Polymer-Enhanced Ultrafiltration of Fe(III) and Cu(II) Aqueous Solutions Using Poly(Vinyl Alcohol)-Alginic Acid/Cellulose Membranes

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This study deals with the removal of Fe(III) and Cu(II) from dilute aqueous solutions using a polymer-enhanced ultrafiltration process. The ultrafiltration studies were carried out in batch stirred cell and the applied pressure was controlled by nitrogen gas. Properties of the composite membranes and its application in metal removal from aqueous solutions were studied. A composite poly(vinyl alcohol)-alginic acid/cellulose membranes were prepared by coating poly(vinyl alcohol)-alginic acid mixture solutions on the filter paper. Poly(vinyl alcohol) and alginic acid were also used as complexing agents to enhance the retention of metal ions. In the filtration of Fe(III) and Cu(II) solutions, the effects of membrane contents, pressure and pH on the retention and the flux were studied. The maximum retention of metals was found as 99% for Fe(III) solution at pressure of 45 psi, pH of 3 in the presence of poly(vinyl alcohol) as complexing agent by using 0.50 (w/v)% [(75 Poly(vinyl alcohol)/25 Alginic acid) (w/w)]/cellulose composite membranes.

Keywords: Complexing agent, composite membranes, polymer-enhanced ultrafiltration, metal removal

1 Introduction

Membranes have been used for separation of species from mixture (1). Some of the properties of the membranes affecting the separation are their chemical nature, surface morphology and presence of charge (2). Solution components have been separated into the retantate and permeate by the membranes. Retention of component by the membrane depends on many parameters such as, pore size of membrane, contents of membrane, pH of solution (3). Membranes have been made from different materials such as polysulfone (4), polysaccharide (5), cellulose derivatives (6). In order to combine the advantages of some polymers, composite membranes have been made. Yang et al. (7) made chitosan/cellulose composite membranes for developing an affinity of membrane with good mechanical and chemical properties. Sodium alginate was blended with flexible polymer poly(vinyl alcohol) (PVA) to reduce the relaxation taking place during pervaporation in the Lastra and et al. (8) study.

Polymer membranes can be used in a large number of separation processes such as nanofiltration and polymer-enhanced ultrafiltration (PEUF). Lastra and et al. (9) investigated the treatment of Fe(II) and Mn(II) ions from wastewater by nanofiltration. Gzara and Dhahbi studied the recovering of chromium(V) ions from liquid solutions by ultrafiltration (10).

The PEUF technique is the combination of binding of metal ions to complexing the agent polymer and ultrafiltration. Since the pore size of membranes is not small enough to separate metal ions, complexing agent polymers are used to bind the metals to obtain large complexes (11, 12). In the PEUF process generally water soluble polymers are used to bind the metals to form macromolecular complexes. These large molecules are retained, while the non-complexed ions pass through the membrane (13). For example, alginic acid (AA) is a biopolymer carrying carboxyl groups capable of forming complexes with metal ions (14), and PVA is carrying hydroxyl groups (15), and it also is used for complexion of metals (16).

Heavy metals are discharged into the environment through different industrial processes. Heavy metals such as, nickel, lead, cadmium and copper in waste water are hazardous to the environment. In order to reduce the heavy metal pollution problem, heavy metals in the environment are removed by some processes such as adsorption, chemical precipitation and membrane (17).

In this study, PVA-AA/cellulose composite membranes were prepared, characterized and used in batch cell

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ultrafiltration for removal of Fe(III) and Cu(II) metal ions from aqueous solutions in the presence of AA and PVA as complexing agents. The effects of applied pressure, pH and contents of membranes on the percent retention and permeate flux were investigated.

2 Experimental

2.1 Materials

AA was supplied from Sigma as sodium salt. PVA with molecular weight of 72,000 g/mol was supplied from Fluka. Glutaricdialdehyde (GA) (25 wt% content in water) was purchased from Sigma. Filter paper was purchased from Machery-Nagel (MN 640de, blue band). $FeCl_3.6H_2O$, $CuCl_2.2H_2O$, HCl, NH_3 and KSCN were all Merck products.

2.2 Preparation of Membranes

Aqueous solutions with 0.25, 0.50, 0.75 (w/v)% [75PVA/25AA(w/w)] were prepared. Then, 20 mL of casting solution was poured onto the filter paper (7.6 cm, diameter) placed in a Petri dish (10 cm, diameter) and allowed the casting solvent (water) to evaporate completely at 60°C. Membranes were then crosslinked for 2.5 h at room temperature by a contacting with a crosslinking solution. Membranes were first immersed in pure water for 2.5 h at room temperature, then washed with pure water numerous times to remove the residual solution. The crosslinking solution contains 59.95(v/v)% of acetone in water containing 10(v/v)% of GA as crosslinking agent and 0.0125(v/v)% of HCl as catalyst (18).

### 2.3 Experimental Apparatus and the Filtration of Solutions

A batch stirred ultrafiltration cell apparatus (Millipore, Amicon 8400) was used for filtration experiments. A membrane was placed into the filtration cell (effective area of 45.36 cm^2), and the applied pressure was controlled by nitrogen gas. For each run, the cell was filled with the volume of 300 mL of 1×10^{-4} M feed solutions at desired ion and 2×10^{-4} unit weight (g/L) complexing agent (AA, PVA) concentration at different pH values and pressurized under nitrogen atmosphere. pH Adjustments were made using 0.1 M NH_3 and HCl solutions. The stirring speed of cell was adjusted to 300 rpm using a magnetic stirrer.
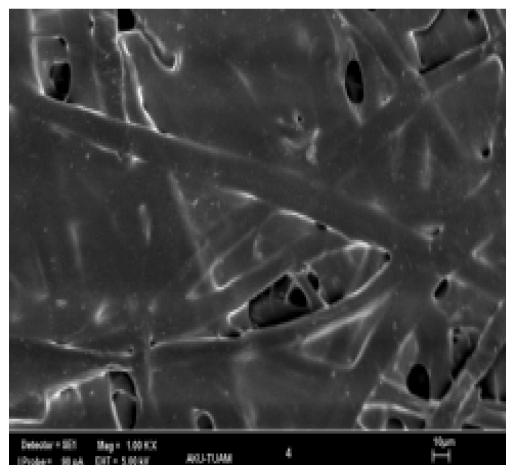
2.4 Analysis

Fe(III) concentrations were determined spectrophotometrically (Shimadzu, 1700 Pharma). 0.1 mL of 0.1 M HCl and 0.1 M KSCN were added to the 3.5 mL of filtrate samples and absorbance was measured at 456 nm. Cu(II)

(a)
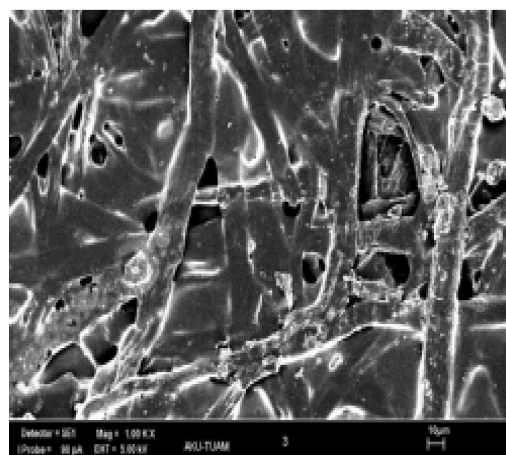
(a)

(c)
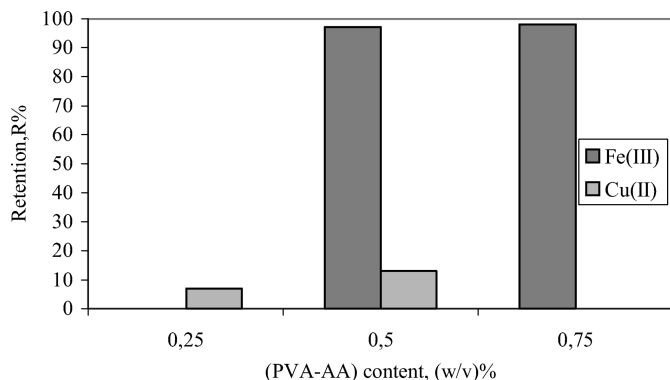
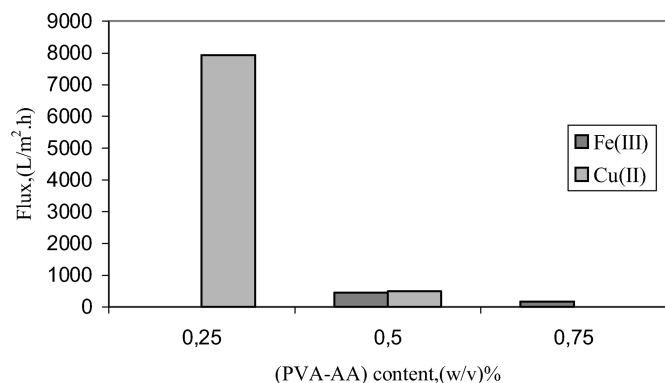**Fig. 1.** SEM micrographs of the composite membranes prepared by coating with different (PVA-AA) concentration: (a) 0(w/v)% [(75 PVA/25 AA) (w/w)] I; (b) 0.50(w/v)% [(75 PVA/25 AA) (w/w)]; (c) 0.75(w/v)% [(75 PVA/25 AA) (w/w)] Magnification: $1000 \times 10 \mu m$.

concentrations were determined using inductively coupled plasma-optical emission spectrometry ICP-OES (Perkin-Elmer, 4300 DV).

Fig. 2. Effect of (PVA-AA) content of the membrane on (a) percent retention of metal ions and; (b) flux in the presence of AA ($C_{Fe(III)} = C_{Cu(II)} = 1 \times 10^{-4}$ M, $C_{AA} = 2 \times 10^{-4}$ unit weight (g/L), pH = 3.0 for Fe(III), pH = 6.0 for Cu(II), P = 60 psi).

Fig. 3. Effect of (PVA-AA) content of the membrane on (a) percent retention of metal ions and; (b) flux in the presence of PVA ($C_{Fe(III)} = C_{Cu(II)} = 1 \times 10^{-4}$ M, $C_{PVA} = 2 \times 10^{-4}$ unit weight (g/L), pH = 3.0 for Fe(III), pH = 6.0 for Cu(II), P = 60 psi).

2.5 Scanning Electron Microscopy

The morphology of the composite membranes was observed by scanning electron microscopy (SEM)(LEO 1430VP). The dried membrane was coated with gold powder before scanning.
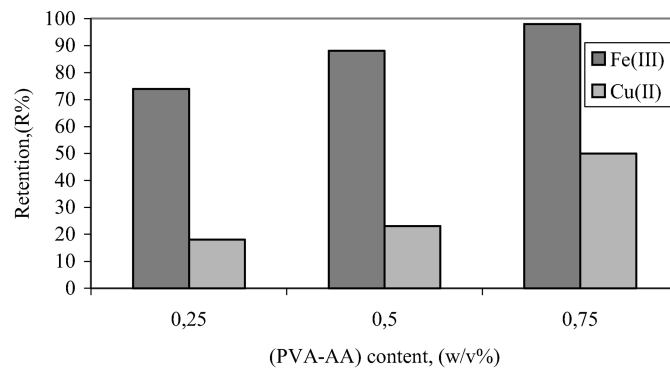
2.6 Measurement of the Permeate Flux and Percent Retention

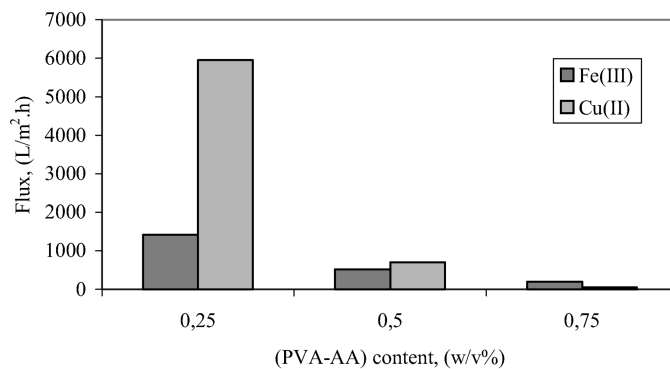Percent retention values were calculated from the formula (Equation 1):

$$R\% = (1 - C_p/C_f) \times 100 \qquad (1)$$

Table 1. Properties of the membranes

Membrane	(w/v)% [(75PVA/ 25AA) (w/w)]	g[(75 PVA/25AA) (w/w)]/g cellulose filter	Thickness (μm)
Cellulose filter	—	—	200
I	0.25	0.063	215
II	0.50	0.126	230
III	0.75	0.189	250

Where C_p and C_f are metal ion concentrations of the permeate and the feed solutions, respectively. The permeate flux was calculated from the formula (Equation 2):

$$J = Q/(A \times \Delta t) \qquad (2)$$

Where Q = 0.3 (permeate volume, L), A = 45.36×10^{-4} (area of membrane, m^2), Δt (sampling time, h).

3 Results and Discussion

3.1 Characterization of the Membranes

(PVA-AA) contents and thicknesses of membranes are shown in Table 1. As is seen from the table, the amount of (PVA-AA) on the composite membranes and thicknesses of membranes increased and the water contents of membranes decreased as expected with increasing the (PVA-AA) concentration of the coating solutions. Figure 1 presents the morphologies of composite membranes made by solutions of different (PVA-AA) concentrations. As is seen from this figure, when the concentration of (PVA-AA) solutions increased, a large amount of (PVA-AA) is coated on the cellulose filter.
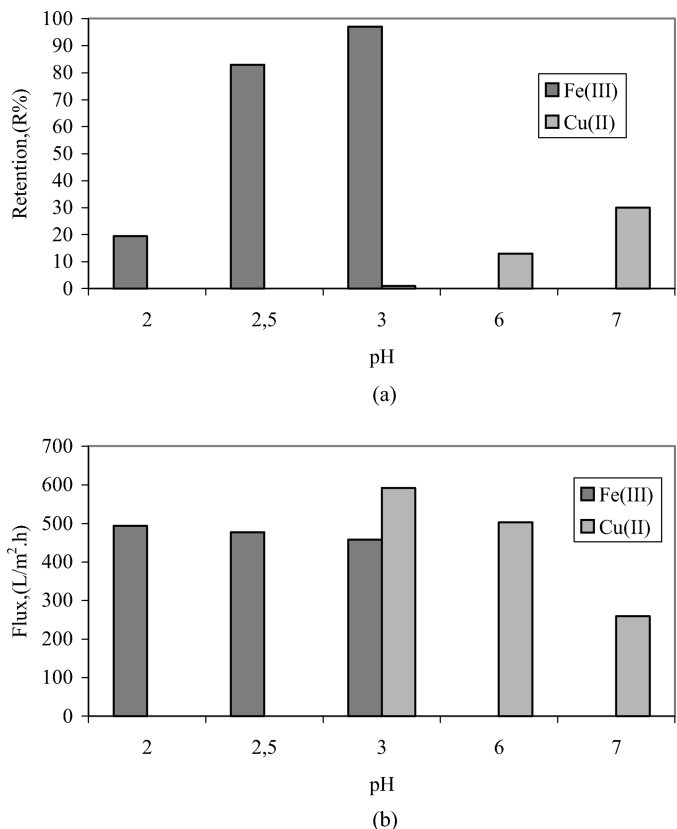
Fig. 4. Effect of pH on (a) percent retention of metal ions and, (b) flux in the presence of AA ($C_{Fe(III)} = C_{Cu(II)} = 1 \times 10^{-4}$ M, $C_{AA} = 2 \times 10^{-4}$ unit weight (g/L), Membrane II, P = 60 psi).

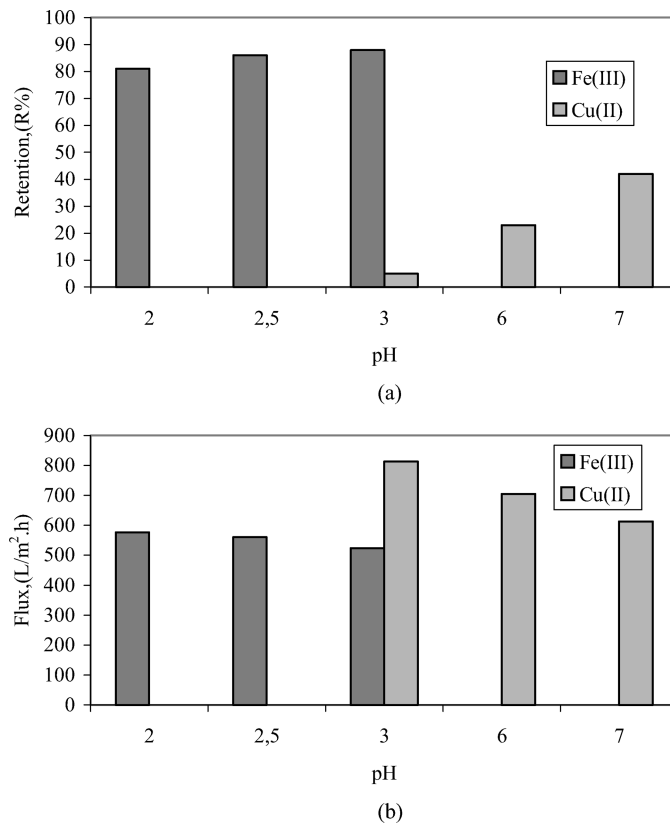**Fig. 5.** Effect of pH on (a) percent retention of metal ions and (b) flux in the presence of PVA ($C_{Fe(III)} = C_{Cu(II)} = 1 \times 10^{-4}$ M, $C_{PVA} = 2 \times 10^{-4}$ unit weight (g/L), Membrane II, P = 60 psi).

3.2 Effects of Membrane Content on Percent Retention and Flux

For complex formation of AA with Fe(III) and Cu(II) ions, a series of experiments were carried out in the literature. Complex formation characterized by a wavelength shift (274–290 nm), which is an indicator of structural changes that occur on the molecules (3), Fe(III) form strong carbonyl complexes as a result of interaction of Fe(III) with nonbonding electrons in a carbonyl group of alginic acid. Solpan and Sahan (19) studied the separation of Cu(II) and Ni(II) from Fe(III) ions by complexation of ions with AA. PVA is carrying hydroxyl groups and also it is used for complexion of metals. Asman and Sanlı (20) investigated ultrafiltration of the Fe(III) solution in the presence of PVA using modified poly(methyl methacrylate-co-methacrylic acid) membranes. Solpan and Sahan (16) investigated the separation and concentration of Cu(II), Ni(II) and Fe(III) ions by complexation of ions with PVA.

The effects of the (PVA-AA) content of the membrane on the percent retention and the permeate flux are shown in Figures 2 and 3 for the membrane I, II and III. All of the metal ion concentrations were 1×10^{-4} M and complexing agent (AA, PVA) concentrations were kept constant as 2×10^{-4} repeating unit weight (g/L) in this study. As the

(PVA-AA) content of the membrane increases, a significant decline in permeate flux and increasing in percent retention are observed. As the (PVA-AA) content of the membrane increases, the pore size of the cellulose support decreases and the resulting permeate flux becomes lower, therefore, percent retention becomes higher, since small pore size prevents the passing of metal ions complexed with the AA and PVA. Similar results were obtained in the studies of G. K. Elyashevic et al. (21). They have reported that the increasing of polyacrylonitrile layer on the porous polyethylene microfiltration film leads to the lowering of permeate rate through the composite membrane.

3.3 Effects of Solution pH on Percent Retention and Flux

Figures 4 and 5 show metal percent retention and permeate flux at different pH values in the presence of complexing agents AA and PVA, respectively. The effects of pH of Fe(III) solution were studied using three different pH values which were 2.0, 2.5, and 3.0. Hydrolysis of Fe(III) takes place at higher than pH of 3. Therefore, pH values were not chosen higher than 3 in this study. Also, for Cu(II) solutions, the effects of pH were studied at pH of 3.0, 6.0, 7.0. As is seen from Figures 4 and 5, as the pH, the permeate flux decreases and percent retention of metal ions increases.
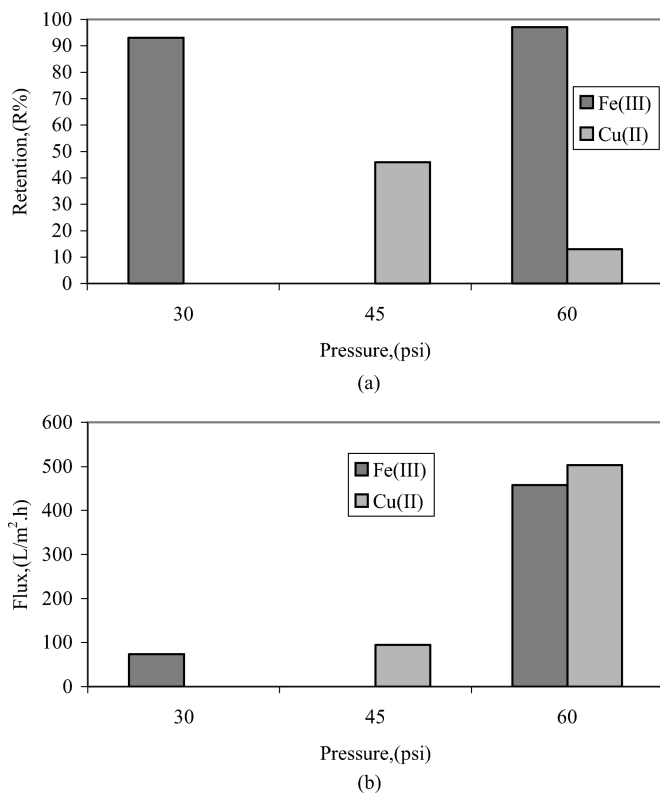
Fig. 6. Effect of applied pressure on (a) percent retention of metal ions and, (b) flux in the presence of AA ($C_{Fe(III)} = C_{Cu(II)} = 1 \times 10^{-4}$ M, $C_{AA} = 2 \times 10^{-4}$ unit weight (g/)L, pH = 3.0 for Fe(III), pH = 6.0 for Cu(II), Membrane II)

An increase in the retention percent by raising the pH of metal ions solution at the presence of complexing agents is the result of the high binding of metals to complexing agent polymers. At low pH values, the retention percentage of metal ions are lower than at high pH values, since at low pH values more H^+ ions repel positively charged of Fe(III) and Cu(II) ions and then relatively prevent the binding of metals to complexing agent polymers. The permeate flux decreases with increasing pH because the metal-AA complexes are coated and blocked the original pores on the cellulose support. Similar results concerning the effect of pH on the retention percent and permeate flux were reported in the literature (19, 20). Solpan and Sahan (19) studied the separation of Cu(II) and Ni(II) from Fe(III) ions by complexation with AA and using a suitable membrane. They observed that as pH increased, the retention of metallic ions increased. Asman and Sanlı (20) investigated ultrafiltration of Fe(III) solution in the presence of PVA using modified poly(methyl methacrylate-co-methacrylic acid) membranes. They concluded that retention was low at low pH values.

3.4 Effects of Applied Pressure on Percent Retention and Flux

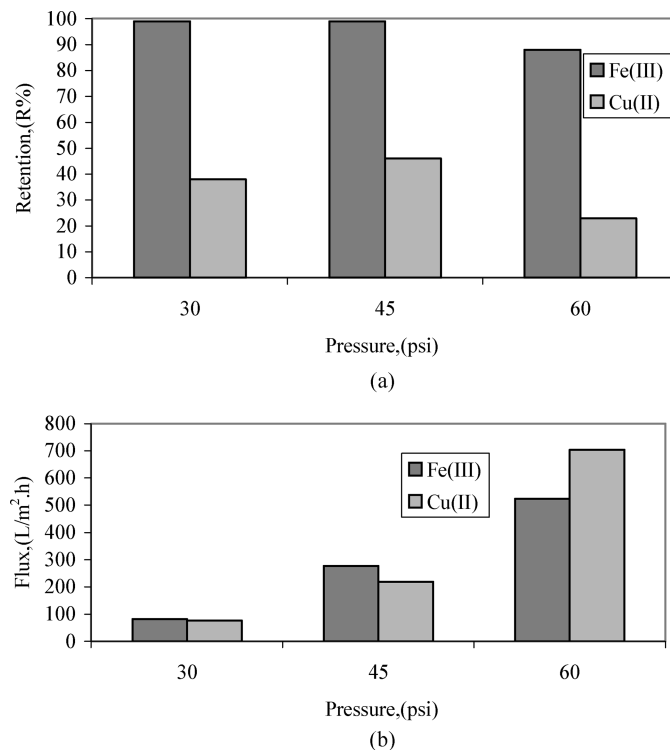The effects of applied pressure on the metal percent retention and permeate flux are shown in Figures 6 and 7.

Fig. 7. Effect of applied pressure on (a) percent retention of metal ions and, (b) flux in the presence of PVA ($C_{Fe(III)} = C_{Cu(II)} = \times 10^{-4}$ M, $C_{PVA} = 2 \times 10^{-4}$ unit weight (g/L), pH = 3.0 for Fe(III), pH = 6.0 for Cu(II), Membrane II).

Applied pressures used were 30, 45, and 60 psi. As is seen from the figures, the permeate fluxes increase as expected with increasing applied pressure. Also, it is shown in these figures that the percent retention ratio of Fe(III) ions is high with the presence of AA and PVA for all applied pressures. However, the percent retention of Cu(II) ions at a pressure of 45 psi, is higher than other applied pressures at under the presence of AA and PVA. Similar results were obtained for permeate flux in the studies of Arthanareeswaran et al. (22). It was observed that the increasing of applied pressure leads to an increase of permeate flux of chromium (III) ion through the ultrafiltration membrane.

4 Conclusions

In this study, (PVA-AA)/cellulose composite membranes were prepared by coating (PVA-AA) mixtures solutions on the filter paper. The effects of membrane content, pH of solution and applied pressure on percent retention and flux were studied for removal of Fe(III) and Cu(II) ions from aqueous solutions by a batch stirred cell. PVA and AA were also used as complexing agents to enhance the retention of metal ions. As the AA content in membrane and the pH of solution increased, the permeate flux decreased, and the percent retention increased. The permeate flux increased with increasing applied pressure for all filtration of

solutions. The percent retention ratio of Fe(III) ions was high for all applied pressures, but the percent retention of Cu(II) ions at a pressure of 45 psi is higher than other applied pressures.

The maximum retention was found as 99% for Fe(III) by complexing with PVA at a pressure of 45 psi, pH of 3.0 and by using 0.50 (w/v)% [(75 PVA/25 AA) (w/w)]/cellulose composite membranes.

Acknowledgments

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