Adsorption Behavior of Copper(II) Ion from Aqueous Solution on Methacrylic Acid-Grafted Poly(ethylene terephthalate) Fibers

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ABSTRACT: The adsorption behavior of methacrylic acid-grafted poly(ethylene terephthalate) fibers was studied toward the copper(II) ion in aqueous solutions by a batch equilibriation technique. The influence of treatment time, temperature, pH of the solution, metal ion concentration, and graft yield were considered. One hour of adsorption time was found sufficient to reach adsorption equilibrium for the copper(II) ion. It was found that the adsorption isotherm of Cu(II) fits Langmuir-type isotherms. The adsorption process is not affected by the temperature when treated with low ion concentration, but is remarkably decreased at a high ion concentration. The heat of adsorption value was calculated as 0.71 kcal/mol. It was found that the reactive fibers are stable and regenerable by acid without losing their activity. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 766–772, 2000

Key words: adsorption; metal ions; fibrous adsorbant; methacrylic acid-grafted polyester fibers

INTRODUCTION

The removal of toxic heavy metal ions from sewage and industrial waste water has received much attention in recent years. Heavy metals can be removed by adsorption on solid matrices. Activated carbon, metal oxides, and agricultural products such as peanut skins, onion skins, wool, and cotton[1–3] have been used as adsorbants for the adsorption of toxic heavy metal ions.

Polymer-supported reactive agents have been considered for the selective extraction processes of metals from aqueous solutions.[4–8] Because of their high specific surface areas, leading to a great adsorption capacity and a high adsorption rate of metal ions, fibrous reactive agents have shown many advantages. Thus, many studies concerning the use of fibrous materials for the adsorption of metal ions have been fullfilled.[9–13]

The fibrous materials grafted with various vinyl monomers are other potential groups which can be used for the adsorption of heavy metals. Although grafting is a well-known method for the modification of a polymer structure,[14,15] it has been used for this purpose only recently. Grafted polymers can be shown to have superior properties, that is, high moisture regain,[14] improved dyeability,[15,16] and good support for the immobilization of enzymes,[17,18] when compared with the host polymer.

In the our previous work,[19] the adsorption behavior of pure poly(ethylene terephthalate) (PET) fibers was studied toward heavy metal ions in

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aqueous solutions by a batch equilibriation technique. In the present study, we aimed to investigate the usability of methacrylic acid-grafted PET fibers for the removal of copper(II) ion from an aqueous solution.

EXPERIMENTAL

Materials

An analytical grade of $CuSO_4 \cdot 6H_2O$ (Merck) was used without purification. pH values were controlled with 0.1*M* KCl/HCl, 0.1*M* CH_3COOH/CH_3COONa, and 0.1*M* KH_2PO_4/K_2PO_4 buffer solutions. Methacrylic acid (MAA, Merck, Germany) was treated with NaCl, dried over $CaCl_2$, and distilled in a vacuum at 40°C. Benzoyl peroxide (Bz_2O_2) was twice precipitated from a chloroform solution in methanol and dried in a vacuum desiccator for 2 days. Benzene was crystallized by cooling in the refrigerator at 4°C; then, the crystallized part was used to prepare the Bz_2O_2 solutions. Middle-oriented PET fibers (100 denier, 28 flaments) were supplied by Sasa Co. (Adana, Turkey).

Graft Copolymerization

The fiber samples were washed with distilled water at 40°C and Soxhlet-extracted for 6 h with acetone and at ambient conditions before grafting. The fibers (0.10 ± 0.01 g samples) were placed in 45 mL deionized water containing 0.94 × 10^{-4} mol of MAA. Then, 5 mL of a Bz_2O_2 solution prepared in benzene (9.68 g/L) was added. The mixture was put in a water bath (Lauda D 40 S) at 80 ± 0.1°C. The grafted PET fibers were taken at specified time intervals (15–120 min) in order to obtain different graft yields[20] and subjected to a prewashing procedure with distilled water at 25°C for 2 h before being washed in boiling water for 1 h. The grafted fibers were Soxhlet-extracted with acetone for 8 h, dried, and weighted. The percentage graft yield was calculated from the difference between the weights of the original and grafted samples.

Adsorption Procedure

A volume of a 30 cm^3 copper(II) ion solution (0.3 mmol/L) adjusted to the desired pH was added onto 0.10 g of MAA-grafted PET fibers in a 100 mL Erlenmayer. The contents were shaken at 200 rpm for a predetermined period of time at 25°C using an orbital shaker (Nuve Model, ST-402). After filtration of the solution, the copper ion concentration of the filtrates was measured by a spectrophotometrical method of dithiocarbamates[21] using a spectrophotometer (Ultraspec 2000 UV-vis). The adsorption capacity of the MAA-grafted PET fibers was evaluated using the following expression:

$$q = (C_0 - C)V/m$$

where q is the amount of ion adsorbed onto the unit mass of the MAA-grafted PET fiber (mmol/g); C_0 and C, the concentration of the ion in the initial solution and in the aqueous phase after treatment for a certain period of time (mmol/L); V, the volume of the aqueous phase (L); and m, the amount of MAA-grafted PET fiber used (g). The metal ion was recovered by treating with 30 mL 1*M* HNO_3 for 1 h, then analyzed by the method mentioned above.

RESULTS AND DISCUSSION

Chemical grafting involves the formation of active centers upon the PET backbone. Once these centers are formed, polymer chains start to grow on them, resulting in branches. Bz_2O_2 undergoes thermal dissociation as

$$C_6H_5COOOOH_5C_6 \rightarrow 2C_6H_5COO^\bullet$$

$$C_6H_5COO^\bullet \rightarrow C_6H_5^\bullet + CO_2$$

The $C_6H_5COO^\bullet$ and $C_6H_5^\bullet$ radicals formed in the polymerization medium may initiate the production of PET radicals:

$$C_6H_5COO^\bullet + PET \rightarrow PET^\bullet$$

$$C_6H_5^\bullet + PET \rightarrow PET^\bullet$$

Also, the $C_6H_5COO^\bullet$ and $C_6H_5^\bullet$ radicals may initiate the homopolymerization of MAA:

$$C_6H_5COO^\bullet + MAA \rightarrow MAA^\bullet$$

$$C_6H_5^\bullet + MAA \rightarrow MAA^\bullet$$

The chain-transfer reaction between growing polyMAA chains and PET which forms active sites upon PET is

$$\text{homopolyPMAA}^{\bullet} + \text{PET} \rightarrow \text{PET}^{\bullet} + \text{homopolyPMAA}$$

Once the PET radicals are produced, the monomer adds to it to give a graft polymer:

$$\text{PET}^{\bullet} + \text{MAA} \rightarrow \text{PET-P}^{\bullet}$$

where PET–P$^{\bullet}$ is the growing PET graft polymer.

Termination of the polymerization process may take place in one of the chain-transfer or combination reactions involving the growing chain radical given below:

$$\text{PET-P}^{\bullet} + \text{homopolyPMAA} \rightarrow \text{graft copolymer} + \text{homopolyPMAA}^{\bullet}$$

$$\text{PET-P}^{\bullet} + \text{MAA} \rightarrow \text{graft copolymer} + \text{MAA}^{\bullet}$$

$$\text{PET-P}^{\bullet} + \text{initiator} \rightarrow \text{graft copolymer} + \text{initiator}^{\bullet}$$

$$\text{PET-P}^{\bullet} + \text{solvent} \rightarrow \text{graft copolymer} + \text{solvent}^{\bullet}$$

$$\text{PET-P}^{\bullet} + \text{homopolyMAA}^{\bullet} \rightarrow \text{graft copolymer}$$

$$\text{PET-P}^{\bullet} + \text{PET-P}^{\bullet} \rightarrow \text{graft copolymer}$$

The effect of the graft yield on the adsorption amount of copper(II) was investigated at 25°C, while keeping all other conditions constant. The results are shown in Figure 1.

It is seen that the adsorption takes place rapidly at first, then slows down and levels off. The adsorption equilibrium was attained within 1 h for all of grafting levels examined. Similar dependence on treatment time was obtained in the studies of other reseachers[11,22–24] with different adsorption equilibrium times for the ions and adsorbants under different conditions.

The results of the adsorption behavior of the fibers indicated that the adsorption ability of 47.0% MAA-grafted PET fibers is higher than that of the other grafted fibers. The increase in the adsorption with increasing graft yield may be attributed to a higher surface area and more active sites. The relation between the nature of the polymer and sorption rate is generally complicated by many possible interactions on the surface. The carboxylic acid groups of MAA-grafted PET fibers are responsible for the interaction of the metal ions with the fiber. Since the electrons are pulled strongly toward oxygen atoms, carboxyl carbon is electron-deficient, carboxyl oxygens are electron-rich, and the copper metal ion acts as an electron acceptor and is taken up by coordination to the donor oxygens of the carboxyl groups of the MAA-grafted PET.

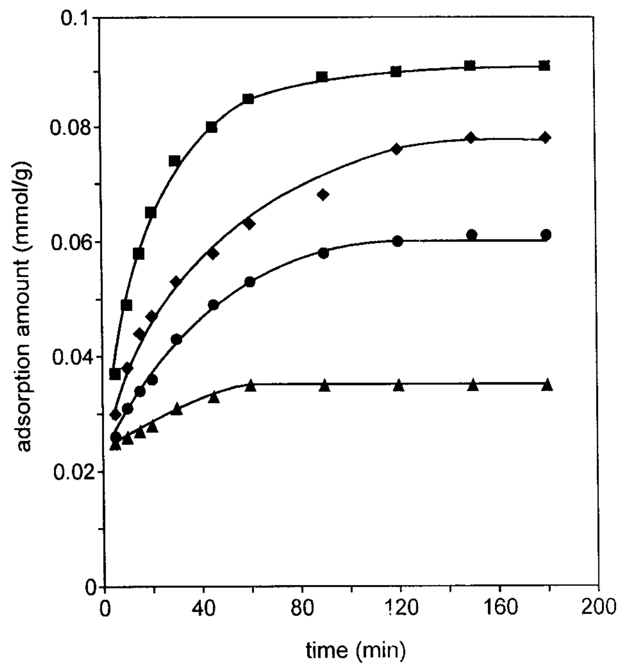

Figure 1 Relationship between adsorption time and adsorption amount of copper(II) with MAA-grafted PET fibers at 25°C. Graft yields: (▲) 0.0%; (●) 23.2%; (♦) 33.4%; (■) 47.0%.

The adsorption equation may be described[11,25,26] by using the following expression:

$$-\text{Ln}(1 - F) = Kt + c$$

where t is the adsorption time; K, an adsorption rate constant; q_t, the adsorption amount at time t; and q_e, an equilibrium adsorption amount; thus, $F = q_t/q_e$ and c is a constant.

According to the adsorption equation, the experimental result of Figure 1 can be converted into the plots of $-\ln(1 - F)$ versus t as shown in Figure 2. Thus, the adsorption rate constants of the fiber calculated from the slopes of the plots are listed in Table I. It is seen that the adsorption

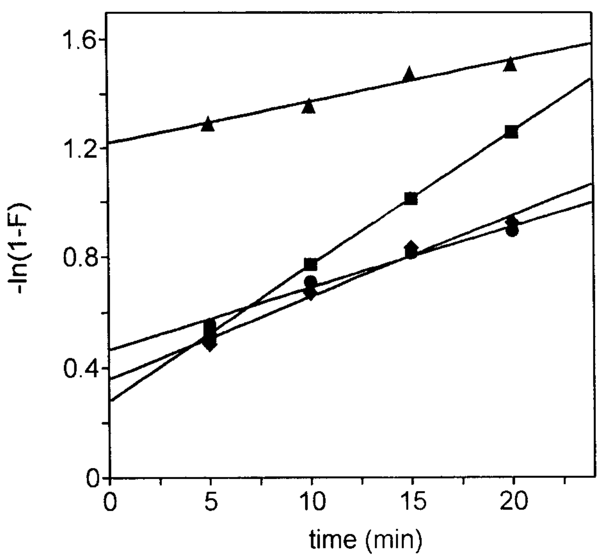

Figure 2 Plots of time versus $-\ln(1 - F)$.

rate constants increase with an increasing percentage graft yield.

Figure 3 shows the relationship between pH and the adsorption amount. With increasing the pH value of the copper(II) aqueous solution from 2 to 5, the adsorption amount increases significantly and reaches the maximum value at pH 5, then levels off. In the rest of the study, experiments were carried out at pH 5.

At a low pH value, the high hydrogen 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.[19]

The relationship between ion concentration and adsorption amount is represented in Figure 4. It is clear from the figure that as the concentration of the ions increased adsorption increased rapidly, then leveled off. The adsorption saturation value was reached at 5.8 mmol ions per gram MAA-grafted PET against 110 mmol copper(II)

Table I Adsorption Rate Constants (*K*) of the Pure PET and MAA-grafted PET Fibers

Graft Yield (%)	$K \times 10^4$ (s^{-1})
0.0	2.55
23.2	3.72
33.4	4.95
47.0	8.30

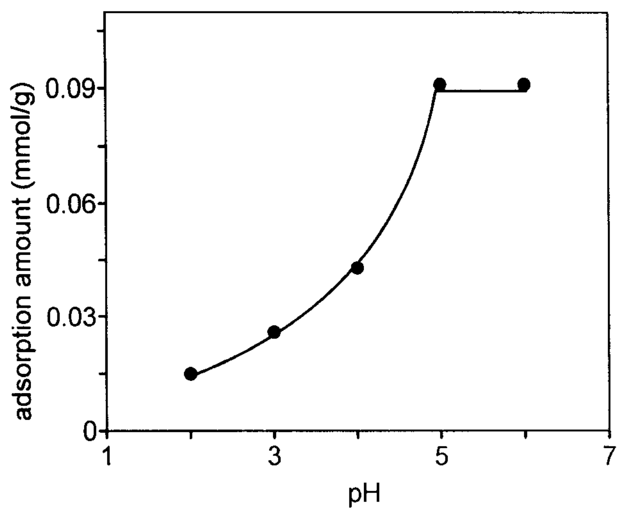

Figure 3 pH dependence of copper(II) ion adsorbed by MAA-grafted PET fibers. Ion concentration = 0.30 mmol/L; temperature = 25°C; contact time = 2 h; graft yield = 47.0%.

ions per liter, indicating that the MAA-grafted PET fiber is capable of a great adsorption capacity.

However, the metal-ion binding abilities and structures of functionalized fibers could be further analyzed. The adsorption ability of an adsorbant can be described by two parameters, that is, the saturation constant K_s (mmol/g) and the equilibrium binding constant K_b (L/mmol).[4,27] These

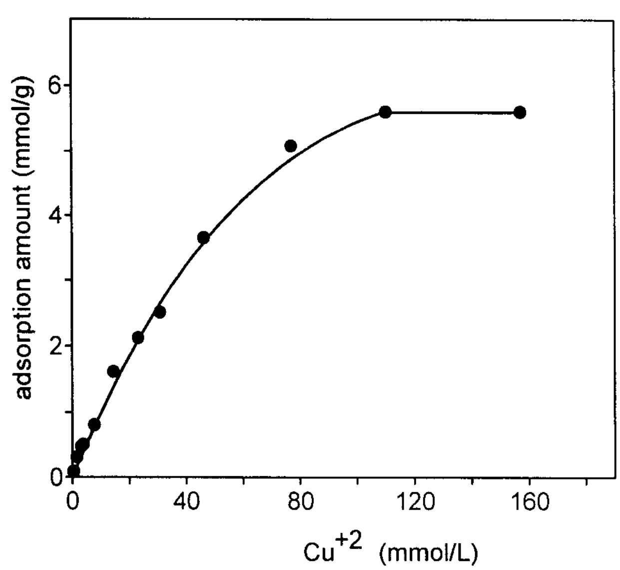

Figure 4 Effect of concentration of copper(II) ions on adsorption. Temperature = 25°C; contact time = 2 h; pH 5; graft yield = 47.0%.

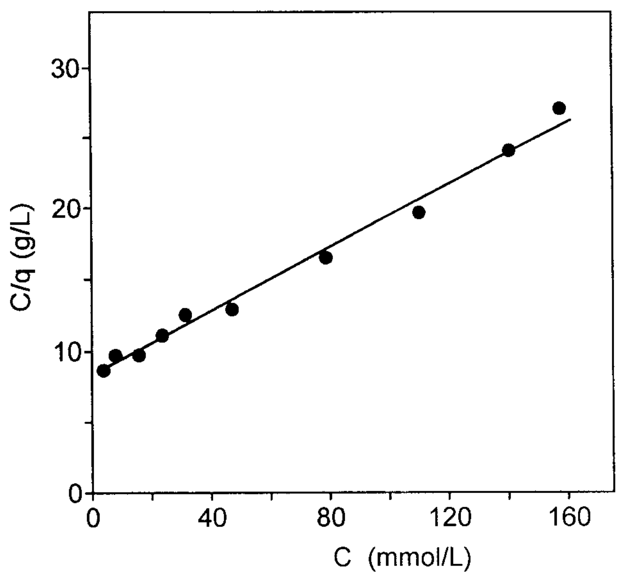

Figure 5 Langmuir plot of the removal of copper(II) ion on MAA-grafted PET fibers.

constants can be calculated from the adsorption isotherm data according to the Langmuir equation:

$$C/q = 1/K_b K_s + C/K_s$$

where C and q are the quantities of ions remaining in the solution and adsorbed on the fibers at equilibrium, respectively. Thus, a plot of C/q versus C should yield a straight line having a slope of $1/K_s$ and intercept of $1/K_b K_s$. Therefore, the relevant experimental data were treated and it was observed that the relationship between C/q and C is linear, indicating that the adsorption behaviors follow the Langmuir adsorption isotherm (Fig. 5).

This suggested that the adsorption sites of MAA-grafted PET fibers were one species. The K_b and K_s values are 0.014 L/mmol and 8.85 mmol/g, respectively.

It has been recognized that the adsorption of copper ion from an aqueous solution by MAA-grafted PET fiber is not affected in the temperature range between 20 and 60°C when treated with low ion concentrations (Fig. 6). However, the adsorption of the copper(II) ion decreased remarkably at high ion concentrations as the temperature increased in the same temperature range (20–60°C). The results are consistent with the literature.[10] The heat of adsorption value was calculated as 0.17 kcal/mol from Figure 7, which was obtained using the data of Figure 6.

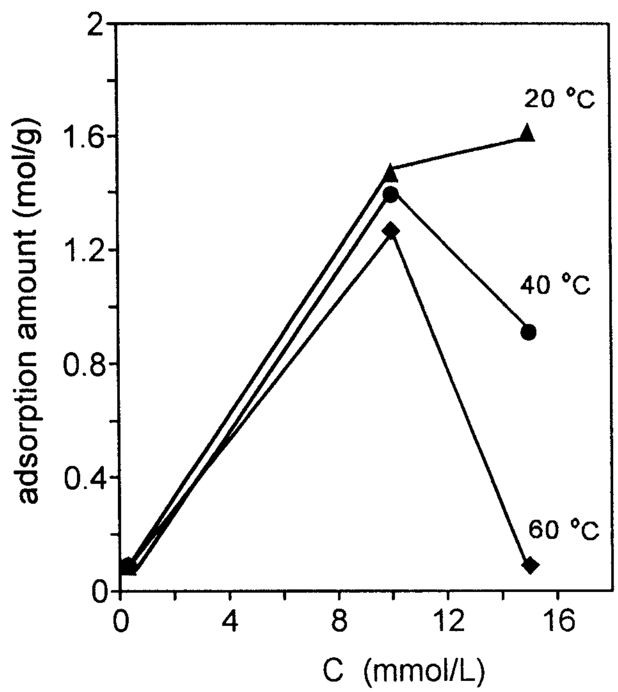

Figure 6 Effect of temperature on adsorption of copper(II) ion. Contact time = 2 h; pH 5; graft yield = 47.0%.

The heat of adsorption value shows that physical adsorption takes place in the adsorption of copper(II) ion on MAA-grafted PET fibers. De-

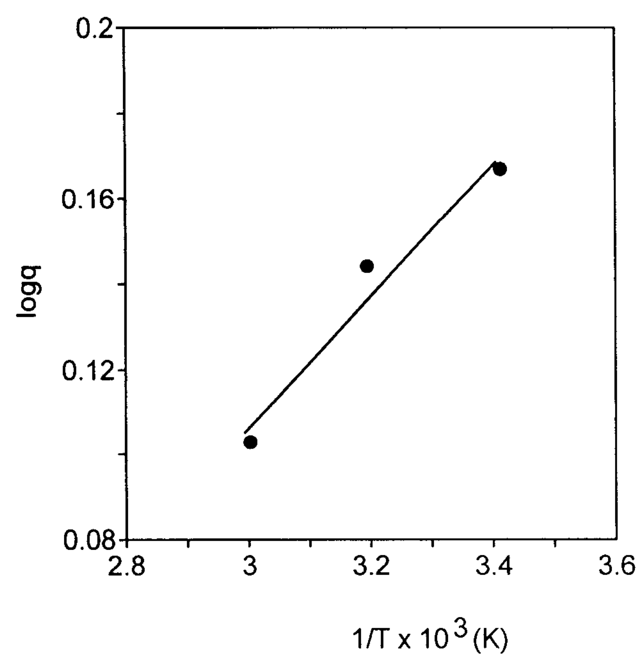

Figure 7 Log q versus to $1/T$ of copper(II) ions.

sorption and readsorption of copper(II) ions are represented in Figure 8. The copper(II) ions adsorbed were easily desorbed by treating with 1*M* HNO_3 at room temperature for 2 h. The desorbed MAA-grafted PET fibers were highly effective for the readsorption of metal ions, even though the adsorption ability of MAA-grafted PET fibers were kept constant after several repetitions of the adsorption–desorption cycle.

The effect of anions on the adsorption of the copper(II) ion was also investigated. The results are listed in Table II. In comparing the anions, with the same concentration of copper(II) ion, the highest adsorption amount was obtained with a sulfate solution. The rate of adsorption should be influenced by the hydration state of the copper(II) ion in the buffer solution or by the diffusion rate of the hydrated copper(II) ion onto the fiber surface.[8]

CONCLUSIONS

1. The results show that the adsorption process was affected by the graft yield.
2. One hour of treatment time was found sufficient to reach the adsorption equilibrium value.
3. The adsorption process is not affected by the temperature at a low ion concentration but decreased at a high ion concentration.
4. It was observed that the reactive fibers are stable and regenerable by acid without losing their activity.
5. It was recognized that the adsorption capacity of the grafted fiber is remarkably high, so that the material is a potential for the waste water treatment for a copper ion.

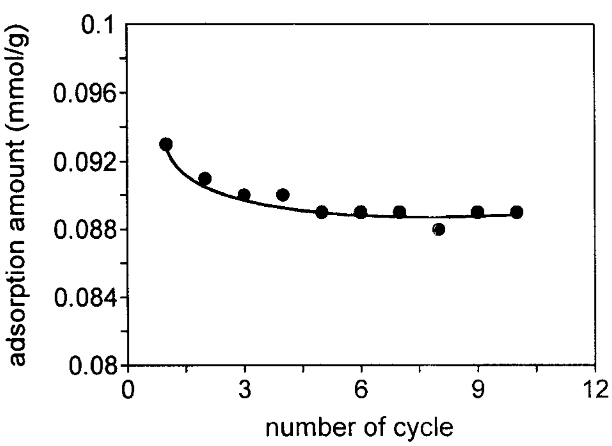

Figure 8 Adsorption–desorption cycles of copper(II) ions on MAA-grafted PET fibers. Ion concentration = 0.3 mmol/L; temperature = 25°C; pH 5; contact time = 2 h; graft yield = 47.0%.

Table II Effect of Anions on the Adsorption of Copper(II) Ion

Anion	Adsorption Amount (mmol/g)
Cl^-	0.553
CH_3COO^-	0.582
SO_4^{-2}	1.067
NO_3^-	0.501

Temperature, 25°C; ion concentration, 0.3 mmol/L; contact time, 2 h; pH 5; graft yield, 47.0%.

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