Desalination and Water Treatment
www.deswater.com

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doi: 10/5004/dwt.2012.3046

37(2012)321–330
January

Taylor & Francis
Taylor & Francis Group

Polymer enhanced ultrafiltration of mercury using chitosan impregnated ceramic membrane

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Received 8 June 2011; Accepted 2 August 2011

ABSTRACT

This work reports the removal of mercury from synthetic wastewater by polymer enhanced ultrafiltration (PEUF). A ceramic membrane was prepared from locally available clay and the membrane surface was impregnated using chitosan to reduce the pore size to ultrafiltration range. The average pore size of the membrane was determined from air permeability data and found to be 12 nm. Polyvinyl alcohol (PVA) was used as the chelating agent. The effects of PVA dose, mercury concentration, pH and transmembrane pressure on mercury rejection were investigated. Rejection increased with the increase of PVA dose and decreased with the increase of initial mercury concentration and transmembrane pressure. The maximum rejection of mercury and PVA was found to be 85% and 99.7% respectively. The optimum pH for the operation was also determined. The flux declination rate was observed to be more at higher PVA dose and less at higher pressure. A preliminary membrane cost estimation approach was adopted based on the manufacturing cost of raw materials and reported.

Keywords: Ceramic membrane; Mercury removal; Polymer enhanced ultrafiltration; Water treatment

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1. Introduction

Mercury and its compounds are toxins and hazardous to human health even at very low concentrations. Acute exposure to mercury may cause chest pain, labored breathing, vomiting, diarrhea, fever, or skin rash whereas chronic exposure may lead to limb weakness, loss of appetite, headache, memory loss, kidney failure, or damage of central nervous system [1]. The safe limit for mercury exposure as set by the US Environmental Protection Agency (EPA) and Food and Drug Administration (FDA) for drinking water is 2 μg/1 The sources of mercury in wastewater is the effluents of chloro-alkali industry, electrical equipment like thermometers, barometers, batteries, fluorescent lamps, wood pulping industries, agricultural, chemical and paints industries [2]. Mercury also enters the food chain as organometallic compound methyl mercury (MeHg) which is very quickly bioaccumulated by fish [3].

The different techniques for the removal of mercury ions from aqueous solution are adsorption, chelation enhanced method and electrocoagulation [4–8]. However, these methods have several disadvantages like poor removal efficiency, generation of toxic sludge, produce other waste material which require further treatment [9]. Blue et al. have reported good removal of mercury with 1,3-benzenediamidoethanethiolate as the chelation agent but, their work limited to 1260 ppb or less than that [7].

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In this context, membrane processes provide an excellent alternative method for the removal of mercury from aqueous solutions. Generally to separate dilute solutions containing ions of different metals, reverse osmosis (RO) is applied. For overcoming the problem of lower permeate flow rate of RO, a combined method that comprises chelation and ultrafiltration can be used. The crux of the method follows the addition of a high molecular weight polyelectrolyte (a chelating agent) into the solution of the ions of metal to be separated. Size of the complexes is much greater than that of the unbounded ions and sufficient to be retained by a UF membrane. The solution is then ultrafiltered through an appropriate membrane selected to ensure good rejection of the macrocomplex so that a metal ion–free filtrate is obtained. This method is named polymer-assisted ultrafiltration (PAUF) or polymer enhanced ultrafiltration (PEUF). The key advantage of this method is: a high selectivity by virtue of the use of selective poly-ligands and a high productivity at lower power consumption. Further, by operating in continuous mode, the process can be automated.

Used polymers for PEUF may be from natural origin like chitosan or alginate or of synthetic origin like poly (acrylic acid), poly(ethyleneimine) or polyvinyl alcohol (PVA) [10–14]. Different studies were reported for the removal of heavy metals using PVA as chelation agent by UF membrane. Lin and Lan studied the recovery of PVA chelated complex from synthetic wastewater by both hydrophilic and hydrophobic ultrafiltration polymeric membrane [13]. Mercury was successfully removed by PEUF using complexation and or ligand formation [15–22]. Mimoune and Amrani worked on the removal of cupric ions, complexed beforehand with PVA. They have also reported the performances of different molecular weight of PVA [23]. Labanda et al. reported the removal of Chromium(III) by PAUF with PVA [12].

Critical reviews of the above literatures convey that the polymer enhanced ultrafiltration of Mercury using surface modified ceramic membrane might be a further scope of research. Again, the literature on the removal of mercury by PEUF using ceramic membrane with PVA as chelating agent is scant. Thus, in this work, a low cost disc shaped ceramic support was fabricated from clay and kaolin with minimum amount of binding materials. Crosslinked chitosan with glutaraldehyde was impregnated over the top surface of the ceramic support in order to reduce the pore size in ultrafiltration range. The prepared membrane was used for the removal of mercury from synthetic wastewater by PEUF using PVA as the chelating agent. The mercury removal efficiencies were investigated at different operating conditions and analyzed. Concentrations of PVA in permeate were also measured and reported. The flux declination profiles with the progress of PEUF were observed for various experimental conditions and analyzed in detail.

2. Experimental procedure

2.1. Raw materials

Clay powder (–150 mesh, sieve size 104 μm, collected from IIT Guwahati campus), sodium metasilicate (Loba Chemie Pvt. Ltd.), sodium carbonate (Rankem, India), boric acid (Loba Chemie Pvt. Ltd.) and kaolin (CDH Pvt. Ltd.) were used for the preparation of membrane support. Total component analysis and preparation method of the clay powder were given in detail elsewhere [24]. Each component has its individual role during membrane preparation. Kaolin provides low plasticity and high refractory properties to the membrane. Sodium metasilicate increases mechanical strength by creating silicate bonds. Sodium carbonate improves dispersion properties, thereby creating homogeneity. Boric acid also increases mechanical strength by creating metaborates during sintering. Chitosan (Hi Media Laboratories Pvt. Ltd., India) was used to impregnate the top surface of the ceramic support by using acetic acid (Merck, India) and glutaraldehyde (Merck, India). Mercuric chloride (Merck, India) was used as the source of mercury. Polyvinyl alcohol (Loba Chemie Pvt. Ltd) with a molecular weight of 115 kDa was used as the chelating agent whereas, elemental iodine (Merck, India) and boric acid (Loba Chemie Pvt. Ltd.) were utilized during the spectrometric determination of PVA. Stannous chloride (Merck, India) was used during the analysis of mercury using atomic absorption spectroscopy (AAS).

2.2. Preparation of the ceramic support and ultrafiltration membrane

Disc shaped ceramic support (50 mm diameter and 5 mm thickness) was prepared from local clay (56%), kaolin (18%), sodium carbonate (4.8%), sodium metasilicate (2.4%), boric acid (2.4%) and water (20%) by paste casting followed by sintering at 1000°C. The details of the preparation method were described elsewhere [24]. The ultrafiltration membrane was prepared by impregnating the crosslinked chitosan over the top layer of ceramic support using dip-coating technique. During this period, the micropores of the ceramic support were altered to ultrafiltration range. The chitosan solution (2 wt.%) was prepared by dissolving chitosan flakes in a 2 wt.% aqueous acetic acid solution. The solution was then mixed with 0.12 % (v/v) glutaraldehyde solution in 1:1 ratio and stirred for 1 min at 298 K. During this step the crosslink reaction took place [25]. To restrict the pore penetration of chitosan during the coating process, the ceramic support was dipped in water for 3–4 h before dip-coating. During this, all the air present in the porous structure inside the support was displaced by water. The support (except the top surface) after taking out from water was covered by aluminum foil for preventing chitosan deposition. The support was then placed in a 250 ml beaker and chitosan/glutaraldehyde solution was poured over it in such a way that the top surface was completely covered by the solution. The dipping time was 800 s. After the coating process, the membrane was taken out from the solution and dried at 100°C for 6 h in a hot air oven for complete removal of water from the membrane.

2.3. Characterizations of the support and the membrane

The characterization of both support and ultrafiltration membranes were performed by scanning electron microscopic analysis and permeation experiments (air and water). The broad intension of the SEM (Make: Oxford; Model: LEO 1430VP) experiment was the morphological study aimed to evaluate the effect of dip coating parameters (solution concentration and dipping time) on ceramic matrix blocking and top layer growth as well as checking the sequential change of membrane morphology during dip-coating process with respect to the coating parameters. SEM also detects the presence of surface/cross sectional defects such as pinholes and cracks (if any). Air flux characterization aims to quantify membrane morphological parameters such as average pore size and Viscous/Knudsen flux that contribute to transport. The ultrafiltration membrane was subjected to gas permeation test. Based on the gas permeation data, average pore radius (r_g, μm) was estimated according to the following expression [26]:

$$K = 2.133\frac{r_g \nu \varepsilon}{l q^2} + 1.6\frac{r_g^2 \varepsilon}{l \eta q^2} p \tag{1}$$

where p (Pa) is the average pressure on the membrane, ν (m/s) is the molecular mean velocity of the gas, l (m) is the pore length, q is the tortuosity, η (Pa s) is the viscosity of gas, K (m/s) is the effective permeability factor evaluated as:

$$K = \frac{QP_2}{S\Delta P} \tag{2}$$

where, S (m^2) is the permeable area of the membrane, Q (m^3/s) is the volumetric flow rate, P_2 is the membrane pressure at permeate side (Pa) and ΔP is the trans -membrane pressure drop (Pa). In Eq. (1), the first term corresponds to Knudsen permeance and the second term corresponds to the viscous permeance. Therefore, Eq. (1) can be represented as a straight line in a graph drawn between K and p where the slope and intercept represents the viscous and Knudsen permeability of the membrane respectively. Henceforth the values of the slope and intercept obtained from the graph can be used to evaluate the percentage contribution of pores (and pore sizes) that contribute towards viscous and Knudsen flow transport mechanisms. In other words, gaseous flux characterization of the ceramic support can yield qualitative information with respect to the pore size distribution applicable for the contribution of Knudsen or viscous flow regimes towards the overall ultrafiltration membrane flux. The average pore radius (r_g) of the membrane can be evaluated using the intercept (A) and slope (B) of the straight line expressed as:

$$r_g = 1.333\frac{B}{A}\nu\eta \tag{3}$$

The hydraulic permeability experiments were conducted using deionized water and were determined by the following Eq. (4) [27]:

$$J = L_h \Delta P \tag{4}$$

where, J is the liquid flux ($m^3/m^2/s$), L_h is the hydraulic permeability ($m^3/m^2/s/kPa$) and ΔP is the transmembrane pressure (kPa). The air and hydraulic permeability experiments were conducted in a dead end permeation cell. Details of the experimental set up were given elsewhere [24].

3. Studies on heavy metal removal

3.1. Rejection of mercury with the ceramic support and chitosan impregnated membrane

Before PEUF experiments, mercury rejection was determined for the ceramic support and chitosan impregnated membrane separately by passing different concentrations of mercury solutions (10, 25 and 50 mg/l). The permeate metal concentrations were determined by AAS (Varian; AA240FS) using cold-vapor mode and stannous chloride was used as reducing agent for Hg.

3.2. Preparation of the feed solution

The feed solutions were prepared by mixing required amount of PVA and mercuric chloride in aqueous medium and shaked overnight to achieve complete dissolution. The mercury concentrations studied were: 10 mg/l, 25 mg/l and 50 mg/l whereas the PVA concentrations were 1.0%, 0.50% and 0.25% (w/v). The maximum concentration of PVA was kept below 1.0%

because with higher concentration of the polymer, the solution viscosity increased which eventually reduced the flux.

3.3. PEUF experiment

The feed solutions were passed through the prepared UF membrane with pore size ~12 nm. The experimental set up was a dead end permeation cell with 250 ml capacity and approximately 12.56×10^{-4} m^2 membrane area. The detailed description of the cell was shown elsewhere [24]. The experiment was conducted up to 2 h for all the prepared solutions. During the experiment, permeate was collected at different time intervals from the bottom of the cell and were analyzed in AAS to determine the residual Hg concentration.

3.4. Rejection of the heavy metal and PVA

The % rejections (R) of mercury and PVA were determined using the following formula,

$$R = \left(1 - \frac{C_f}{C_i}\right) \times 100 \tag{5}$$

where, C_i is the concentration of mercury/PVA in the feed and C_f is the concentrations of mercury/PVA in the permeate which was determined by spectrometric method using boric acid as complex formation agent and elemental iodine as the coloring agent [28].

The experiments were performed to observe the effect of the concentrations of both PVA and mercury and transmembrane pressure on the mercury removal efficiency. The mercury ions are attached with the PVA chelate through ionic interaction and remains on the retentate side of the membrane. The first set of solution was prepared with a fixed concentration of metal ion (30 mg/l) and varying PVA concentrations. Again, another set of solutions were prepared with a fixed PVA concentration (0.50%) and varying metal ion concentrations. After mixing the required amount of PVA and heavy metal in aqueous solution, the mixture was kept in a shaker for overnight to ensure the maximum transformation of the metal ions towards the chelate compound. Further, the effect of transmembrane pressure on mercury rejection was studied by varying the transmembrane pressure (103.4 kPa, 137.9 kPa and 206.8 kPa) at a fixed concentration of PVA (0.50%) and mercury (30 mg/l). The rejections of PVA with respect to time for different PVA concentrations were also investigated at a fixed pressure of 137.9 kPa. All the above experiments were conducted at a fixed pH of 7.0.

The effects of PVA concentration and transmembrane pressure over the flux decline profiles with the progress of the experiment were also studied. PVA concentrations were varied with a fixed pressure of 137.9 kPa and transmembrane pressure was varied with a fixed PVA (0.50%) and mercury (30 mg/l) concentration. This was achieved by collecting the permeate from the bottom and continuously measuring the cumulative mass. Then the cumulative mass was converted to cumulative volume and from the slope of the cumulative volume versus time curve, the permeate flux was obtained as a function of operating time. The variation of rejection (at 5 min of the filtration) with pH for fixed initial mercury concentration (30 mg/l), PVA concentration (0.50%) and transmembrane pressure (172.4 kPa) was also conducted with the aim of finding the optimum pH for the operation.

3.5. Membrane cleaning

The membrane was thoroughly washed in hot water (90°C) and dried in hot air oven at 120°C for 12 h after each PEUF experiment. Air and water permeabilities of the membrane were determined and compared with that of the unused membrane. Less than 0.5% increase in permeabilities was observed. This increase may be attributed to the marginal corrosive loss of the chitosan during the cleaning operation.

4. Results and discussion

4.1. Characterizations of the ceramic support and ultrafiltration membrane

4.1.1. Morphological assessment

The SEM images of the top surface of both ceramic support and ultrafiltration membrane are presented in Fig. 1. From the figures it was clear that the surface of the support was covered with the coating material. The rough surface of the ceramic support became smooth and some cluster of coating materials were observed on the top surface of the ultrafiltration membrane. It was also clear from the SEM images that there were no cracks or discontinuous coating over the membrane surface.

4.1.2. Gas permeation

Fig. 2 shows the variation of effective permeability factor (K) with average pressure (p) for the support and the chitosan impregnated membrane. Table 1 summarizes parameters evaluated from the graphical analysis of transmembrane flux data. As shown in the table, the permeability of the support was found to be 6.90×10^{-1} m^3/m^2/kPa/s and that of for the chitosan impregnated ultrafiltration membrane was 3.07×10^{-3} m^3/m^2/kPa/s.

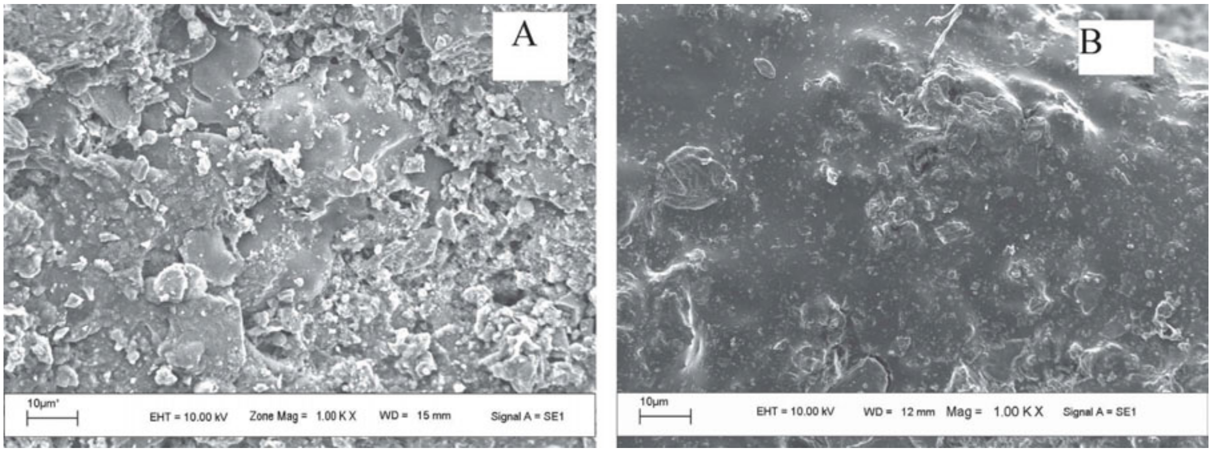

Fig. 1. SEM images of (A) ceramic support and (B) chitosan impregnated ultrafiltration membrane.

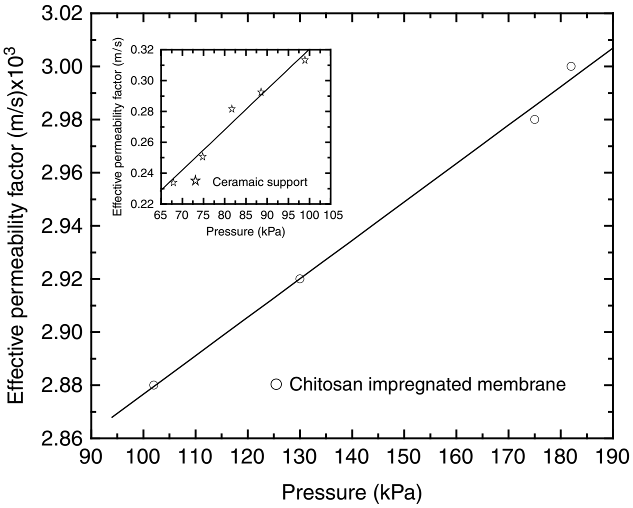

Fig. 2. Variation of effective permeability factor with average pressure for the ceramic support and chitosan impregnated ultrafiltration membrane.

The average pore size of the support was found to be 1093 nm and that of for chitosan impregnated membrane was 12 nm. Another observation was that during air permeability, the contribution of viscous flux decreased (from 81% to 5%) and Knudsen flux increased (from 19% to 95%) for the UF membrane. This was due to the decrease in the pore sizes during dip coating, which was also confirmed from the SEM images. Nandi et al. also reported similar trend for the membranes prepared by dip coating of cellulose acetate over ceramic support [26].

4.1.3. Hydraulic permeability

From the hydraulic permeabilities of the support and chitosan impregnated membrane (Table 1), it was observed that the permeability decreased after dip coating. The permeability of the support and chitosan impregnated membrane were found to be 1.2 × 10^{-5} $m^3/m^2/Pa/s$ and 3.3 × 10^{-8} $m^3/m^2/Pa/s$ respectively. This decrease was due to the reduction in average pore size of the membrane during the impregnation process. The hydraulic permeability was observed to be lesser than the air permeability. This was because of higher density and viscosity of water with respect to air.

4.2. Polymer enhanced ultrafiltration (PEUF)

4.2.1. Mercury rejection efficiencies

Fig. 3 describes the variation of mercury rejection at different transmembrane pressure. It was observed that the

Table 1
Various parameters evaluated from air and water permeability experiment

Membrane	Slope (×10^7)	Intercept (×10^2) (m/s/Pa) (m/s)	Air permeability[*] ($m^3/m^2/kPa/s$)	Pore size (nm)	Viscous flux (%)	Knudsen flux (%)	Hydraulic permeability ($m^3/m^2/kPa/s$)
Support	26.15	5.89	6.90 × 10^{-01}	1093	60–81	19–40	1.2 × 10^{-5}
Ultrafiltration membrane	0.014	0.27	3.07 × 10^{-03}	12	05–12	88–95	3.3 × 10^{-8}

[*] At 241.3 kPa transmembrane pressure.

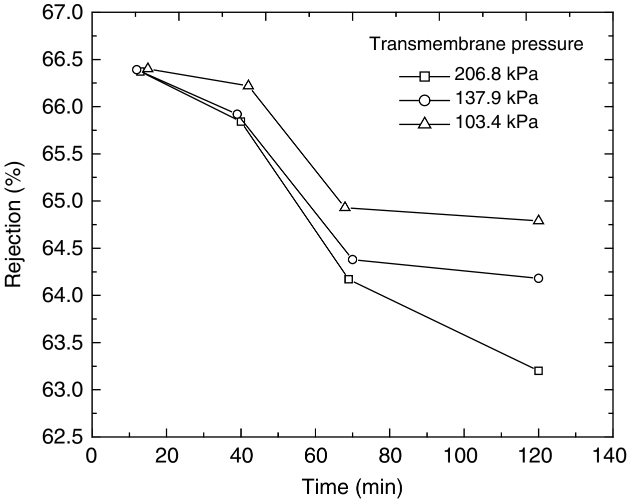

Fig. 3. Effect of transmembrane pressure on mercury rejection (PVA concentration: 0.50%, mercury concentration: 30 mg/l, pH: 7.0).

rejection decreased with the increase of transmembrane pressure. The mercury rejection increased from 63.2% to 64.7% when pressure decreased from 206.8 kPa to 103.4 kPa at the end of 120 min of operation. This was due to the fact that, with the increase of pressure, some chelate complexes passed through the membrane pore resulting higher mercury concentration in the permeate. Further, same decreasing trends of the rejection with progress of the experiment were observed for all the pressures. The reason was already discussed in the preceding section.

Fig. 4 presents the mercury removal efficiency with time at different PVA concentrations. It was observed that, higher concentration of PVA lead to better removal of mercury. From the figure it was clear that 24.3% and 85.1% rejection was observed using 0.25% and 1.0% PVA at the end of 12 min for 30 mg/l mercury, respectively. Up to 1% rejection was observed without using PVA. The metal ions react with the PVA molecule to form chelate compound which were then rejected by the UF membrane. The increase in rejection efficiency with PVA concentration was due to the formation of more numbers of chelate compound which subsequently rejected by the UF membrane. It was also clear from the figure that mercury rejection decreased marginally with time. This was due to the deposition of more chelate molecules over the membrane surface, leading to an increase in the membrane surface concentration (concentration polarization). This resulted in an increase in the convective transport of the mercury to the permeate side thereby increasing the permeate side mercury concentration. Thus, the permeate mercury concentration was increased and rejection was decreased. Similar observation was also reported during micellar enhanced ultrafiltration (MEUF) of eosin dye using polyamide membrane of 1000 Da cutoff [29].

The variation in mercury removal efficiency with time at constant pressure and PVA concentration is shown in Fig. 5 for three different initial mercury concentrations. It was observed that the mercury concentration in permeate increased with initial mercury concentration. The rejection increased from 63.7% to 72.3% when initial mercury concentration decreased from 50 mg/l to 10 mg/l at the end of 12 min of the PEUF experiment. This was due to the extent of chelating reaction between

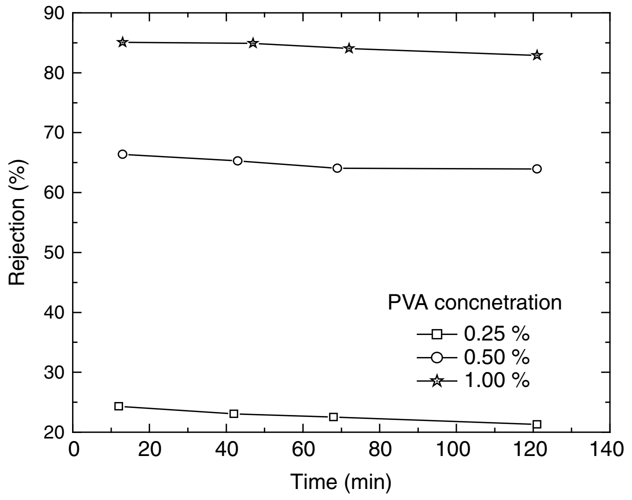

Fig. 4. The effect of PVA concentration on mercury rejection (initial mercury concentration: 30 mg/l, transmembrane pressure: 172.4 kPa, pH: 7.0).

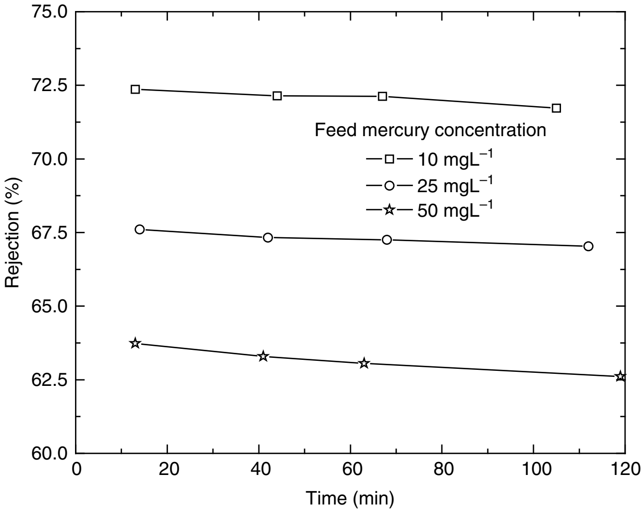

Fig. 5. Effects of feed mercury concentration on mercury rejection (PVA concentration: 0.50%, transmembrane pressure: 172.4 kPa, pH: 7.0).

mercury ions with fixed concentration of PVA. As the mercury concentration increased, all the mercury ions could not bind to the chelating agent and remains as free ions in the solution. This un-reacted mercury passed through the UF membrane resulting in lower mercury rejection. From Fig. 5 it was also clear that the rejection decreased with the progress of the experiment marginally. For example, rejection decreased from 72.4% to 69.3% when operating time increased from 12 min to 120 min for the initial mercury concentration of 10 mg/l. The decrease in mercury rejection was due to increase in convective transport as discussed in the preceding section.

Fig. 6 shows the variation of mercury rejection with solution pH at a fixed transmembrane pressure of 172.4 kPa and constant concentrations of mercury (30 mg/l) and PVA (0.50%). It was observed that rejection increased with pH of up to 7.0 and decreased thereafter. Maximum rejection was observed at pH of 7.0. The mercury removal was found to be 38.9%, 65.9% and 54.3% at pH of 3, 7 and 12, respectively. The maximum rejection was due the formation of more stable mercury - PVA chelate at pH 7 that reduced the free mercury in solution and hence lowered the permeate mercury concentration. The decrease in mercury removal beyond pH 7 was due to the formation of mercury hydroxide rather than mercury - PVA chelate. Other researchers also reported similar trends for the removal of copper with PVA as the chelating agent [14].

Fig. 7 shows the variation of PVA rejection during PEUF. It may be seen from the figure that more than 98.7% PVA was rejected even after 120 min of operation for all the cases. It may also be found that rejection marginally increased with PVA concentration. The slight increase of PVA rejection with initial PVA concentration was probably due to the formation of larger chelate by coalescence of the smaller chelates. Similar trends were reported by Chakrabarty et al. for the removal of crude oil with polysulfone membrane [30]. The decreasing trend of mercury rejection with the progress of the experiment was also due to the convective transport as discussed in case of mercury removal.

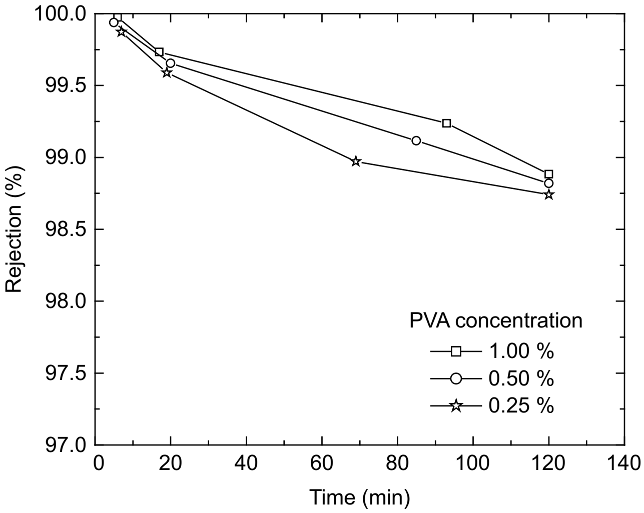

Fig. 7. Rejection of PVA (transmembrane pressure: 137.9 kPa, initial mercury concentration: 30 mg/l, pH: 7.0).

4.2.2. Flux declination during PEUF

The variation of the permeate flux at different transmembrane pressure is shown in Fig. 8. Two trends can be

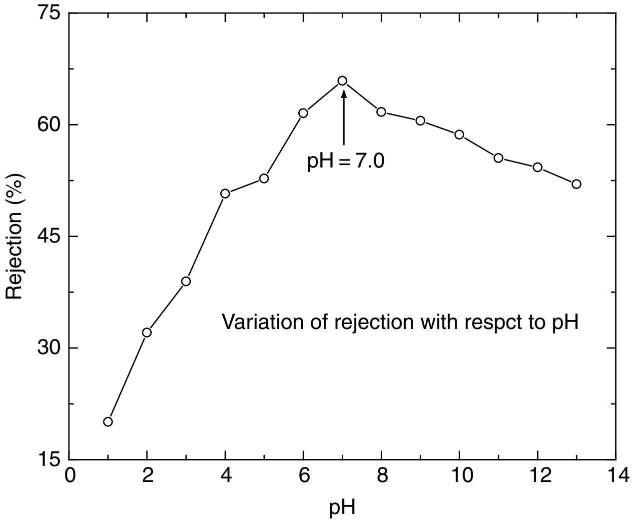

Fig. 6. Variation of mercury rejection with solution pH (initial mercury concentration: 30 mg/l, PVA concentration: 0.50%, transmembrane pressure: 172.4 kPa, time of operation: 15 min).

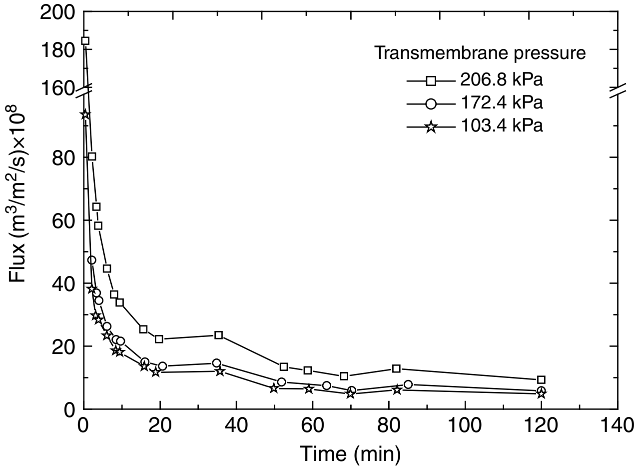

Fig. 8. Flux decline profile during PEUF at different initial mercury concentration (transmembrane pressure: 137.9 kPa, mercury concentration: 30 mg/l, pH: 7.0).

observed from this figure. First, the permeate flux declined over the time of operation and second, the permeate flux was more at higher operating pressure at a given time. As discussed earlier, due to concentration polarization, the membrane surface concentration increased with time. This increased the osmotic pressure at the membrane solution interface and therefore reduced the driving force for the permeating solution. This lead to a decline of the permeate flux with the time of operation. Again, flux decreased sharply up to around 20 min of operation and became gradual thereafter. For example, the permeate flux decreased from about 114 × 10^{-8} $m^3/m^2/s$ (at 0.5 min) to 13.6 × 10^{-8} $m^3/m^2/s$ (at 20 min) and further decreased to 5.79 × 10^{-8} $m^3/m^2/s$ (at 95 min) at 172.4 kPa. This resulted in a flux drop of about 88% and 94 % during 20 min and 95 min of operation, respectively. The initial sharp flux decline was due to membrane pore blocking and the gradual flux decline was due to the formation of gel type layer of mercury-PVA chelate over the membrane surface. At the same instance of time, increase in operating pressure simply increased the driving force across the membrane; thereby flux was more at higher pressure. For example, at the end of the experiment (100 min), the permeate flux is 4.81 × 10^{-8} $m^3/m^2/s$ at 103.4 kPa pressure and it is 9.31 × $10^{-8}/m^3/m^2/s$ at 206.8 kPa. This resulted in about 94% increase in flux.

The effects of PVA concentration for a fixed mercury concentration of 10 mg $l^{?1}$ on the permeate flux are presented in Fig. 9. The figure shows that the permeate flux decreases with PVA concentration at a fixed operating pressure. It may also be found that the initial flux decline is very sharp and become gradual thereafter. For example, at 0.5% PVA concentration, the flux decreases from 46.5 × 10^{-8} $m^3/m^2/s$ (at 3.2 min) to 5.9 × 10^{-8} $m^3/m^2/s$ (at 33 min) and further decreased to 6.51 × 10^{-8} $m^3/m^2/s$ (at 120 min). Again, the flux increases from 1.08 × 10^{-8} $m^3/m^2/s$ to 16.95 × 10^{-8} $m^3/m^2/s$ at the end of 120 min and at 137.9 kPa when the PVA concentration decreases from 1% to 0.25%. This trend may be explained by the increase in resistance against the solvent flux due to deposition of mercury-PVA chelate over the membrane surface. Mueller et al. also reported similar type of phenomenon while working with oily wastewater with polyacrylonitrile membrane [31].

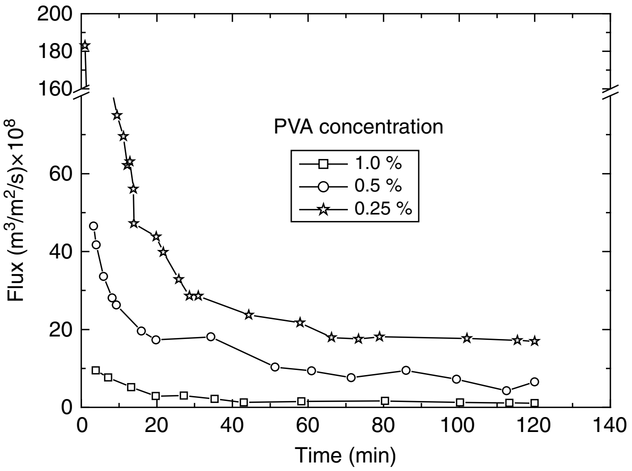

Fig. 9. Flux decline profile during PEUF at different PVA concentration (transmembrane pressure: 137.9 kPa, mercury concentration: 30 mg/l, pH: 7.0).

4.2.3. Cost estimation of the prepared membrane

Preliminary cost estimation was undertaken based on the unit costs of raw materials used for preparing chitosan impregnated UF membrane. In general, ceramic membranes are ten times costlier than polymer membranes. Conventional industrial scale polymeric and ceramic membranes are available for USD 50–200 m^{-2} and USD 500–2000 m^{-2} respectively [32,33]. Manufacturing cost of all the raw materials considered for membrane preparation was reported in Table 2. The total material cost was

Table 2
Cost analysis of prepared ultrafiltration membrane from the unit cost of raw materials

Components	Unit price (USD/kg)	Materials required/m^2 (kg)*	Cost/m^2 (USD)
Clay	–	7.130	–
Kaolin	7.36	1.833	13.494
Sodium carbonate	7.36	0.611	4.498
Sodium metasilicate	14.23	0.306	4.348
Boric acid	8.59	0.306	2.625
Chitosan	671.34	0.050	33.567
Glutaraldehyde	23.68 (per l)	0.012 (l)	0.284
Acetic acid	8.96 (per l)	0.050 (l)	0.448
Total		10.298	59.265

*5 cm diameter and 5 mm thickness ceramic support was prepared from total 20 gm raw materials and 0.03 g chitosan was required for coating of the said ceramic support. The required amounts of glutaraldehyde and acetic acid were reported in the section 3.3.

around USD 60 m^{-2}. Including manufacturing and shipment costs, the average cost of the inorganic membrane for industrial applications based on bulk production methods would be closer to the value of USD 150 m^{-2} that is often quoted for polymeric membrane configurations. Therefore, it can be inferred from cost analysis that the inorganic membrane based on kaolin would be closer to the cost of the polymeric membranes deployed for industrial configurations and could be slightly expensive than the modules prepared with polymeric membranes owing to the costs involved in manufacturing and bare module costs. The reported value of the membrane cost is conceptual in nature and may vary significantly depending, on the fouling characteristics, time performance and long term stability of the ceramic membrane in process applications.

5. Conclusion

Mercury was successfully removed from aqueous medium by PEUF. Chitosan impregnated ultrafiltration membrane was prepared from ceramic support and used for PEUF experiments. Mercury ions were attached with chelating agent (PVA) and retained by the ultrafiltration membrane. The rejection of mercury increased substantially by adding the PVA demonstrating the viability of the PEUF process. The feed PVA concentration ranged from 0.25 to 1.0% (w/v) and mercury concentration ranged from 10 to 50×10^{-3} kg/m^3 with pressure varying from 103.4 to 206.8 kPa. Flux and retention characteristics of both mercury and PVA were investigated at different pH, initial PVA and mercury concentration and transmembrane pressure. Rejection was observed to increase with feed PVA concentration and decreased with initial mercury concentration and transmembrane pressure. The maximum rejection of mercury was found to be about 85% at 172.4 kPa pressure with PVA concentration of 0.25% at the end of 20 min of operation for the initial mercury concentration of to 30×10^{-3} kg/m^3. More than 98.5% removal of chelating agent was achieved even after 120 min of batch operation. Optimum pH for the rejection was found as 7.0. The flux declination rate was higher at high feed PVA concentration and lower at higher pressure. It is well known that the cross flow operation will improve the rejection efficiency of both mercury and PVA. Cost for the membrane composition was estimated as around USD 60 m^{-2}. In summary, the PEUF process may be used as a potential alternative technique for the removal of mercury from the wastewater.

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