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Removal of heavy metal ions from aqueous solutions by poly(methyl methacrylate-co-ethyl acrylate) and poly(methyl methacrylate-co-buthyl methacrylate) membranes

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ABSTRACT

This study deals with the removal of Fe(III), Cu(II) and Co(II) ions from dilute aqueous solutions by using batch equilibration technique. Poly(methyl methacrylate-co-ethyl acrylate) and poly(methyl methacrylate-co-butyl methacrylate) membranes were used for adsorption of metal ions from aqueous solutions. The effects of contact time, pH and concentration of metal ions on the adsorption properties of membranes were studied. As the pH of solution and initial concentration of metal ions increased, the adsorption of metal ions on the membranes also almost increased in our studies. Adsorption equilibrium was reached in about 120 min for Fe(III) ions and 75 min for Cu(II) and Co(II) ions. The maximum adsorption of metals was found as 2.56 mmol/m^2 for 1×10^{-3} Cu(II) solutions at pH of 6.0 by using poly(methyl methacrylate-co-ethyl acrylate) membrane. All adsorption values were provided by the Langmuir adsorption isotherm model.

Keywords: Adsorption; Poly(methyl methacrylate-co-ethyl acrylate); Poly(methyl methacrylate-co-butyl methacrylate); Membrane

1. Introduction

Heavy metals are discharged into environment through different industrial processes. Heavy metals such as nickel, lead, cadmium and copper in wastewater are hazardous to the environment. In order to reduce heavy metal pollution problem, heavy metals in the environment are removed by some processes such as adsorption, chemical precipitation and membrane processes [1].

Adsorption process has been considered as important separation technique because of its simple processing. Traditional adsorbents have been designed in particle forms in adsorption process. When particle form adsorbents are applied in batch operation, filtration is generally required for removing them from liquid solution. Nowadays, membranes have been used to remove heavy metals from effluents with many advantages [2]. Several advantages of membranes are large surface area, easily removable from fluid without extra filtration, low pressure drop and short diffusion path for adsorption [3–8].

Membranes have been used for separation of species from mixture [9]. Some of the properties of the membranes affecting the separation are their chemical nature, surface morphology and presence of charge [10]. Membranes have been made from different materials such as polysulfone [11], polysaccharide [12], and cellulose derivatives [13]. In order to combine advantages of some polymers, composite membranes have been made. Chitosan/cellulose composite membranes were made for developing an affinity of membrane with good mechanical and chemical properties [14]. Sodium alginate was blended with flexible polymer poly(vinyl alcohol) (PVA) to reduce the relaxation taking place during pervaporation [15].

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Poly(methyl methacrylates) have some properties such as chemical stability and mechanical strength, and they have been used for the development of membranes and application in separation techniques [16]. Poly(methyl methacrylate-co-ethyl acrylate) P(MMA-co-EA) and poly(methyl methacrylate-co-butyl methacrylate) P(MMA-co-BMA) chains contain carbonyl groups to provide interaction between metals and polymers [17]. In this study, P(MMA-co-EA) and P(MMA-co-BMA) membranes were prepared, and used in batch equilibration technique for removal of Fe(III), Cu(II) and Co(II) ions from aqueous solutions. The effects of contact time, pH and concentration of metal ions on the adsorption were investigated.

2. Experimental

2.1. Material

P(MMA-co-EA) with molecular weight of 101,000 and P(MMA-co-BMA) with molecular weight of 75,000 were supplied from Aldrich. *N*,*N*-dimethyl formamide (DMF) was supplied from Fluka. Filter paper was purchased from Machery-Nagel (MN 640de, blue band). $FeCl_3 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $CoCl_2 \cdot 6H_2O$, HCl, NH_3 were all Merck products. Potassium thiocyanate and sodium diethyldithiocarbamate trihydrate were supplied from Riedel and Aldrich, respectively.

2.2. Preparation of membranes

The P(MMA-co-EA) membrane (MI) was prepared as follows: A 1 (w/v)% of P(MMA-co-EA) solution was prepared in DMF. Then 10 ml of casting solution was poured in a Petri dish (6.7 cm, diameter) and allowed the casting solvent to evaporate completely at 30°C for 96 h. Membranes were then immersed in a bath of pure water for 1 h at room temperature.

P(MMA-co-BMA) membrane (MII) was prepared as follows: A 1 (w/v)% of P(MMA-co-BMA) solution was prepared in DMF. Then 10 ml of casting solution was poured in a Petri dish (6.7 cm, diameter) and allowed the casting solvent to evaporate completely at 50°C for 19 h. Membranes were then immersed in a bath of pure water for 1 h at room temperature.

The membranes were cut into pieces of 15 cm^2 area for further uses. Properties of P(MMA-co-EA) and P(MMA-co-BMA) membranes are shown in Table 1.

2.3. Scanning electron microscopy

The morphology of the membranes was observed by scanning electron microscopy (SEM) (LEO 1430VP). The dried membranes were coated with gold powder before scanning. Fig. 1 presents the morphologies of our homogeneous membranes.

2.4. Batch adsorption experiments

Adsorption of Fe(III), Cu(II) and Co(II) ions from aqueous solutions was investigated in batch experiments. The pieces of membrane were placed into the 100 ml beaker. For each run the beaker was filled with the volume of 50 ml of metal ion solutions at desired ion and at different pH values. pH adjustments were made by using 0.1 M NH_3 and HCl solutions. The contents were stirred at known stirring rate for predetermined period of time at room temperature.

2.5. Analysis

After the desired treatment periods, the concentrations of the Fe(III) and Co(II) ions in the aqueous phase were determined with potassium thiocyanate and the

Table 1
Properties of the membranes (for one piece)

Membrane	Content of membrane	Average thickness (μm)	Average weight (g)	Average surface area (cm^2)
MI	P(MMA-co-EA)	35	0.043	15
MII	P(MMA-co-BMA)	35	0.043	15

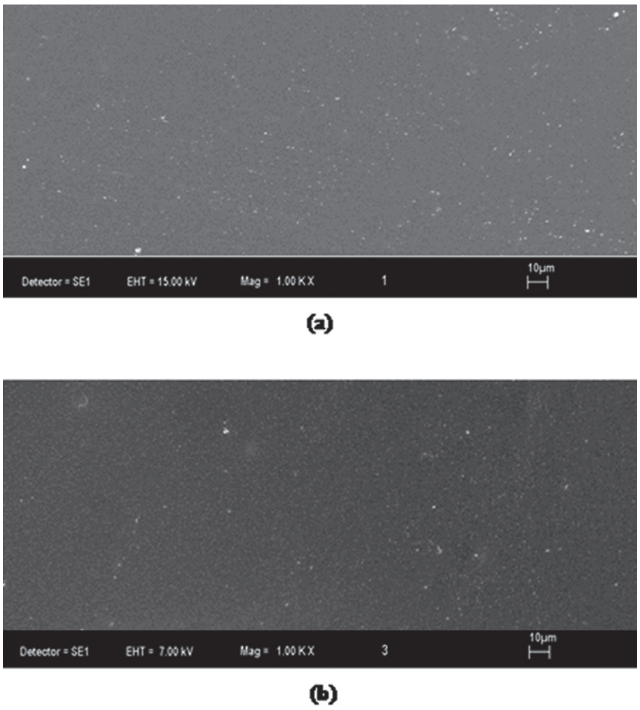

Fig. 1. SEM micrographs of the membranes (a) P(MMA-co-EA) membrane (b) P(MMA-co-BMA) membrane. Magnification: 1000 × 10 μm.

concentrations of Cu(II) ions in the aqueous phase were determined with sodium diethyldithiocarbamate trihydrate spectrophotometrically by using spectrophotometer (Shimadzu, 1700 Pharma).

2.6. Measurement of the adsorption capacity of the membranes

The amount of adsorption per unit surface area of the membranes was evaluated by using the following formula:

$$Q = [(C_0 - C)V] / A \qquad (1)$$

In this equation (Eq. (1)), Q is the amount of metal ions adsorbed onto unit surface area of the membranes (mmol/m^2), C_0 and C are the concentrations of the metal ions in the initial solution and in the aqueous phase after treatment for certain period of time, respectively (mmol/l), V is the volume of the aqueous phase (l) and A is the total surface area of the membranes used (m^2).

3. Results and discussion

3.1. Effect of contact time on adsorption

The relation between the nature of the polymer membrane and adsorption rate is generally complicated by many possible interaction on the surface of the membrane. Oxygen in the carbonyl groups of MI and MII membranes are responsible for the interaction of the metal ions with membranes. Since the mobile π electrons are pulled strongly towards oxygen, carbonyl carbon is electron-deficient, carbonyl-oxygen is electron rich and metals act as electron acceptors and taken up by coordination to the donor oxygen of the carbonyl groups of the polymer membranes [18].

Fig. 2 shows the contact time on adsorption of metal ions on membrane MI and MII. As seen from this figure adsorption rates increase rapidly at first, then the increasing of adsorption rates slow down and finally almost levels off. As the adsorption of metal ions on membranes occurs, the carbonyl groups of membranes blocked by metal ions, then the increasing of adsorption rates slow down and finally almost levels off. Adsorption equilibrium was reached in about 120 min for Fe(III) ions and 75 min for Cu(II) and Co(II) ions. A similar dependence on treatment time was obtained in the studies of other researchers with different adsorption equilibrium times for the metal ions and adsorbents under different conditions [4,18].

3.2. Effect of solution pH on adsorption of metal ions

Fig. 3 shows metal adsorption on membranes at different pH values. The effects of pH of solution were studied using different pH values which were 3.0, 4.0, 5.0 and 6.0. As it is seen from Fig. 3, as the pH increases adsorption of metal ions also increases. An increase in the adsorption by raising the pH of metal ions solution is the result of the high binding of metals to carbonyl groups of membranes. 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), Cu(II) and Co(II) ions and then relatively prevent the binding of metals to membranes. Similar results were obtained in DemirataOzturk et al.'s study [17]. They investigated preconcentration of copper ion in aqueous phase on methacrylate polymers.

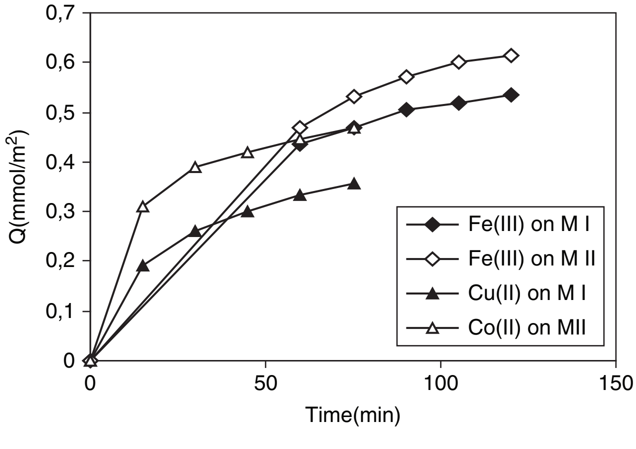

Fig. 2. Effect of contact time on adsorption of metal ions ($C_{Fe(III)} = C_{Cu(II)} = C_{Co(II)} = 1 \times 10^{-4}$ M, pH = 6.0, stirring rate 300 rpm; for Fe(III) on MI, Fe(III) on MII and Co(II) on MII, stirring rate 400 rpm; for Cu(II) on MI, piece of membrane 2; for Fe(III) on MI, Fe(III) on MII and Co(II) on MII, piece of membrane 3; for Cu(II) on MI).

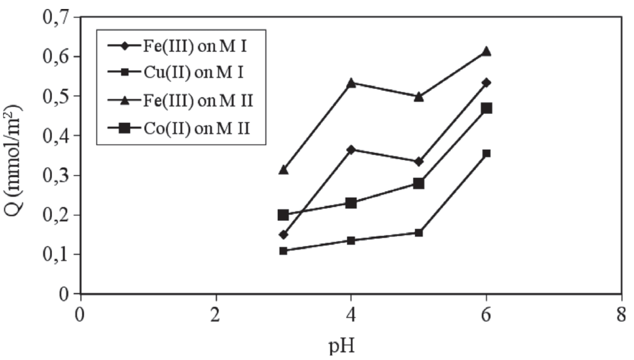

Fig. 3. Effect of pH on adsorption of metal ions ($C_{Fe(III)} = C_{Cu(II)} = C_{Co(II)} = 1 \times 10^{-4}$ M, stirring rate 300 rpm; for Fe(III) on MI, Fe(III) on MII and Co(II) on MII, stirring rate 400 rpm; for Cu(II) on MI, piece of membrane 2; for Fe(III) on MI and Fe(III) on MII, piece of membrane 3; for Cu(II) on MI).

They observed that low retention values at low pH values. Because at low pH values, the high H^+ ion concentration at the interface electrostatically repels positively charged metal ions and preventing their approach to the polymer surface.

3.3. *Effect of concentration of metal ions on adsorption*

The effect of initial concentration of metal ions on adsorption is shown in Fig. 4. Concentration of metal ions used were 0.1, 0.5 and 1.0 mmol/l, respectively. As the concentration of the metal ions increased, adsorption increased first rapidly then slowed down. The higher initial metal concentration provided a higher driving force to overcome all mass transfer resistance of metals between aqueous and membrane and also accelerated the probable collision between metal ion and membrane [19]. The relationship between the amount of metal adsorbed and the metal ion concentration in the aqueous solution is obtained by adsorption isotherms.

The Langmuir adsorption equation is described by the equation:

$$C / Q = 1 / Q_0 \cdot b + C / Q_0 \qquad (2)$$

In this equation (Eq. (2)), Q is the amount of metal ions adsorbed onto unit surface area of the membranes (mmol/m^2), Q_0 is the theoretical monolayer saturation capacity (mmol/m^2), C is the concentrations of the metal ions in the aqueous phase after treatment for certain period of time (mmol/l), and b is constant (L/mg).

The values of isotherm constants and correlation coefficients (R^2) were given in Table 2. According to these values and Fig. 5, our adsorption curves are fit Langmuir adsorption isotherm.

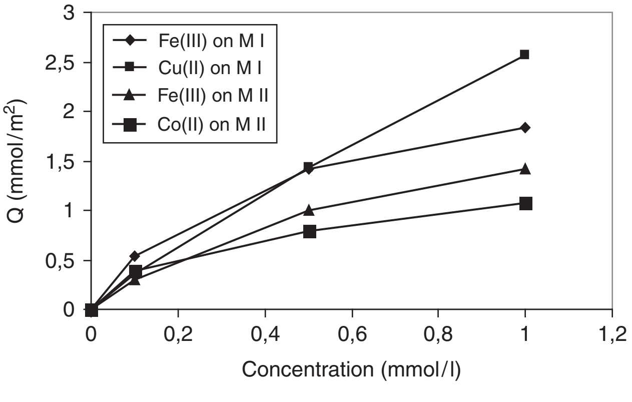

Fig. 4. Effect of concentration of metal ions on adsorption (pH = 6.0, stirring rate 300 rpm; for Fe(III) on MI, Fe(III) on MII and Co(II) on MII, stirring rate 400 rpm; for Cu(II) on MI, piece of membrane 2; for Fe(III) on MI, piece of membrane 3; for Cu(II) on MI, piece of membrane 4; for Fe(III) on MII and Co(II) on MII).

Table 2
Langmuir constants and correlation coefficients (R^2)

Adsorptions of metal ions on the membranes	Q_0 (mmol/m^2)	b (L/mg)	R^2
Co(II) on MII	1.3541	3.4704	0.9846
Fe(III) on MII	2.4067	1.6799	1.0000
Fe(III) on MI	2.5100	2.6649	0.9996
Cu(II) on MI	8.2034	0.4444	0.9668

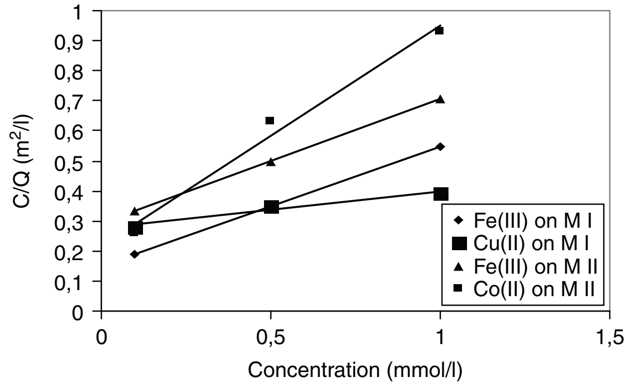

Fig. 5. Langmuir adsorption isotherms of metal ions on the membranes (pH = 6.0, stirring rate 300 rpm; for Fe(III) on MI, Fe(III) on MII and Co(II) on MII, stirring rate 400 rpm; for Cu(II) on MI, piece of membrane 2; for Fe(III) on MI, piece of membrane 3; for Cu(II) on MI, piece of membrane 4; for Fe(III) on MII and Co(II) on MII).

4. Conclusions

In this study, MI and MII membranes were prepared and used in the adsorption of metals from aqueous solutions. The effects of contact time, pH and concentration of metal ions on adsorption were studied for removal of Fe(III), Cu(II) and Co(II) metal ions from aqueous solutions by a batch equilibration technique. As the pH of solution and initial concentration of metal ions increased, the adsorption of metal ions on the membranes also increased.

Adsorption equilibrium was reached in about 120 min for Fe(III) ions and 75 min. for Cu(II) and Co(II) ions. The maximum adsorption of metals was found as 2.56 mmol/m^2 for 1×10^{-3} Cu(II) solutions at pH of 6.0 by using poly(methyl methacrylate-co-ethyl acrylate) membrane. All adsorption values were provided by the Langmur adsorption isotherm type.

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