SYNOPSIS OF THE THESIS

TITLED

STUDIES ON THE FUNCTIONALIZED CARBON NANOTUBES INCORPORATED POLYMERIC COMPOSITE MEMBRANES FOR LOW PRESSURE SEPARATIONS

SUBMITTED TO

THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

APPLIED CHEMISTRY

SUBMITTED BY

Km Nikita

Registration No. FOTE/907 **Date: 05/07/2016**

THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA
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STUDIES ON THE FUNCTIONALIZED CARBON NANOTUBES INCORPORATED POLYMERIC COMPOSITE MEMBRANES FOR LOW PRESSURE SEPARATIONS

Introduction

There has been immense use of polymeric as well as ceramic membranes in the field of water treatment, but some of the disadvantages of these membranes are fouling, low chemical and thermal stability, low permeability and selectivity & lower rejection of specific contaminants. Thus, the idea of composite or mixed matrix membranes came in existence, which can overcome the above mentioned limitations to a large extent. Zimmerman et. al first reported about the mixed matrix membranes[1]. These membranes contain a polymeric substrate as continuous phase and inorganic/organic fillers as dispersed phase. Fillers improve the performance of membranes in terms of pure water flux as well as rejection [2-6]. There are several reports on mixed matrix membranes, however in all the previously reported work of mixed matrix membranes there is no uniformity in the pore sizes reported and in fact there are contradictory results. Some report a reduction in the pore dimensions as compared to the pristine matrix [7, 8], some report an increase in the pore dimensions [9, 10] and one report mentions no change in the pore dimensions [11]. Yet the mixed matrix membrane performance with respect to pure water flux was found to be enhanced in all the cases. Therefore there is no clarity on the role of the pores in the mixed matrix membranes even as the above mentioned references show that polymer based mixed matrix membranes which comprise of a polymer continuous phase and a dispersed phase (zeolites, porous silica, carbon molecular sieves, carbon nano tubes etc.) provides promising solution of low permeation to salt/contaminant and high water flux, higher mechanical strength and also thermal stability. Carbon nanotubes (CNT) are attractive approach for designing of new membranes for advanced molecular separation because of their unique transport properties [12]. Hence we have chosen nanotubes as a filler material in our work. To the best of our knowledge no one has studied the pore dimensions and porosity of membranes using small angle neutron scattering as the density difference between the pore and the matrix would give rise to different scattering characteristics. On the basis of above literature we have chosen the problem of our research on the study of pore dimensions, distribution of pores and other morphological studies for functionalized MWCNT/polymeric composite membranes and their correlation to the rejection observed.

Chapter 1: Introduction

This chapter gives the history of emergence of different kind of membranes (asymmetric, thin film composite, mixed matrix) since the discovery of the synthetic membranes. The complete review of literature on membrane preparation techniques, different polymers and fillers used, reports on the morphological survey of membranes is presented. Moreover, an overview to studies on the heavy metal removal, effluent water treatment, membrane antifouling studies is discussed. Additionally, scattering techniques which could be used to reveal the morphology of membranes are also depicted.

Chapter 2: Scope of Research

This chapter discusses scope and objectives of the thesis.

Chapter 3: Experimental route

This chapter includes the experimental procedure of functionalization of multiwall carbon nanotubes and scheme of the sulfonation of polyethersulfone (PES). The technique for the preparation of all the membranes which comprises of PES and sulfonated PES mixed matrix membranes having different concentration of functionalized nanotubes as fillers is specified here. The functionalization of multiwall carbon nanotubes is confirmed by Fourier Transform Infrared (FTIR) and sulfonation of polyethersulfone is ensured by Fourier Transform Infrared (FTIR) as well as Nuclear magnetic resonance (NMR). The thermal properties of nanotubes, sulfonated PES and all the membranes were measured by Thermo gravimetric analysis (TGA). Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) are also used to analyze the sulfonated polyethersulfone. The solubility studies of PES and sulfonated PES are also studied. The morphology of membranes is studied by Field Emission Scanning Electron Microscopy (FESEM), Capillary Flow Porometry, Mercury Porosimeter as well as Small Angle Neutron Scattering. The membrane hydrophilicity is measured from the sessile drop method measuring the contact angle using a Goniometer. The impedance analyzer is used to observe the conducting nature of membranes. The mechanical strength of all the membranes is analyzed using Tensile testing. The structure of the polymer matrix & the membranes made from them are shown below in Figure 1 & Figure 2:

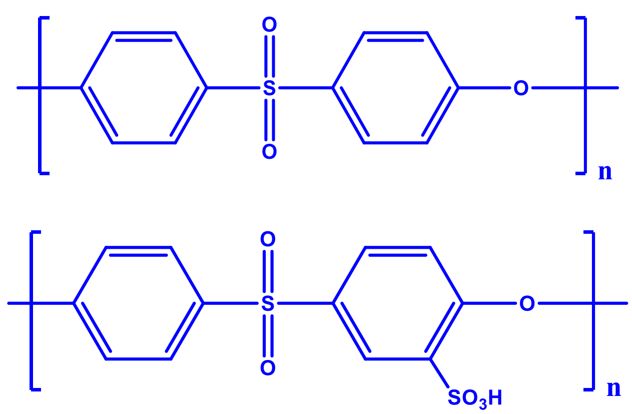

Figure 1. Structure of polyether sulfone and sulfonated Polyethersulfone.

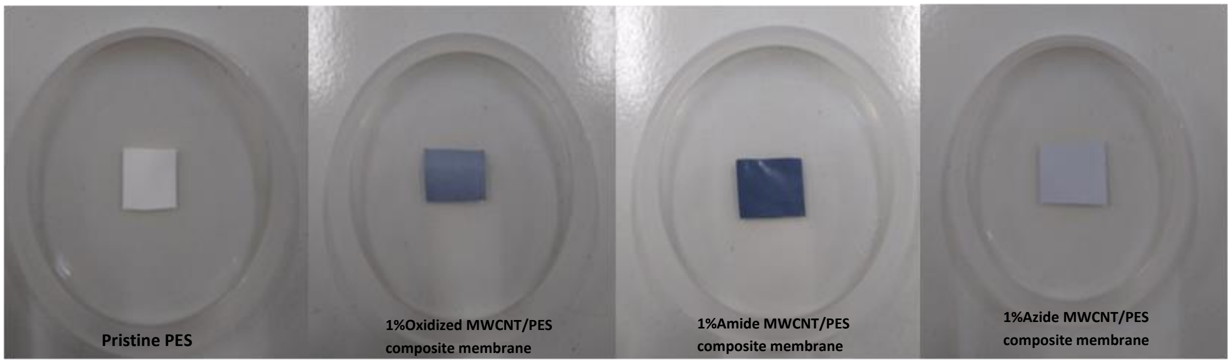

Figure 2. Membrane samples prepared from PES & functionalized CNTs.

Chapter 4: Filtration performance of membranes

This Chapter covers the permeation studies of all the membranes. Heavy metals are one of the hazardous and major sources of pollutant in the waste-water and industrial effluents. The effluent water from the treatment plants still contain substantial concentration of pollutants. The flux of the membranes is flow rate of filtrate passing through it. The pure water flux (PWF) of composite as well pristine polymeric membranes were measured. Effect of pressure and different pH on water flux was also studied for all the membranes. We have selected chromium, lead, cadmium, copper, arsenic for our study to test the effectiveness of our membranes. 1000 ppm concentration feed solution was prepared by dissolving heavy metals in de-ionized water which is used for studying flux, rejection and selectivity of all the membranes at varying time, pressure and pH. The results obtained are highlighted in Figure 3. The azide functionalized nanotubes containing membranes showed the best rejection characteristics. Similarly, proteins extensively reside in the wastewater effluent being large molecules. One of the severe limitations of existing membranes is protein fouling. The antifouling behaviour of prepared membranes was investigated by protein filtration experiments which notify reusability of the membranes.

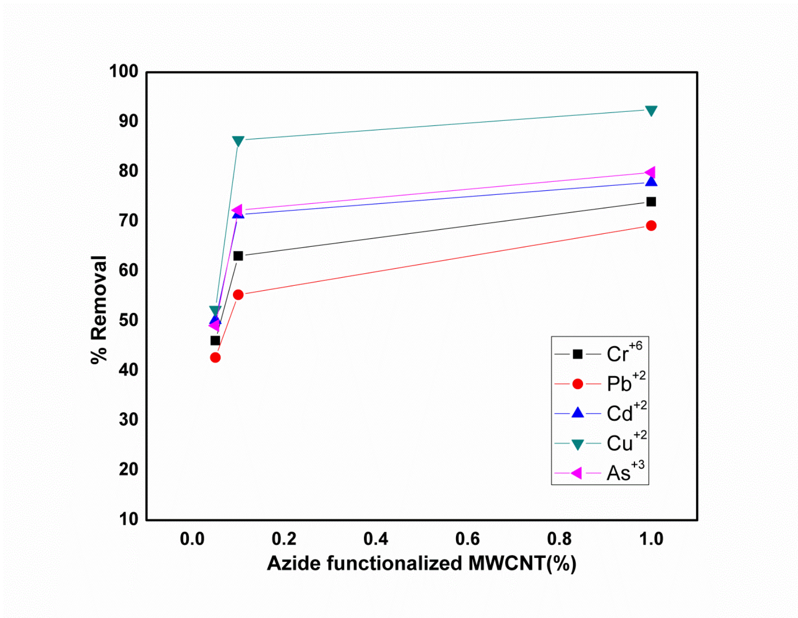

Figure 3. Percentage rejection of metal ions at pH 2.5 for mixed matrix azide functionalized MWCNT/PES membranes containing different % of nanotubes at 71 psi pressure

Chapter 5: Results and Discussion

This Chapter deals with the interpretation of thermal, chemical, morphological analysis of nanotubes, functionalized polymer and membranes, as well as permeation studies of membranes. It includes the correlation of the filtration test results with morphological studies. Presence of nanotubes caused the enhancement in flux of the membranes and are explained in this Chapter. The effect of addition of different functionalized nanotubes on membrane morphology, rejection capability and hydrophilicity is explained here. Flux recovery ratio, reversible fouling ratio and irreversible fouling ratio with respect to all membranes is calculated for the better understanding of antifouling characteristics.

Chapter 6: Summary, Conclusions & Future Prospects

Summary of each chapter and outcome of the work have been discussed in this Chapter. Furthermore the possible future effort based on the limitation of the work is reported here.

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❖ Publications

1. Porous structure studies of the mixed-matrix polymeric membranes of polyether sulfone incorporated with functionalized multiwalled carbon nanotubes, Km Nikita, S. Kumar, V.K. Aswal, D.K. Kanchan, C.N. Murthy*, *Desal. Wat. Treat.*, **2019,** doi:10.5004/dwt.2019.23624. (Accepted)
2. Understanding the surface morphology of MWCNT/PES membranes using SANS: Interpretation & Rejection Performance, Km Nikita, P. Karkare, D. Ray, V. K. Aswal, P. S. Singh, C. N. Murthy*, *J. App. Wat. Sci.* (Paper submitted)
3. Studies on the sulfonated polyethersulfone/MWCNT membranes for water purification, Km Nikita, D. Ray, V.K. Aswal, C. N. Murthy* (Paper under preparation).

❖ Paper presented in conferences

1. Km Nikita, Murthy CN., Aswal VK., (**2016**) Synthesis of functionalized carbon nanotubes blended polyethersulfone membranes with controlled pore size for low pressure desalination application, V. Vidyanagar, Gujarat, India, Advances in separation and purification science and Technology(NSST), G H Patel College of Engineering and Technology, 23rd 24th September. (**Oral Presentation**)
2. Km Nikita, Murthy CN., Aswal VK., (**2017**) Thin Film Composite Membranes Containing Functionalized Carbon Nanotubes for Low Pressure Desalination Process, Trivendram, Kerala, India, Macro2017, Hotel Uday Samudra, 8th 9th 10th11th January. (**Poster Presentation**)
3. Km Nikita, Murthy CN., Aswal VK., (**2017**) Studies on the pore dimension controlled polymeric thin film composite membranes of MWCNT incorporated polyethersulfone,

Tiruchirappalli, Tamilnadu, India, International Conference on Membrane Separation Process (MEMSEP), NIT Trichy, 21, 22, 23 February. (**Oral Presentation**)

4. Km Nikita, Karkare P.,Aswal VK., Murthy CN.,(**2018**) Poly ether sulfone (PES) and modified PES based mixed matrix membranes containing functionalized MWCNTs for waste-water treatment, Goa, India, DAE-BRNS Sponsered Eighth Bienniel Symposium on Emerging Trends in Deparation Science and Technology (SESTEC 2018), BITS Pilani, K.K. Birla Goa Campus, 23rd, 24th, 25th, 26th May.(**Oral Presentation**)

5. Km Nikita, Karkare P., Aswal VK., Murthy CN., (**2018**) Polyethersulfone/functionalized MWCNT mixed matrix membranes for the application of heavy metal removal and waste water treatment, Udaipur, Rajasthan, India, International conference on Chemical Sciences in New Era, Pacific University, 5th, 6th October.(**Poster presentation**)

6. Km Nikita, Karkare P., Aswal VK., Murthy CN., (2018) Functionalized MWCNTs incorporated Poly ether sulfone (PES) and modified PES based mixed matrix membranes for heavy metals removal, Vadodara, Gujarat, India, National Conference on Recent Advances in Material Sciences, The M.S. University of Baroda, 23rd, 24th November. (**Poster Presentation/Second Prize**)

7. Km Nikita, P. Karkare, D. Ray, V.K. Aswal, C.N. Murthy (**2018**) Studies of the polyether sulfone/functionalized Multiwalled Carbon Nanotube mixed matrix membranes for heavy metal removal, Vadodara, India, The 6th International Water Association-Regional Membrane Technology Conference (IWA-RMTC 2018), The M.S. University of Baroda, 10th, 11th, 12th December (**Poster Presentation**)

8. Km Nikita, P. Karkare, D. Ray, V.K. Aswal, C.N. Murthy (**2019**) Studies of the protein fouling behaviour of polyether sulfone/functionalized MWCNT mixed matrix membranes

during water filtration, V. Vidyanagar, Gujarat, India, National Seminar on Applied Polymer Science and Technology, S. P. University, 24th, 25th January (**Poster Presentation**).

- **Conference attended/participation in workshop**

1. Km Nikita attended 'National Conference on Study of Matter Using Intense Radiation Sources and Under Extreme Conditions' on November 3-November 6, 2016 at UGC-DAE Consortium for Scientific Research, University Campus, Indore, M.P.
2. Km Nikita participated in 'XVIII School on Neutrons as Probes of Condensed Matter' on October 22-November 1, 2018 at Bhabha Atomic Research Centre, Mumbai, Maharashtra.

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