

**Synopsis of the thesis**

**titled**

**STUDIES OF THE SEPARATION CHARACTERISTICS OF  
POLYMERIC MIXED MATRIX MEMBRANE INCORPORATED WITH  
CARBON ALLOTROPES**

**Submitted to**

**THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA**

**For the degree of**

***DOCTOR OF PHILOSOPHY***

**In**

**Applied Chemistry**

**Submitted by**

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**Date:30/12/2020**

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## **General Introduction:**

Membrane technology has gained significant popularity across diverse industries, including water and wastewater treatment, food processing, chemical industry, biotechnology, medical and pharmaceutical sectors, water desalination, blood purification, and fuel cells for energy applications. The utilization of membrane technology has expanded due to its numerous benefits, including improved energy efficiency, cost-effectiveness in operations, scalability, and user-friendly operation. Notably, the chemical industry is witnessing high growth in the adoption of membrane materials known for their remarkable stability. A membrane that incorporates fillers like carbon nanotubes, graphene oxide, metal oxides, zeolites etc. into its polymer matrix can be referred to as a Mixed Matrix Membrane (MMM). Loeb and Sourirajan were the pioneers in preparing the first asymmetric membrane by utilizing cellulose acetate through a phase inversion method for water desalination[1]. Cellulose acetate remains the commonly employed polymer for membrane preparation, despite its limited chemical and thermal resistance properties. Polyether sulphone (PES) and Polysulphone (PSU) are widely used for membrane preparation due to their exceptional mechanical, thermal, and chemical properties. To enhance the membrane properties, these polymers were incorporated with various functionalized multiwalled carbon nanotubes (MWCNTs) to prepare mixed matrix membranes with diverse functional groups on their surfaces. These mixed matrix membranes, incorporating different functionalized MWCNTs, have already been characterized and exhibited improved performance in heavy metal rejection, porosity, permeability, and fouling resistance[2–4]. Furthermore, the mixed matrix membranes surfaces were modified to enhance metal rejection by increasing the number of functionalities on the membrane surface[5].

Surface modification on a prepared mixed matrix membrane offers novel properties including better separation characteristics, energy efficiency, and chemical

efficiency compared to the unmodified membrane. Chemical resistance, such as swelling resistance, fouling or solvent resistance, control of pore size, and removal of membrane irregularities that enhance flux or selectivity will all be possible with the modification. Surface modification is generally aimed at enhancing the permeability and antifouling properties of membranes by increasing the hydrophilicity of the membrane surface. Additionally, it improves chemical stability and introduces surface charge to facilitate the rejection of specific types of ions through the membrane[6,7]. There are various approaches to achieve membrane surface modification, such as blending polymers and incorporating fillers during the membrane preparation stage[8,9]. However, there are also post-preparation techniques for membrane surface modification, including plasma treatment[10], UV irradiation[11], gas or wet phase coating[12,13], and grafting, which involve the formation of covalent bonds during the modification process[14]. The application of click reaction for the surface modification of polyethersulfone/azide-CNT mixed matrix membrane leads to the development of a hydrophilic surface and enhanced antifouling properties[5]. Therefore, we chose to conduct surface modification on the membrane, incorporating a range of functional groups including amine, azide, and others. Subsequently, we characterized the modified membranes to evaluate their performance in terms of heavy metal rejection, permeability, morphology, and antifouling properties.

## **Chapter 1: Introduction**

In this chapter, we provide a comprehensive overview of the evolution of various types of membranes, including asymmetric, thin film composite, and mixed matrix membranes, since the introduction of synthetic membranes. We conduct an extensive literature review encompassing membrane surface modification techniques, as well as studies focusing on the

morphological analysis of membranes. Furthermore, we discuss the research conducted on heavy metal removal, treatment of effluent water, and studies related to membrane antifouling of the modified membranes.

## **Chapter 2: Scope of research**

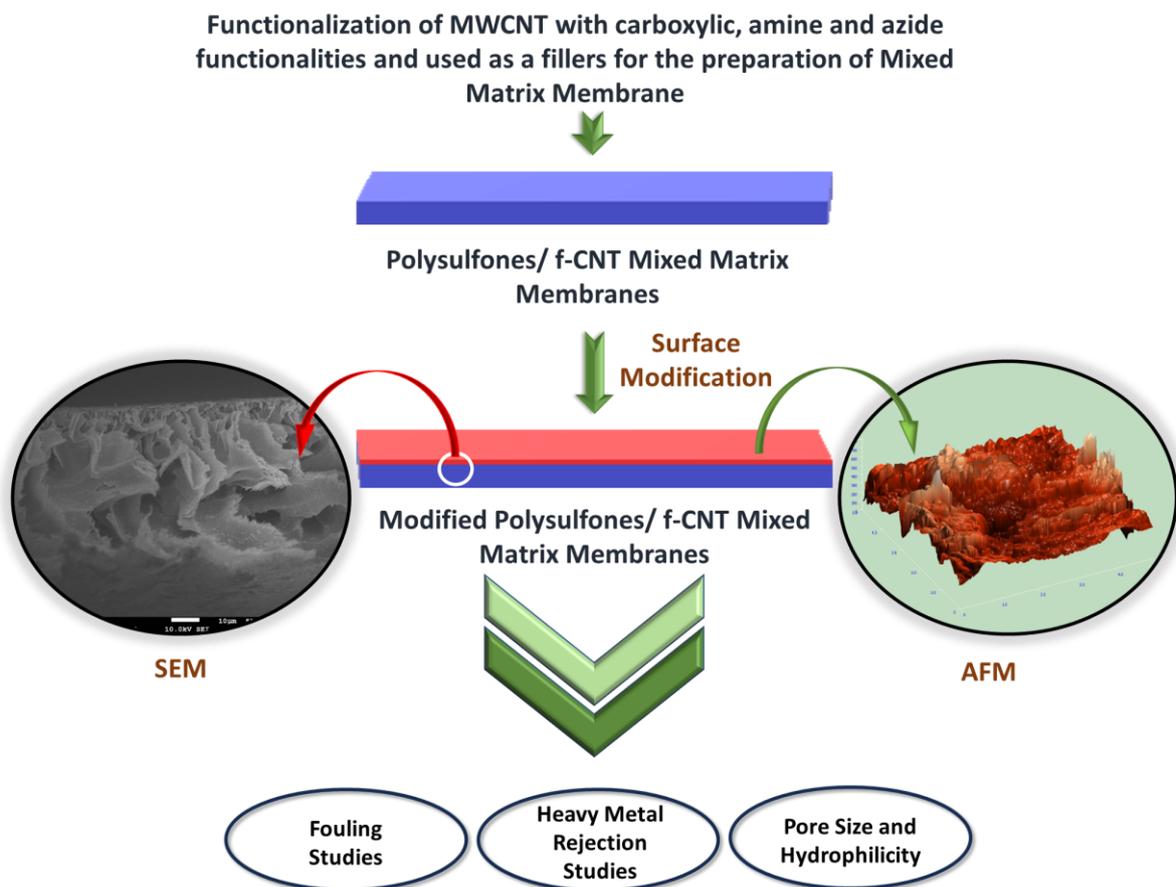
In this chapter, we explore the scope and objectives of the thesis.

- Functionalization of MWCNTs with carboxylic, amine and azide functionalities and used as fillers for the preparation of polysulphones mixed matrix membranes.
- Polysulphones mixed matrix membranes having carboxylic, amine and azide functionalities on their surface undergoes surface modification using different methods like click reaction, reaction with trimesoyl chloride (TMC) and cyanuric chloride (CC) and treatment with Polyethylenimine (PEI).

## **Chapter 3: Experimental route**

This chapter focuses on the study of functionalizing multiwalled carbon nanotubes (MWCNTs) and surface modification of mixed matrix membranes. The specific techniques for modifying various membranes with different functional groups are outlined. The functionalization of MWCNTs is characterized using Fourier Transform Infrared (FT-IR), while their morphology is observed through transmission electron microscopy (TEM). The method for modifying Polysulphone or Polyether sulphone/ Azide-CNTs mixed matrix membranes via click reaction is described, with confirmation through X-ray photoelectron spectroscopy (XPS). Additionally, other surface modifications of mixed matrix membranes incorporating amine-functionalized carbon nanotubes using cyanuric chloride and trimesoyl

chloride are detailed in this chapter, with confirmation through Fourier Transform Infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS). The surface morphology of both modified and unmodified membranes is studied using Field Emission Scanning Electron Microscopy (FESEM), Atomic force microscopy (AFM), and small angle neutron scattering (SANS). The hydrophilicity of the membranes is measured using the sessile drop method, where the contact angle is determined using a Goniometer.



**Figure 1.** Surface modification of mixed matrix membrane

## Chapter 4: Membrane Performance

This chapter is dedicated to the permeation studies conducted on all membranes. The pure water flux of both modified and unmodified membranes was measured. Additionally, a heavy metal rejection study was carried out using selected hazardous heavy metals, namely chromium, copper, lead, cadmium, and mercury. The effectiveness of the modified membranes in comparison to the unmodified membranes was tested under specific conditions. The heavy metal rejection study was performed at 50 psi transmembrane pressure, at an acidic pH of 2.6, and at room temperature (25 °C), which represents the optimal conditions established by Prachi et al.[2]. The results obtained are presented in Table 1 below. Notably, mixed matrix membranes modified with cynuric chloride and trimesoyl chloride exhibit superior heavy metal rejection, particularly for copper. This can be attributed to the presence of functional groups like amine, benzenecarbonyl, and triazine on the membrane surface, which promote both adsorption and complexation, thereby aiding in the rejection of heavy metal ions. These functional groups contribute significantly to the higher rejection rates observed. Protein fouling stands out as a significant drawback of current membranes. To assess the antifouling properties of the prepared membranes, protein filtration experiments were conducted, highlighting their potential for reuse.

**Table 1.** Heavy metal rejection study of surface modified and unmodified membrane

Membranes	% Rejection of heavy metals				
	Cr(VI)	Cu(II)	Pb(II)	Cd(II)	Hg(II)
PSU/ AM-CNT/CC	95.2 ± 0.59	98.9 ± 0.52	96.7 ± 0.65	96.5 ± 0.63	97.8 ± 0.79
PES/ AM-CNT/CC	94.6 ± 0.42	98.8 ± 0.41	95.3 ± 0.60	95.96 ± 0.56	97.2 ± 0.79
PSU/AM-CNT/TMC	86.9 ± 3.2	96.6 ± 0.82	90.6 ± 0.62	84.5 ± 0.56	92.4 ± 0.51
PES/AM-CNT/TMC	96.3 ± 0.58	98.2 ± 0.85	97.6 ± 0.61	95.3 ± 0.29	97.6 ± 0.47
PSU/ AM-CNT	96.0 ± 0.81	98.2 ± 0.42	96.9 ± 0.62	95.4 ± 0.83	96.9 ± 0.67
PES/AM-CNT	85.7 ± 0.86	95.6 ± 0.81	92.4 ± 0.61	83.5 ± 0.26	92.2 ± 0.61

## **Chapter 5: Results and Discussion**

In this chapter, we focus into the morphological study of both modified and unmodified membranes, exploring the correlation between their morphology and permeation and rejection properties. The presence of distinct functional groups on the membrane surface is demonstrated to enhance the efficiency of heavy metal removal compared to the unmodified membrane. Furthermore, we examine the impact of introducing additional functional groups to the membrane surface on aspects such as membrane morphology, rejection capabilities, and hydrophilicity. Detailed explanations regarding these effects are provided within this chapter.

## **Chapter 6: Summary, Conclusions & Future Prospects**

In this chapter, a comprehensive overview of each chapter is provided, including a summary of the main points and findings derived from the research conducted. Moreover, this chapter also highlights potential future efforts that can be pursued to address the limitations identified in the study.

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## **Publications:**

1. Modification of surface characteristics of functionalized multi-walled carbon nanotubes containing mixed matrix membrane using click chemistry. Priyanka Mistry, Km Nikita, V.K. Aswal, S. Kumar, C.N. Murthy\*, *Desal. Wat. Treat.*, **2023**, doi: 10.5004/dwt.2023.29589. (Accepted on 27 April, 2023)
2. Book Chapter: Studies on the f-MWCNT/PES Mixed Matrix Membranes for Water and Wastewater Treatment. Priyanka Mistry and C.N. Murthy. Environmental Pollution, Climate Change and Altered Lifestyle during COVID, PART 2 - Pollution: Management Strategies, **2022**, Daya Publishing House® A Division of Astral International Pvt. Ltd. New Delhi – 110 002. ISBN: 978-93-5461-317-3 (HB).

## **Conferences:**

1. Oral Presentation: IWA, The 6<sup>th</sup> International Water Accusation Regional Membrane Technology Conference 11th December 2018
2. Poster Presentation: 56<sup>th</sup> Annual Convention of Chemist 2019 organized by 'INDIAN CHEMICAL SOCIETY' NOVEMBER 14-16, 2019, Raipur-492010, Chhattisgarh, India
3. Attended: UGC-CPEPA Sponsored, National Seminar on Applied Polymer Science and Technology (NSAPST-2019) Organized by Department of Chemistry, Sardar Patel University, Vallabh Vidhyanagar-388120, Gujarat, India.
4. Poster Presentation/Second Prize: National symposium on Climate Change, Pollution and Harmony with Nature, 25 January, 2020, organized by Department of Geography, The Maharaja Sayajirao University of Baroda, The Institution of Engineers (India) Vadodara, Indian Association of Air Pollution Control.
5. Oral presentation: 9<sup>th</sup> DAE - BRNS biennial symposium (Webinar) on "Emerging trends in separation science and technology (e-SESTEC-2020) Organized by BARC, Mumbai, India
6. Poster presentation: Virtual International Conference on "Advances in Sustainable Research for Energy and Environmental Management (ASREEM-2021)", August 6th,

2021, Department of Chemical Engineering, Sardar Vallabhbhai National Institute of Technology Surat-395007, Gujarat, India

7. Oral presentation: 12<sup>th</sup> International Conference (Virtual) on “Advancements in polymeric (APM-2021)”, March 9<sup>th</sup>, 2021, Bhubaneswar, India.
8. Oral Presentation: 1<sup>st</sup> International Conference on “Advances in Water Treatment and Management” (ICAWTM-22) 25-26 March 2022, organized by Pandit Deendayal Energy University, Gandhinagar, Gujarat, India.
9. Poster Presentation: 16<sup>th</sup> International Conference on Science and Technology of Polymers and Advanced Materials through Innovation, Entrepreneurship and Industry 2<sup>nd</sup> to 4<sup>th</sup> November, 2022, (SPSI - MACRO – 2022) organized by CSIR - NCL, Pune, India.

### **Work shop:**

1. One- week STUTI Training Program on the theme SPECTROMETRIC ANALYSIS AND IMAGING OF BIOLOGICAL SAMPLES organized by Sophisticated analytical and Technical Help Institute (SATHI), Banaras Hindu University and National Institute of Technology, Warangal during 25 April, 2023 – 1 May, 2023 at Central Discovery Centre, BHU, Varanasi.

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