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Synthesis and characterization of polymer membranes using advance analytical tools and techniques for water purification

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ABSTRACT

In this paper we studied the synthesis of polymer membrane materials and their characterization by various techniques such as Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), CHNS/O analysis, scanning electron microscopy (SEM), and performance in the form of volumetric flux and salt rejection. Herewith we have discussed about these techniques simply in details. The techniques are discussed as follows along with examples. Herewith we used polysulfone (PSf) membrane as a support membrane for our studies and we use all aforementioned techniques for polymer membrane characterizations. Novel thin film composite (TFC) membrane was prepared via interfacial polymerization (IP) on the surface of PSf membrane. The selective layer was prepared by the interfacial polymerization of 1, 3-benzenedithiol (BDT), and trimesoyl chloride (TMC) for water purification and the results have been discussed well in this paper. The result indicated that volumetric flux depends on the hydrophilicity of thin film. BDT 2 wt % and TMC 0.1 wt % solutions were found appropriate for high performance membrane. Such membrane exhibited 98.3 % salt rejection and as high as 79 L m^2 h water flux. Copyright © 2016 VBRI Press.

Keywords: Polymer membrane; characterization techniques; interfacial polymerization; volumetric flux; salt rejection.

Introduction

There is an urgent need for governments, industries, and proprietors around the world to explore new technologies to produce the pure water at low cost. Nowadays different polymer membranes are the favorable candidate materials for the water purification because of its low-cost, effectiveness and reliability in numerous industrial separation processes [**1- 4**]. Therefore, the characterizations of these polymer membranes for original properties are tremendously significant for couture membrane for specific separations. From the last few decades polysulfone membranes are broadly used in membrane separation processes because of their elevated mechanical potency, superior thermal stability, and resistance to acid/alkali solution. Preparation of polysulfone membrane with an accurate pore size and narrow pore size distribution in bid to accomplish an successful sieving with an acceptable fluid flow is a difficult task. Generally the phase inversion technique is used for the preparation of polysulfone membranes. Yun et al reported the preparation of polysulfone membranes by phase inversion processes for water vapor separation [**5**].

However, most polymeric membranes have porous structures without a dense selective layer which limit their use to a great extent. Therefore, in order to solve this problem, interfacial polymerization method has been utilized to fabricate thin film composite (TFC) membranes due to its promising results as a highly dense and selective layer [**6-12**]. Effect of monomer concentrations [**13-16**] and reaction conditions [**17**] have been studied in great detail and researchers have managed to outline optimum reaction conditions to fabricate thin film composite membranes with excellent properties. To further improve the performance of TFC polyester membranes various surface treatments and additives have been utilized. Modification of polyamide membrane by atomic layer deposition [**18**], graft polymerization [**19**], addition of amino cyclodextrin [**20**] and electrostatic self-assembly [**21**] has been studied in great detail.

In this work the membrane preparation/fabrication condition was systematically investigated. After the development of polymeric PSf membranes, the design of novel thin-film composite (TFC) membranes was a significant advancement in membrane technology. TFC membranes are composed of an upper poly (thiol ester) active layer fabricated via interfacial polymerization (IP) of 1,3-benzenedithiol (BDT) in an aqueous solution and trimesoyl chloride (TMC) in an organic solution, a porous middle polysulfone (PSf) ultrafiltration (UF) support, and a non-woven fabric base. The TFC-PSf membranes show with reasonably high water flux. Results obtained in this study are useful for the design the membrane conditions for reverse osmosis (RO). These types of fundamental studies are very important for those researchers who are working in the field of RO technology for the development of suitable membrane materials. In our study we have characterized prepared membrane using the modern instrumentation technology.

Experimental

Materials

Polysulfone ultrafiltration membranes (molecular weight cut off = 6000). The monomers 1,3-benzenedithiol (BDT) and 1, 3, 5-benzenetricarbonyl chloride (TMC) for interfacial polymerization were purchased from Sigma-Aldrich. Deionized water (DI) from Milli-Q ultrapure water purification system (Millipore) was used as a solvent for BDT while n-hexane (99.9%, Fisher Scientific, NJ) was used as solvent for TMC.

Casting of polysulfone membranes

The 15 wt.% of polysulfone was dissolved in A. R. grade *N*, *N*-dimethylformamide (DMF) to make homogeneous solution. By using the well know technique a phase inversion processes the prepared polymer solution was cast on a non-woven fabric Nordyls T-100 from a water bath consisting a fixed amount of DMF and 0.1 wt.% CTAB surfactant. The roofed casting chamber of the membrane casting unit was maintained at about 36 °C and relative humidity of about 22% for to maintain the membrane quality. The polysulfone membrane fabric was rolled from a supply roller in to the casting base where the thin film of casting liquid was formed on the fabric to make flat sheet membrane of known thickness. After the flat sheet membrane casting the casting chamber then immediately passed into the coagulation bath where precipitation of liquid film into solid membrane was done. The prepared polysulfone flat sheet membrane was rinsed carefully with distilled water and used for the further study as explain in this paper. Table 1 shows the all parameters those used for the casting of polysulfone flat sheet membrane.

Table 1. Parameters for casting of PSf flat sheet membrane.

Entry	Characteristics	Value
1	Polymer concentration in casting solution	15% by weight
2	Thickness (μm)	60
3	Molecular weight cut off (MWCO)	120 KDa
4	Bubble point pressure (psi)	48.345
5	Bubble point diameter (μm)	0.0663

ATR-FTIR

Attenuated total reflectance (ATR) – Fourier transformed infrared spectroscopy (FTIR) was performed to identify the characteristic functional groups of interfacially polymerized poly (thiol ester) layer as well as the surface chemistry of the modified membranes. ATR-FTIR technique has been widely used instead of conventional transmission mode because it is more comfortable and the measurement can be performed in few seconds. Moreover, there is no need for extensive sample preparation as all kinds of samples such as fibers, pellets, powders and pastes can easily be mounted on the ATR crystal. After cleaning the dry membrane sample was carefully cut and mounted on the crystal with the poly (thiol ester) layer facing the crystal. The ATR-FTIR analysis was done using ALPHA-P Spectrometer (Bruker Optik GmbH) with a diamond crystal in the range of 600-4000 cm^{-1}.

FE-SEM

Field emission – scanning electron microscopy (FE-SEM) was used to investigate the surface morphology of the modified thin film composite membrane. The prepared membrane samples were first immersed in distilled water followed by immediate cooling in liquid nitrogen to freeze for the easy visualization of the membrane cross-section structure. TFC membrane cross section was visualized by SEM, S-4800, Hitachi, with the stub and sputter coated thin layer of gold using sputter coater (Balzers union SCD 040).

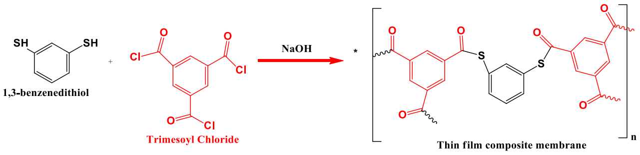

Fig. 1. Thin film composite membrane structure prepared by interfacial polymerization method.

Results and discussion

Preparation and characterization of composite membrane for water purification

Thoroughly washed polysulfone flat sheet membrane was immersed in an 2.0% aqueous solution of 1,3-benzenedithiol (7.03 mmol) for 5 min followed by draining off for 5 min to remove excess solution. To make the homogeneous solution with water maintain the pH of thiol monomer (1, 3-benzenedithiol) is very important, and need to maintain it in between 12-13 using NaOH solution. Further the membrane was then immersed into TMC solution of 0.1% (0.4 mmol) for 1 min followed by draining off excess solution. The polymerization reaction occurs on the surface of PSf flat sheet membrane resulting in the formation of an ultrathin layer of cross-linked poly (thiol ester)polymer, as we called here thin film composite membrane. The obtained thin film composite membrane was cured in hot air circulation at 70-80 °C for 10 min whereby polyester layer attains chemical stability. Furthermore, remove the membrane from oven, cool it for 2 h and after the cooling dipped the membrane overnight in RO water and at the second day tests the membrane for water purification. The schematic representation of interfacial reaction by using BDT and TMC is depicted as **Fig. 1**.

Fig. 2 shows the ATR-FTIR spectra of the PSf membrane support and thin film composite (TFC) membranes. The spectra of PSf flat sheet membrane shows typical characteristic peaks at 1586 cm^{-1}, 1323 cm^{-1}, 1295 cm^{-1}, and 1240/1157 cm^{-1} that are assigned to C-C stretching in the aromatic rings, C-SO_2-C symmetric stretching, S-O stretching, and C-O-C symmetric stretching respectively. Furthermore, the vibrational bands at 1080 cm^{-1}, 1014 cm^{-1}, and 873 cm^{-1} are due to the aliphatic

C-C/aromatic C-H bending and rocking in the polysulfone polymer chain [**22**]. In the ATR-FTIR spectra of the thin-film composite (thiol ester) membrane shows characteristic peak at wave number 1730 cm^{-1} for S–C=O (thiol ester) group [**23**].

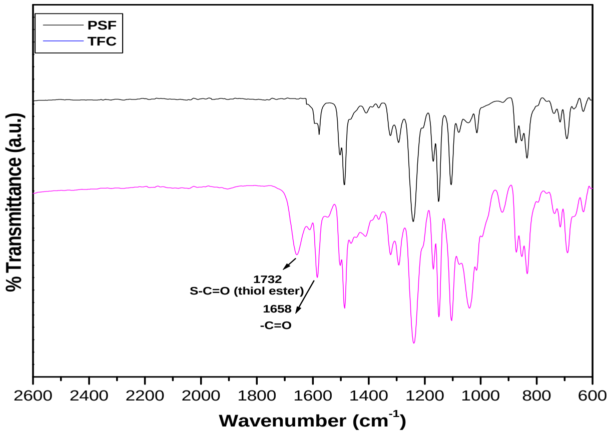

Fig. 2. ATR-FTIR spectra of the PSf and thin film composite (TFC) membranes.

The aforesaid results of ATR-FTIR show the confirmation of the presence of poly(thiol ester) thin film on the surface of polysulfone membrane support. In the range of 1200–1600 cm^{-1} numerous strong bands were found, which correspond to the typical stretching modes of CN heterocycles [**23**]. The absence of abovementioned characteristic band in the IR spectra of PSf membrane support confirms the formation of composite membrane.

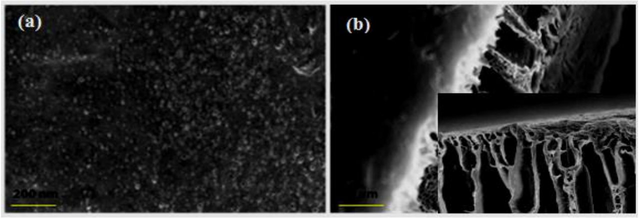

Fig. 3. SEM images of thin film composite membrane for water purification, (a) Surface view, (b) Cross-sectional view.

Fig. 3 shows the surface morphology of TFC membrane viewed under scanning electron microscope using dried, fractured (for transverse section) and gold sputtered samples. The electron micrographs of TFC membrane surface and transverse section are shown in **Fig. 3 (a**, **b)** respectively. In **Fig. 3b** clearly found the existence of three layers non-woven polyester fabric, micro porous polysulfone layer and thin film composite layer are observed. In the surface image of thin film composite membrane **(Fig. 3a)** shows a dispersed granular surface with visible open pore structures. By using this TFC membrane the effect of different concentration feed solution towards water flux are measured and results are depicted in **Fig. 4**.

CHNS/O analysis

The elemental analysis of TFC membrane was done using CHNS/P analyser. First measure the sample weight in mg (milligram) into a quartz tube at 1020 °C with constant helium flow (carrier gas) for the analysis. The chemical compositions of coating layer mention in **Table 2**. CHNS/O analysis of the barrier layer provided tentative chemical composition of the barrier layer. The theoretical as well as determined values of C, H, S and O in the barrier layer material have been given in **Table 2**. The theoretical values indicated in the table have been calculated presuming 99% thiol ester bond formation in the polymerization reaction between BDT and TMC.

Table 2. CHNS/O analysis of the thin film coating layer of membranes.

Elements	**Theoretical values (%)**	**Experimentally determined values coated membrane, 2% (w/v) m- (BDT) and 0.1% (w/v) (TMC) (%)**
C	67.95	65.78
H	3.75	4.56
S	13.2	13.42
O	15.1	16.24

Thin film composite membrane for water purification

During the interfacial polymerization of multifunctional thiol and multifunctional carboxyl chloride normally two types of reactions are possible depending upon the concentration of monomers at the interface. One is the formation of a cross-linked poly (thiol ester) structure due to the reaction between thiol groups of BTD and acid chloride groups of TMC and second one is because of the hydrolysis of acid chloride group of TMC to carboxylic acid group. Though the concentration of both the monomers (BDT and TMC) is important however the rate of polymer formation and growth of poly (thiol ester) chain depends on the concentration of TMC solution.

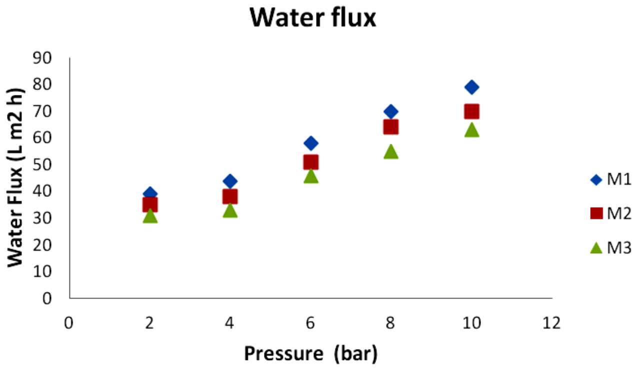

Fig. 4. The volumetric flux against trans-membrane pressure using salt concentration M1 200, M2 500 and M3 1000 ppm NaCl solutions.

The formation of thin polymer layer on flexible support in situ through interfacial polymerization using solutions of reactive monomers in suitable solvents is unique and is widely used for the fabrication of porous and non-porous composite membranes shows the best results regarding volumetric flux and salt rejection. The volumetric flux was plotted against trans-membrane pressure (**Fig. 4**). For optimization studies, the concentrations of feed solutions were taken as M1 200, M2 500 and M3 1000 ppm NaCl solutions. The volumetric flux was found to increase with trans-membrane pressure, in consonance with Hagen-Poiseuille equation; however, an irregular increase was observed for volumetric flux. The variation observed is attributable to Tortuosity factor, related to bend in shape of pores in membranes under pressure. During the experimental process, an increased surface hydrophilicity due to thin selective layer will facilitate the solubilization of water molecules on membrane surface, and thus improve water flux as mentioned in **Fig. 4**. In addition, the concentrated solution was pragmatic to permeate gradually in association to its diluted solution underneath identical investigational circumstances.

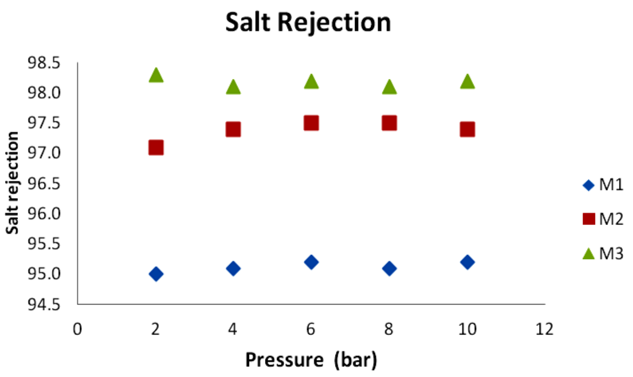

Fig. 5. The salt rejection against trans-membrane pressure using salt concentration M1 200, M2 500 and M3 1000 ppm NaCl solutions.

Salt rejection and water flux of three different concentration feed solution through this thin film composite membrane have been shown in **Fig. 4** and **Fig. 5** respectively. Salt rejection varies from 95.0% to 98.3% depending upon the concentrations of salt used in the feed solution. Using concentration (M3) which was passed through membrane prepared using BDT solution of 2% and TMC solution of 0.1% exhibited salt rejection optimum 98.3%. The membranes prepared from solutions other than 2% BDT and 0.1% TMC exhibited inferior performance because of this reason herewith we didn't show remaining results. Lower concentrations of feed solution exhibited low salt rejection and high water flux as shown in **Fig. 5**. Therefore, optimum concentration of feed solution is 1000 ppm shows higher salt rejection but decrease water flux.

Conclusion

This work explored the impact of thin active layers on water purification. This layer was prepared using BDT 2 wt.% monomer solution as a novel material. In conclusion, the techniques are discussed herewith along with examples considering TFC membrane for our studies are useful for the researcher those are working in the membrane field. After characterization finally as a results the volumetric flux and salt rejection of TFC membrane was measured at different pressures and at pressure 10 bar we got volumetric flux 79 L m^2 h. Furthermore, the volumetric flux was plotted against trans-membrane pressure, for optimization studies, the concentrations of feed solutions were taken as M1 200, M2 500 and M3 1000 ppm NaCl solution. The volumetric flux was found to increase with trans-membrane pressure. With concentration (M3), which was passed through membrane prepared using BDT solution of 2% and TMC solution of 0.1% exhibited optimum 98.3% of salt rejection.

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