Preparation and Characterization of Acrylonitrile Butadiene Styrene and Trifluoroacetylethyl Cellulose Blend Nanofiltration Membrane and Performance in the Separation of Mercury

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Abstract— **In the present work, an attempt has been made to prepare a new blend membrane with 75% of acrylonitrile butadiene styrene and 25% of trifluoroacetyl ethyl cellulose by casting method. The membrane was characterized using scanning electron microscope and thermogravimetric analysis. This membrane was used to separate mercury ions from aqueous solutions using nanofiltration. The experiments were carried out at different feed concentrations (5, 10, 50 and 100 ppm), feed pressures (0.2, 0.4, 0.6, 0.8 and 1.0 MPa), feed flowrates (4, 8, 12, 16 L/min) and corresponding permeate flux (J_v) and observed rejection (R_O) were measured. The experimental studies showed that this membrane gave highest observed rejection of 59.3% at feed concentration of 5 ppm and applied pressure of 1MPa.**

Index Terms— **Nanofiltration, mercury, acrylonitrile butadiene styrene, blend membrane**

I. INTRODUCTION

Fresh water resources in the world are limited and water stress in the dry or highly urbanized regions is rather common. Currently about one third of the world's population lives in areas with moderate to severe water shortage. One of the severely hazardous water contaminants is heavy metal, such as mercury, whose both organic and inorganic forms are toxic. A large amount of mercury is contaminated in the effluent generated from the industries. The aquatic environments are effected by the mercury, in the form of Hg(II), which is mostly generated from industrial and nuclear wastes. Severe health problems take place in both animals and humans due to presence of mercury in the environment [1].

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Mercury is carcinogenic, mutagenic, teratogenic and promotes tyrosinemia. The main toxicological effects of mercury include neurological damage, paralysis, chromosome breakage, impairment of pulmonary and kidney functions, chest pain, etc. Hence, it is necessity to develop cheap methods to decontaminate mercury polluted water [2]. Though lot of research has been conducted for the removal of mercury from aqueous solutions, most of this has been done on the removal of relatively high concentrations of oxidized mercury from synthetic solutions [3]. Due to increasing environmental awareness and strict regulations on acceptable levels of mercury emissions, it is necessary to remove mercury [4]. The Central Pollution Control Board (CPCB), India, limit for mercury is $1 \mu g \, L^{-1}$ for drinking water and $5 \mu g \, L^{-1}$ for wastewater discharge [5]. There is greater interest in removing mercury from streams containing relatively low concentration of mercury.

Membrane technology had gained wide acceptability in the separation and rejection of metals by reverse osmosis (RO) and ultrafiltration (UF), but the problems like high operation and maintenance costs for application of high pressure to system and pretreatment necessity have led to the production of nanofiltration (NF) membranes [6]. The properties of NF membrane lies in between UF and RO, with special advantages of lower osmotic pressure difference, higher permeate flux, higher retention of multivalent salts and molecular weight compounds (>300), relatively low investment and low operation and maintenance costs [7].

The main aim of the present work is to prepare a new blend membrane by using acrylonitrile butadiene styrene (ABS) and trifluoroacetyl ethyl cellulose (TFAEC) to provide balanced quantities of hydrophobic and hydrophilic moieties, so that it can be used to investigate the effects of applied pressures and feed concentrations on permeate flux and observed rejection of mercury ions by NF.

II. MATERIALS AND METHOD

A. Materials

The main materials used are ethyl cellulose (EC) (National Chemicals, Vadodara, India), trifluoro acetic

anhydride (Spectrochem, Mumbai, India) in a boiling range 39-40^{0}C and density 1.508-1.511 g/mL, chloroform (Finer Chemicals, Ahmedabad, India) in a boiling range 60-62^{0}C, density 1.475-1.480 g/mL and refractive index 1.444-1.445, pyridine (Merck Limited, Mumbai, India), tetrahydrofuran (Molychem, Mumbai, India) with refractive index 1.407-1.409 and density 0.886-0.888 g/mL, acrylonitrile butadiene styrene (Heny Fine Chemicals), dichloromethane (Molychem, Mumbai, India) with refractive index 1.4235-1.4250 and density 1.323-1.327 g/mL, ethyl alcohol and mercury chloride (Merck, Mumbai, India). Distilled water with pH 5.9 ± 0.2, conductivity 1.0 µS/cm (Millipore, Elix, Bangalore, India) is used throughout the experiments.

B. Procedure to Prepare Ttrifluoroacetylated Ethyl Cellulose

Ethyl cellulose had been dried in vacuum at 60^{0}C for 2h to remove the moisture content. It was then dissolved in a pyridine/chloroform mixture (1/1 by volume) to give a solution with 5% (w/v) EC. Trifluoroacetic anhydride (TFAA) was added drop wise as a 20% solution in chloroform to the EC solution, with stirring at 400 rpm, to give complete reaction. After a reaction time up to 24 h, the trifuoroacetyl products were isolated by pouring the reaction mixture into a large amount of distilled water, then filtered and washed several times with distilled water to remove unreacted reagent and pyridine. The products were further purified by re-dissolving in tetrahydrofuran (THF) and re-precipitating in distilled water several times. Final products were dried under vacuum at 65^{0}C for at least 7-8 h,which is then called TFAEC [8].

C. Membrane Preparation

Acrylonitrile butadiene styrene (15 g) was dissolved in dichloromethane (85 g). The solution was then stirred (REMI model-R 24, India) at 400 rpm for 4h. The resultant homogeneous solution was kept airtight for overnight in a refrigerator for the removal of entrapped air bubbles. Similar procedure was followed for preparing solutions of TFAEC (15 wt% in dichloromethane). ABS and TFAEC polymers were mixed in a definite weight ratio. The prepared solution (polymers in solvent) was continuously stirred for 8 h in order to obtain homogeneous polymer solution. It was further kept airtight for overnight for the removal of any traces of entrapped air bubbles. The casting of membrane was carried out on a glass plate using a thin film applicator (ACME, India). After around 4 h of solvent evaporation, the membrane was placed in an oven at 50^{0}C for another 4 h for the removal of residual traces of solvent.

D. Characterization of Membrane

Scanning Electron Microscope

Top surface and cross-sectional views of the blend membranes were characterized by using scanning electro microscope (SEM) analysis. For the analysis, blend membranes were cut into pieces of various sizes and wiped with filter paper. These pieces were dipped into liquid nitrogen for 20–30 s and frozen. The frozen pieces of the blend membranes were broken and kept in desiccators till they are used for SEM analysis.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) (TGA-7, PerkinElmer, and Norwalk, CT) was used to investigate the loss of water from membrane material and degradation of membrane material during heating. The temperature range used was from 30 to 500°C, and heating rate employed was at 10°C/min. For flushing purpose, nitrogen gas was used at the rate of 20 mL/min.

E. Experimental Procedure

The feed solutions of different concentrations were prepared by adding appropriate amount of mercury chloride salt to distilled water. The NF experiments were carried out using a Perma®-pilot scale membrane system (Permionics Membranes, Vadodara, India) shown in Fig.1. The NF experiments were performed using the blend membrane prepared from TFAEC and ABS. The effective surface area of the membrane was 150 cm^2 (length 15 cm and width 10 cm). In order to avoid possible membrane compaction the membrane was stabilized for 2 h at 10 atm (maximum pressure used in the experiments) before performing the experiments. The experiments were performed in batch cross-flow circulation mode and hence, the samples of permeate were collected from high pressure to low pressure for a particular feed concentration and feed flow rate. Permeate and retentate were recycled to the feed vessel in order to keep the constant feed concentration. The experiments were carried out for different feed concentrations (5, 10, 50 and 100 ppm), feed pressures (0.2, 0.4, 0.6, 0.8 and 1.0 MPa), feed flow rates (4, 8, 12, 16 L/min) and corresponding permeate flux (J_v) and observed rejection (R_O) were measured. The mercury ions concentration in permeate samples were measured by an UV–vis spectrophotometer (HACH-DR 5000) according to standard methods [9]. It is necessary to measure the pure water permeability (PWP) of the membrane after each set of experiments in order to ensure that the initial membrane PWP is restored for every experiment.
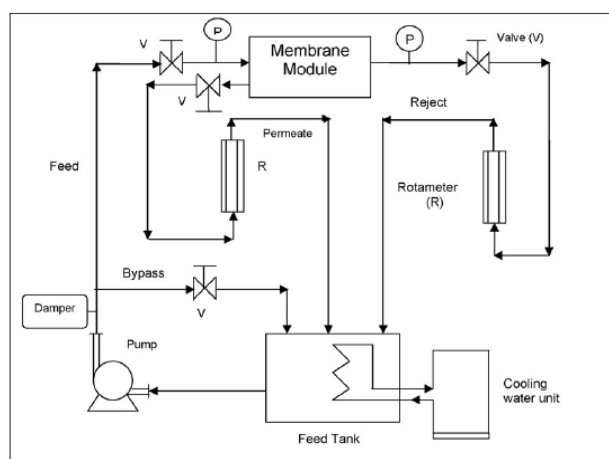

Fig. 1. Parma®-pilot scale membrane system

III. RESULTS AND DISCUSSION

A. Membrane Characterization

SEM

Figures 2 and 3 display the SEM images of cross-section and top surface of blend membrane. The minimum thickness of membrane was 131.2 µm. The top surface of membrane indicates that there are less number of pores due to less quantity of hydrophilic polymer.

TGA

The thermal stability of membranes was checked by TGA analysis (see Fig. 4). As the temperature increases the thermal stability plots show the mass loss of the membrane. All the plots start at 100% mass and end at almost total mass loss of a membrane. Figure 4 indicates that new membrane was thermally stable up to 250^0C beyond this temperature there was a small loss of membrane material.
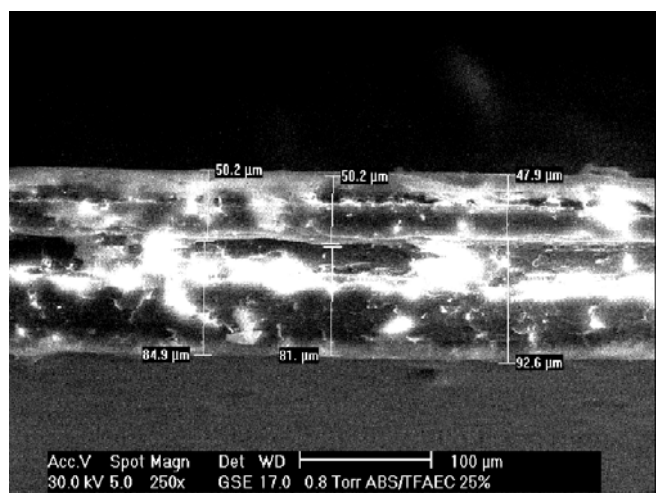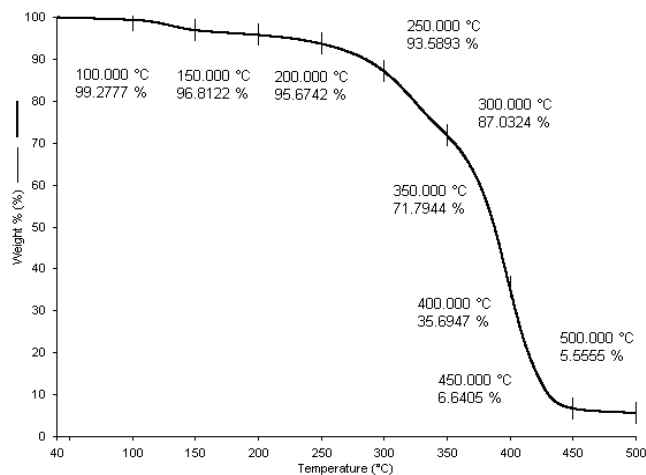

Fig. 4. TGA curve of blend membrane

B. Effect of Applied Pressure and Feed Concentration on Observed Rejection in Nanofiltration

Figures 5 and 6 show the effect of applied pressure on the mercury ions rejection with varying feed concentrations (5, 10, 50 and 100 ppm) at feed rates of 16 and 12 L/min (LPM), respectively. It can be seen from Figs. 5 and 6 that the percent observed rejection of mercury ions increases with increase in applied pressure, which is in line with the reported results on NF [4, 10, 11]. The rejection of mercury ions decreases with increase in the feed concentration because as we increase the feed concentration, the solute concentration gradient across the membrane increases as a result the concentration adjacent to the membrane also increases, which will in turn leads to decrease in rejection of solutes. By comparing Figs. 5 and 6, it can be concluded that the percentage rejection of solute increases on increasing the feed flow rate at the same operating pressure. The main aim of increasing the feed flow rate is to increase the mass transfer coefficient across the membrane.

Fig. 2. SEM micrograph of cross-section of membrane
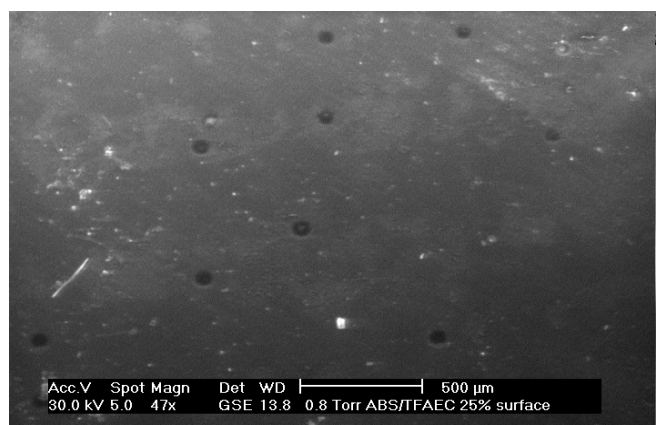
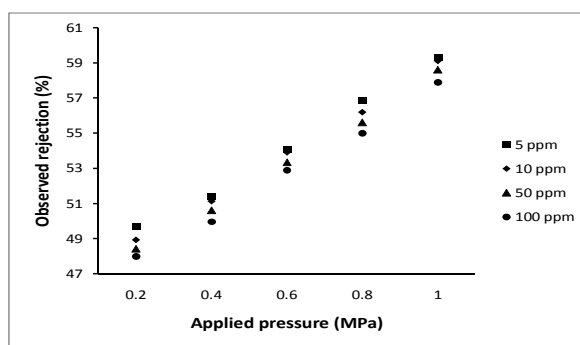Fig. 3. SEM micrograph of top surface of membrane

Fig. 5. Influence of applied pressure on the % observed rejection of mercury chloride salt for different feed concentrations (feed rate= 16 L/min)
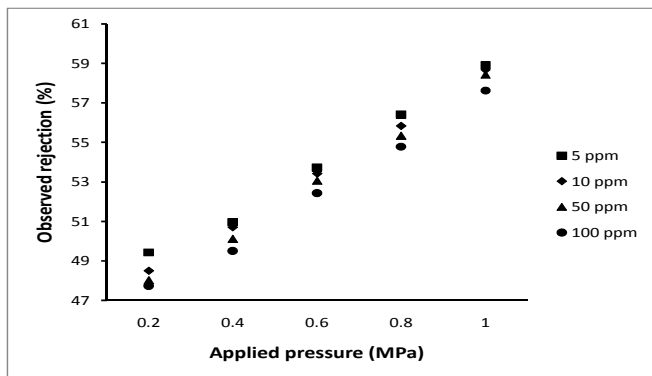
Fig. 6. Influence of applied pressure on the % observed rejection of mercury chloride salt for different feed concentrations (feed rate= 12 L/min)

C. Effect of Applied Pressure and Feed Concentration on Permeate Flux in Nanofiltration

It is clear from the Figs. 7 and 8 that the permeate flux increases as we increase the applied pressure which shows that there may be negligible concentration polarization in the membrane cell. As the feed concentration increases the permeate flux decreases due to the increase of concentration difference across the membrane as well as the osmotic pressure which opposes permeate flux [4, 10, 11].
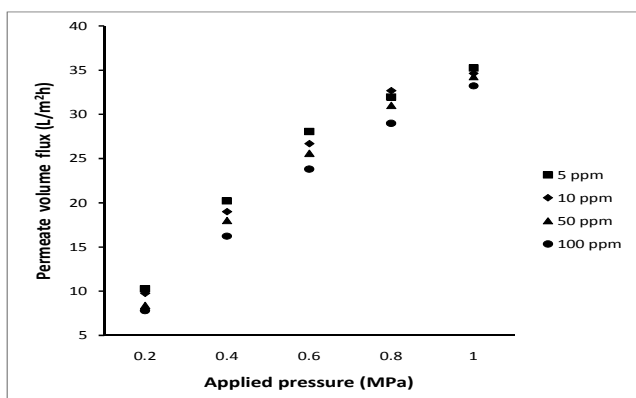

Fig. 7. Influence of applied pressure on the permeate volume flux of mercury chloride salt for different feed concentrations (feed rate= 12 L/min)
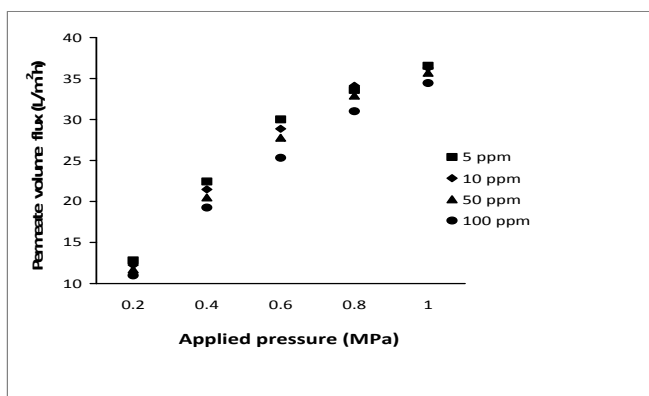

Fig. 8. Influence of applied pressure on the permeate flux of mercury chloride salt for different feed concentrations (feed rate= 16 L/min)

IV. Conclusions

In the present study, trifluoroacetyl ethyl cellulose (TFAEC) powder was prepared from ethyl cellulose (EC). A new blend membrane was prepared with 75% composition of acrylonitrile butadiene styrene (ABS) and 25% composition of TFAEC polymer solution. The prepared blend membrane was characterized with the help of SEM and TGA. This membrane was used to separate mercury ions from aqueous solutions using nanofiltration (NF) at different operating conditions. The experimental studies showed that this membrane gave highest observed rejection of 59.3% for a feed concentration of 5 ppm and applied pressure of 1 MPa.

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