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The adsorption of Fe (III) ion from aqueous solution by fibrous adsorbent

A.Ahmady*, A.Bagheri

Department of Chemistry, Faculty of Science, Islamic Azad University, Central Tehran Branch, Tehran, (IRAN)

E-mail : shayan_iran@yahoo.com

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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 Fe(III) 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 1h. It was observed that the adsorbed Fe(III) ion upon acrylic acid grafted poly(ethylene terephthalate) fibers could be recovered in acidic media. The fiber could also readsorb Fe(III) ions without losing its activity.

KEYWORDS

Adsorption;
Metal ions;
Acrylic acid grafted poly- (ethylene terephthalate);
Fibrous adsorbent.

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 adsorbents for adsorption of heavy metal ions. Reactive polymers are 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 methacrylic 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 Fe (III) ions from the aqueous solutions by the use of acrylic acid grafted poly (ethylene terephthalate) fibers.

EXPERIMENTAL

The poly (ethylene terephthalate) (PET) fibers used (28 filaments) were supplied from SASA Co.(Adana, Turkey). The fiber samples, prepared as small bundles (0.15-0.01g), were extracted with acetone in Soxhlet device for 6h and dried in air. Benzoyl peroxide Bz_2O_2) was recrystallized from a methanol/chloroform mixture twice and dried in vacuum. Acrylic acid (AA) was distilled at 30°C using a column filled with copper wires. The fixed pH solutions were prepared by the use of 0.1M KCl–HCl, 0.1M CH_3COOH– CH_3COONa, and 0.1 M KH_2PO4–K_3PO4 buffer solutions.

Graft copolymerization

Graft copolymerization experiments were carried out in 100mL 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 50mL with deionized water. The mixture was placed in a thermostated water bath adjusted to the grafting temperature. The fiber samples removed from the system after the polymerization process were washed in boiling water for 4h, changing the wash water at least three times. The samples were finally extracted in Soxhlet with methanol for 8h 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 30mL Fe (III) ion solution at an appropriate concentration at fixed pH was added onto AA grafted PET fiber in a 100mL Erlenmayer. The mixture was stirred throughout the experiment at 25°C. The solution was filtered and the Fe(III) ion concentration of the filtrates was measured by the atomic absorption spectroscopy. The adsorption capacities of the AA grafted PET fibers were calculated by the use of following expression:

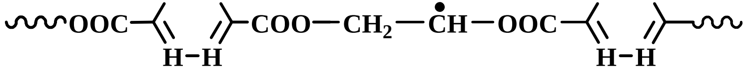
$$q = (C_0 - C_t)V/m$$

Here, q is the amount of adsorbed Fe(III) ion onto unit mass of the AA grafted PET fiber(mmol g^{-1}). The C_0 and C_t are the amount of Fe(III) 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 Fe (III) ion adsorbed upon AA grafted PET fiber was recovered by treating with 30mL 1M HNO3 for 1h, 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(see I, II structure), whose structures are given below[22,23] : (radicals III and IV have been produced from radical I and II after reaction with acrylic acid).

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: 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 ad-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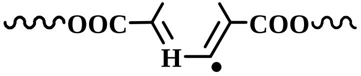
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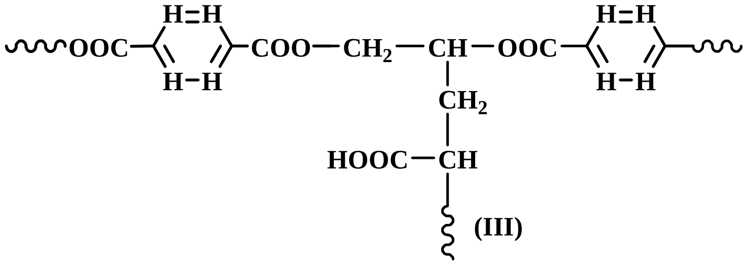
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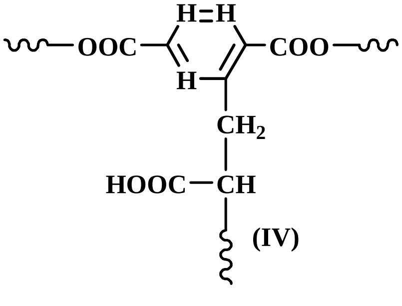
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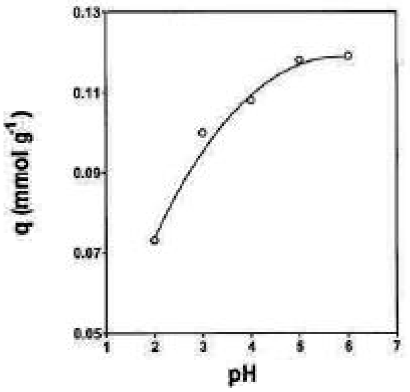

Figure 1: The change of the adsorption amount of Fe (III) ion adsorbed upon AA grafted PET fibers with pH (Graft yield, % 13.2; Fe(III) ion concentration, 0.25mmol L^{-1}; contact time, 3h; temperature, 25°C)

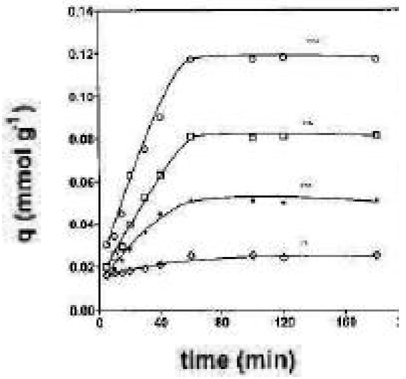

Figure 2: The change of amount of Fe(III) ion adsorbed upon PET fibers, grafted with different amounts of AA, with time(Graft yields: 13.2%; 8.8%; 3.6%; 0.0% PET. Temperature: 25°C; pH, 5)

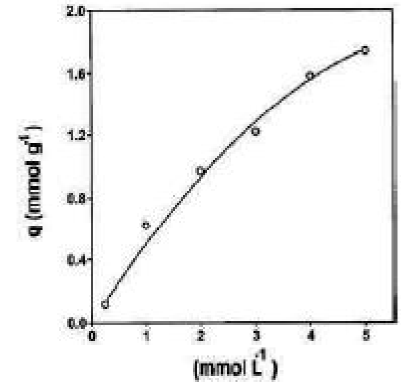

Figure 3 : The effect of Fe (III) ion concentration on the amount of Fe (III) ion adsorbed upon AA grafted PET fibers Graft yield, 13.2%; pH, 5; contact time, 3 h; temperature, 25°C

TABLE 1: The Change of Fe(III) Ion Adsorption upon AA Grafted PET Fibers with temperature Graft yield, 13.2%; Fe (III) ion concentration, 2.5mmol L^{-1}; pH, 5; contact time, 3h

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

sorption experiments in the Fe(III) ion solutions at various pH values(Figure 1). It was observed that the increase of the pH of aqueous Fe(III) 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.

At low pH values, the high hydrogen ion concentration at the interface repel 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 Fe(III) ion was investigated at 25^0C, keeping all other conditions constant. The results are plotted in figure 2. As seen from the figure, the Fe(III) 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 0.025mmol g^{-1}, this value increased up to 0.118mmol 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 Fe(III) ions compared with pure PET fiber. The Fe(III) 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 1h for each grafting value. It was observed that the equilibrium adsorption value was0.118mmol 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. Fe(III) ions act as electron acceptors and are coordinated to the electron-rich oxygen atoms of the carboxyl groups.

From figure 3, by increasing in Fe (III) ion concentration increased the adsorption amount.

TABLE 1 reveals the effect of temperature on the adsorption of Fe(III) ions upon AA grafted PET fibers. The table shows that when a Fe(III) ion concentration of 0.4mmol L^{-1} or higher is employed the amount of Fe(III) ion adsorbed upon the reactive PET fiber at20°C is higher than that of 60^0C. This proves that the complex formed with Fe (III) ions and the carboxyl groups upon the fiber at lower temperatures is much more stable.

CONCLUSION

Our results show that AA grafted PET fibers have much higher Fe (III) 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 adsorbent for Fe (III) ions without losing their activity.

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