Crossflow Filtration of Iron(III), Copper(II), and Cadmium(II) Aqueous Solutions with Alginic Acid/Cellulose Composite Membranes

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ABSTRACT: The removal of Fe(III), Cu(II), and Cd(II) ions from aqueous solutions was investigated with a crossflow filtration technique. Alginic acid (AA)/cellulose composite membranes were used for retention. In the filtration of Fe(III) solutions, the effects of the crossflow velocity, applied pressure, AA content of the membranes, and pH on the retention percentage and the permeate flux were examined. The maximum retention percentage was found to be 89% for a 1×10^{-4} M Fe(III) solution at the flow velocity of 100 mL/min and the pressure of 60 kPa with 0.50% (w/v) AA/cellulose composite membranes at pH 3. Aqueous solutions of Cu(II) and Cd(II) were filtered at the flow velocity of 100 mL/min and pressure of 10 kPa. The effects of the AA content of the membranes and pH of the waste medium on the retention percentage and the permeate flux were determined. For 1×10^{-4} M Cu(II) and Cd(II) solutions, the maximum retention percentages were found to be 94 and 75%, respectively, at pH 7 with 0.50% (w/v) AA/cellulose composite membranes. When metal-ion mixtures were used, the retention percentages of Fe(III), Cu(II), and Cd(II) were found to be 89, 48, and 10%, respectively, at pH 3 with 0.50% (w/v) AA/cellulose composite membranes. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 616–623, 2010

Key words: composites; membranes; waste

INTRODUCTION

Membrane technology can be used in a large number of separation processes. Reverse osmosis filtration and nanofiltration membranes have been used in the treatment of wastewater containing Mn(II) and Fe(II).[1,2] In a study by Gzara and Dhahbi,[3] commercial polysulfone membranes were used in recovering chromium(VI) by ultrafiltration. Chang and Hwang[4] used a crossflow microfiltration technique for the removal of metal ions from liquid solutions. Crossflow filtration is used to reduce the formation of sublayers on membranes due to the flow of the feed solution tangential to the membranes.[5–8]

Some of the properties of membranes affecting separation are their chemical nature and surface morphology.[5] Solution components have been separated into retentate and permeate components. The retention of a component by a membrane depends on many parameters such as the pH, membrane pore size, and membrane material.[9]

Membranes have been made from numerous materials, such as cellulose derivatives,[10] polysulfone,[11] and polysaccharide.[12] Composite membranes have been made to combine the advantages of polymers.[13] To develop an affinity membrane with good mechanical and chemical properties for large-scale affinity purification, Yang et al.[14] prepared chitosan/cellulose composite membranes. Alginic acid (AA) is a biopolymer carrying carboxyl groups capable of forming complexes with metal ions.[15] AA has been used in controlled release, ion exchange, and vapor permeation membrane separation.[16] Alginate membranes crosslinked with glutaraldehyde have been used to separate ethanol–water mixtures because the water molecules easily adsorb into hydrophilic alginate membranes.[17]

Heavy metals such as copper, lead, and cadmium, discharged into the environment through different industrial processes, are hazardous to the environment and health. The problems associated with heavy metals in the environment are their accumulation in the food chain and their persistence in nature.[18] These aspects result in a health hazard. To reduce heavy-metal pollution, heavy metals in the environment must be removed by processes such as adsorption, chemical precipitation, and membrane technology.[19] Membrane separation processes can

TABLE I
Physical Properties of the Filter Paper Used as a Support

Type	Filtrak grade 391 (blue band)
Diameter (cm)	12.5
Thickness (cm)	0.0135
Weight (mg/piece)	995
Volume (mL)	1.656

reduce the amounts of heavy metals with a low energy requirement.[20]

In this study, AA/cellulose composite membranes were used for the removal of single ions and mixtures of Fe(III), Cu(II), and Cd(II) ions from aqueous solutions by crossflow filtration. The effects of the applied pressure, crossflow velocity, AA content of the membranes, and pH on the permeate flux and retention percentage were investigated.

EXPERIMENTAL

Materials

AA was supplied by Sigma (St. Louis, MO) as a sodium salt (medium viscosity). Cellulose as filter paper was acquired from Filtrak; (Niederschalag, Germany) the physical properties are listed in Table I. $FeCl_3 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $CdCl_2 \cdot H_2O$, HCl, KSCN, and NH_3 were all Merck (Darmstadt, Germany) products.

Preparation of the membranes

Aqueous solutions with sodium alginate concentrations of 0.25, 0.50, and 0.75% (w/v) were prepared. Then, a 40-mL AA solution was poured onto cellulose filter paper placed on a glass plate (9 cm × 14 cm), and the casting solvent (water) was allowed to evaporate completely at 60°C. The membranes were then immersed in 1M HCl for 24 h.[21]

Experimental apparatus and the filtration of solutions

Feed solutions (500 mL) with predetermined ion concentrations and different pH values were prepared. pH adjustments were made with 0.1M NH_3 and 0.1M HCl solutions. Membranes were placed into the

filtration cell (area = 30 cm^2). Then, the feed solutions were pumped through a crossflow filtration unit (Millipore, Bedford, MA) at a predetermined velocity and pressure. The permeate and retentate were returned to the feed tank for circulation. During the filtration, 3.5-mL filtrate samples were collected at different time intervals for the analysis of the metal concentrations. For the crossflow filtration of the solution, the effects of the crossflow velocity, applied pressure, AA content of the membranes, and pH on the retention percentage and the permeate flux were investigated.

Analysis

Fe(III) concentrations were determined spectrophotometrically (model 20D, Spectronic, Rochester, NY); 0.1 mL of 0.1M HCl and 0.1M KSCN was added to the 3.5-mL filtrate samples, and the absorbance of the red complex was measured at 456 nm. Cu(II), Cd(II), and metal-ion concentrations in the mixtures were determined with an atomic absorption spectrophotometer (PU 9285, Philips, Eindhoven, The Netherlands).

Scanning electron microscopy

The morphology of the composite membranes was observed with scanning electron microscopy. The dried membrane specimen was coated with gold powder before scanning. The magnification was 3000×.

Measurement of the permeate flux and retention percentage

The permeate flux was determined by the collection of the filtrate in a graduated cylinder at a specific time interval. Retention values were calculated with the following formula:

$$\text{Retention}(\%) = (1 - C_p/C_f) \times 100 \qquad (1)$$

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

Sorption capacity

The crosslinked membranes were immersed into water. The swollen membranes were wiped with cleaning tissue as quickly as possible only for the

TABLE II
Properties of the Membranes

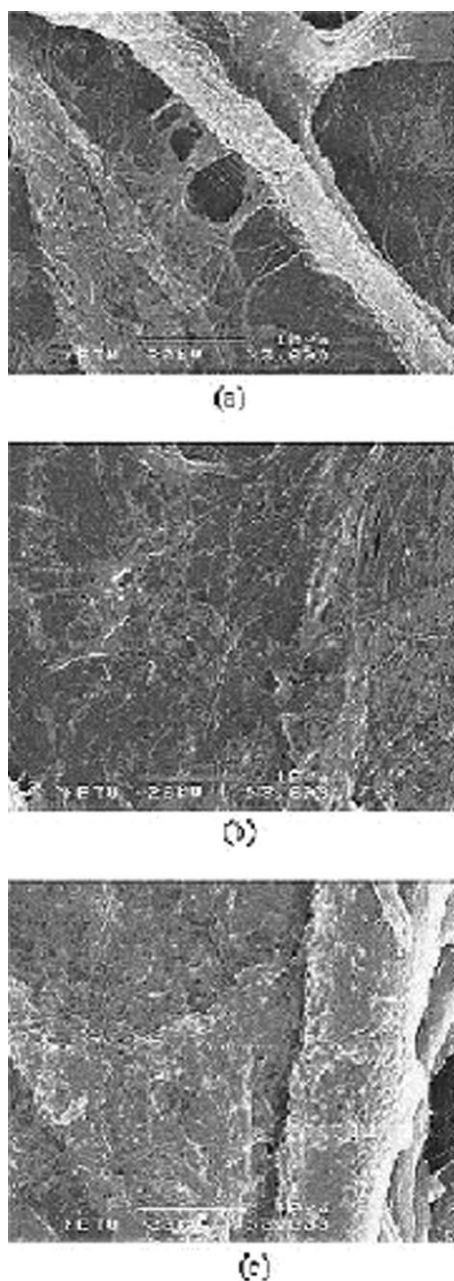| Membrane	AA [% (w/v)]	AA/cellulose filter (g/g)	Thickness (μm)	Sorption capacity [% (w/w)]
Cellulose filter	—	—	135	159
I	0.25	0.101	140	134
II	0.50	0.150	145	129
III	0.75	0.209	150	118

Figure 1 Scanning electron micrographs of the composite membranes prepared via coating with different AA concentrations: (a) membrane I [0.25% (w/v) AA/cellulose], (b) membrane II [0.50% (w/v) AA/cellulose], and (c) membrane III [0.75% (w/v) AA/cellulose]. The magnification is 3000×.

removal of the excess water and then weighed as quickly as possible. Then, the membranes were dried at 60°C until a constant weight was obtained. The swelling degrees of the membranes were calculated as follows:

$$\text{Swelling degree} = (W_S/W_D - 1) \times 100 \qquad (2)$$

where W_D and W_S are the masses of the membranes before and after swelling, respectively.

RESULTS AND DISCUSSION

Characterization of the membranes

The AA contents, thicknesses, and water contents of the membranes are shown in Table II. The amount of AA in the composite membranes and the thickness of the membranes increase and the water contents of the membranes decrease with the AA concentration of the coating solutions increasing. Figure 1 presents the morphologies of composite membranes made with solutions of different AA concentrations. As the concentration of the AA solution increases, the pore size of the surface of the cellulose filter decreases (Fig. 1). Because the original pores on the cellulose support are blocked by much more AA, very little AA is coated onto the cellulose by a 0.25% AA solution, and a large amount of AA is coated onto the cellulose by 0.50 and 0.75% AA solutions (Table II). Fewer pores can be observed on the 0.75% membrane, and fewer pores lead to a lower flow rate of the solution through the membrane.

Similar results were obtained by Yang et al.[14] They reported that the flux of membranes based on chitosan on a cellulose support decreased as the concentration of the chitosan solution increased because
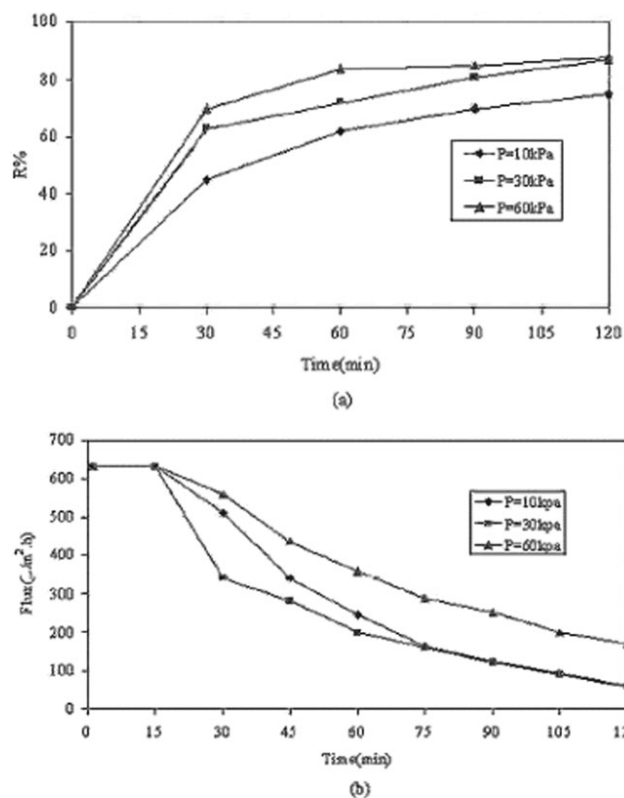

Figure 2 Effect of the applied pressure (*P*) on (a) the retention percentage (*R*%) and (b) flux of Fe(III) solutions [Fe(III) concentration = 1×10^{-4} *M*, velocity = 30 mL/min, pH = 3.0, membrane II].
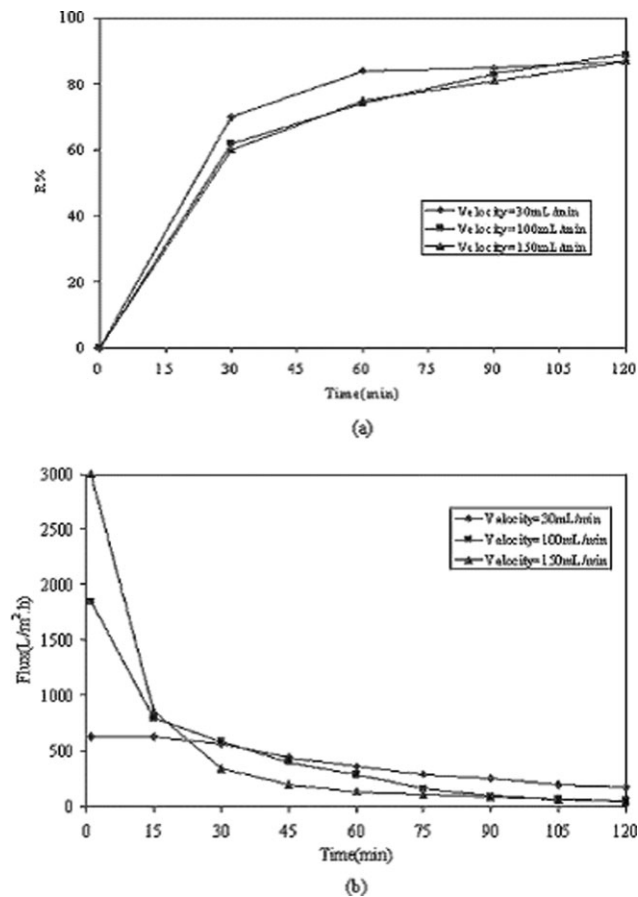
(a)

(b)

Figure 3 Effect of the crossflow velocity on (a) the retention percentage ($R\%$) and (b) flux of Fe(III) solutions [Fe(III) concentration = 1×10^{-4} M, pressure = 60 kPa, pH = 3.0, membrane II].

the original pores of the cellulose support were blocked.

Filtration of Fe(III) solutions

The effect of the applied pressure on the retention percentage and permeate flux of Fe(III) solutions is shown in Figure 2. The applied pressures were 10, 30, and 60 kPa. The initial permeate flux for membrane II is the same at different applied pressures because there is no effective cake formation at the beginning of filtration. On the other hand, the retention percentage ratio of Fe(III) ions first increases sharply and slows with increasing applied pressure. As the pressure increases, the retention is increased, probably because of cake formation on the membrane, which produces an additional barrier for filtration. The hydrolysis of Fe(III) starts at pH 3 and causes cake formation. At a high pressure, a high retention ratio can be seen (Fig. 2), probably because of the high cake formation, which contains more Fe(III).

The effects of the velocity on the retention percentage of Fe(III) and permeate flux with crossflow

velocities of 30, 100, and 150 mL/min are shown in Figure 3. At the same pressure, the initial permeate flux increases with increasing crossflow velocity because there is no effective cake formation at the beginning of the filtration. As shown in Figure 3, the effect of the crossflow velocity on the permeate flux and retention percentage is not significant.

The effect of pH was studied at three different pH values: 2.0, 2.5, and 3.0. As shown in Figure 4, the retention percentage of Fe(III) ions decreases with decreasing pH. At low pH values, the high H^+-ion concentration at the interface electrostatically repels positively charged Fe(III) ions, preventing their approach for adsorption onto the membrane surface. The permeate flux decreases with increasing pH, probably on account of cake formation on the membrane, because the hydrolysis of Fe(III) starts at pH 3.

Similar results concerning the effect of pH on the retention percentage and permeate flux have been reported in the literature.[4,22]

Şolpan and Şahan[22] studied the separation of Cu(II) and Ni(II) from Fe(III) ions by complexation with AA and with a suitable membrane. They
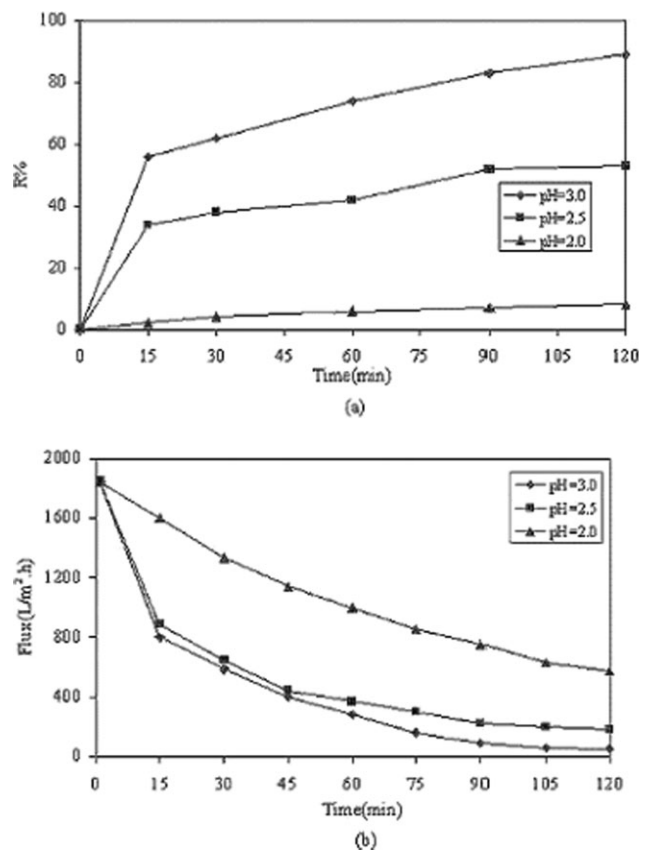

(a)

(b)

Figure 4 Effect of pH on (a) the retention percentage ($R\%$) of Fe(III) and (b) flux [Fe(III) concentration = 1×10^{-4} M, pressure = 60 kPa, velocity = 100 mL/min, membrane II].
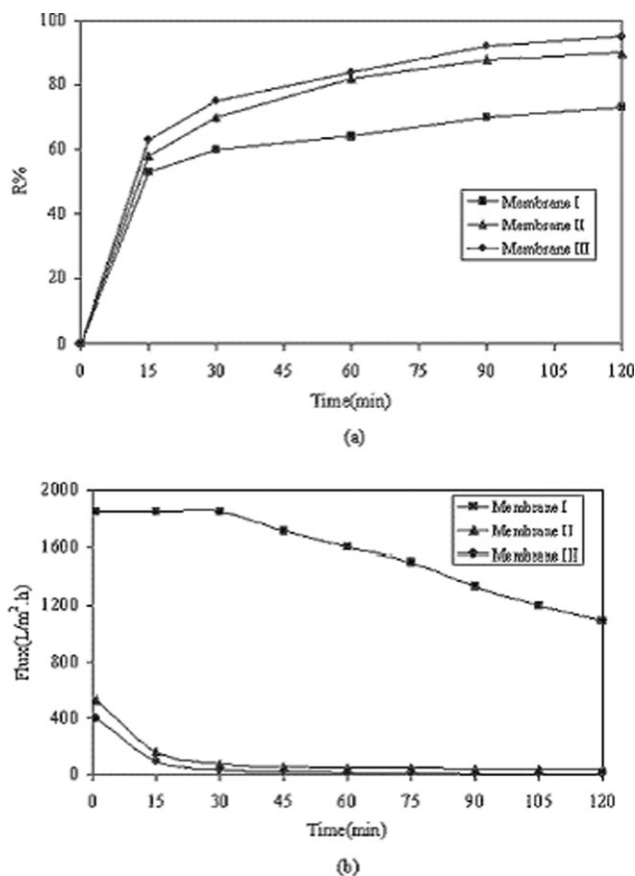
Filtration of Cu(II) solutions

The dependence of the permeate flux and retention percentage on the AA content of the membrane is presented in Figure 6. With the AA content of the membrane increasing, the permeate flux decreases, whereas the retention percentage increases similarly to the filtration of Fe(III) solutions and to filtration in the literature.

Jegal et al.[24] reported that the flux through a membrane based on poly(vinyl alcohol)/sodium alginate on a polysulfone support increased as the active layer thickness decreased.

The permeate flux and retention percentage as a function of pH were studied at pHs 3, 6, and 7, and the results are presented in Figure 7. An increase in the pH reduces the permeate flux but increases the retention percentage.

Asman and Şanlı[25] studied the ultrafiltration of Fe(III) solutions in the presence of poly(vinyl alcohol) with modified poly(methyl methacrylate-co-methacrylic acid) membranes. They concluded that retention was low because of the mostly un-ionized poly(methacrylic acid) units of the membrane at low pH values.

For a 1×10^{-4} M Cu(II) solution, the maximum retention percentage was found to be 94% at the

Figure 5 Effect of the AA content of the membrane on (a) the retention percentage (R%) of Fe(III) and (b) flux [Fe(III) concentration $= 1 \times 10^{-4}$ M, pressure $= 10$ kPa, velocity $= 100$ mL/min, pH $= 3.0$].

concluded that as the pH increased, the retention of metallic ions increased.

Chang and Hwang[4] investigated the removal of metal ions from liquid solutions by crossflow micro-filtration. They observed that the permeate flux for crossflow microfiltration increased as the pH of the solutions increased.

The effect of the AA content of the membrane on the retention percentage and the permeate flux is shown in Figure 5 for membranes I, II, and III. Figure 5 shows that as the AA content of the membrane increases, a significant decline in the permeate flux and an increase in the retention percentage can be observed.

Similar results were obtained by Elyashevic et al.[23] They reported that an increase in a polyacrylonitrile layer on a porous polyethylene microfiltration film led to the lowering of the permeation rate through the composite membrane.

The maximum retention was found to be 89% for a 1×10^{-4} M Fe(III) solution at the flow velocity of 100 mL/min and pressure of 60 kPa with 0.5% (w/v) AA cellulose composite membranes at pH 3.

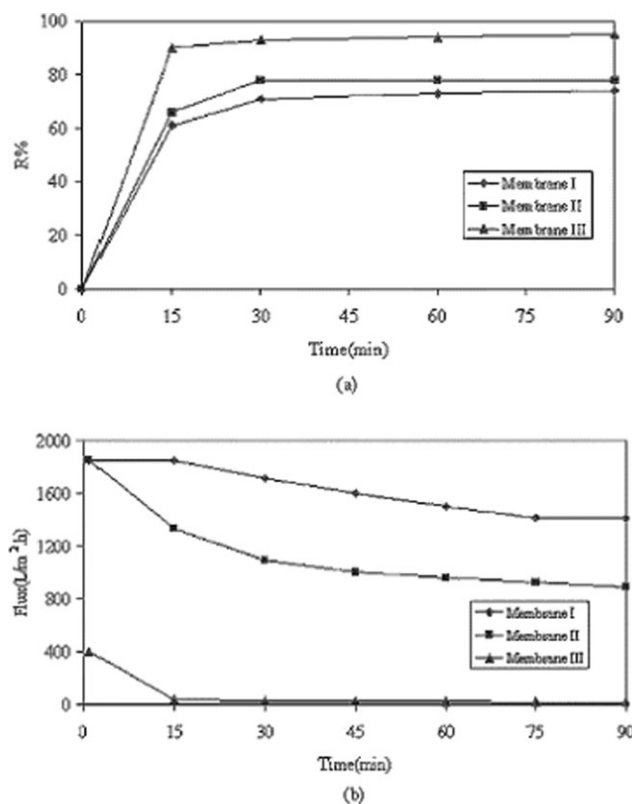**Figure 6** Effect of the AA content of the membrane on (a) the retention percentage (R%) of Cu(II) and (b) flux [Cu(II) concentration $= 1 \times 10^{-4}$ M, velocity $= 100$ mL/min, pH $= 6.0$, pressure $= 10$ kPa].
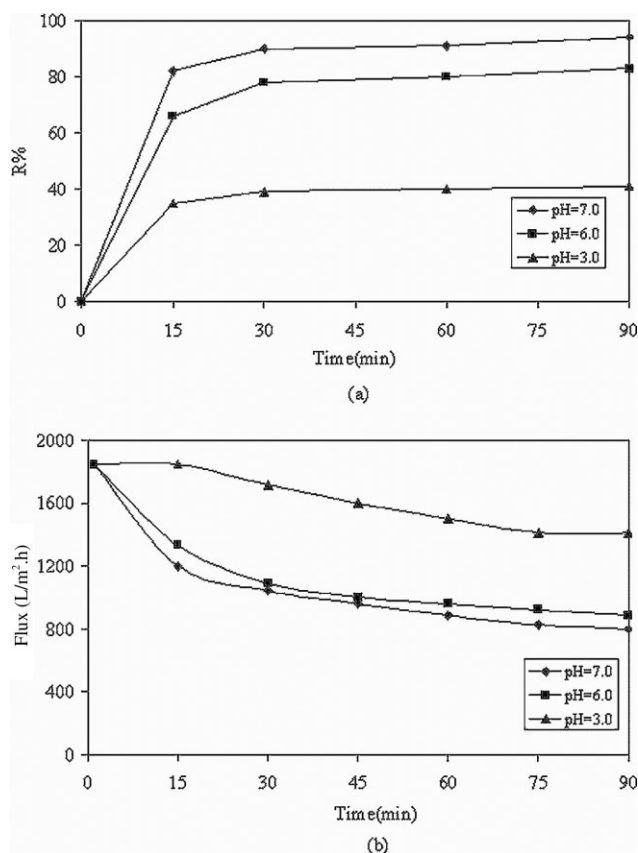
Figure 7 Effect of pH on (a) the retention percentage ($R\%$) of Cu(II) and (b) flux [Cu(II) concentration $= 1 \times 10^{-4}$ M, velocity $= 100$ mL/min, pH $= 6.0$, pressure $= 10$ kPa, membrane II].

velocity of 100 mL/min and pressure of 10 kPa with 0.5% (w/v) AA/cellulose composite membranes at pH 7.

Filtration of Cd(II) solutions

The effect of the AA content of the membrane on the retention percentage and the permeate flux is shown in Figure 8. Membranes I, II, and III were used to study the effects of the AA content of the membranes on the retention percentage of Cd(II) and permeate flux similarly to Fe(III) and Cu(II).

Similar results have been reported in the literature. Jegal et al.[26] reported that the flux of membranes based on poly(vinyl alcohol)/sodium alginate on a polysulfone support decreased on account of the blocking of polysulfone pores with much more poly(vinyl alcohol)/sodium alginate as the concentration of the poly(vinyl alcohol)/sodium alginate solution increased.

Shown in Figure 9 is the effect of pH on the permeate flux and retention percentage at pHs 3, 6, and 7. As reflected in the figure, first the permeate flux decreases and the retention percentage increases, and then both the permeate flux and retention percentage level off with increasing pH.

Demirata Ozturk et al.[27] investigated the preconcentration of copper ions in an aqueous phase on methacrylate polymers. They observed low retention values at low pH values.

For a 1×10^{-4} M Cd(II) solution, the maximum retention percentage was found to be 75% with 0.5% (w/v) AA/cellulose composite membranes at pH 7.

Filtration of Fe(III), Cu(II), and Cd(II) mixtures

The retention percentage and permeate flux of metal-ion mixtures and single metal ions at pH 3 are shown in Figure 10. The retention percentages of Fe(III), Cu(II), and Cd (II) are 88, 41, and 28%, respectively, for single metal ions and 89, 48, and 10%, respectively, for metal-ion mixtures at pH 3. The retention percentage of Fe(III) is not affected, the retention percentage of Cu(II) increases, and the retention percentage of Cd(II) decreases in the presence of the other metal ions. The retention percentage of Fe(III) is higher than those of Cu(II) and Cd(II) ions in mixtures of ions because of the high ionic valence number of Fe(III). For the same ionic valence number, the retention percentage of Cu(II) is higher than that of Cd(II) because of the smaller
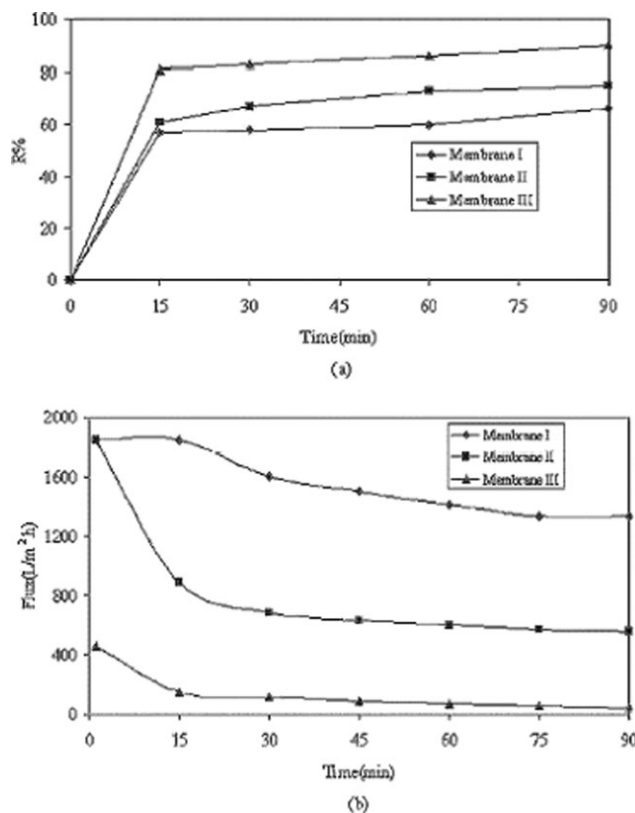

Figure 8 Effect of the AA content of the membrane on (a) the retention percentage ($R\%$) of Cd(II) and (b) flux [Cd(II) concentration $= 1 \times 10^{-4}$ M, velocity $= 100$ mL/min, pH $= 7.0$, pressure $= 10$ kPa].
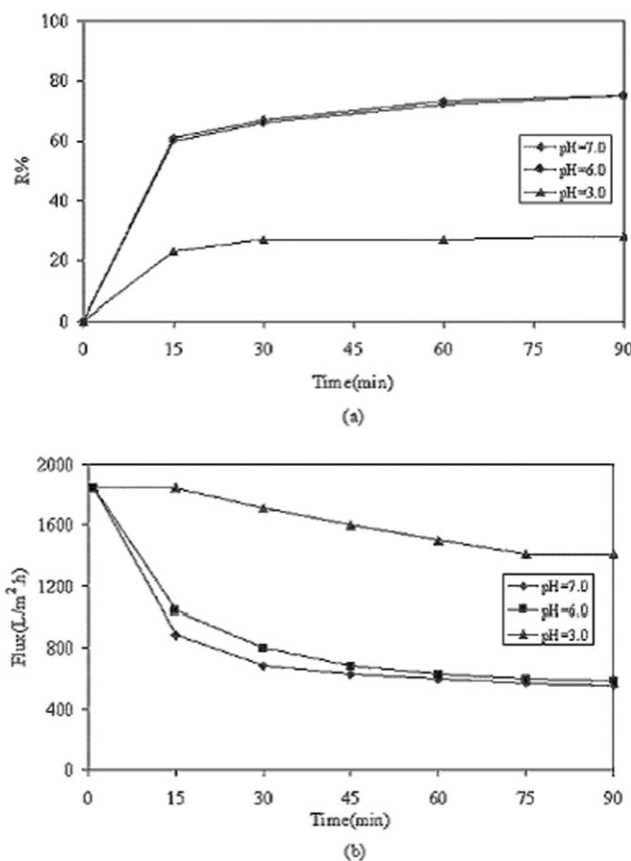
Figure 9 Effect of pH on the retention percentage (R%) of Cd(II) and (b) flux [Cd(II) concentration = 1 × 10⁻⁴ M, pressure = 10 kPa, velocity = 100 mL/min, membrane II].

ionic radius of Cu(II). The permeate flux of metal-ion mixtures becomes lower than that of single metal ions because of high cake formation on the membrane. Because the total ion concentration is high for the mixture of ions, high cake formation on the membrane occurs.

Choo et al.[28] studied iron and manganese removal and membrane fouling during ultrafiltration in conjunction with perchlorination for drinking water treatment. They concluded that manganese and iron particles offer a relatively low specific resistance in the cake in comparison with their mixtures.

CONCLUSIONS

In this study, AA/cellulose composite membranes were used for the crossflow filtration separation of single ions and mixtures of Fe(III), Cu(II), and Cd(II) ions from aqueous solutions.

The effects of the applied pressure and crossflow velocity on the retention percentage and permeate flux were investigated for Fe(III) solutions. The retention percentage ratio of Fe(III) ions first increased sharply, and then the increase slowed

with increasing applied pressure. The effects of the crossflow velocity on the permeate flux and retention percentage were found to be insignificant.

The effects of the AA content of the membrane and pH on the permeate flux and retention percentage were studied for Fe(III), Cu(II), and Cd(II) solutions. As the AA content of the membrane and the pH of the solution increased, the permeate flux decreased, and the retention percentage increased.

The maximum retention percentage was found to be 89% for Fe(III) solutions at the crossflow velocity of 100 mL/min and pressure of 60 kPa with 0.5 (w/v) AA/cellulose composite membranes at pH 3.

For Cu(II) and Cd(II) solutions, the maximum retention percentages were found to be 94 and 75%, respectively, at the flow velocity of 100 mL/min and pressure drop of 10 kPa with 0.5 (w/v) AA/cellulose composite membranes at pH 7.

The retention percentages of Fe(III), Cu(II), and Cd(II) for mixtures of metals were found to be 89, 48, and 10%, respectively, with 0.5 (w/v) AA/cellulose composite membranes at pH 3.
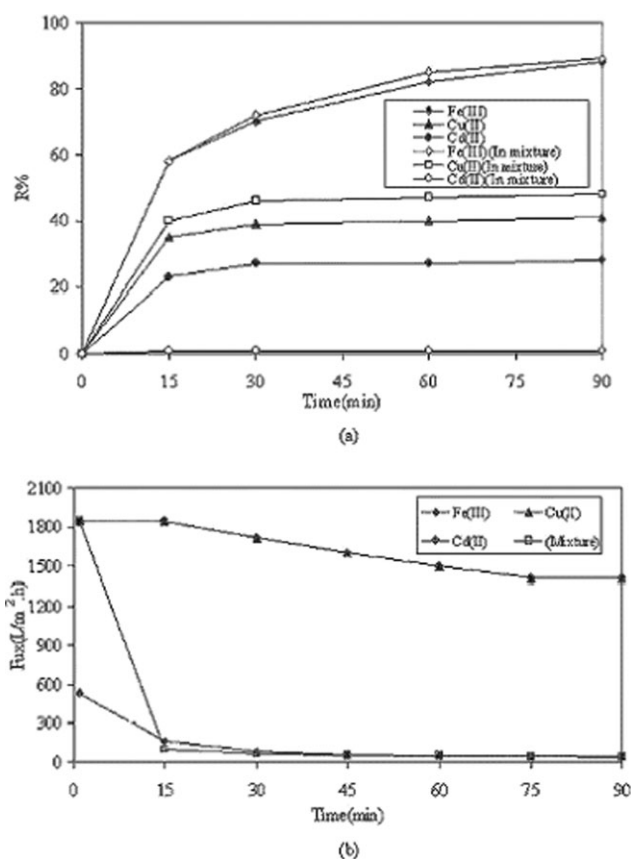

Figure 10 (a) Retention percentage (R%) and (b) flux of metal-ion mixtures and single metal ions [pH = 3.0, velocity = 100 mL/min, pressure = 10 kPa, membrane II, Fe(III) concentration = Cu(II) concentration = Cd(II) concentration = 1 × 10⁻⁴ M].

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