The Adsorption of Cu(II) Ion from Aqueous Solution upon Acrylic Acid Grafted Poly(ethylene terephthalate) Fibers

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ABSTRACT: This study is concerned with the investigation of the adsorption properties of acrylic acid grafted poly(ethylene terephthalate) fibers by the use of Cu(II) ions in aqueous solutions. Influence of pH, graft yield, contact time, concentration of the ion, and reaction temperature on the amount of ion adsorbed upon reactive fiber were investigated. The time in which the adsorption reached to the equilibrium value was determined as 1 h. The adsorption isotherm of Cu(II) ion was found to be a Langmuir type and the heat of adsorption was calculated as -10.1 kJ mol^{-1}. It was observed that the adsorbed Cu(II) ion upon acrylic acid grafted poly(ethylene terephthalate) fibers could be recovered in acidic media. The fiber could also readsorb Cu(II) ions without losing its activity. J Appl Polym Sci 87: 1216–1220, 2003

Key words: adsorption; metal ions; acrylic acid grafted poly(ethylene terephthalate); fibrous adsorbant

INTRODUCTION

Municipal wastewaters such as sewer and industrial drainage contain toxic heavy metals. The removal of heavy metals from these waters has been a highly important issue in recent years.

Active carbon, metal oxides, peanut skins, wool, and cotton[1–4] have been used as adsorbants for adsorption of heavy metal ions. Reactive polymers is another group of materials that are used in the selective extraction of metals from aqueous solutions.[5–8] In particular, the fibrous reactive materials have a very high adsorption capacity due to their very large surface area. That is why these materials are also widely utilized in enzyme immobilization[9,10] and removal of various gases.[11,12]

There are mainly two ways to prepare reactive fibers—namely, the exchange of the existing groups on the fiber with other reactive groups having higher adsorption ability[13–15] and grafting of various vinyl monomers upon the fiber by graft copolymerization.[16–18] Polypropylene fibers grafted with acrylic acid[19] and poly(ethylene terephthalate) fibers grafted with metacrylic acid[20] are examples of such applications. Grafting improves the adsorption capacity of fiber significantly by forming many reactive groups upon the polymer chains.

This study is concerned with the removal of Cu(II) ions from the aqueous solutions by the use of acrylic acid grafted poly(ethylene terephthalate) fibers.

EXPERIMENTAL

Materials

The poly(ethylene terephthalate) (PET) fibers used (28 filaments) were supplied from SASA Co. (Adana, Turkey). The fiber samples, prepared as small bundles (0.15 ± 0.01 g), were extracted with acetone in Soxhlet device for 6 h and dried in air. Benzoyl peroxide (Bz_2O_2) was recrystallized from a methanol/chloroform mixture twice and dried in vacuum. Acrylic acid (AA) were distilled at 30°C using a column filled with copper wires. The fixed pH solutions were prepared by the use of 0.1*M* KCl–HCl, 0.1*M* CH_3COOH–CH_3COONa, and 0.1*M* KH_2PO_4–K_2PO_4 buffer solutions.

Graft copolymerization

Graft copolymerization experiments were carried out in 100 mL Pyrex tubes. Appropriate amounts of Bz_2O_2 solution in 5 mL acetone and monomer were added to the polymerization tube containing the fiber sample, and they were made up to 50 mL with deionized water. The mixture was placed in a thermostated water bath (Lauda D 40 S) adjusted to the grafting temperature. The fiber samples removed from the system after the polymerization process were washed in boiling water for 4 h, changing the wash water at least three times. The samples were

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finally extracted in Soxhlet with methanol for 8 h and dried. The graft yield was calculated gravimetrically from the difference between the weight of the grafted and ungrafted fibers.

Adsorption procedure

A volume of a 30 mL Cu(II) ion solution at an appropriate concentration at fixed pH was added onto AA grafted PET fiber in a 100 mL Erlenmayer. The mixture was stirred throughout the experiment at 25°C. The solution was filtered and the copper ion concentration of the filtrates was measured by the spectrophotometric method of dithiocarbamates.[21]

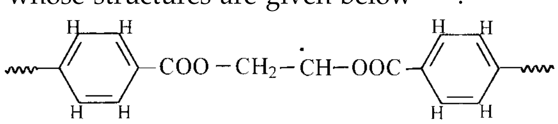
The adsorption capacity of the AA grafted PET fibers were calculated by the use of following expression:

$$q = \frac{(C_o - C_t)V}{m}$$

Here, q is the amount of adsorbed Cu(II) ion onto unit mass of the AA grafted PET fiber (mmol g^{-1}). The c_0 and c_t are the amount of Cu(II) ion in the initial solution and the aqueous phase after the adsorption procedure (mmol L^{-1}), respectively. V is the total volume of the aqueous phase, and m is the weight of the AA grafted PET fiber. The Cu(II) ion adsorbed upon AA grafted PET fiber was recovered by treating with 30 mL 1M HNO_3 for 1 h, then analyzed by the method mentioned above.

RESULTS AND DISCUSSION

The electron spin resonance (ESR) studies carried out on PET revealed that there formed two types of radical, whose structures are given below[22,23]:



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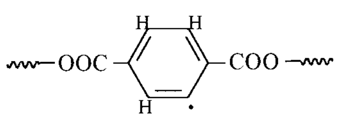


II

These radical sites can be created either by the direct interaction of the initiator with the fibers or by the transfer reaction between the active homopolyAA chains and PET fibers.[24–26] AA molecules are added to the active sites in succession to form AA grafted PET molecules as follows:

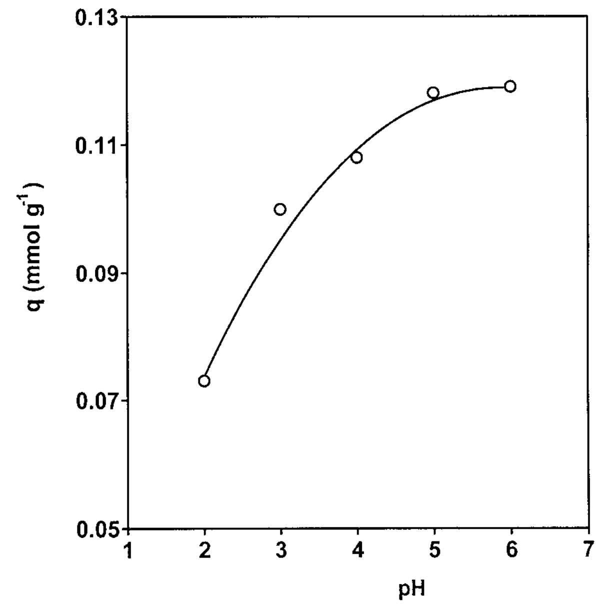
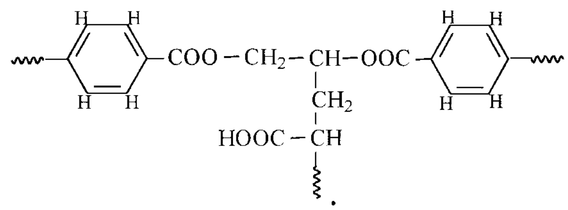
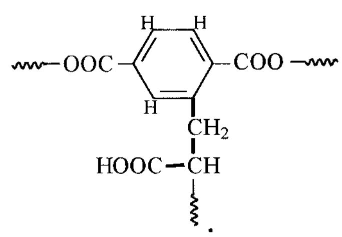


Figure 1 The change of the adsorption amount of Cu(II) ion adsorbed upon AA grafted PET fibers with pH. (Graft yield, % 13.2; Cu(II) ion concentration, 0.25 mmol L^{-1}; contact time, 3 h; temperature, 25°C.)



III



IV

Type II PET radicals are known to be predominant.[27] Therefore the AA grafted PET samples used may be said to be mainly of structure IV.

It has been known that the metal ion adsorption of reactive fibers was changed with the pH of solution.[17,21,28] To find the optimum pH value, fiber samples having the highest graft yield (13.2%) were subjected to the adsorption experiments in the Cu(II) ion solutions at various pH values (Fig. 1). It was observed that the increase of the pH of aqueous Cu(II) ion solution from 4 to 6 caused a significant increase in the amount of adsorption and reached the maximum value at a pH value of 5. The experiments were carried out at pH 5, where the highest adsorption was obtained.

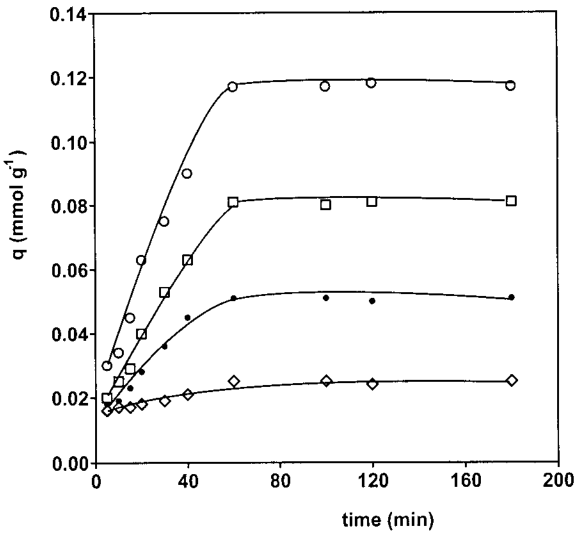


Figure 2 The change of amount of Cu(II) ion adsorbed upon PET fibers, grafted with different amounts of AA, with time. Graft yields: (○) 13.2%; (□) 8.8%; (●) 3.6%; (◇) 0.0% PET. Temperature: 25°C; pH, 5.

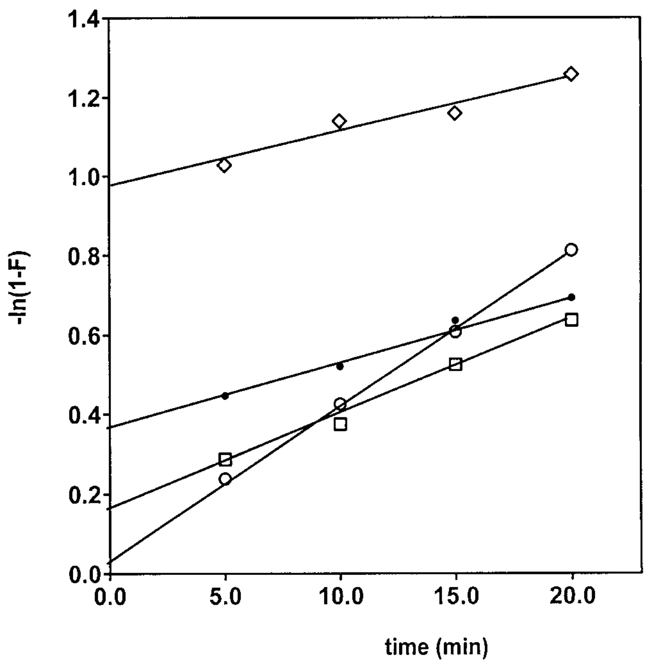


Figure 3 The graph of adsorption time $-\ln(1-F)$ vs time according to the adsorption equation.

At low pH values, the high hydrogen ion concentration at the interface repels positively charged the metal ions electrostatically and prevents their approach to the fiber surface. Therefore, the lower adsorption values were observed at lower pH values, as seen in Figure 1.[29]

The effect of the amount of AA grafting and contact time on the adsorption of the Cu(II) ion was investigated at 25°C, keeping all other conditions constant. The results are plotted in Figure 2. As seen from the figure, the Cu(II) ion adsorption of AA grafted PET fibers is higher than that of pure PET fiber. While the equilibrium concentration of the pure PET fiber was 0.025 mmol g^{-1}, this value increased up to 0.118 mmol g^{-1} for 13.2% AA grafted PET fiber. This shows that AA grafting converts the PET fiber into a highly effective fibrous reactive material that can be used for the adsorption of Cu(II) ions compared with pure PET fiber.

The Cu(II) ion adsorption of the fiber shows a rapid increase with the amount of AA grafting at first, then slows down and reaches an equilibrium value. The time for reaching the adsorption equilibrium is approximately 1 h for each grafting value. It was observed that the equilibrium adsorption value was 0.118 mmol g^{-1} in 13.2% AA grafted fibers.

The increase in adsorption amount with the graft yield may be attributed to the increase in the carboxyl groups inserted in fiber structure by graft copolymerization. The carboxylic acid groups in AA grafted PET fibers are responsible for the interaction between the fiber and the metal ion. The electrons of carboxyl are strongly pulled toward the oxygen atoms, and the carboxyl carbon becomes poor in electrons. Cu(II) ions act as electron acceptors and are coordinated to the electron-rich oxygen atoms of the carboxyl groups.

The adsorption equation for the system investigated is given as follows[17,30,31]:

$$-\ln(1-F) = Kt + a$$

Here, a is a constant, t is the adsorption time, and K is the adsorption rate constant. F is given as

$$F = q_t/q_e$$

where q_t and q_e are the amount of adsorption at time t and equilibrium, respectively.

Figure 3, drawn using experimental data given in Figure 2, is the plot of $-\ln(1-F)$ vs t. The adsorption rate constants (K) calculated from the slopes of the lines in Figure 3 are given in Table I.

Figure 4 shows the relation between the Cu(II) ion concentration and the amount of adsorption. As seen

TABLE I
The Change of Adsorption Rate Constant with the Graft Yield

Graft yield (%)	$K \times 10^4$ (s^{-1})
0.0	2.55
3.6	2.74
8.8	3.88
13.2	6.30

Cu(II) ion concentration, 0.25 mmol L^{-1}; pH, 5; temperature, 25°C; contact time, 3 h.

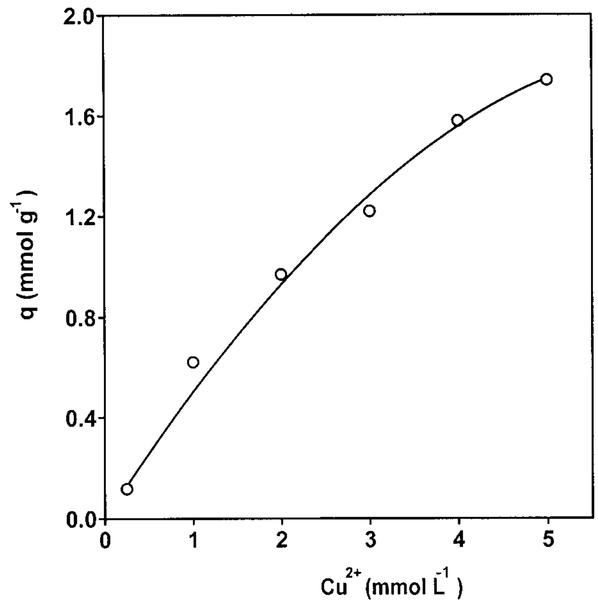


Figure 4 The effect of Cu(II) ion concentration on the amount of Cu(II) ion adsorbed upon AA grafted PET fibers (Graft yield, 13.2%; pH, 5; contact time, 3 h; temperature, 25°C.)

from Figure 4, the increase in Cu(II) ion concentration increased the adsorption amount.

The adsorption ability of an adsorbant is described by two parameters—namely, equilibrium binding constant (K_b), which is related to the binding strengths between the functional groups and the metal ions, and saturation constant (K_s), which is the measure of the binding ability and the accessibility of functional groups toward the ions.[19,32]

TABLE II
The Change of Cu(II) Ion Adsorption upon AA Grafted PET Fibers with Temperature

Temperature (°C)	q (mmol g^{-1})
20	1.132
40	1.107
60	1.080

Graft yield, 13.2%; Cu(II) ion concentration, 2.5 mmol L^{-1}; pH, 5; contact time, 3 h.

K_b and K_s constants were calculated according to the Langmuir equation given below:

$$c_e/q_e = 1/K_bK_s + c_e/K_s$$

Here, c_e and q_e are the amount of ions remained in the solution and adsorbed upon the fibers at equilibrium, respectively. The plot of c_e/q_e vs c_e in Figure 5 was drawn from the adsorption data given in Figure 4. The linear relation between c_e and c_e/q_e shows us that the adsorption behavior of AA grafted PET fibers fits the Langmuir isotherm (Fig. 5).

K_b and K_s values were calculated as 0.19 mmol L^{-1} and 3.85 mmol g^{-1} from Figure 5.

Table II reveals the effect of temperature on the adsorption of Cu(II) ions upon AA grafted PET fibers. The table shows that when a Cu(II) ion concentration of 0.4 mmol L^{-1} or higher is employed the amount of Cu(II) ion adsorbed upon the reactive PET fiber at 20°C is higher than that of 60°C. This proves that the

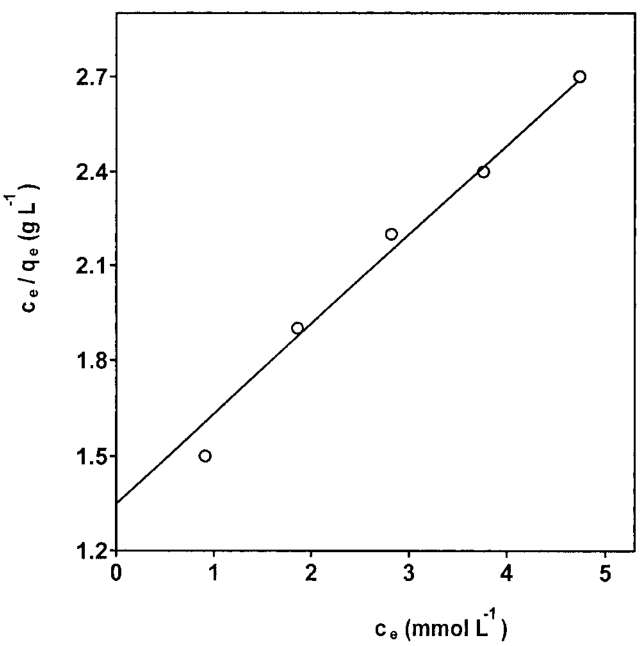


Figure 5 The plot of c_e/q_e vs c_e drawn according to Langmuir equation.

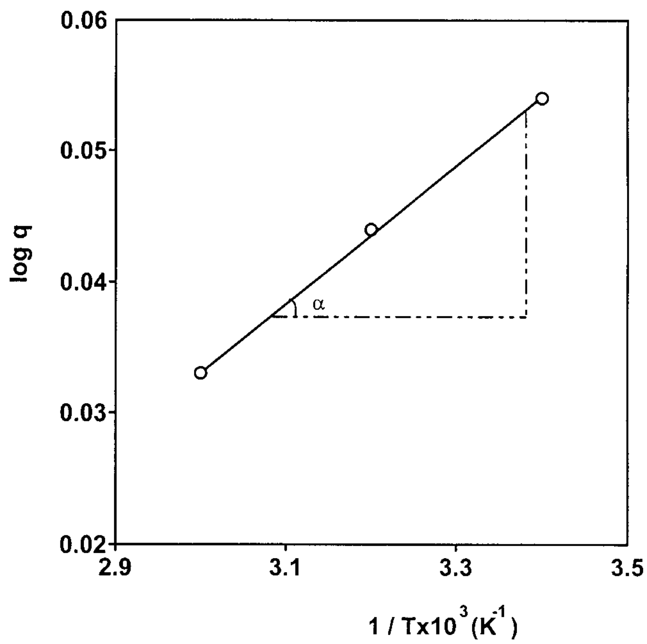


Figure 6 The consecutive adsorption/desorption cycles of Cu(II) ion upon AA grafted PET fibers.

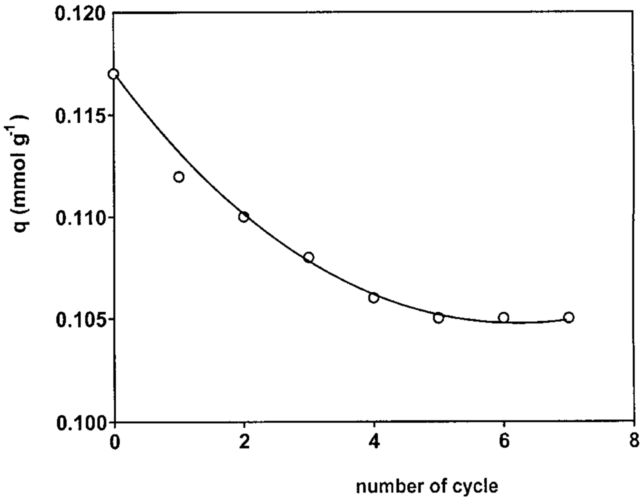


Figure 7 Results of the consecutive Cu(II) adsorption/desorption experiments of AA grafted PET fibers.

complex formed with Cu(II) ions and the carboxyl groups upon the fiber at lower temperatures is much more stable.

From the slope of the line in Figure 6 plotted using data in Table II, the heat of adsorption was calculated as -10.1 kJ mol^{-1}. The value of the heat of adsorption reveals that the type of adsorption of Cu(II) ion upon AA grafted PET fibers is physical.

Figure 7 shows the results of the consecutive Cu(II) adsorption/desorption experiments of AA grafted PET fibers. The Cu(II) ions adsorbed upon AA grafted PET fibers were desorbed by treating them with 1*M* HNO_3 for 1 h at ambient temperature. The adsorption ability of AA grafted PET fibers shows a slight decrease after a few adsorption/desorption cycles and remain stables at a value of 0.092 mmol g^{-1} (Fig. 7). This shows that AA grafted PET fibers are highly effective fibrous materials for the adsorption of Cu(II) ions.

CONCLUSION

Our results show that AA grafted PET fibers have much higher Cu(II) ion adsorption capacity than pure PET fibers. It was also seen that the adsorption capacity increased with the grafting yield. The time to reach the adsorption equilibrium was found to be approximately 1 h and independent of graft yield. It was also found that AA grafted PET fibers can be used as an active adsorbant for Cu(II) ions without losing their activity.

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