SYNTHESIS AND REMOVAL OF HEAVY METALS USING PS BASED MEMBRANES

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Abstract:This study has been undertaken to investigate the efficiency of prepared membranes. For our research work we have selected polysulfone (PS) – Polyetherimide blend membranes. Removal of heavy metal test carried out using self-fabricated salinity checking equipment. A new set of membranes prepared are subjected to study their heavy metals removal efficiency. Our team successfully able to remove around 80 -88% cadmium and mercury with respect to different applied pressure. Along with rejection percentage, prepared membranes also characterized in terms of water absorption, hydrophilicity, FTIR and DSC analysis

Key words: Polysulfone, synthesis, rejection, heavy metals

I. INTRODUCTION

In recent times membrane technology emerging as one of the important tools in water purification. From our household RO system to multi stage desalination technique, membranes take major role [1]. Globally water system under severe threat with increase in human and industrial activity. The main contaminants inwaterof grave concern are heavy metals such as mercury, lead, cadmium, etc. The heavy metals are among the most common pollutants found in contaminated water. Even at low concentration these metals can pose a toxic threat to human beings and animals. Heavy metals, due to their versatile physical and chemical properties,they are widely used in electronic industry, machinery parts and in making of different tools which are used in our daily life. As a result heavy metals easily enters into aquatic and food chain system [2]. Consumption of heavy metals through water or food may pose serious health threat. For example consumption of lead more than 0.1 mg/L (Regulation of water qualityin India) may cause brain damage, hypertension, etc, consumption of Nickel more than 0.1 mg/L (Regulation of water quality in India) may cause DNA damage, high phytotoxicity, etc, dosage of chromium more than 0.1 mg/L (Regulation of water quality in India) may result in irritation of gastrointestinal mucos, etc, when zinc concentration exceeds 0.1 mg/L (Regulation of water quality in India) may cause phytotoxic, abdominal pain, anemia etc, more dosage of cadmium (0.001 mg/L allowed as per regulation of water quality in India) may result in serious damage to kidneys and bones in humans, bronchitis, emphysema, anemia, etc mercury (0.004 mg/L allowed as per regulation of water quality in India) is the another poisonous heavy metal which may cause mutagenic effects, etc,arsenic (0.05 mg/L allowed as per regulation of water quality in India) causes toxicological and carcinogenic effects, melanosis, keratosis, hyperpigmentation, immunotoxic, etc. By considering above mentioned ill effects of heavy metals, it is very important to remove heavy metals from consumable food stuff especially water. There are several methods of heavy metals removal such as coagulation, precipitation, membrane filtration, adsorption by adsorbent, ion exchange, heterogeneous photocatalysis and bioremediation. In this work we have adopted membrane filtration for the removal of mercury and cadmium [3]

II. EXPERIMENT: 2.1 Materials and method:

Polysulfone (PS) having molecular weight of 35,000, Polyetherimide (PEI) were obtained from Sigma Aldrich. Reagent grade N-methyl pyrrolidone, NMP was obtained from Merck-India and was used without any further purification. Mercury and cadmium salts are purchased from Merck, India.Lapox L-12 hardener was purchased from local market. Both PS and PEI in required amount were dried in vacuum oven for 10 hours. Then a specified amount of NMP was added and heated to dissolve the polymer. The solution was stirred for 4 hours for completion of dissolution. 0.1ml of hardener was added.Further stirring was stopped for 30 minutes and polymer solution was casted over nonwoven porous support KC 270 using a casting knife. Further excess of solvent was removed by allowing membrane for room temperature for about 2 hrs. The membranes were separated by dipping the glass plates in distilled water [4].Further obtained membrane carefully dried and was used for performance study. Prepared membranes summarized in Table 1. Fig 1 depicts synthetic route for synthesis of blend membrane

Table. 1: Solutions containing different wt. % of PS and PEI

Membrane Code	Nonwoven support	Wt % composition (PS)	Wt % composition (PEI)	Hardener (ml)
M1	K.C.270	90	10	0.1
M2	K.C.270	80	20	0.1
M3	K.C.270	70	30	0.1
M4	K.C.270	60	40	0.1

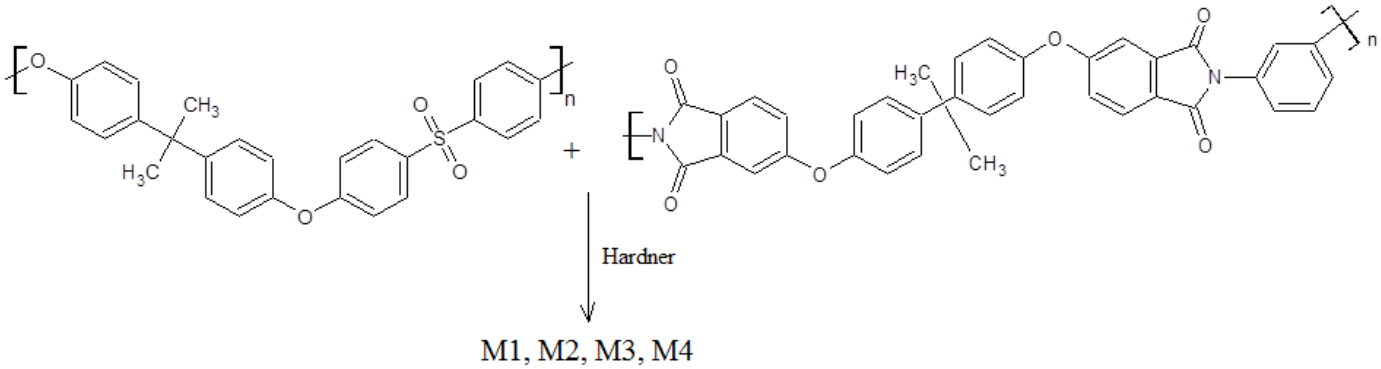

Fig. 1 Synthetic route for membrane preparation

2.2. Infra-red spectral studies

In order to obtain detailed information about the formation of the blend membranes, FTIR spectra of the membrane were recorded using Nicolet Avatar 5700 FTIR (Thermo Electron Corporation) spectrometer. Samples for infrared (IR) measurements were prepared by grinding a quantity of the sample with a specially purified KBr salt finely. This powder mixture is then crushed in a mechanical die press to form a translucent pellet.

2.3. Morphology of the membranes:

To analyze surface and cross section image of the membranes, we used scanning electron microscope (SEM)Jeol JSM-6380LA.To obtain the best result, membrane was cryogenically fractured in liquid nitrogen and then sputtered with gold. SEM provides information on surface porosity and layer thickness.

2.4. Water uptake measurement:

The swelling characteristics were determined by water uptake measurements. The membrane samples were first immersed in deionized water until there was no weight difference in the membrane. Further wet membrane then blotted to dry to remove surface droplets and quickly weighted. The wet membranes were vacuum dried at 50°C and weighted again. The water uptake of the membranes was calculated by weight gain of absorbed water with reference to the dry membrane and reported as weight percent water absorption. The water uptake can be calculated using following equation, [5].

$$\text{Water uptake} = m_{wet} - m_{dry}/m_{dry} \quad \ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where, m_{wet} is the weight of wet membrane and m_{dry} is the weight of dry membrane.

2.5. Hydrophilicity – hydrophobicity of the membranes:

The water contact angle (CA) of the membraneswasmeasured to study theirhydrophobicity/-philicity. TheCAmeasurementswere performed using the VCA-Optima (AST productsInc. MA, USA). Samples of 4 cm^2 area (2cm×2 cm) at random positionswere prepared from each membrane. The samples were thenplaced on the glass plate holder and fixed with scotch tape. Theequipment syringe filled with distilledwaterwas installed to standvertically. 2µl of water was deposited on the membrane surface.The CA was measured at five different spots on each membranesample for both top and bottom surfaces.

2.6. DSC analysis:

Differential scanning calorimetry (DSC) is a thermodynamic technique widely used for studying thermal characteristics of the membrane. The ability to monitor phase transitions in polymeric membrane has not only provided data on thermodynamic stability for these important molecules, but also made it possible to examine the details of unfolding processes and to analyze the characteristics of intermediate states involved in the melting of membrane polymers. A DSC-60 Shimadzu calorimeter was used to analyze the thermal behavior of differently processed membranes, with the heating rate of 10 ºC /min up to 300 ºC.DSC curve of the resultant membranes were studied with increase in temperature at the rate of 10ºC/min. Each sample was subjected to several heating/cooling cycles to obtain reproducible Tg values. The initial onset of the change midpoint of slope in the DSC curve is taken to be the Tg.

2.7. Permeation - Rejection study:

Mercury and cadmium salts were used to study flux - rejection performance of the membrane. The permeability of pure water through membrane was also measured. Flux, F(l / m^2 h), was calculated as Eq. 2

$$F = W/ A\ t \ldots\ldots\ldots 2$$

Where W(l) is the total volume of the water or solution permeated during the experiment, A(m^2) is the membrane area, and *t* (h) is the operation time. Rejection, *R*, is calculated as Eq.3

R= (1-concentrate permeates/ concentrate feed) …….3

Schematic diagram of lab scale filtration set up is shown in Fig. 2. The feed was taken from the feed tank and was pumped into themodule. The pressure difference betweenthe feed inlet and the outlet during operation was adjusted from 1 to 12 Bar. The rate of the permeate stream was measuredby a rotameter and a gauged cylinder whereas rejection (%) was studied by conductivity measurements.

Fig.2. Photograph of the self-made permeation / rejection equipment

III. RESULTS AND DISCUSSION

3.1. Spectral study:

In order to obtain detailed information about the formation of the blend membranes, FTIR spectra of the membrane were recorded. IR spectroscopy has several advantages for membrane studies. Firstly, variations in frequency, line width, and intensity are sensitive to structural transitions of membrane components. Fig.3 shows IR spectrum of the PS-PIE membrane. Following observed stretching frequencies confirms formation of blend membrane,

3600 -3200 cm^{-1} for O-H stretching vibrations, 2980 -2880 cm^{-1} for Asymmetric and symmetric C-H stretching vibrations involving entire methyl group,1412 cm^{-1} for Asymmetric C-H bending deformation of methyl group,1365 cm^{-1} for Symmetric C-H bending deformation of methyl group ,1325 -1298 cm^{-1} for Doublet resulting from asymmetric O═S═O stretching of sulfone group, 244 cm^{-1} for symmetric C-O-C stretching of aryl ether group,1170 cm^{-1} for Asymmetric O═S═O stretching of sulfonate ,1150 cm^{-1} for Symmetric O═S═O stretching of sulfone group ,1107 -1092 cm^{-1} for Aromatic ring vibrations ,1027 cm^{-1} for Symmetric O═S═O stretching of sulfonate group

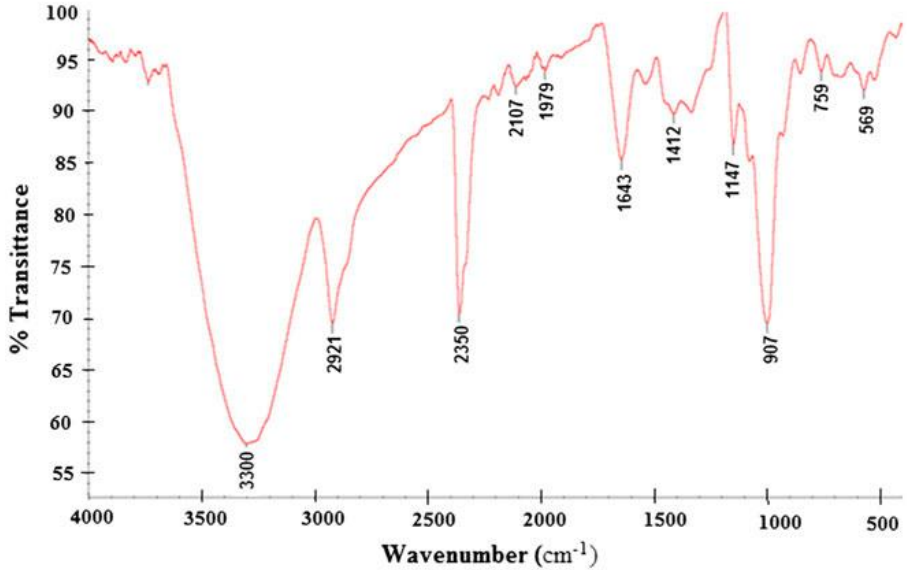

Fig. 3. IR spectrum of membrane

3.2. Morphology of the membranes

The SEM pictures show similar densestructure for the surface area of the synthesized membranes. Surface image shows distribution of nano/micro pores in membranes. Fig.4a shows surface image of the M1 with pe pore size less than 5 µm. Cross section image of the M1 membranes showsdense and channel-like microvoids (Fig.4b) which eases the flow of mass transport within the membrane matrix. It can be concluded that SEM study of the membranes however does not clearly signify the effects of concentration of either PS or PEI on the membrane structure.

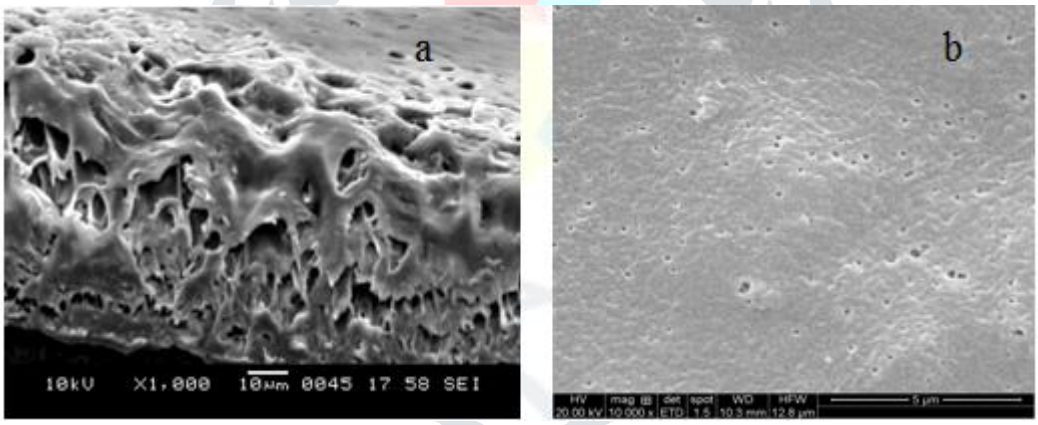

Fig.4. Cross section (a) and surface image (b) of the membrane

3.3. Water uptake measurement:

The water uptake, swellingcharacteristics play important roles in overall membrane performance. Obtained results were tabulated in Table.2. It is evident that membrane having higher concentration of PS gives lesser water uptake. It may be due to the fact that PS is relatively hydrophobic hence it cannot hold more water content

Table2. Water uptake value for different membranes

Membrane code	Water uptake
M1	17
M2	32
M3	41
M4	57

3.4. Hydrophilicity – hydrophobicity of the membranes:

It is well known fact that membrane showing contact angle more than 30^{o} possess more hydrophobicity than hydrophilicity. From the obtained results it is observed that membranes exhibit hydrophobic nature than hydrophilic. In general these membranes wettability character is very less. Table.3 Illustrates variation of contact angle with polysulfone concentration,as polysulfone concentration increases contact angle also increases hence it implies that PEI gives comparitively hydrophilicity to the membranes.membrane having highest water uptake value shows increased contact angle measuments

Table3. Contact angle values of different membranes

Membrane code	Contact angle in degree
M1	69±3
M2	61±3
M3	53±3
M4	49±3

3.5. DSC analysis:

Fig.5shows the thermograms of DSC measurement of the membranes. The Tg values of the M1, M2, M3, M4 membranes are 222, 212, 201, 200 ˚C, respectively.The relationship between Tgand the composition of blended membranes depends upon percentage of polysulfone, lower PS composite membrane shows Tg range from 200˚C to 203˚C whereas higher PS composition show Tg range from 212˚C to 222˚C.Hence it concludes that polysulfone concentration plays vital role in thermal stability of the present membranes [6]

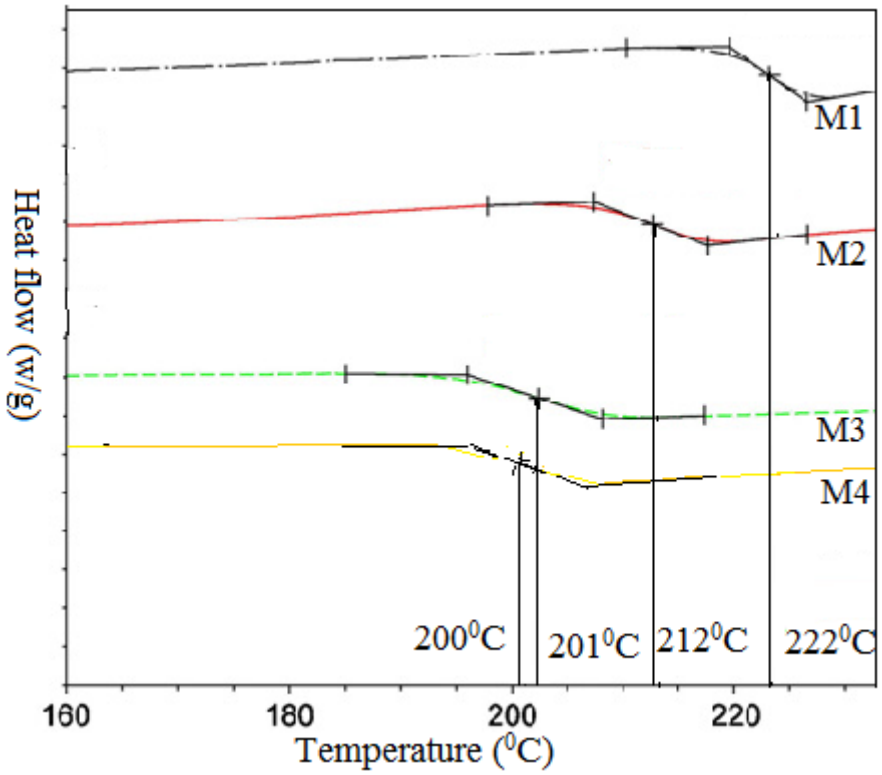

Fig.5. DSC curve of the M1, M2, M3 & M4 membranes

3.6. Permeation - Rejection study:

At different pressure (bar), flux for pure water with respect to unsupported membranesis shown in Fig.6.The plot depicts a linear relationship between the pure water flux and transmembrane pressure. It is seen that slow and steady increase of pure water flux with respect to decrease in PS wt% . This is due to the fact that PEI leads predominantly to swelling rather than leaching out from the membrane-forming system. Consequently, the flow path in the membrane was reduced and hence the increase in the flux was not steep. Flux values of M1 and M2further reinforces above explanation.

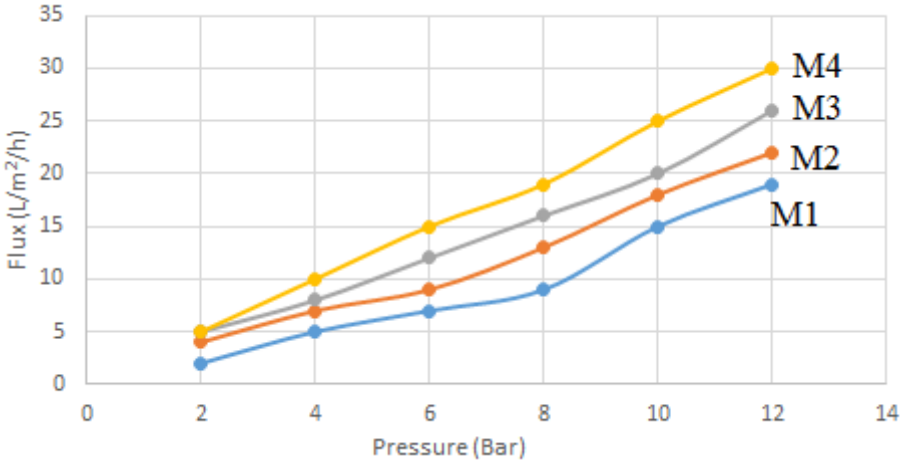

Fig.6 water flux of the membranes

For the rejection study a solution of $Cd(NO_3)_2 \cdot 4H_2O$ with cadmium 0.001mg/l and $Hg(NO_3)_2 \cdot H_2O$ with mercury 0.004 mg/l was prepared.

The factors responsible for separation of different salts by different membranes were discussed here. The rejections to cadmium and mercury salts by four different membranes were studied and the results are shown in Fig.7. - Fig.8 respectively. The membrane salt selectivity appears to be a function of both Donnan exclusion (the rejection of ionic components as a result of charge interactions between the membrane surface and the ions) and size effects. This suggests that the membrane discriminates on the basis of both ionic size and charge repulsion/attraction. All of the ions in aqueous solution became hydrated by water molecules. It is observed that M1 membranes shows more rejection rate. Between Cd and Hg, cadmium rejected to more extent than mercury.

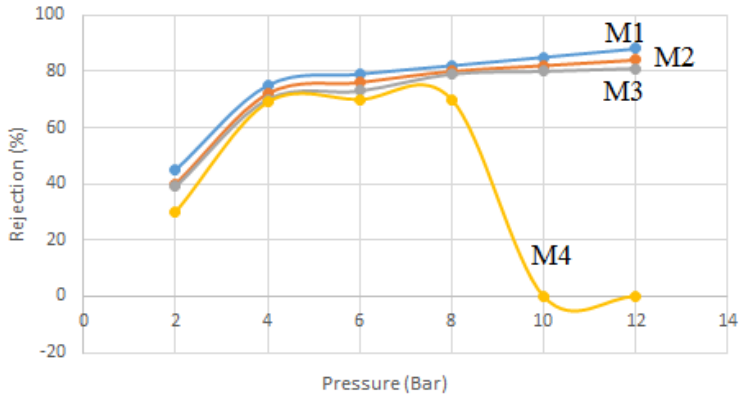

Fig.7. Rejection rate for cadmium

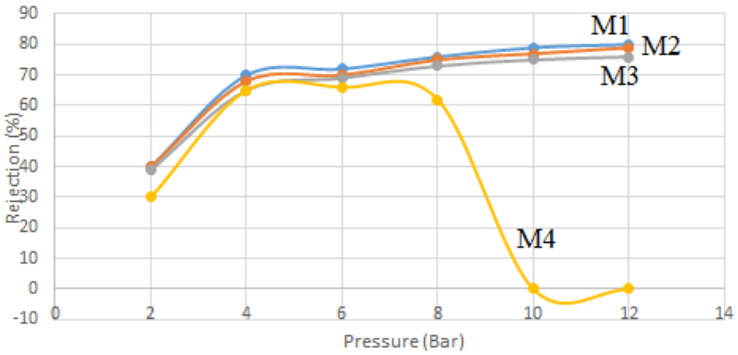

Fig.8. Rejection rate for mercury

IV. CONCLUSION

It is observed that prepared membranes show good thermal stability. Synthesised membranes are confirmed by IR spectra. Contact angle measurements give wettability of the membranes. Membranes exhibit higher contact angle value and this value increases with increase in PS concentration. Hence it is understood that concentration of PS increases hydrophobic nature of the membranes. Membranes shown good rejection of mercury and cadmium at lower pressure.

REFERENCES

[1]WilfM, BartelsC, Optimization of seawater RO systems design (2005) Desalination, 173, 1-12

[2]Hansen, H.K., Nunez, P. and Jil, C. (2008) Removal of arsenic from wastewaters by airlift electrocoagulation. Part 1: Batch reactor experiments, Sep. Sci. Technol., 43, 212-224

[3]Khulbe, Kailash & Matsuura, T. (2018). Removal of heavy metals and pollutants by membrane adsorption techniques. Applied Water Science.

[4] Chitrakara Hegde, Mahesh Padaki, Arun Isloor, Pikulwanichapichart,YuLiangdeng (2011) Synthesis and desalination performance of Ar^{+}-N^{+} irradiated polysulfone based new NF membrane. *Desalination* 265, 153–158

[5] Munari S, Bottino A, Capannelli G, Moretti P, (1985) Membrane morphology and transport properties, Desalination, 53, 11-23

[6]Vinodhini A, Kirubhanandan S, Gomathi T, Sudha P N, Venkatesan J and Sukumaran A(2017) FTIR, XRD and DSC Studies of Nanochitosan, Cellulose acetate and Polyethylene glycol Blend Ultrafiltration Membranes, International Journal of biological macromolecule, 04, 1721-1729

[7] Kirk Johnston H (1975) Reverse osmosis rejection of heavy metal cations, Desalination, 16, 205-224