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Abstract: The removal of Fe(III), Cu(II), and Cd(II) ions from aqueous solutions was studied by polymer-enhanced crossflow filtration technique. Alginic acid polymer was used as complexing agents to enhance the retention. Alginic acid/cellulose composite membranes were used in the filtration. In the filtration of metal ion solutions the effects of alginic acid content of the membranes and pH on the percent retention and the permeate flux were examined. The maximum percent retention was found as 98% for 1×10^{-4} M Fe(III) solution at the flow velocity of 100 mL/min, pH of 3.0, pressure of 60 kPa in the presence of alginic acid as complexing agent by using 0.25 (w/v)% alginic acid/cellulose composite membranes. For 1×10^{-4} M Cu(II) and Cd(II) solutions the maximum percent retentions were found as 71% and 80% respectively using 0.50 (w/v)% Alginic acid/cellulose composite membranes when the filtration was carried out in the presence of alginic acid at pressure of 10 kPa, flow velocity of 100 mL/min and pH of 7.0.

Keywords: Alginic acid/cellulose membrane, complexing agent, composite membranes, crossflow filtration, retention of metal ions

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INTRODUCTION

Heavy metals in waste water that are discharged into the environment through different industrial processes (1) are hazardous to the environment. For reducing pollution problems, heavy metals in the environment must be separated by different processes such as adsorption, chemical precipitation, and membrane processes (2).

Membranes can be used in a large number of separation processes. Reverse osmosis filtration and nanofiltration membranes were used in the treatment of wastewater containing Mn(II) and Fe(II) (3,4). In a study by Gzara et al. (5) polysulfone membranes were used in recovering chromium(VI) by ultrafiltration. Membranes have been made from different materials such as polysulfone (6), polysaccharide (7), and cellulose derivatives (8). Cellulose membranes have low mechanical and chemical properties. In order to develop properties of cellulose, composite membranes can be produced. Composite membranes have been made for combining advantages of some polymers in order to develop membrane with good mechanical and chemical properties. For example L.Yang et al. (9) made chitosan/cellulose composite membranes for this purpose. The characterization of membranes require a study of parameters such as the porosity and the permeability to the solvent and the selectivity for macromolecular retention (10–13).

Crossflow filtration is used to reduce the sublayer formation on the membrane due to the flow of the feed solution tangential to the membrane (14–16). Chang and Hwang (17) used the crossflow microfiltration technique for the removal the 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. Since pore sizes of membranes are not small to separate metal ions, complexing agent polymers are used to bind the metals to obtain big complexes (18,19). In membrane processes 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 (20). For example, Alginic acid (AA) is a biopolymer carrying carboxyl groups capable of forming complexes with metal ions and also it has been used as membranes such as in ion exchange processes (21,22).

In this study, Alginic acid (AA)/cellulose composite membranes were used in crossflow filtration for removal of single and in the mixture of Fe(III), Cu(II), and Cd(II) ions from aqueous solutions in the presence of AA as complexing agent. The effects of AA content of the membrane and pH on the permeate flux and percent retention were investigated.

EXPERIMENTAL

Materials

AA was supplied from Sigma as sodium salt (medium viscosity). Filter paper used was from Filtrak (Germany, grade: 391). $(FeCl_3) \cdot 6H_2O$, $(CuCl_2) \cdot 2H_2O$, $(CdCl_2) \cdot H_2O$, HCl, and NH_3 were all Merck products.

Preparation of the Membranes

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 the glass plate (dimensions of 9 cm $\times$ 14 cm) and allowed the casting solvent (water) to evaporate completely at 60°C. Membranes were then immersed in 1 M HCl for 24 hour. Properties of prepared membranes were given in Table 1.

Experimental Apparatus and the Filtration of Solutions

Experimental set up was shown in Fig. 1. 500 mL of feed solutions for the desired ion and the 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 purpose built filtration unit (Millipore) was constructed from plastic and stainless steel. Membranes were placed into the filtration cell (made of plastic material) with an area of 30 cm^2. During an experiment feed liquid flowed through the filtration cell tangential to the membrane. Permeate and retentate were returned to the feed tank for circulation. During filtrations 3.5 mL filtrate samples were collected at different time intervals for analysis of metal concentrations from the permeate. Desired filtration conditions were maintained by two manually operated valves. For crossflow filtration of solution the effects of the AA content of the membranes and pH on percent retention and the permeate flux were investigated.

Table 1. Properties of the Membranes

Membrane	% AA (w/v)	g AA/g cellulose filter	Thickness (mm)
Cellulose filter	–	–	135
I	0.25	0.101	140
II	0.50	0.150	145
III	0.75	0.209	150

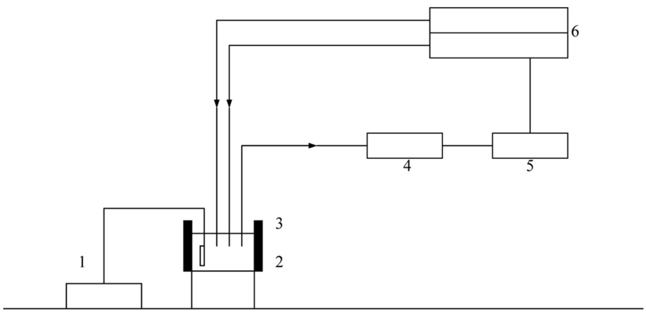

Figure 1. Shematic of experimental set up. 1. pH meter, 2. Magnetic stirrer, 3. Feed tank, 4. Pump, 5. Pressure gauge measurement, 6. Filtration unit.

Analysis

Fe(III) concentrations were determined spectrophotometrically. 3.5 mL of filtrate samples were taken and the absorbance of the complex was measured at 290 nm (Spectronic 20D). Cu(II), Cd(II) concentrations were determined using an atomic absorption spectrophotometer (Philips, PU 9285).

Measurement of the Permeate Flux and Percent Retention

The permeate flux expressed as L/m^2h was determined by collecting filtrate samples in a graduated cylinder at a specific time interval. Percent retention values were calculated from the formula:

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

where C_p and C_f are metal ion concentrations of the permeate (final metal ion concentration) and the feed solutions (initial metal ion concentration), respectively.

RESULTS AND DISCUSSION

Filtration of Fe(III) Solutions in the Presence of AA

AA is a polysaccharide consisting of D-mannuronic acid and L-guluronic acid units. The product used in the present study was polyuronic acid which was composed of primarily of anhydrous mannuronic acid with 1–4 linkages. It is a hydrophilic, non-crosslinked polymer and has great molecular mass difference compared to the interacting species used in the study; thus complexing with this reagent will help in the retention of the ions. However, it is necessary to evaluate the complex formulation and determine the required amount of AA for complex formation.

For this purpose a series of experiments was carried out to evaluate complex formation of AA with Fe(III). Complex formation characterized by wave length shift (274–290) which is an indicator of structural changes that occur on the molecules (23) Fe(III) form strong carbonyl complexes as a result of interaction of Fe(III) with nonbonding electrons in the carbonyl group of alginic acid so a shift in the wave length maxima takes place. This is due to $\Pi \rightarrow \Pi^*$ transitions (24).

The required amount of AA for complex formation was determined as 2 repeating unit weight (g) of AA for each (mole) of Fe(III) by using different repeating unit weight g/L of AA added to 1×10^{-4} M Fe(III) solutions to obtain different ratios.

The effects of the AA content of the membrane on the percent retention of Fe(III) and the permeate flux are shown in Fig. 2 in the presence of AA. Membrane I and membrane II were used in this study but not membrane III. As the AA concentration increased to 0.75% for membrane III, a significant decline in the flow rate is observed because much more AA was coated on and blocked the original pores on the cellulose support. From Fig. 3, sharp increase retention occurs in the initial filtration period and then levels off. However, flux first drops sharply and then levels off. On the other hand, as the AA content of the membrane increases, a significant decline in permeate flux is observed. Similar results were obtained in the studies of Elyashevic G.K. et al. (25). They have reported that the increasing of polyacrylonitrile layer on the porous polyethylene microfiltration film leads to the lowering of the permeate rate through the composite membrane.

The effect of pH was studied using three different pH values: 2.0, 2.5, and 3.0. The effect of pH at higher values than 3.0 was not studied due to hydrolysis of Fe(III) ions. As it is seen from Fig. 3, at the initial filtration period high fluxes and low retentions were obtained and then reached steady state values in fluxes and retentions. Furthermore, as the pH increases the permeate flux decreases and the percent retention of metal ions increases. At low pH values the retention percentage of metal ions are low, since the high H^+ ions repel positively charged Fe(III) ions and then prevent the binding of metals to complexing agent polymers. The permeate flux decreases with increasing pH due to cake formation possibility on the membrane. A similar result concerning the effect of pH on the retention percent and permeate flux were reported in literature. Solpan and Shan (24) 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 the pH increased the retention of metallic ions also increased. Asman and Sanlı (26) investigated ultrafiltration of the Fe(III) solution in the presence of PVA using a

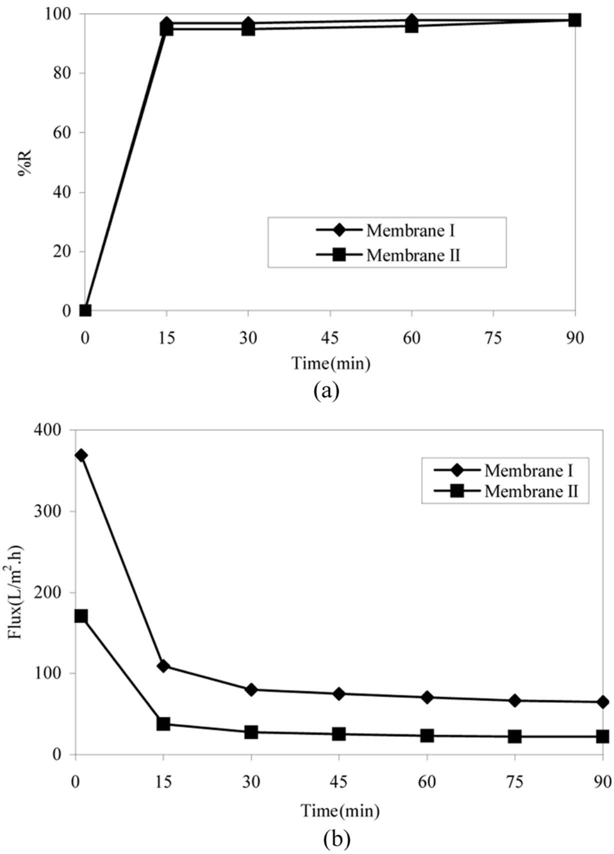

Figure 2. Effect of AA content of the membrane on (a) percent retention of Fe(III) and (b) flux in the presence of AA ($C_{Fe(III)} = 1 \times 10^{-4}$ M, $C_{AA} = 2 \times 10^{-4}$ unit weight (g/L), pH = 3.0, P = 60 kPa, Velocity = 100 mL/min).

modified poly(methyl methacrylate-co-methacrylic acid) membranes. They have concluded that retention was low at low pH values.

In this study, the maximum percent retention was found as 98% for 1×10^{-4} M Fe(III) solution at the flow velocity of 100 mL/min, pressure of 60 kPa in the presence of AA as complexing agent by using 0.25 (w/v)% AA/cellulose composite membranes at pH 3.

Filtration of Cu(II) Solutions in the Presence of AA

AA-Cu(II) complex formation was searched as in AA-Fe(III) complex formation by the shift of absorption value and complex have absorption

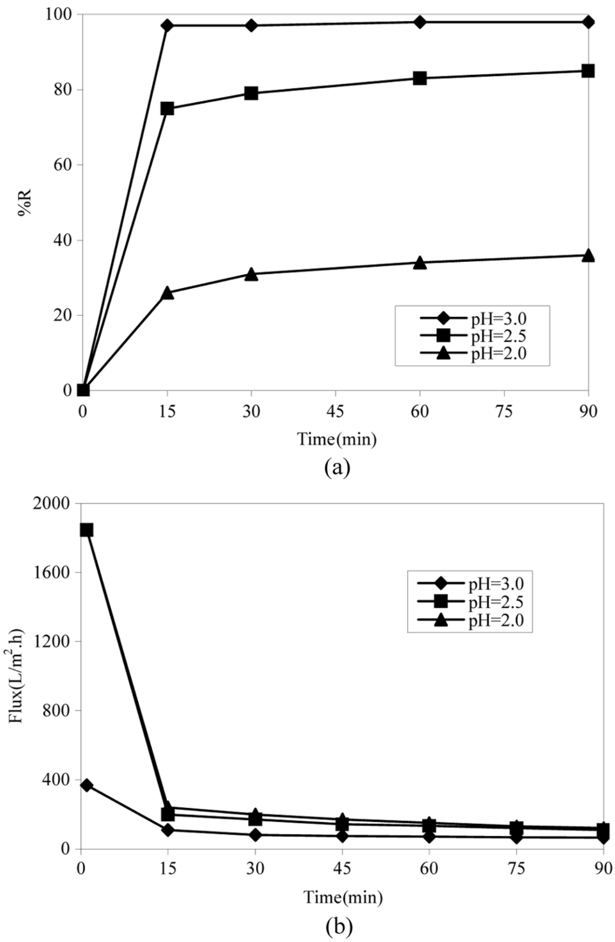

Figure 3. Effect of pH on (a) percent retention of Fe(III) and (b) flux in the presence of AA ($C_{Fe(III)} = 1 \times 10^{-4}$ M, $C_{AA} = 2 \times 10^{-4}$ unit weight (g/L), P = 60 kPa, Velocity = 100 mL/min, Membrane I).

at 238 nm. The necessary amount of AA for the complex formation was determined as 2 repeating unit weight (g) of AA for each (mole) of Fe(III).

The dependencies of the permeate flux and percent retention of AA-Cu(II) complex on the AA content of the membrane are presented in Fig. 4. According to this figure, at the beginning of filtration higher fluxes and lower retention were obtained. However, decrease in flux and sharp increase in retention occurs at high filtration periods. On the other hand, with increasing AA content of membranes the permeate flux decreases and the percent retention increases.

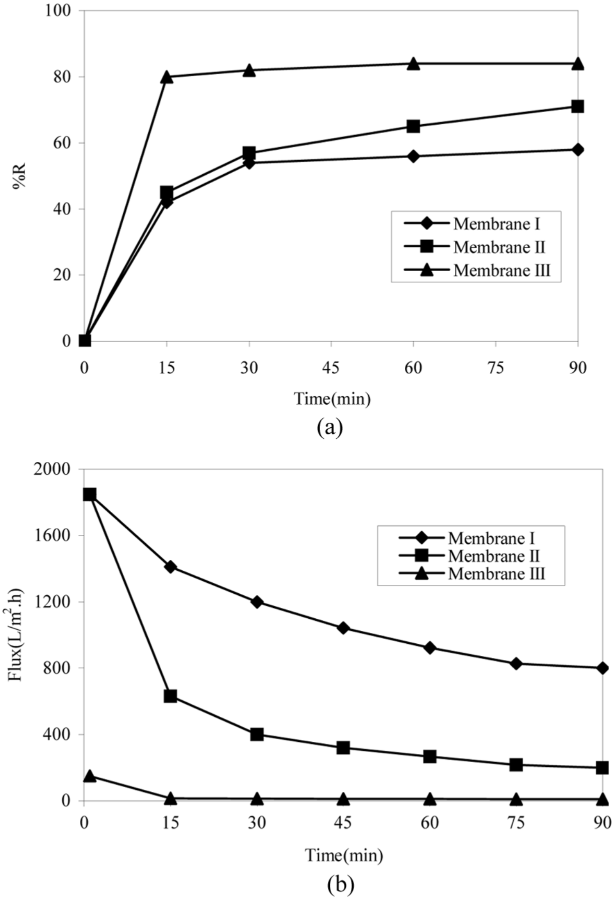

Figure 4. Effect of AA content of the membrane on (a) percent retention of Cu(II) and (b) flux in the presence of AA ($C_{Cu(II)} = 1 \times 10^{-4}$ M, $C_{AA} = 2 \times 10^{-4}$ unit weight (g/L), Velocity = 100 mL/min, pH = 7.0, P = 10 kPa).

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. 5. This figure reflects that, as the pH increases the permeate flux decreases and the percent retention increases. 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. The permeate flux decreases at high pH values due to high cake formation on the membrane.

In this study the maximum percent retentions for 1×10^{-4} M Cu(II) solutions were found as 71% by using 0.50 (w/v)% AA/cellulose

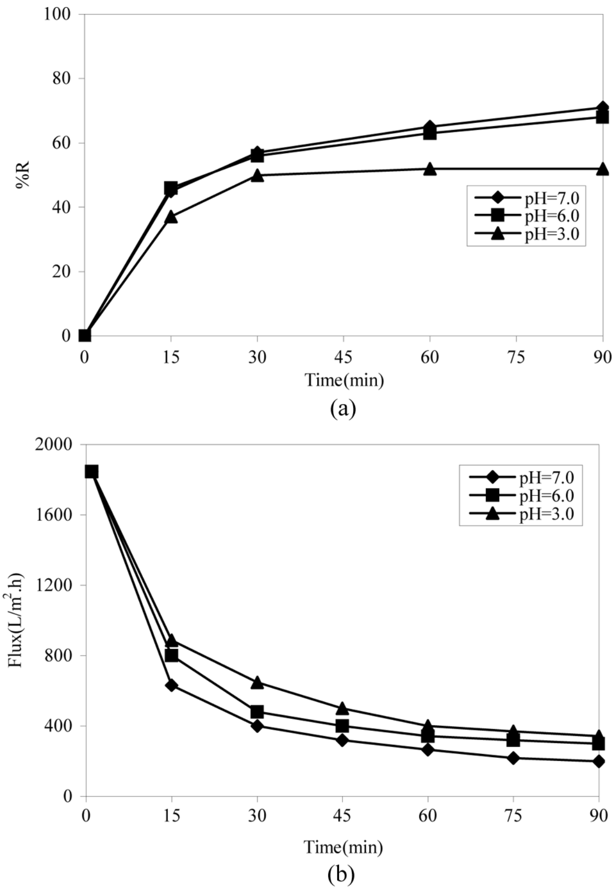

Figure 5. Effect of pH on (a) percent retention of Cu(II) and (b) flux in the presence of AA ($C_{Cu(II)} = 1 \times 10^{-4}$ M, $C_{AA} = 2 \times 10^{-4}$ unit weight (g/L), Velocity = 100 mL/min, P = 10 kPa, Membrane II).

composite membranes when the filtration was carried out in the presence of AA at pH of 7.0, a pressure of 10 kPa, and flow velocity of 100 mL/min.

Filtration of Cd(II) Solutions

AA-Cd(II) complex formation was examined as in Fe(III) and Cu(II) and found that complex have absorption at 250 nm and 2 repeating unit weight (g) of AA is found enough for complex formation for each (mole) of Cd(II). Effect of AA content of the membrane on the percent retention

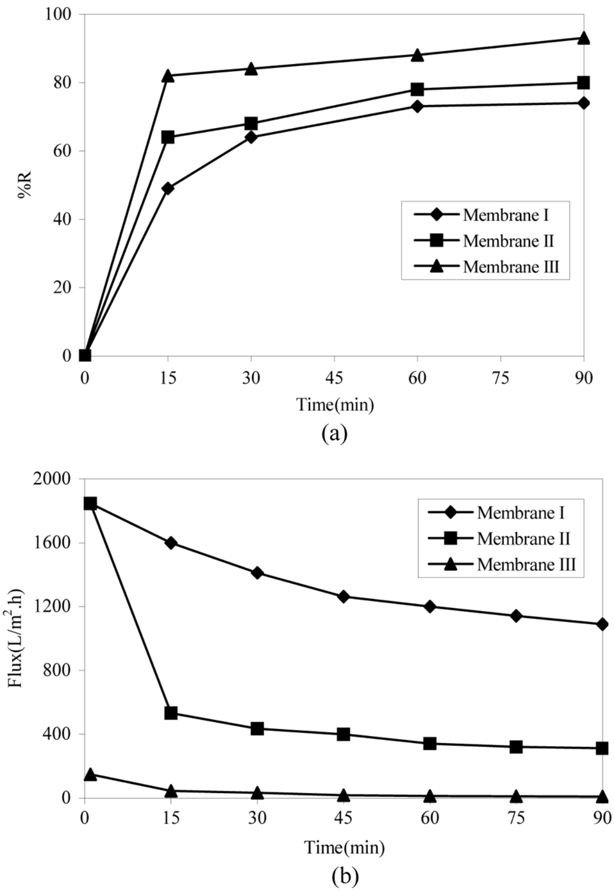

Figure 6. Effect of AA content of the membrane on (a) percent retention of Cd(II) and (b) flux in the presence of AA ($C_{Cd(II)} = 1 \times 10^{-4}$ M, $C_{AA} = 2 \times 10^{-4}$ unit weight (g/L), Velocity = 100 mL/min, pH = 7.0, P = 10 kPa).

and permeate flux of Cu(II) in the presence of AA are shown in Fig. 6. As shown in this figure, at the beginning of the filtration, membranes have lower cake resistance on their surface, and thus a higher flux and lower retention are obtained. Also, due to higher fluxes, the cakes grow faster on the surface of membranes. As a result, a sharp drop of flux and a sharp increase of retention occur. Furthermore, as the AA content of the membrane increases the percent retention increases and the permeate flux decreases as in the filtration of Fe(II), Cu(II) solutions. Similar results were obtained in the studies of Jegal et al. (27). They have 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.

Figure 7 shows the effect of pH on the permeate flux and percent retention at pH 3, 6, and 7. As is reflected from the figure that the first permeate flux decreases and the percent retention increases then both the permeate flux and the percent retention level off with increasing

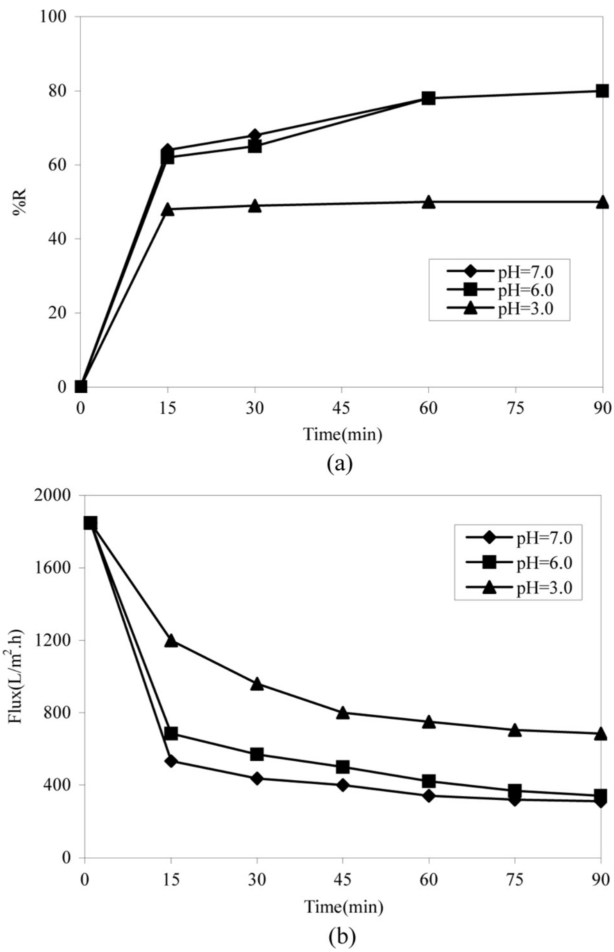

Figure 7. Effect of pH on (a) percent retention of Cd(II) and (b) flux in the presence of AA ($C_{Cd(II)} = 1 \times 10^{-4}$ M, $C_{AA} = 2 \times 10^{-4}$ unit weight (g/L), P = 10 kPa, Velocity = 100 mL/min, Membrane II).

pH. Low percent retention and high permeate flux are observed due to the low binding of metals to complexing agent polymers at low pH values.

For 1×10^{-4} M Cd(II) solutions the maximum percent retentions were found as 80% in this work by using 0.50 (w/v)% AA/cellulose composite membranes when the filtration was carried out in the presence of AA at pH of 7.0, a pressure of 10 kPa, and a flow velocity of 100 mL/min.

Filtration of Fe(III), Cu(III), Cd(III) Mixture in the Presence of AA

The percent retention and permeate flux of individual metal ions and in the mixture for AA enhanced cross flow filtration were shown in Fig. 8. All of the metal ion concentrations were 1×10^{-4} M and AA concentration was kept constant as 2×10^{-4} repeating unit weight (g/L) in the study.

The maximum percent retention of Fe(III), Cu(II), and Cd(II) for single metal ions were found as 98%, 71%, 80%, respectively in the presence of AA. However, in the mixture these values were found as 89%, 96%, 98% respectively in the presence of AA for membrane II at pH 7. It is reflected from the results, AA enhanced cross-flow filtration through alginic acid–cellulose composite membranes works also successfully for the retention of the ions in the mixture.

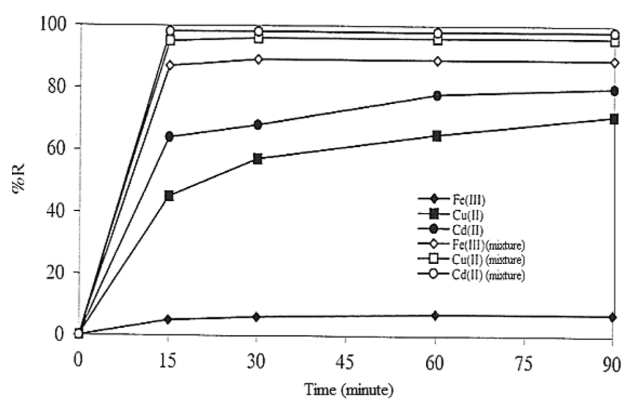

Figure 8. Comparasion of retention of Fe(III), Cu(II), Cd(II) ions individually and with in the mixture. (pH = 7.0, Velocity = 100 mL/min., P = 10 kPa, Membrane II, $C_{Fe(III)} = C_{Cu(II)} = C_{Cd(II)} = 1 \times 10^{-4}$ M, $C_{AA} = 2 \times 10^{-4}$ unit weight (g/L)).

CONCLUSION

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

The effects of AA content of membrane and pH on permeate flux and percent retention were studied for Fe(III), Cu(II), and Cd(II) solutions in the presence of AA. As the AA content in the membrane and the pH of solution increased the permeate flux decreased, and the percent retention either increased or first increased and then reached a constant value.

The maximum percent retention was found as 98% for 1×10^{-4} M Fe(III) solution at the flow velocity of 100 mL/min, pH of 3.0, and a pressure of 60 kPa in the presence of AA as complexing agent by using 0.25 (w/v)% AA/cellulose composite membranes at pH 3. For 1×10^{-4} M Cu(II) and Cd(II) solutions the maximum percent retentions were found as 71% and 80% 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 AA as complexing agent. This method also works successfully for the mixture of 1×10^{-4} M Fe(III), Cu(II) and Cd(II) ions giving the retentions of 89%, 96%, 98% respectively in the presence of AA for membrane II at pH 7.

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