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Poly(vinyl pyrrolidone)-enhanced crossflow filtration of Fe(III), Cu(II) and Cd(II) ions using alginic acid/cellulose composite membranes

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ABSTRACT

Removal of Fe(III), Cu(II) and Cd(II) ions from aqueous solutions was studied by polymer-enhanced crossflow filtration. Poly(vinyl pyrrolidone) (PVP) was used as complexing agent to enhance the retention. Alginic acid (AA)/cellulose composite membranes were used in the separation. The effects of AA content of the membranes and pH of the solution on the retention efficiency and the permeate flux were examined. Maximum retention efficiency was found as 93% for 1×10^{-4} M Fe(III) solutions at a flow velocity of 100 mL/min, pH of 3.0, pressure of 10 kPa in the presence of PVP by using 0.50 (w/v)% AA/cellulose composite membranes whereas for 1×10^{-4} M Cu(II) and Cd(II) solutions the maximum retention efficiencies were found as 98% and 81% respectively at pH 7.0.

Keywords: Composite membranes; Complexation; Crossflow filtration; Metal removal; Poly(vinyl pyrrolidone)

1. Introduction

Heavy metals in wastewater are discharged into environment through different industrial processes [1]. Heavy metals such as, nickel, lead, cadmium and copper in wastewater are hazardous to the environmental. For reducing heavy metal pollution problems, heavy metals in the environment must be separated [2].

Membrane filtration is a common process in water treatment and is gaining increasing importance nowadays [3]. Some of the properties of the membranes affecting the separation are their chemical nature, surface morphology and presence of charge [4]. Solution components have been separated into the retentate 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 [5].

Polymer membranes can be used in large number of separation processes such as nanofiltration, ultrafiltration and crossflow filtration. Lastra and et al. [6] investigated the treatment of Fe(II) and Mn(II) ions from wastewater by nanofiltration. Ultrafiltration membrane was used in recovering chromium(VI) in the study of Gzara [7]. Crossflow filtration is used to reduce the sublayer formation on the membrane due to the flow of the feed solution tangential to the membrane [8–10]. Chang and Hwang used crossflow microfiltration technique for the removal of metal ions from aqueous solutions [11]. Membranes can also be used in polymer-enhanced crossflow filtration technique for the separation of metal ions from aqueous solutions. Polymer-enhanced crossflow filtration technique is the combination of binding of metal ions to complexing agent polymer and crossflow filtration [12,13] to increase the retention.

Composite membranes have been prepared for combining advantages of some polymers in order to develop

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an affinity membrane with good mechanical and chemical properties. Yang and et al. [14] made chitosan/cellulose composite membranes. Sodium alginate was blended with flexible polymer poly(vinyl alcohol) to reduce the relaxation taking place during pervaporation [15].

Membranes have been made from different materials such as polysulfone [16], cellulose derivatives [17] and polysaccharide [18]. AA is a well known natural polysaccharide, which contain four-linked β-D-mannuronic acid, and α-L-guluronic acid. Due to the presence of the carboxylic acid groups in saccharide residues, AA has an anionic nature, forming alginate salts with cationic metals, such as Ca^{2+} and Na^{+} [19]. For this reason AA has been used in the field of ion exchange, controlled release and membrane processes [20–22].

In the membrane processes generally water soluble polymers (as AA) are used to bind the metals to form macromolecular complexes. These large molecules are retained, while the non-complexed ions pass through the membrane [21,22]. Polymer also carries carbonyl groups capable of forming complexes with metal ions [23]. For this reason it is a useful polymer for polymer enhanced filtration.

We have previously studied crossflow filtration removal of single of Fe(III), Cu(II) and Cd(II) metal ions from aqueous solutions using AA/cellulose composite membranes [24,25]. As a continuation of the studies, in this study we have used AA/cellulose composite membranes in the filtration using PVP as complexing agent. The effects of AA content of membrane and pH on the permeate flux and retention efficiencies were investigated.

2. Experimental

2.1. Materials

AA was supplied from Sigma as sodium salt (medium viscosity). PVP (MW, 40000) was purchased from Sigma. Cellulose as filter paper was from Filtrak (Germany, grade: 391). $(FeCl_3).6H_2O$, $(CuCl_2).2H_2O$, $(CdCl_2).H_2O$, HCl, NH_3 were all Merck products.

2.2. Preparation of the membranes

AA/cellulose composite membranes were prepared as described previously [24]. Briefly, aqueous solutions with 0.25, 0.50, 0.75(w/v)% sodium alginate content were prepared. Then 40 mL of AA solution was poured onto the filter paper placed in a glass plate (dimensions of 9 cm × 14 cm) and allowed the casting solvent (water) to evaporate completely at 60°C. Membranes were then immersed in 1 M HCl for 24 h. Membranes of 0.25 (w/v)% AA, 0.50 (w/v)% AA, 0.75 (w/v)% AA content were named as membrane I, membrane II, membrane III, respectively. Properties and the characterization of the membranes were given in our previous study [24].

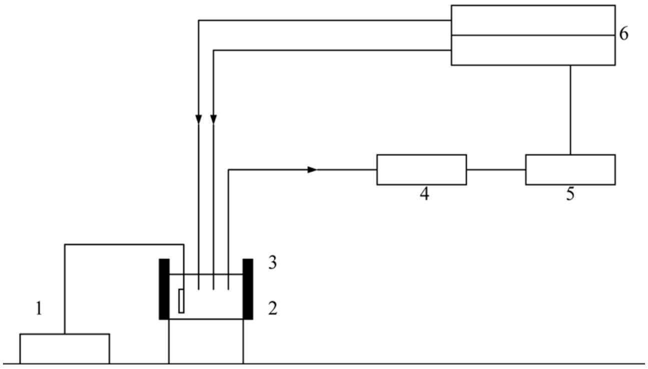


Fig. 1. Schematic diagram of the crossflow filtration apparatus. 1. pH meter, 2. Magnetic stirrer, 3. Feed tank, 4. Pump, 5. Pressure gauge measurement, 6. Filtration unit.

2.3. Crossflow filtration of solutions

Schematic diagram of the crossflow filtration apparatus is shown in Fig. 1. 500 mL of feed solutions at desired ion and complexing agent concentration were prepared at different pH values. pH adjustments were made using 0.1 M NH_3 and 0.1 M HCl solutions. The feed solutions were pumped through a crossflow filtration unit (Millipore) at a predetermined velocity (100 mL/min) and pressure (10 kPa) [24]. Membranes were placed into the filtration cell (area of 30 cm^2). Permeate and retentate were returned to feed tank for circulation. During the filtrations 3.5 mL filtrate samples were collected at different time intervals for analysis of metal ion concentrations. At least two runs were carried out for each data point.

2.4. Analysis

Fe(III) concentrations were determined spectrophotometrically. 3.5 mL of filtrate samples were taken and absorbance of the complex was measured at 293 nm. Cu(II), Cd(II) concentrations were determined using an atomic absorption spectrophotometer (Philips, PU 9285).

2.5. Measurement of the permeate flux and retention efficiency

The permeate flux:

$$J = V / A \cdot t \quad (1)$$

was expressed as $L/m^2.h$ where V is the volume of filtrate in L collected in a graduated cylinder at a specific time interval (h) and A is the area in m^2.

Retention efficiency values were calculated from the equation:

$$R\% = \left(1 - C_p / C_f\right) \times 100 \quad (2)$$

where C_p and C_f are metal ion concentrations of the permeate and the feed solutions, respectively.

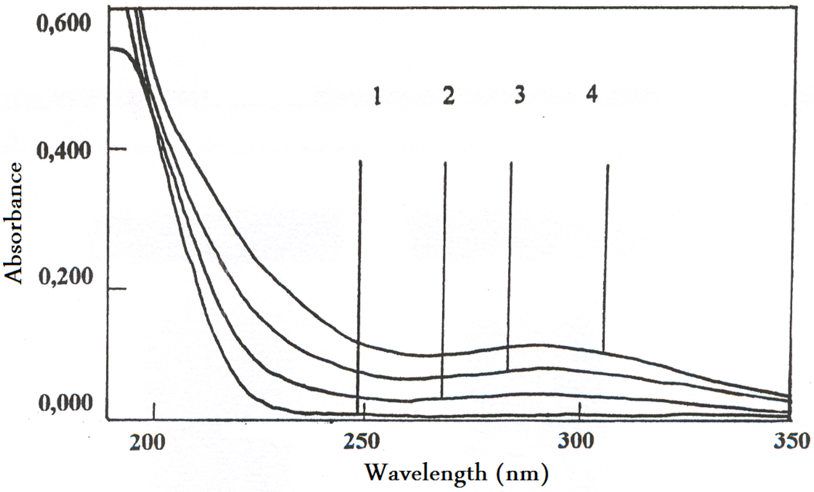


Fig. 2. Complexing of Fe(III) with PVP. 1. PVP, 2. (4 mL PVP + 1 mL Fe(III)), 3. (3 mL PVP + 2 mL Fe(III)), 4.(2 mL PVP + 3 mL Fe(III)).

3. Results and discussion

3.1. Filtration of Fe(III) solutions in the presence of PVP

PVP is soluble in water and has a tendency for complex formation with small molecules. It is a hydrophilic polymer and has great molecular mass difference comparing to the interacting species used in the study; thus complexing with this reagent will help to the retention of the ions. However, it is necessary to evaluate the complex formation and determine the required amount of PVP for complex formation.

For this purpose a series of experiments were carried out to evaluate the complex formation of PVP with metal ions. The complexing of Fe(III) ions with PVP was investigated spectrophotometrically (Fig. 2). Wavelength at 293 nm for PVP was shifted with Fe(III) addition. Guner et al. [23] reported that the n–π* excitations were shifted to the longer wavelengths in PVP-metal chloride aqueous systems. They have also stated that it is possible to explain the observed shifting phenomena in aqueous metal chloride solutions of PVP as a result of the interaction of the polymer with metal cations.

The required amount of PVP for complex formation was determined by mixing different unit weight (g)/L of PVP with 1×10^{-4} M Fe(III) solutions to obtain different ratios. Results are shown in Fig. 3. As it is seen from the figure, 2 unit weight (g) of PVP is necessary for each mole of Fe(III).

Experiments were carried out to filtrate PVP–Fe(III) complexes solutions and the effect of AA content of the membrane on the percent retention of Fe(III) and the permeate flux are shown in Fig. 4. Membrane I and membrane II were used in the study, membrane III cannot be used due to high cake formation on the surface of the membrane. As it is seen from the figure, a sharp increase of retention occurs in the initial filtration period and then levels off. However, flux first drop sharply and then levels off. On the other hand, increase in the AA content of the membrane caused a significant decline in permeate flux. As the AA content of the membrane increases, the pore size of the cellulose support decreases and resulting in a decrease in the permeate flux and an increase in the retention efficiency since small pore size prevents the passing of metal ions complex. Similar results were obtained in the studies of Elyashevich et al. [26]. They have reported that the increasing of polyacrylonitrile layer on the porous

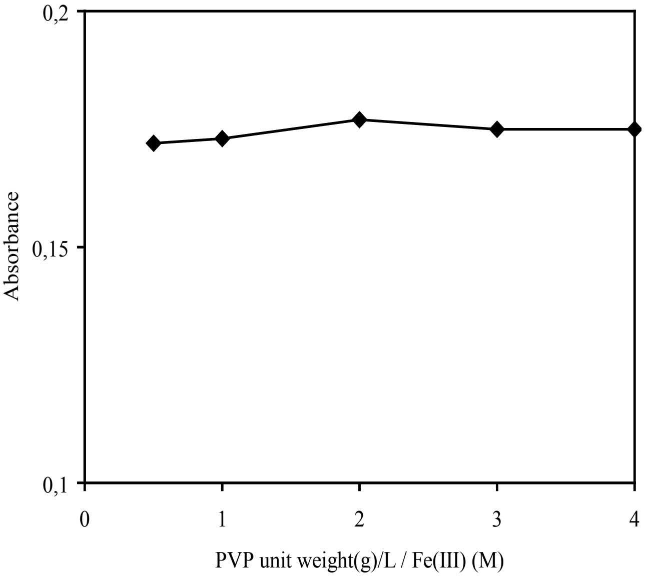
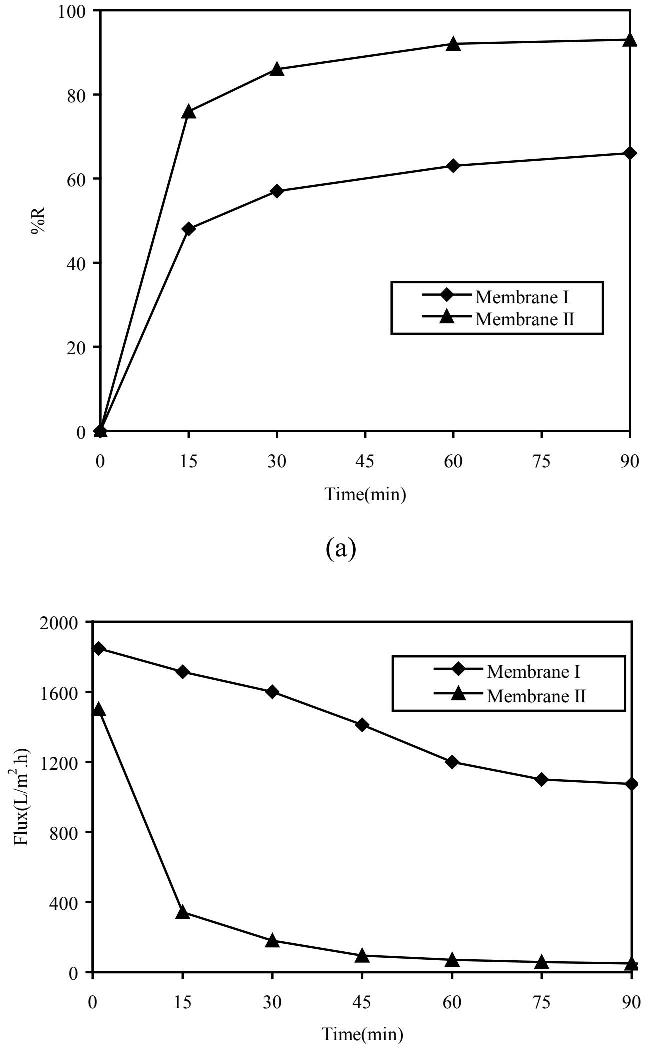
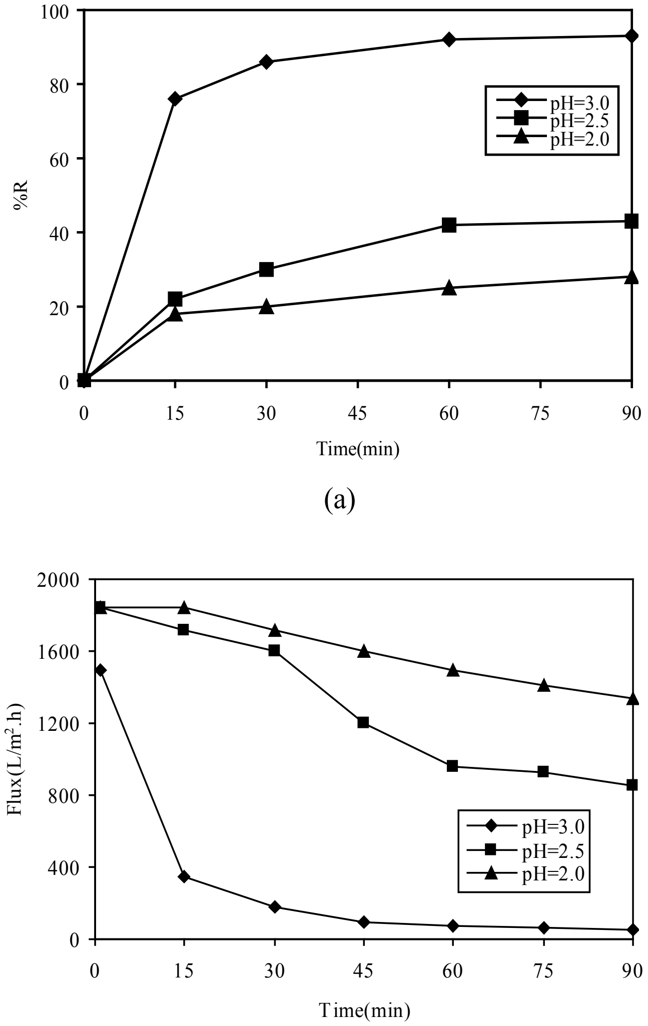


Fig. 3. Evaluation of the necessary amount of PVP for complex formation with Fe(III) ($\lambda = 293$ nm, $C_{\mathrm{Fe(III)}} = 1\times10^{-4}$ M, pH = 3.0).



(b)

Fig. 4. Effect of AA content of the membrane on (a) percent retention of Fe(III) and (b) flux in the presence of PVP ($C_{Fe(III)}$ = 1×10^{-4} M, C_{PVP} = 2×10^{-4} unit weight(g)/L, pH = 3.0, P = 10 kPa, velocity = 100 mL/min).



(b)

Fig. 5. Effect of pH on (a) percent retention of Fe(III) and (b) flux in the presence of PVP ($C_{Fe(III)}$ = 1×10^{-4} M, C_{PVP} = 2×10^{-4} unit weight(g)/L, P = 10 kPa, velocity = 100 mL/min, Membrane II).

polyethylene microfiltration film lead to the lowering of permeation rate through the composite membrane.

The effect of pH was studied using three different pH values: 2.0, 2.5 and 3.0. pH values higher than 3.0 was not studied due to hydrolysis of Fe(III) at high pH values. As it is seen from Fig. 5, at the initial filtration period high fluxes and low retentions were obtained and then reached steady state values. Furthermore, as the pH increases the permeate flux decreases, whereas retention efficiency of metal ions increases. At low pH values H$^+$ ions which are in high concentration repel the positively charged Fe(III) ions preventing the binding of metal ions to complexing agent polymer. The permeate flux decrease with increasing pH is probably due to high cake formation on the membrane. Similar results concerning the effect of pH on the retention and permeate flux were reported in the literature. Solpan and Shan [27] studied the separation of Cu(II) and Ni(II) from Fe(III) ions by complexation with AA using a suitable membrane. They have observed that as the pH increased the retention of metal ions increased. Asman and Sanlı [28] investigated ultrafiltration of Fe(III) solution in the presence of poly(vinyl alcohol) using modified poly(methyl methacrylate-co-methacrylic acid) membranes. They have also concluded that retention was low at low pH values. Similar results were also observed in our previous study in that alginic acid polymer was used as complexing agent to enhance the retention [25] of the ions.

In this study, the maximum retention efficiency was found as 93% for 1×10^{-4} M Fe(III) solution at the flow velocity of 100 mL/min, pH of 3.0, pressure of 10 kPa in the presence of PVP as complexing agent by using 0.50 (w/v)% AA/cellulose composite membranes.

3.2. *Filtration of Cu(II) solutions in the presence of PVP*

PVP–Cu(II) complex formation was also searched as in PVP–Fe complex formation by the shift of absorption value and complex have absorption at 250 nm (Fig. 6). The necessary amount of PVP for the complex formation was determined as 2 unit weight (g) of PVP for each mole of Fe(III) (Fig. 4). The dependencies of the permeate flux and percent retention of PVP–Cu complex on the AA content of the membrane are presented in Fig. 8. As the AA content of membrane increased, retention also increased similar to the case of alginic acid enhanced ultrafiltration of Cu(II) solution [25].

The permeate flux and percent retention as a function of pH were studied at pH 3, 6, 7 and the results are presented in Fig. 9. As is seen from the figure, as the pH increases the permeate flux decreases and retention efficiency increases.

For this study the maximum retention efficiency for 1×10^{-4} M Cu(II) solutions were found as 98% by using 0.50 (w/v)% AA/cellulose composite membranes when the filtration was carried out in the presence of PVP at pH of 7.0, pressure of 10 kPa and flow velocity of 100 mL/min.

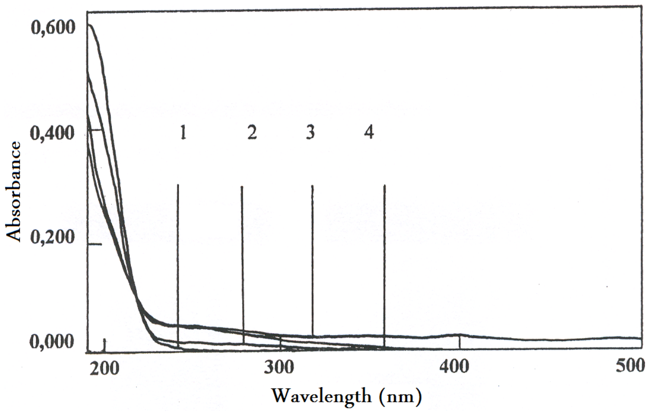


Fig. 6. Complexing of Cu(II) with PVP 1. PVP 2. (4 mL PVP + 1 mL Cu(II)), 3. (3 mL PVP + 2 mL Cu(II)), 4. (2 mL PVP + 3 mL Cu(II)).

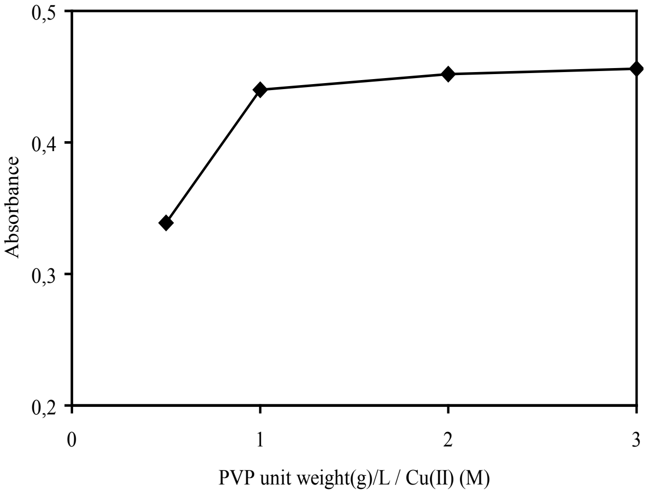
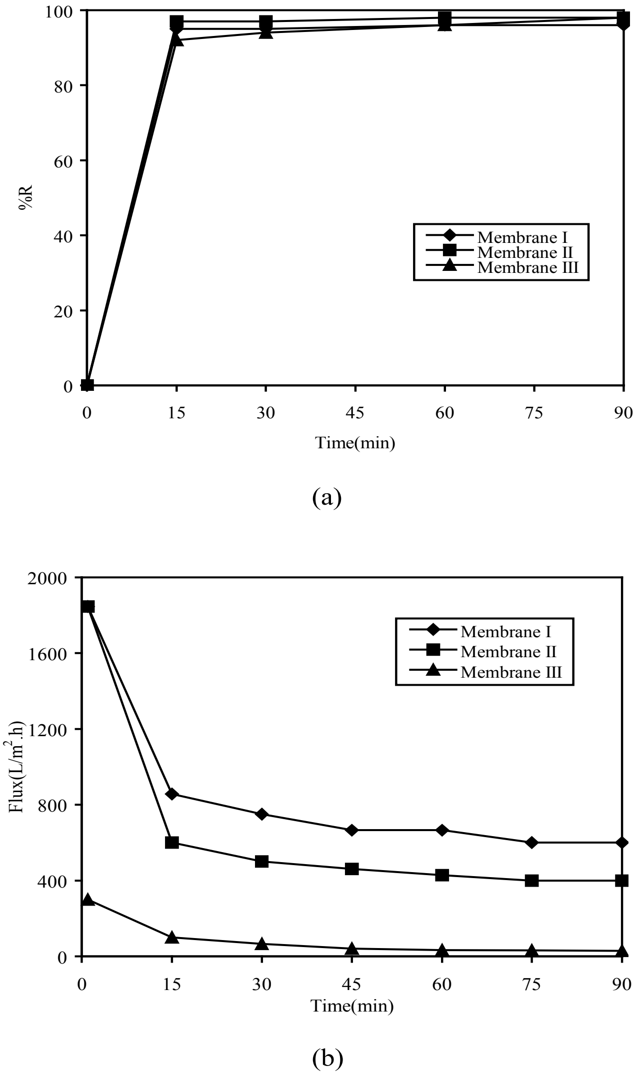


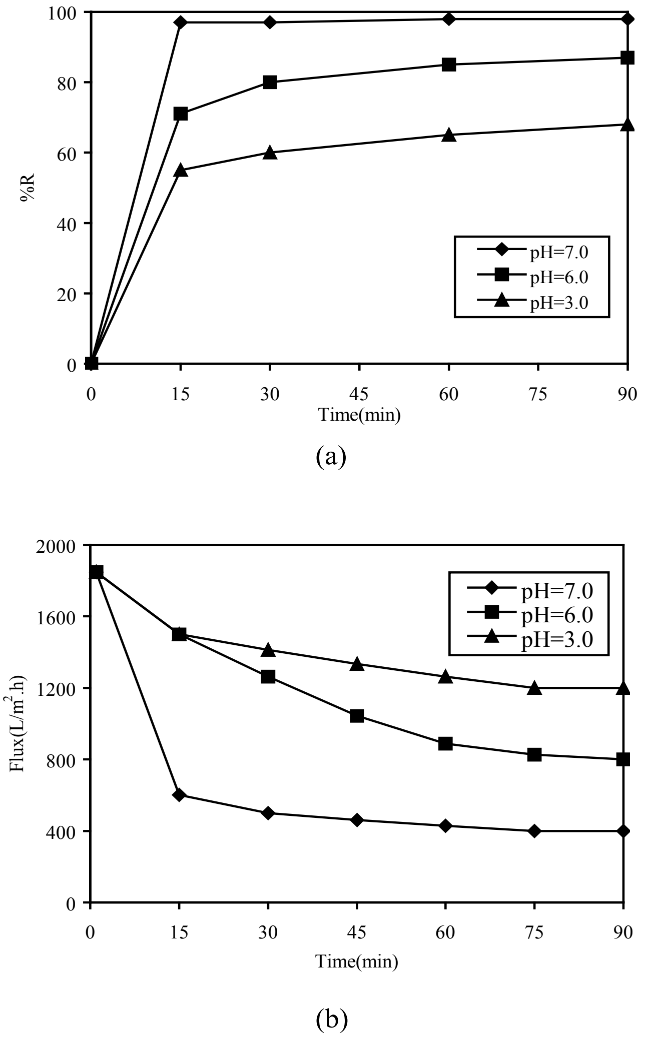
Fig. 7. Determination of necessary amount of PVP for complex formation with Cu(II) ($C_{Cu(II)} = 2\times10^{-4}$ M, $\lambda = 250$ nm, pH = 7.0).



(a)

(b)

Fig. 8. Effect of AA content of the membrane on (a) percent retention of Cu(II) and (b) flux in the presence of PVP ($C_{Cu(II)} = 1\times10^{-4}$ M, $C_{PVP} = 2\times10^{-4}$ unit weight(g)/L, velocity = 100 mL/min, pH = 7.0, P = 10 kPa).



(a)

(b)

Fig. 9. Effect of pH on (a) percent retention of Cu(II) and (b) flux in the presence of PVP ($C_{Cu(II)}$ = 1×10^{-4} M, C_{PVP} = 2×10^{-4} unit weight(g)/L, velocity = 100 mL/min, P = 10 kPa, Membrane II).

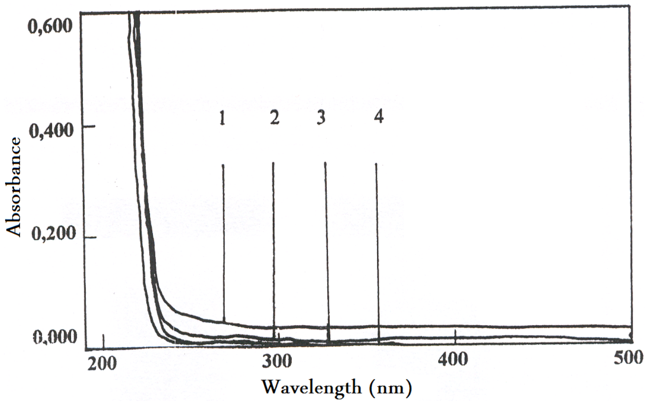


Fig. 10. Complexing of Cd(II) with PVP 1. PVP 2. (4 mL PVP + 1 mL Cd(II)), 3. (3 mL PVP + 2 mL Cd(II)), 4. (2 mL PVP + 3 mL Cd(II)).

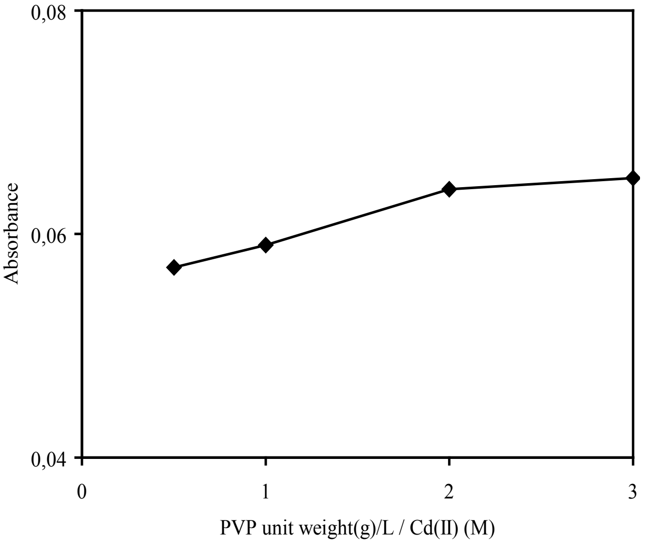


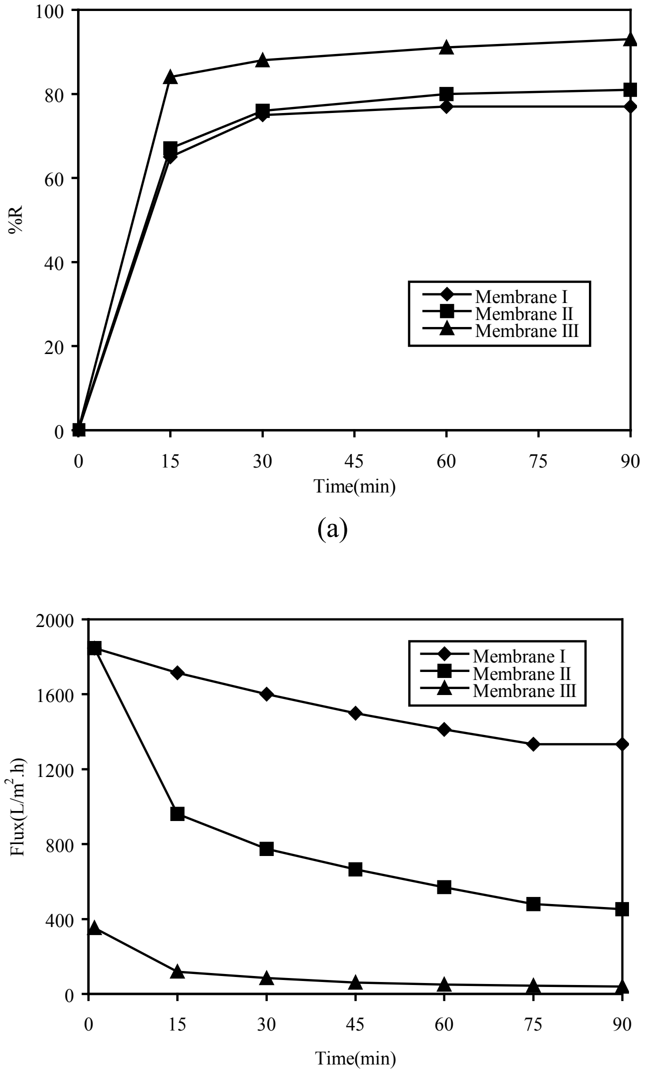
Fig. 11. Determination of necessary amount of PVP for complex formation with Cd(II) ($C_{Cd(II)}$ = 2×10^{-3} M, λ = 275 nm, pH = 6.0).

3.3. Filtration of Cd(II) solutions in the presence of PVP

PVP–Cd(II) complex formation was examined as in Fe(III), Cu(II) and found that wavelength was shifted at 275 nm for PVP with Cd(II) addition (Fig. 10). Also, 2 unit weight (g) of PVP was found enough for the complex formation (Fig. 11). Membranes I, II and III were used in this study. The effect of AA content of the membrane on the retention efficiency of Cd(II) and permeate flux are shown in Fig. 12 in the presence of PVP. Similar trends were observed in the retention and the flux as in the case of PVP–Fe and PVP–Cu complex. Jegal et al. [29] have also reported that the flux of membranes based on poly(vinyl alcohol)/sodium alginate on polysulfone support decreased as the concentration of the poly(vinyl alcohol)/sodium alginate mixture solution increased.

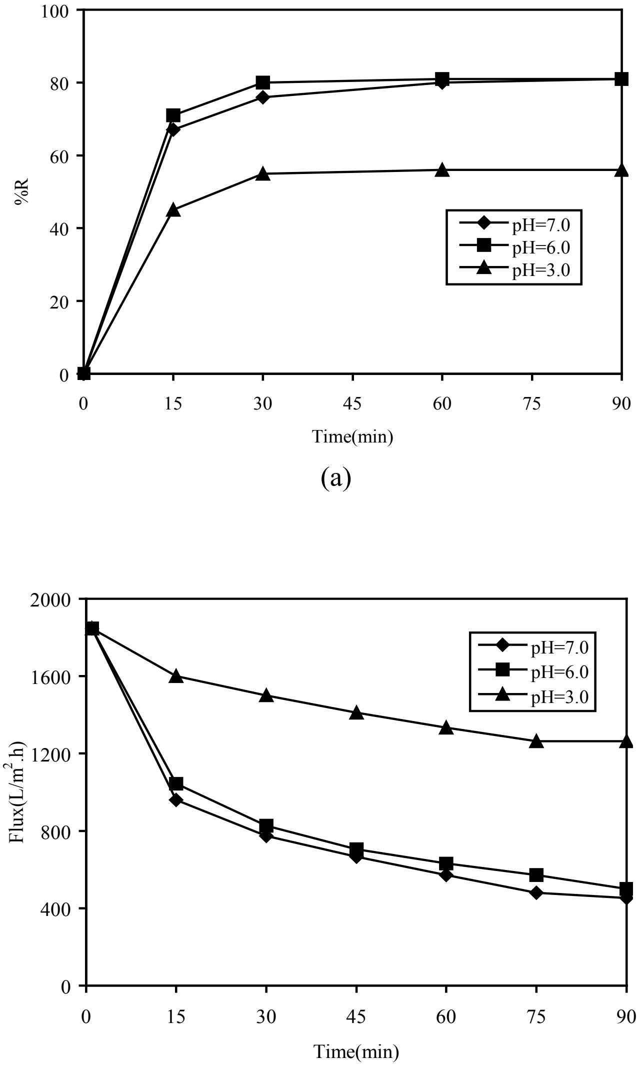
Fig. 13 shows the effect of pH on the permeate flux and retention efficiency at pH 3, 6 and 7. Low percent retention and high permeate flux were observed at low pH values due to the low binding of metals to complexing agent polymers.

For 1×10–4 M Cd(II) solutions the maximum retention efficiency was found as 81% by using 0.50 (w/v)% AA/cellulose composite membranes when the filtration was carried out in the presence of PVP at pH of 7.0, pressure of 10 kpa and flow velocity of 100 mL/min.



(b)

Fig. 12. Effect of AA content of the membrane on (a) percent retention of Cd(II) and (b) flux in the presence of PVP ($C_{Cd(II)}$ = 1×10^{-4} M, C_{PVP} = 2×10^{-4} unit weight (g)/L, velocity=100 mL/min, pH = 7.0, P = 10 kPa).



(b)

Fig. 13. Effect of pH on percent retention of Cd(II) and (b) flux in the presence of PVP ($C_{Cd(II)}$ = 1×10^{-4} M, C_{PVP} = 2×10^{-4} unit weight (g)/L, P = 10 kPa, velocity = 100 mL/min, Membrane II).

3.4. Filtration of Fe(III), Cu(II), Cd(II) mixture in the presence of PVP

The retention efficiency of individual metal ions and in the mixture for PVP enhanced cross flow filtration is shown in Fig. 14. All of the metal ion concentrations were 1×10^{-4} M and PVP concentration was kept constant as 2×10^{-4} unit weight (g)/L in this study. The maximum retention efficiencies of Fe(III), Cu(II) and Cd(II) for single metal ions were found as 93%, 98%, 81%, respectively in the presence of PVP. However in the mixture, these values were found as 87%, 88%, 87% respectively in the presence of PVP for membrane II at pH 7. It can be seen from Fig. 14 that the retention efficiency of Cd(II) ions is increased by the presence of other metal ions while retention efficiency of the other ions are reduced. In reality, the retention efficiency of metal ions must decrease in the presence of other metal ions in the medium due to the existence of competition between ions for the complex formation with PVP. But there is an increase in the retention efficiency in Cd(II) ions in the mixture. This can be explained by the fact that Fe(III) and Cu(II) ions firstly form a complex with PVP due to the high ionic valence number of Fe(III) and the small ionic radius of Cu(II) and also this situation

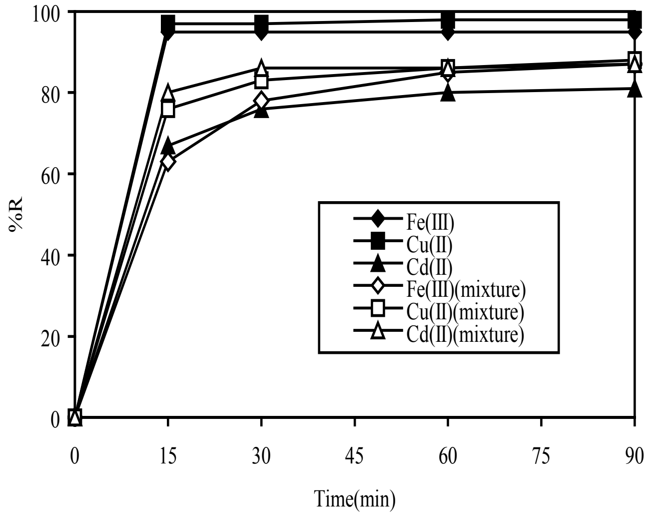


Fig. 14. Comparison of retention of Fe(III), Cu(II), Cd(II) ions individually and with in the mixture. (pH = 7.0, velocity = 100 mL/min, P = 10 kPa, Membrane II, $C_{\mathrm{Fe(III)}} = C_{\mathrm{Cu(II)}} = C_{\mathrm{Cd(II)}} = 1\times10^{-4}$ M, $C_{\mathrm{PVP}} = 2\times10^{-4}$ unit weight(g)/L).

results in additional barrier for the filtration and can cause high retention efficiency for Cd(II) ions.

It is reflected from the results that PVP enhanced cross flow filtration through alginic acid–cellulose composite membranes works also successfully for the retention of the ions in the mixture.

4. Conclusion

In this study, removal of Fe(III), Cu(II),and Cd(II) ions from aqueous solutions by polymer-enhanced crossflow filtration was investigated. PVP was used as complexing agent polymer. AA/cellulose composite membranes were used in the filtration.

As the AA content of the membrane and the pH of solution increased the permeate flux decreased, whereas the retention efficiency increased.

The maximum percent retention was found as 93% for 1×10^{-4} M Fe(III) solution at the flow velocity of 100 mL/min, pH of 3.0, pressure of 10 kPa in the presence of PVP by using 0.50 (w/v)% AA/cellulose composite membranes at pH 3.

For 1×10^{-4} M Cu(II) and Cd(II) solutions the maximum retention efficiencies were found as 98% and 81% respectively by using 0.50 (w/v)% AA/cellulose composite membranes at pH of 7.0, pressure of 10 kPa and flow velocity of 100 mL/min in the presence of PVP.

The method also works successfully for the mixture of 1×10^{-4} M Fe(III), Cu(II) and Cd(II) ions giving the retention of 87%, 88%, 87% respectively in the presence of PVP for 0.50 (w/v)% AA/cellulose composite membrane at pH 7, pressure of 10 kPa and flow velocity of 100 mL/min.

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