Adsorption of Copper(II), Cobalt(II), and Iron(III) Ions from Aqueous Solutions on Poly(ethylene terephthalate) Fibers

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ABSTRACT: The adsorption behavior of poly(ethylene terephthalate) (PET) fibers towards copper(II), cobalt(II), and iron(III) ions in aqueous solutions was studied by a batch equilibriation technique. Influence of treatment time, temperature, pH of the solution, and metal ion concentration on the adsorption were investigated. Adsorption values for metal ion intake followed the following order: Co(II) > Cu(II) > Fe(III). One hour of adsorption time was found sufficient to reach adsorption equilibrium for all the ions. The rate of adsorption was found to decrease with the increase in the temperature. Langmuir adsorption isoterm curves were found to be significant for all the ions studied. The heat of adsorption values were calculated as −5, −2.8, and −3.6 kcal/mol for Cu(II), Co(II), and Fe(III) ions, respectively. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1935–1939, 1998

Key words: adsorption; fibrous adsorbant; poly(ethylene terephthalate) fibers; metal ions; industrial waste treatment

INTRODUCTION

The presence of heavy metals in the environment is a major concern due to their toxicities. Treatment of aqueous wastes containing soluble heavy metals requires concentration of the metals into a smaller volume, followed by recovery or secure disposal. For these reasons, development of analysis methods capable of determining trace amounts of such materials and removal of the impurities in any process have become an important subject of chemistry.

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Heavy metals can be removed by adsorption on solid matrices. Activated carbon, metal oxides, and ion exchange resins have been used as nonspecific adsorbants in the literature.[1,2] Recently, specific adsorbants[2–12] consists of chelating resins, carrier matrix, polymeric hydrogels, and microspheres have been considered for the selective extraction of metals from industrial wastes.

Lezzi et al.[3] synthesized chelating resins containing thiol groups as chelating functions from styrene–divinyl benzene copolymer grafted with various polyethylene glycols and reported that adsorption values for metal ions intake followed the following order: Ag(II) > Cu(II) > Pb(II).

Lezzi and Cobianco[4] used chelating resins supporting dithiocarbamate and methyl thiourea groups in the adsorption of heavy metal ions and found the order of metal adsorption for dithiocarbamate-supported resins to be Hg(II) > Pb(II) ≫ Cd(II) > Cu(II) and for methyl thiourea supported resins to be Hg(II) ≫ Cu(II) > Cd(II) ≫ Pb(II).

Kato et al.[5] prepared poly(1-vinyl imidazole) resin with Ni^{2+}, Co^{2+}, and Zn^{2+} as a template to study the adsorption of metal ions. Saraydin et al.[6] used acrylamide–maleic acid hydrogels for the adsorption of uranyl ions. Pişkin et al.[8] prepared dithiocarbamate incorporated monodisperse polystyrene microspheres for the adsorption of cadmium ion.

Membrane processes were also used for the concentration and removal of metal ions. Asman and Şanli[9] prepared methyl methacrylate-*co*-methacrylic acid membranes modified with polyethylene glycol and used in the ultrafiltration of Fe(III) solutions.

Studies concerning the use of fibrous materials for the adsorption of metal ions are limited. Kabay et al.[10] used acrylonitrile-grafted polypropylene fiber and polyethylene (PE) hollow fiber for the uptake of copper and uranyl ions from seawater. They have reported that polypropylene-based fibrous adsorbants achieved a rapid uptake for Cu(II) and uranyl ions. Saito et al.[11] also suggested a novel adsorption system using hollow-fiber adsorbants containing amidoxime groups by grafting of acrylonitrile onto PE hollow fiber.

PET fiber is one of the most important synthetic fiber used in the textile industry today. It possesses desirable properties, such as strength, resistance to stretch, and shrinkage. In this study, we have aimed to investigate the useability of PET fibers for the removal of Cu(II), Co(II), and Fe(III) ions from wastewater.

EXPERIMENTAL

Materials

Analytical grade reagents (Carlo-Erba) of ferric chloride ($FeCl_3 \cdot 6H_2O$), cobalt (II) chloride ($CoCl_2$), and cupric sulphate ($CuSO_4 \cdot 6H_2O$) were used without purification. pH values were controlled with $0.1M$ KCl–HCl, $0.1M$ CH_3COOH–CH_3COONa, and $0.1M$ KH_2PO_4–K_2PO_4 buffer solutions. Middle oriented PET fibers (126 denier, 28 filaments) used in this experiment were provided by SaSa co. of Adana, Turkey. The fiber samples were Soxhlet-extracted for 6 h with acetone and dried at ambient temperature before the adsorption experiments were carried out.

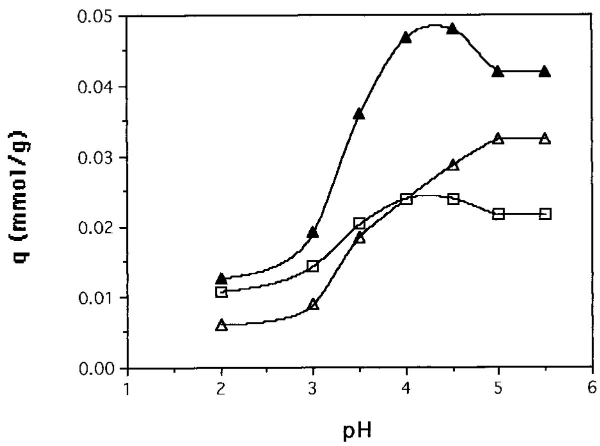

Figure 1 The pH dependence of (△) Cu(II), (▲) Co(II), and (□) Fe(III) ions adsorbed by PET fibers.

Adsorption Procedure

Volumes of 30 cm^3 of each of the metal ion solutions (0.4 mmol/L) adjusted to desired pH were added onto 0.1 g of PET fibers placed in 100-mL erlen-mayer. The contents were shaken at 200 rpm for a predetermined period of time at 298 K using an orbital shaker (Nuve Model, ST-402). After filtration of the solutions, the ion concentrations of the filtrates were determined spectrophotometrically with picric acid using a spectrophotometer (Ultraspec 2000 UV-VIS).

Adsorption capacity of the PET fibers were evaluated by using the following expression:

$$q = [(c_0 - c)V]/m$$

where q is the amount of ion adsorbed onto unit mass of the PET fiber (mmol/g), and c_0 and c are the concentration of the ion in the initial solution and in aqueous phase after treatment for a certain period of time, respectively (mmol/mL).

RESULTS AND DISCUSSION

The adsorption behavior of Cu(II), Co(II), and Fe(III) ions on the PET fibers at various pH values was investigated in the batch process at the following conditions: ion concentrations were 0.4 mmol/L, contact time was 4 h, and temperature was 298 K (Fig. 1). As is seen from

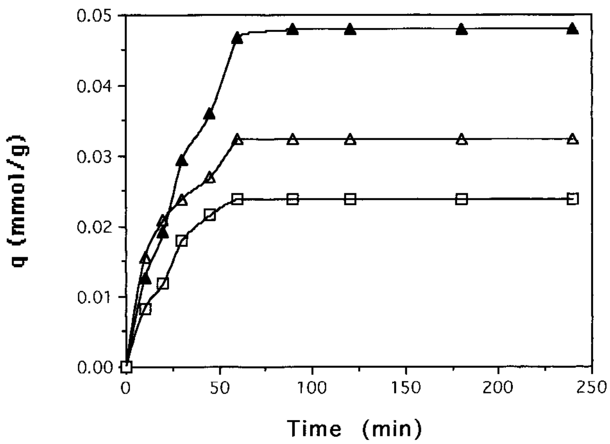

Figure 2 Effect of contact time on adsorption of (△) Cu(II), (▲) Co(II), and (□) Fe(III) ions (ion concentration = 0.4 mmol/L; temperature = 298 K).

Figure 1, adsorption increases up to certain pH values, then decreases. Optimum pH was found to be 4.0 for Co(II) and Fe(III) and 5.0 for Cu(II) ions. In the rest of the study, experiments were carried out at these pH values. At low pH values, the high H^+ ion concentration at the interface electrostatically repels positively charged metal ions, preventing their approach to the fiber surface. Low adsorption values observed at low pH values are in line with expectations. At high pH values, hydrolysis of metal ions or precipitation of hydroxides predominates. pH dependence of metal ion adsorption was also observed in the adsorption of Cu(II) ions on cellulose triacetate polymer containing α-hydroxy oxime groups[12] and in the concentration of Fe(III) ions by dextran.[13]

The time course of Cu(II), Co(II), and Fe(III) ions adsorption on the PET fibers is presented in Figure 2. Adsorption takes place rapidly at first, then slows down and levels off. The adsorption equilibrium was attained within 1 h. A similar dependence on treatment time was obtained in the studies of other researchers[5,14,15,16] with different adsorption equilibrium times for the ions and adsorbants under consideration. The results for the adsorption behavior indicated that the ability of adsorption of PET fibers decreased in the order of Co(II) > Cu(II) > Fe(III). However, according to the crystal field radii for these hexa coordinated metals, the expected order was Co(II) > Fe(III) > Cu(II).[17] Thus, the observed trend of adsorption does not correspond to the relative sizes of the metal ions. Sarkar et al.[18] also found in their study of the preconcentration of Cu(II), Ni(II), and Fe(III) with silica gel modified with salicyl adoxime that, although the crystal field radii for these metals follows the order of Co(II) > Fe(III) > Cu(II) > Ni(II) > Zn(II), the observed adsorption followed the order of Cu(II) < Zn(II) < Co(II) < Ni(II) < Fe(III).

The effect of ion concentration on adsorption was shown in Figure 3. It is clear from the figure that as the concentration of the ions increased, adsorption increased first rapidly, then slowed down, and adsorption saturation values were reached depending on the type of ion.

The relation between the nature of the polymer and sorption rate is generally complicated by many possible interaction on the surface. Oxygen in the carbonyl groups of the polyester are responsible for the interaction of the metal ions with the fiber. Since the mobile π electrons are pulled strongly towards oxygen, carbonyl carbon is electron-deficient, and 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. Uptake efficiency of PET fibers with 28 filaments provides a large surface area for the adsorption and may be suggested as a potential material for wastewater treatment, especially for Co(II) and Cu(II) ions. The adsorption curves for Co(II), Cu(II), and Fe(III) ions appeared to be the Langmuir type (Fig. 4). This suggested that the adsorption sites of PET fibers were one species.

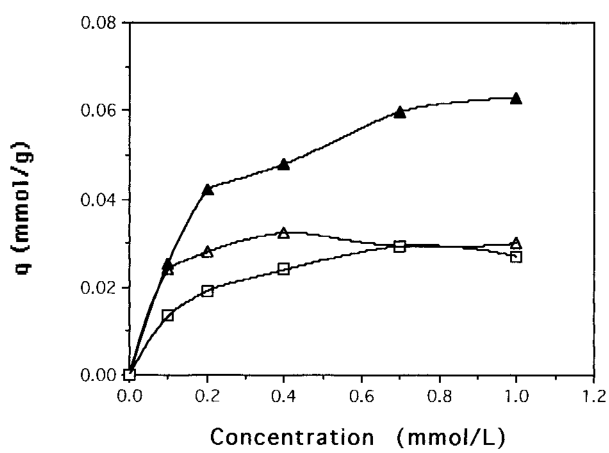

Figure 3 Effect of concentration of (△) Cu(II), (▲) Co(II), and (□) Fe(III) ions on adsorption (contact time = 1 h; temperature = 298 K).

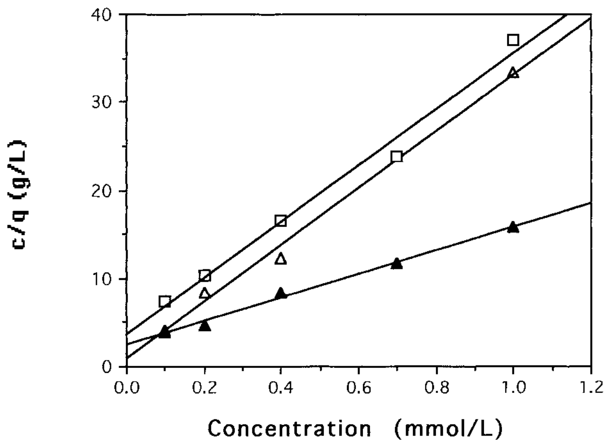

Figure 4 Adsorption isotherms of (△) Cu(II), (▲) Co(II), and (□) Fe(III) ions on PET fibers.

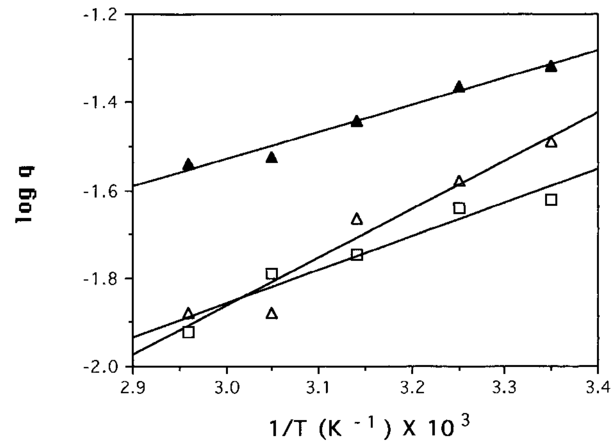

Figure 6 Log q versus to $1/T$ of (△) Cu(II), (▲) Co(II), and (□) Fe(III) ions.

It has been observed that the adsorption of metal ions from aqueous solution is affected by the temperature (Fig. 5) with the adsorption being decreased remarkably as the temperature increased. Using the data of Figure 5, Figure 6 was obtained, and the heat of adsorption values were found as −5.0, −2.8, and −3.6 kcal/mol for Cu(II), Co(II) and Fe(III), respectively. As it is reflected from the negative heat of adsorption values, adsorption is an exothermic process and is responsible for the reduction in adsorption as the temperature increased. Heat of adsorption values show that the physical adsorption take place in the adsorption of Cu(II), Co(II), and Fe(III) ions on PET fibers.

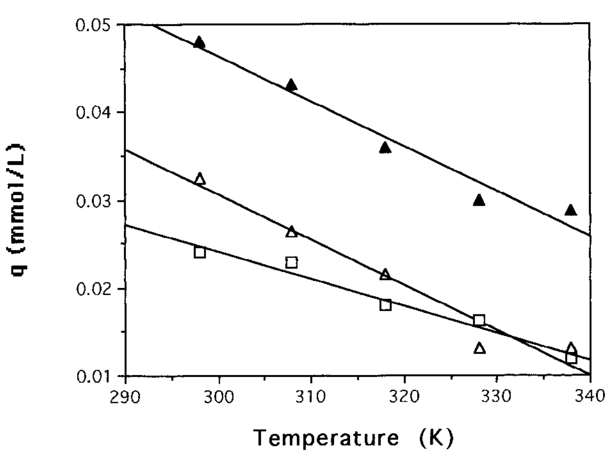

Figure 5 Effect of temperature on adsorption of (△) Cu(II), (▲) Co(II), and (□) Fe(III) ions (ion concentration = 0.4 mmol/L; contact time = 1 h).

CONCLUSIONS

1. The observed trend of adsorption was Co(II) > Cu(II) > Fe(III) in all the experiments fulfilled.
2. One hour of treatment time was found sufficient to reach adsorption equilibrium value.
3. A Langmuir type of adsorption was observed for Cu(II), Co(II), and Fe(III) ions.
4. It was recognized that PET fibers are a potential material of wastewater treatment for the ions studied.

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