$	
Control-Psf	57.1	28.6	42.9	71.5	45.7	22.9	54.3	77.2	
Psf:1 – nano-TiO ₂	57.9	21.1	42.1	63.2	47.4	15.8	52.6	68.4	
Psf:3 – nano-TiO ₂	60	20	40	60	50	15	50	65	
Psf: $F_T/1$ – nano-TiO ₂	65.7	17.1	34.3	51.4	57.1	11.4	42.9	54.3	
Psf: $F_T/3$ – nano-TiO ₂	75	10	25	35	70	7.5	30	37.5	
Psf: $F_C/1$ – nano-TiO ₂	64.7	17.7	35.3	53	55.9	11.8	44.1	55.9	
Psf: $F_C/3$ – nano-TiO ₂	72.1	13.9	27.9	41.8	65.1	9.3	34.9	44.2	

Since the fouling phenomena is intrinsically composed of both reversible and irreversible fouling occurrences, therefore the antifouling properties of the membranes are further investigated by

analyzing the resistances towards solvent fluxes caused by total fouling (R_i), reversible fouling (R_i), and irreversible fouling (R_{ir}).^{254,271} The effect of irreversible fouling seems to be more pronounced in reducing the solvent flux as compared to the reversible fouling since the latter can be well controlled by simple hydraulic cleaning whereas the former exhibits the sign of strong adhesion of the foulants to the membrane surface. It can be seen from the results of Table 6.4 that, during both cyclic UF operations the R_t value declines sharply with use of F_T - nano-TiO₂ and F_C – nano-TiO₂; the component values of R_t , *i.e.*, R_r and R_{ir} reduce successively for Psf: $F_T/1$ – nano-TiO₂ UF, Psf: $F_T/3$ – nano-TiO₂ UF and Psf: $F_C/1$ – nano-TiO₂ UF, Psf: $F_C/3$ – nano-TiO₂ UF to a significant extent as well. The extents of improvement in antifouling characteristics of the mixed-matrix UF membranes developed employing F_T – nano-TiO₂ and F_C – nano



Fig. 6.12: Time-dependent variation of solvent fluxes of the membranes during ultrafiltration of BSA solution following two-steps cyclic operation, which involves three times of pure water ultrafiltration and two times of BSA solution ultrafiltration. After each ultrafiltration of BSA solution, cleaning through pure water flushing was conducted.

A further in-depth comparison of the variations in values of R_r and R_{ir} implies that the former nanoadditives endow sharp and superior antifouling behavior on their use at higher concentration, whilst the use of the latter at similar concentration remains comparatively less distinctive. The study on flux recovery ratio and fouling resistive behaviors thereby explores the capability of both organofunctionalized nanoadditives - F_T - nano-TiO₂ and F_C - nano-TiO₂ as potential antifouling contenders in development of mixed-matrix UF membranes.

6.3. Polysulfone-CNT nanocomposite membrane development

CNT based membranes are very much important owing to the fast mass transport^{272,273} through these tiny hydrophobic channels as well as the ability to offer gate-keeper controlled separation²⁷⁴ by functionalisation of CNT tip and the size wall of the CNTs. There exists four usually practiced approaches²⁷⁵ to the synthesis of membranes based on CNTs:

- 1. Deposition of carbonaceous materials inside preexisting ordered porous membranes, such asanodized alumina, also known as the template synthesized CNT membranes;²⁷⁶
- 2. Membranes based on the interstice between nanotubes in a vertical array of CNTs, referred to as the dense-array outer-wall CNTmembrane;⁹⁴
- 3. Encapsulation of as-grown vertically aligned CNTs by a space-filling inert polymer or ceramic matrix followed by opening up the CNT tips using plasma chemistry, or the open-ended CNTmembrane;^{272,273} and
- 4. Membranes composed of nanotubes as fillers in a polymer matrix, also known as mixedmatrix membranes.

In the present work, the efforts were made to functionalise the CNTs using mixed acids and prepare the membranes by method-4 (as mentioned above) to result in a membrane with superior flux without compromise in selectivity.

6.3.1. Experimental

6.3.1.1. Materials

The base polymer, Polysulfone (Psf; M_W : 30kDa) was obtained from M/s. Solvay Specialties India Pvt. Ltd. The solvent, N-methyl-2-pyrrolidone (NMP) with minimum assay of 99.5% and porogen, Polyvinyl pyrrolidone (PVP, K–30; M_W : 40kDa) of AR grade, as utilized without further purification were procured from SRL Pvt. Ltd. (India).The nanoparticles: single wall carbon nanotube (SWNT) of diameter 0.7-1.3 nm; double walled carbon nanotube (DWNT) of diameter 5 nm and multi wall carbon nanotube (MWNT) of diameter 6-13 nm was procured from Aldrich.For evaluation of membranes' rejection behaviors towards organic solutes, poly(ethylene glycol) (PEG, Mw: 35 kDa) and poly(ethylene oxide) (PEO, Mw: 100kDa) were procured from Sigma–Aldrich. The conductivity of mili-Q ultra-pure water used in the experiments was below 2 μ S/cm.

6.3.1.2. Synthetic routes adopted for surface modification of CNTs

For surface modification of the CNTs, they were first sonicated for 1 h, and then heated at 80 $^{\circ}$ C for 4 h in the mixture of 1:1 concentrated HNO₃ (65%) and HCl (37%) to remove catalyst particles. oxygen containing groups, mainly carboxyl groups on the CNTs was introduced. They

are denoted as C-SWNT, C-DWNT and C-MWNT in the following text. The functionalized CNTs were filtered and washed several times, then dried at 120 °C overnight.^{277,278}

6.3.1.3. Preparation of polymer dope solutions

For the fabrication of mixed-matrix (Psf-CNT) UF membranes in sheet–configurations, polymer dope solutions, each further comprising of two different compositions, were prepared by employing varying proportions of SWNT, DWNT and MWNT and their functionalised counter parts: C-SWNT, C-DWNT and C-MWNT in hermetically sealed glass bottles. More specifically, the extent of the nanoadditive was varied at 0.25 and 1 (w/w_{Psf})% in the dope solutions comprising of 10 gram of Psf, 3 gram of the porogen, PVP and 40 mL of NMP. The dispersion of nanoparticles was undergone ultrasonic treatment for 20 min, prior to the addition and subsequent mixing of dried Psf beads and PVP, maintaining the specified compositions. The dope solutions were then vigorously agitated for several hours to accomplish complete dissolution of Psf and PVP in the solvent with homogeneously dispersed CNTs. For comparison purpose, one dope solution (Control) devoid of any nanoadditive was further prepared following the aforementioned composition of polymer and porogen as well as the methodology. Then, the resultant viscous dope solutions (as descripted in Table 6.5) were kept for overnight in an environmentally controlled atmosphere maintaining the temperature and relative humidity at $25(\pm 1)$ °C and 35-40 %, respectively, to eliminate the trapped air bubbles from the solutions.

6.3.1.4. Preparation of mixed-matrix UF membranes

Prior to fabrication of the desired mixed-matrix UF membranes along with the one required for comparison purpose following non-solvent induced phase inversion method, cleaned glass plates

(without having any fabric-base) were taped onto their parallel ends in such a way that each resulting membrane layer could achieve an estimated thickness of 200 μ m. The as-prepared stable dope solutions and the Control were cast manually onto the taped glass plates at a steady casting shear employing a well-dried, ultra-smooth glass-roller. The entire assemblies comprising of the cast films were immediately then immersed in a precipitation bath containing ultra-pure water as non-solvent, maintained at room temperature, for immersion precipitation.

Membrane code	Psf (in gram)	PVP (in gram)	NMP (in mL)	CNT (in gram)
Psf				
PSf-SWNT-1				0.025
PSf-SWNT-2				0.1
PSf-C-SWNT-1				0.025
PSf-C-SWNT-2				0.1
PSf-DWNT-1				0.025
PSf-DWNT-2	10.0	3.0	40	0.1
PSf-C-DWNT-1				0.025
PSf-C-DWNT-2				0.1
PSf-MWNT-1				0.025
PSf-MWNT-2				0.1
PSf-C-MWNT-1				0.025
PSf-C-MWNT-2				0.1

Table 6.5: Composition of precursor dope compositions and the respective derived membranes.

To ensure the adequate exchange between solvent and non-solvent followed by a resultant absolute removal of the porogen as well as the solvent from the membrane matrices, the prepared membranes were taken out of the water bath and rinsed in fresh water for several instants. The entire casting process was carried out in a controlled environmental atmosphere, where temperature and relative humidity were maintained at 25(±1) °C and 35-40%, respectively. The membranes as developed under invariable casting condition were properly stored in a water-bath. The membranes were categorized based on the difference in the specified compositions and accordingly defined as Psf-SWNT-1, Psf-SWNT-2 &Psf-C-SWNT-1, Psf-C-SWNT-2; Psf-DWNT-1, Psf-DWNT-2 & Psf-C-DWNT-1, Psf-C-DWNT-1, Psf-MWNT-2 & Psf-C-MWNT-1, Psf-C-MWNT-2. The Control is denoted as Psf as presented in Table 6.5.

6.3.1.5. Characterization of the as-synthesized carboxylated CNTs

For X-ray Photoelectron Spectroscopic (XPS) technique, a DESA-150 electron analyzer (Staib Instruments, Germany) equipped with Mg-K α X-ray source (1253.6 eV) was employed for characterization purpose. The spectrometer's binding energy scale was calibrated with Au-4f_{7/2}photo-peak at a binding energy (B.E.) of 83.95 eV. The spectra were recorded as the intensity (number of counts per second) versus B.E. The curve fitting of the multiplex photopeaks was performed using Gaussian functions and then peak area as well as full width at half maximum (FWHM) were also determined.

6.3.1.6. Physicochemical characterizations of the mixed-matrix UF membranes

Static sessile-drop method was adopted to carry out rapid as well as replicate measurements of the contact angles, and thereby analyze the overall surface hydrophilic features of the
investigated membranes having physicochemical heterogeneities. A contact angle measuring instrument (DSA 100 of KRUSS Gmbh, Germany) with DSA 1 v 1.92 software was employed for such evaluation purposes. A specific drop volume of 3 μ l of the probe-solvent (water), deposited from a micro-syringe needle was steadily allowed to produce on each of the membrane surface. The acquisition of the equilibrium contact angle values, at the membrane-solvent-air interface was accomplished with an equal residence time of 60 s. After continuous such measurements being carried out at eight different locations of each membrane surface, the contact angle values were averaged out and by this means reported with their standard deviations for the respective membranes.

The electrokinetic characteristics of the similar sets of membranes were evaluated by employing ZetaCAD electrokinetic analyzer (CAD Inst., France), which consisted of a quartz-cell configuration being capable of holding two flat sheets of each membrane in such a way that the probed membranes remained separated by spacers and their skin layers faced each other creating a slit channel for tangential flow of electrolytic solution across the membranes. The streaming potential, generated due to the bidirectional flow of 10^{-3} M KCl as background electrolyte solution, under applied pressure gradient across the membrane was measured by Ag/AgCl electrodes, equipped with the cell.Zeta potentials (ζ) of the membranes were evaluated using the streaming potential values and on the basis of Helmholtz-Smoluchowski equation(Eq. 2.11). An average value of ζ , derived from three replicates was reported and the measurement error was found to be ± 0.4 mV.

6.3.1.7. Evaluation of ultrafiltration performances of the mixed-matrix UF membranes

For all the membranes, the extents of molecular separationwere evaluated by analyzing the rejection behaviors of them towards neutral organic solutes such as PEG, with average Mw of 35 kDa and PEO, with average Mw of 100kDa. The test solutions were prepared by dissolving preweighed amount of PEG and PEO in ultra-pure water at a concentration of 200 ppm. The membranes having identical effective membrane area of 14.5 cm² were employed in a cross-flow filtration unit, operatedunder a transmembrane pressure of 1 bar at room temperature; and in view of minimizing the effect of experimental error the measurements were repeated with three different coupons of each membrane to obtain the average values. The concentrations of PEG and PEO in both feed and product solutions were measured by analyzing the total organic carbon (TOC) content of the samples using TOC analyzer (ANATOC-II, SGE analytical science, Australia) and employed for estimation of percentage rejection of the probe organic solutes (R_{PEG/PEO}) following Eq. 2.20.

The steady-state solvent flux (J in L.m-2.day⁻¹)was determined by direct as well as replicate measurements of the permeate flow following Eq. 2.21. Prior to all UF test experiments, the membranes were initially subjected to undergo hydraulic compaction for 1 h in water at standard UF test conditions to achieve stabilized performances of the membranes.

6.3.2. Results and discussions

6.3.2.1. Analysis of physicochemical characteristics of the functionalized CNTs

The deconvoluted C-1s spectra of the pristine CNTs, *i.e.*, SWNT, DWNT and MWNT, represented in Fig. 6.13 reveal the presence of intense component peaks at the lowest B.E. of

284.6, 284.7 and 284.6eV(Table 6.6), respectively with respective FWHM of 1.57, 1.44 and 1.27 eV, which are ascribed to the sp²-hybridized non-oxygenated C of C–C or C–H in the graphitic structures. The broader peaks appearing at higher B.E. of 286, 286.1and 286.6 eV, with FWHM of 2.38, 2 and 2.21 eV are referred to the C atoms of different C–O functionalities. In the pristine MWNT, the peak appearing at B.E. of 285.4 eV with FWHM of 1.59 eV corresponds to the defects on the nanotubes' structure. Moreover, the least intense peaks located at 288.4 and 288.9 eV, with FWHM of 4.51 and 6.24 eV are assigned to the O–C=O segments of the pristine SWNT and MWNT, respectively.

The analyses of deconvoluted O-1s spectra of the pristine CNTs further corroborate the inherent presence of different oxygen rich segments in the nanotubes' structures. Unlike the pristine DWNT, both pristine SWNT as well as MWNT exhibit the presence of C–OH and C–O–C segments, since broader peaks (FWHM: 3.14 and 3.22 eV) appear at 533.5 and 533.7 eV, respectively. The extent of presence of such peaks is more in the pristine MWNT as compared to the former *i.e.*, pristine SWNT. The peaks appeared at 532.2 and 532.6 eV corresponded to the C=O and O–C=O segments of the pristine SWNT and DWNT, respectively. However, the deconvoluted O-1s spectra of the pristine MWNT show the absence of such carboxylated segments.



Fig. 6.13: High resolution photoelectron spectra obtained from pristine SWNT, DWNT and MWNT, (line with bullets: experimental data; solid line: curve fit of the experimental data); a) C-1s and b) O-1s.

	C-1s			O-1s			
Codes of Pristine CNTs	BE (eV)	FWHM (eV)	Peak area (%)	BE (eV)	FWHM (eV)	Peak area (%)	
SWNT	284.6	1.57	30.84	532.2	3.95	56.26	
	286.0	2.38	54.23	533.5	3.14	43.74	
	288.4	4.51	14.93				
DWNT	284.7	1.44	54.74	530.5	2.54	39.02	
	286.1	2.0	45.26	532.6	2.94	60.98	
	284.6	1.27	36.39	531.0	2.51	17.19	
MWNT	285.4	1.59	22.32	533.7	3.22	82.81	
	286.6	2.21	21.57				
	288.9	6.24	19.73				

Table 6.6: Curve fitting summary of C-1s and O-1s XPS peaks for pristine SWNT, DWNT and MWNT.

The probed CNTs are modified through controlled chemical oxidation pathway, which seems to introduce more oxygen rich functionalities onto the surfaces of the functionalized CNTs, *i.e.*, C-SWNT, C-DWNT and C-MWNT. The investigation carried out by XPS study, represented in Fig. 6.14 and Table 6.7 establishes the variations observed in the functionalized nanostructures. The deconvoluted C-1s spectra of both C-SWNT and C-DWNT reveal the constitution of three distinct peaks, wherein the peaks ascribed to the sp²-hybridized non-oxygenated C of C–C or C–H in the graphitic structures appear at 284.4 and 284.8 eV, respectively and the peaks appearing at higher B.E. of 286.1and 286.2 eV, with FWHM of2.83 and 1.91 eV are referred to the C atoms of different C–O functionalities.



Fig. 6.14: High resolution photoelectron spectra obtained from functionalized CNTs: C-SWNT, C-DWNT and C-MWNT, (line with bullets: experimental data; solid line: curve fit of the experimental data); a) C-1s and b) O-1s.

Moreover, the peaks corresponded to the carboxylated functionalities appear at higher B.E. of 289.1 and 288 eV for the C-SWNT and C-DWNT, respectively. The deconvolution of C-1s spectrum of C-MWNT shows the presence four constitutional peaks that appear at 284.6, 286, 287.7 and 289.7 eV, wherein the latter three peaks are referred to the oxygen rich functionalities.

The deconvoluted O-1s spectra of the functionalized CNTs also substantiate the differential presence of the oxygen rich functionalities.

	C-1s			O-1s			
Codes of	BE	FWHM	Peak area	BE	FWHM	Peak area	
functionalized	(eV)	(eV)	(%)	(eV)	(eV)	(%)	
CNTs							
C - SWNT	284.4	2.04	39.07	531.4	4.17	50.31	
	286.1	2.83	47.88	533.6	3.49	49.69	
	289.1	3.56	13.05				
C - DWNT	284.8	1.52	48.07	530.0	1.71	11.40	
	286.2	1.91	33.12	531.8	2.68	46.93	
	288.0	5.13	18.81	533.4	2.85	41.67	
TNWM	284.6	1.45	36.94	531.7	2.11	8.65	
	286.0	2.0	39.97	535.0	3.38	91.35	
C - 1	287.7	1.57	5.10				
	289.7	4.25	17.09				

Table 6.7: Curve fitting summary of C-1s and O-1s XPS peaks for functionalized CNTs: C - SWNT, C - DWNT and C - MWNT.

6.3.2.2. Analysis of physicochemical features of the mixed-matrix UF membranes

The hydrophilic characters of the investigated membranes are assessed with respect to the probe solvent – water to evaluate the role of CNTs and functionalised CNTs in modifying the surface chemistry of the control and mixed matrix UF membranes. The variations in hydrophilic characters as shown in Fig. 6.15 reveal that impregnation of CNTs improves the hydrophilicity and such improvement is more pronounced when functionalised CNTs are impregnated on to the membrane surface with progressively higher concentrations. Considering the Control-Psf UF with contact angel value of 70.7° , the same decreases with impregnation of CNTS (SWNT,

DWNT and MWNT) which could be because of the presence of residual oxygen containing functional groups present over the CNT surface as a result of purification of CNTs (usually made by the acid treatment to remove the transition metal catalyst particles). It is also observed that with increase in loading of CNTs, the contact angle value is increasing slightly which could be because of a competition between the hydrophobic surfaces available and the residual oxygen functionalities present. The effect of CNT in decreasing the contact angle value of Control Psf membrane is more pronounced in case of functionalised MWNT (Psf-C-MWNT-2 with contact angle value of 50.9°), which clearly indicates that the extent of carboxylation increases with increase in the available surface area though the conditions and duration of functionalisation has been kept same for all the CNTs. It is important to note that the impregnation of functionalised CNTs influences the direction of migration and subsequent dispersion of the nanoadditives towards the skin surfaces of the membranes owing to the more affinity of them towards the nonsolvent, water. The variations in hydrophilic characters corroborate that the hydrophilic $-CO_2^-H^+$ groups present over the functionalised CNTs significantly enhance the efficacy of CNTs in modifying the intrinsic hydrophobic character of the Control-Psf UF. Furthermore, the facilitated distribution of functionalised CNTs within the polymer matrix of Psf implies that the modified nanoadditives not only influence the physicochemical features of the membranes' skin surfaces but also the skin layers' porous pathways, which collectively contribute in enhancing the hydrophilicity of the mixed-matrix UF membranes.



Fig.6.15: Contact angle values of control Psf and mixed matrix Psf-CNT UF membranes.

Electrokinetic features of the membranes, determined by tangential streaming potential measurements with respect to 10^{-3} M KCl solution are represented in Fig. 6.16. The matrix of Control-Psf UF devoids of any dissociable functionality being capable of creating surface charges, and thus the ζ of – 20.38 mV is attributed to the effect of specific adsorptions of Cl⁻ ions from the electrolyte solution on the hydrophobic membrane surface. However, the investigated mixed-matrix UF membranes provide different weak or strong sources of charges, which arise due to the non-covalently fixed –OH groups on the surface of CNTs or the –CO₂–H⁺ groups of the functionalised CNTs. Therefore, the mixed-matrix UF membrane surfaces exhibit predominant contributions of the tethered functionalities in surpassing the tentative ionic adsorptions by the intrinsic character of the core Psf matrix. The charge carrying sites of the mixed-matrix UF membranes induce surface conductivity in the membranes, and through their variant distributions alter the electrokinetic features of the mixed-matrix UF membranes, as the ζ of the mixed-matrix UF membranes, as the ζ of the mixed-matrix UF membranes, as the ζ of the mixed-matrix UF membranes, as the ζ

changes from -20.38 (Psf) to -15.72 mV for Psf-SWNT-2 UF; to -8.60 mV for Psf-C-SWNT-2 as shown in Fig. 6.16. Similar trend is observed in case of DWNT and MWNT impregnated membranes as evident from Fig. 6.16. The decline in negative ζ values of the mixed-matrix UF membranes as compared to the Control-Psf UF indicates that the occurrence of severe ionic adsorption on the core Psf matrix of the latter gets overcompensated by the occurred electrokinetic events influenced through the modified compositions of electrochemical double layers in the formers. Such influence is also observed to be progressively pronounced on moving from Psf to Psf-CNT to Psf-C-CNT UF irrespective of the CNT being SWNT or DWNT or MWNT.



Fig. 6.16:Electrokinetic features of the membranes: Control Psf and mixed matrix Psf-CNT membranes.

The enhanced impregnations of functionalised CNTs seem to markedly elevate the skin layer conductivities of the respective membranes. This variance can be demonstrated as the result of dragging of the tangentially driven counter-ions from the hydrodynamic slipping plane or plane of shear to the bulk of the membranes charged layer, through the hydrodynamically stagnant layer of counter-ions. The effective streaming currents of the membranes are thus supposed to get reduced because of such diffusive back flow of the streaming current²⁶⁶ the phenomenon which is substantiated by the observed electrokinetic features, as manifested through the decline of ζ of the respective membranes.

6.3.2.3. Study of mixed-matrix UF membranes solute rejection and solvent flux behaviors

The %SR and PWP, measured under a steady operating condition, reflecting the variations in macroscopical features of the mixed-matrix UF membranes are presented in Figs. 6.17a and 6.17b, respectively. The representations signify that the functionalized CNTs, as persuasive nanoadditives, induce noteworthy physicochemical variations in the projected mixed-matrix UF membranes. The %SR towards the probed solutes, PEG and PEO are found to be 89.2 and 94.6%, respectively for Control-Psf UF. The % SR of all the mixed matrix membranes are found to be in the similar line to that of the Control Psf membrane concluding there is no compromise in % SR with addition of CNTs or functionalized CNTs. The analyses of steady state PWP of the membranes indicate gradual change from 2880 LMD for Control-Psf UF to mixed matrix Psf ranging from 3000 to 4320 LMD (for Psf-SWNT/DWNT/MWNTUF membranes) to 5760 LMD (Psf-C-DWNT-2 & Psf-C-MWNT-2 UF membranes). The impregnations of functionalized CNTs within the Psf matrices of the mixed-matrix UF membranes also gives rise to obvious improvement in PWP compared to that of virgin CNTs. Since impregnation of CNTs as well as functionalized CNTs influence the mechanism of pore-formation during phase inversion process by altering (delaying) the rate of both, *i.e.*, non-solvent's indiffusion and the solvent's outdiffusion, the resultant formation of finer pores evidently leads to the enhancement in %SR for the respective mixed-matrix UF membranes.



Fig. 6.17 (a) % Solute rejection (SR) of the membranes: Control-Psf UF, Psf:- SW-1UF, Psf:- SW-2UF Psf:- C-SW-1UF,Psf:- C-SW-2 UF,Psf:- DW-1UF,Psf:- DW-2 UF,Psf:- C-DW-1UF, Psf:- C-DW-2 UFPsf:-MW-1UF,Psf:-MW-2UF,Psf:- C-MW-1UF, Psf:- C-MW-2 UF



Fig. 6.17 (b) PWP of membranes:Control-Psf UF, Psf:– SW-1UF, Psf:– SW-2UF Psf:– C-SW-1UF, Psf:– C-SW-2 UF, Psf:– DW-1UF, Psf:– C-DW-1UF, Psf:– C-DW-2 UFPsf:– MW-1UF, Psf:– MW-2UF, Psf:– C-MW-1UF, Psf:– C-MW-2 UF

The trends obtained for the macroscopical features are in well accordance with the discussed variations in contact angle values. Hence, the concurrent increase in PWP of the membranes also

corroborates with the contributing factor of enhancement in the surface hydrophilicity as discussed earlier. Furthermore, although the molecular transport through a UF membrane gets predominantly controlled by hydrodynamic interactions, but there may also exist the simultaneous contribution of electrostatic interactions for the mixed-matrix UF membranes, wherein the implanted charged sites $(-CO_2^-H^+)$ being part of the entrapped functionalized CNTs exert substantial electrostatic interactions with the diffusing solvent molecules, and thereby improve the hydrodynamic dragging efficiencies of the porous pathways.

6.4. Conclusions

Mixed-matrix UF membranes, namely Psf: F_T - nano-TiO₂ UF and Psf: F_C - nano-TiO₂ UF comprising Psf and the organofunctionalized nanoadditives, F_T - nano-TiO₂ and F_C - nano-TiO₂ have been prepared at variant compositions following the non-solvent induced phase inversion technique.

The precursor anatase nano-TiO₂ was modified through functionalization by chemisorption processes utilizing two different potential organoligands, Tiron and Chromotropic acid to synthesize the desired organofunctionalized nanoadditives, F_{T} - nano-TiO₂ and F_{C} - nano-TiO₂, respectively. The analysis of obtained structural features of the nanoadditives, characterized by XRD, Raman, FTIR and XPS techniques revealed that, the former complexing organoligand favourably resided in both chelating and bridging bidentate geometries, whereas the latter complexing organoligand preferred to stay in both bridging bidentate as well as monodentate geometries at the surface of the nano-TiO₂. Both functionalization processes thus directed towards enrichment of the surfaces of nano-TiO₂ with substantial charged sites (-SO₃'H⁺), ultimately stimulating the surfaces by providing stronger and stable electrostatic environment. The study of solute rejection towards neutral organic solutes like PEG and PEO, and solvent flux behaviors revealed the salient macroscopical features of the membranes as they showed very high solvent throughputs i.e., 3500 - 4000 and 3400 - 4300 LMD at 1 bar of transmembrane pressure, without any significant deterioration in their solute rejection capability.

The antifouling study, conducted by binary cyclic fouling process with respect to the BSA solution as foulant further demonstrated that, both classes of the mixed-matrix UF membranes tuned via impregnation of F_T - nano-TiO₂ and F_C - nano-TiO₂ exhibited superior flux recovery ratios as compared to the membranes developed employing the non-functionalized nano-TiO₂, and the influence was more pronounced on impregnation of the former nanoadditives at higher concentration. Furthermore, noteworthy mitigation of the notorious effect of reversible as well as irreversible fouling was also achieved by the use of both organofunctionalize dnanoadditives, indicating a better prospect for recycling of the mixed-matrix UF membranes for robust UF application.

From the studies carried out on CNT impregnated membranes, it is evident that embedment of carboxylated functionalized CNTs have got tremendous opportunities to tune the surface chemistry of the membrane that in turn can lead to enhanced flux without compromise in selectivity. It is also important to conclude that like organofunctionalised TiO₂, modified CNTs have got the potential to improve the antifouling behvaiour of membranes. Elevated solvent throughputs with optimum solute rejection behaviour obtained with the discussed class of membranes opens up new opportunities for these modulated nanoadditives toward sustainable development of mixed-matrix UF membranes.

CHAPTER –7

Conclusions & Recommendations

In this chapter, the results of the entire work carried out in favour of the area of research, as a part of the thesis, have been summarized. The chapter brings out the achievements and the novel scientific understandings emerged out of this work in line with the objectives targeted. The work encompasses development of mixed matrix membrane with incorporation of different nanomaterials on to polymer host matrix. For the sake of uniformity, in all cases polysulfone (Psf) was chosen as the polymer host matrix. The objective of the work, as highlighted in the first chapter, was to attempt different nanocomposite membrane system in view of minimization/elimination of usual shortcomings associated with any membrane based process. The important disadvantages any membrane process encounter are: trade-off between flux and selectivity and (bio)fouling. The fouling could be due to microorganisms or organic substances present in water streams. Nanomaterials targeted in this work are: reduced graphene oxide (for minimization of trade-off between flux and selectivity); carbon nanotubes and silver (for antibiofouling); TiO_2 (for antifouling) and pyrochlore (for improvement of radiation resistance of polymeric membrane). Only non-supported (without any non-woven fabric support) flat sheet configuration of membrane was prepared in all cases for evaluation of membrane performance. The Conclusions & Recommendations are summarized below:

7.1. Conclusions

 Nanostructured reduced graphene oxide (RGO) is synthesized from graphite powder and characterized. Using non-solvent induced phase inversion technique, a series of nanocomposite ultrafiltration (UF) membranes are developed by in situ impregnation of the as synthesized RGO in Psf polymer matrix with variation of RGO from 1 to 8 w/w%. The physicochemical features and transport properties offered by the membranes are evaluated. Structural characterization of the Psf-RGO composite UF membranes are done by XPS and FTIR spectroscopy. The variation in porous morphology of the membranes, on impregnation of RGO is evaluated by SEM. Variation in skin surface topography is analyzed by AFM. The change in surface hydrophilicity is evaluated by contact angle studies. The thermal and mechanical properties of the membranes are assessed by thermogravimetric analysis and tensile strength measurements, respectively. The studies reveal that an optimum loading of RGO (2 w/w%) in Psf matrix resulted membranes with minimisation of trade-off between the flux and selectivity that exists with the conventional UF membranes. The enhanced permeation ability (4200 LMD) of the Psf-RGO composite UF membranes (beyond that of Psf membrane: 3700 LMD) is attributed to the additional and facilitated transport of water caused by the atomically smooth interconnected inter layers (as novel pathways for water permeation) offered by RGO impregnated in the PSF matrices. The mixed matrix membrane with 2 wt % loading of RGO resulted in a pore size distribution that led to better solute rejection compared to pure Psf membrane (Pure Psf: 65 % and Psf-2 wt% RGO: 92 % rejection against polyethylene glycol 35 kDa). Hence, the trade-off postulate that a membrane with higher flux should offer low solute rejection is violated, which is an important finding. In addition, the optimum loading of RGO resulted in membranes with improved thermal and mechanical stability. A set of transport equations have been derived from Kedem-Katachalsky's irreversible thermodynamic model, by incorporating pore-size distribution of the membrane and molecular weight distribution (derived from size distribution) of polyethyleneimine. The model is able to explain the experimental findings of Psf-RGO composite membranes with respect to flux and selectivity. Thus, impregnation of RGO delivers emerging potential to lead to the development of an ideal membrane with desirable attributes.

A high-performance mixed-matrix UF membrane was developed using non-solvent induced phase inversion technique, utilizing various optimized compositions of polymer -Psf and bactericidal nanostructured material *i.e.*, silver nanoparticles (Ag-nps). Membranes in sheet-configuration with high void volumes were synthesized employing large amount of PVP as porogen. The resultant porous morphology and surface chemistry, *i.e.*, surface hydrophilicity and electrokinetic features were assessed by instrumental techniques. The notable separation performances were observed as the membranes exhibited very high solvent throughput with an extensive anti-microbial activity. It has been substantiated that the nanoparticles being impregnated within such a benign matrix of polymer exerted more pronounced mechanistic role during antimicrobial efficacy on E. Coli, since as a survival mechanism the bacteria undergoing flagellar locomotory motion started experiencing negative chemotactic responses under the modified circumstances. It is confirmed that incorporation of silver (1 % of polymer weight) not only results in a bio-fouling resistant membrane, but also silver has got a pronounced role to play in bacterial rejection only when the membrane matrix is sufficiently porous (~80 %). With an objective of applying the salient features of such membranes, the methodical attempt was utilized in fabricating a domestic water purification device, with the membrane in candle-configuration for treatment of environmentally relevant aquatic media. It has been corroborated that our impactful approach towards an efficient purification methodology (solvent throughput: 2500 LMH/bar and bacterial rejection: 99.99%) intensifies the significance of membrane technology as a green and sustainable process by addressing the issues of easy scale up, energy and cost efficiency.

- With the objective of having improvement over the existing anti-biofouling tendency of Psf membranes, nanocomposites were developed with impregnation of both single walled as well as multi walled CNTs. The performance of the membranes was evaluated in terms of pure water permeability and solute rejection studies. The membranes were characterised using SEM, AFM and contact angle studies. The anti-biofouling performance of the membrane surfaces was examined using E. Coli culture and a comparison of antibiofouling tendency obtained with the nanocomposites over the control Psf membranes has been made. It was confirmed that membranes with impregnation of single walled CNTs possess better antibiofouling behaviour as compared to controlPsf as well as polysulfone membrane embedded with multi walled CNTs. It is important to note that unlike silver, the CNTs were not observed to offer clear cut inhibition zone around the membrane surface for growth of microorganisms. Though antibiofouling tendency of single walled CNT impregnated membranes was found to be better compared to multi walled, however, it is believed that lack of alignment of CNTs and lack of accessibility of CNT tips that are responsible for microorganism killing in a mixed matrix system could be the reason of not obtaining enough bacteria rejection and antibiofouling property with the Psf-CNT membrane surface.
- Pyrochlore (Gd₂Zr₂O7) nanoparticle, prepared by gel-combustion method, was used for development of mixed matrix membrane with polysulfone as host matrix. The

concentration of pyrochlore was varied from 0.1 % to 2 % of polymer weight. The membranes were prepared using phase inversion technique. The pure water permeability and solute rejection studies (with 200 ppm solutes of 35 kDa of PEG) of the synthesized membranes were carried out to evaluate the performance of the membrane. To assess the radiation stability of the membranes, γ (gamma) radiation doses of 40, 80, 240, 500 and 1000 kGy were provided to the membranes in aqueous environment. The membranes were characterized using FTIR, SEM, EDX and XPS. The tensile strength and elongation at break for all the samples (both un-irradiated and irradiated) were carried out using Universal Testing Machine. The extent of damage caused due to 1000 kGy irradiation (correlated with the extent of reduction in elongation at break values) is about 90 % for pure polysulfone whereas the membranes with 2 % nanoparticle loading showed only about 57 % reduction in elongation at break, which resulted in a membrane with improved radiation resistance behaviour of all the membrane samples prepared. However, from membrane performance perspective, 1 % pyrochlore loaded mixed matrix membrane irradiated upto 1000 kGy showed the optimum flux behaviour (~2800 LMD) without compromise in selectivity (~82 % solute rejection for PEG 35kDa) and tensile strength (~2.60 MPa). The enhanced stability of pyrochlore embedded membranes is attributed to the ability of pyrochlore to take up the radiation, which leads to interchanging of the sites occupied by Gd and Zr and in turn dissipation of gamma energy. In this process, polymer host matrix is exposed to gamma radiation to a minimum extent, making the overall composite matrix radiation resistant.

Charged mixed-matrix UF membranes were developed with superior transport characteristics and stimulating antifouling activity. The matrix of fouling susceptible Psf, an usual polymeric contender of UF membrane was customized by impregnating organofunctionalized nanoadditives during fabrication of the membranes following nonsolvent induced phase inversion technique. The anatase nano- TiO_2 was modified by functionalization processes utilizing two different potential organoligands, Tiron and Chromotropic acid to synthesize the organofunctionalized nanoadditives, F_T- nano-TiO₂ and F_C- nano-TiO₂, respectively. The evaluated structural features of the nanoadditives establish that the difference in structural attributes of the two complexing organoligands leads to blending of chelating and bridging bidentate geometries for the former, and bridging bidentate as well as monodentate geometries for the latter. The surface chemistry of the probed membranes, Psf: F_T- nano-TiO₂UF and Psf: F_C- nano-TiO₂UF gets profoundly influenced by the benign distribution of the nanoadditives enriched with distinct charged sites (-SO3⁻H⁺), as evidenced by enhanced surface hydrophilicity and altered electrokinetic features. The membranes exhibit very high solvent throughputs (Psf: ~2300 LMD; Psf: F_T/3 - nano-TiO₂: ~5760 LMD; Psf: F_C/3 - nano-TiO₂: 6000 LMD) times that of control Psf membrane) without notable detrimental effect in their solute rejection capabilities. The flux recovery ratios in 2nd cycle (Control Psf: 45.7 %; Psf: F_T/3 - nano-TiO₂: 70 %; Psf: F_C/3 - nano-TiO₂: 65.1%) and fouling resistive behaviors of the mixed-matrix UF membranes towards bovine serum albumin (BSA) solution explore that enhanced hydrophilicity and strong long-range repulsive forces as induced by both organofunctionalized nanoadditives impart stable and extensive antifouling activity, further ensuring a cost-effective and energy-efficient UF prospect for the treatment of environmentally concerned aquatic media.

Mixed matrix (Psf-CNT) UF membranes in sheet-configurations were prepared by employing varying proportions of SWNT, DWNT and MWNT and their functionalised counter parts: C-SWNT, C-DWNT and C-MWNT. The CNTs were carboxylated with mixed acids concentrated HNO₃ (65%) and HCl (37%) and characterized using XPS. The membranes were characterized with streaming potential analyser and Drop shape analyser to ascertain the extent of charge and hydrophilicity enhancement caused by charged nanoparticle incorporation on to the polymer host matrix. Pure water permeability and solute rejection studies were carried out to analyse the effect of charge on the enhancement of performance of the membranes. It is observed that though the incorporation of CNTs onto Psf hardly leads to any improvement in flux and rejection behaviour, whereas the incorporation of charged (carboxyl acid group) CNTs leads to a 1.5 to 2 times flux enhancement (Psf membrane: 2880 LMD; Nanocomposite Psf: 4320 to 5760 LMD) without compromise in the solute rejection abilities (about 90 % solute rejection against PEO of 100 kDa) of the membranes. The enhancement in flux is attributed to the charged surface (more hydrophilic) of the membrane brought about by functionalized nanomaterials. It is confirmed that charged nanocomposite UF membranes offer better separation performance compared to nanocomposite as well as pure polymeric membranes.

7.2. Recommendations

- When Nanotechnology based products are potential providers of unprecedented opportunities to many environmental problems including climate change, energy conversion, gas separation, biomedical applications and clean drinking water, at the same time, challenges still need to be addressed to optimize the design of the nanocomposite membranes for industrial applications at a large scale. Understanding needs to be developed to have deeper insight into the effects of nanomaterials on membrane structures and correlate them with the membrane performance outcomes. If the specific contributions of different nanomaterials to tune the surface hydrophilicity, pore size, charge density and membrane porosity *vis a vis* membrane performance is understood, then it would open up new ways to develop membranes with hybrid nanomaterials (combination of two or more nanomaterials) that can pave the path for idea membrane having all the desirable attributes.
- Efforts can be taken up to align CNTs in a polymeric matrix to exploit the maximum utility of CNTs. The approach to alignment can be through application of magnetic/electric field based upon the type of CNTs and polymer of concern. State-of-art methodologies need to be looked during membrane fabrication for taking advantage of magnetic/electric field.
- Pyrochlores (A₂B₂O₇) of different combination of A & B can be tried to analyse and assess the effect of radiation on the type of pyrochlores and more importantly, the effect of varieties of pyrochlore impregnation on the overall membrane performance under a radioactive environment.

- Agglomeration/aggregation prevents nanomaterials from being homogeneously dispersed inside polymer matrices. Polymer and nanomaterials properties can be tuned to make the nanomaterials well dispersed and stable in the host matrix, which would minimize the obvious interfacial defects and enable extraction of the maximum useful properties of nanomaterials onto nanocomposite membranes. Leaching of nanomaterials from the membranes into the environment, its risk assessment and environmental toxicity also need to be systematically evaluated.
- In the present work, only mixed matrix based composites were targeted wherein the nanomaterial are present in the bulk of the membrane. The method to preferentially locate the nanomaterials onto the membrane surface was not adapted. Membrane process being primarily a surface influenced phenomena, efforts can be oriented to fabricate surface located nanocomposite membranes with still superior properties. This method can effectively be used to functionalise commercially available membranes to introduce unique functionalities over it. Also, capillary configurations of nanocomposites can be tried to assess the prons and cons the configuration could offer in comparison with the flat sheet one.
- Finally, the raw materials, the process and the final product (membrane) have to be amenable for large scale production and industrial application. There is a need to evaluate the cost-effectiveness of large scale nanocomposite membrane fabrication including the batch size of nanomaterials synthesis, methodologies for effective nanomaterial impregnation, and monitoring the long-term stability of mixed matrix membranes under practical application/operating environment.

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