



## Selective removal of Cr(VI) ions from aqueous solutions including Cr(VI), Cu(II) and Cd(II) ions by 4-vinyl pyridine/2-hydroxyethylmethacrylate monomer mixture grafted poly(ethylene terephthalate) fiber

Mustafa Yiğitoğlu\*, Metin Arslan

Kırıkkale University, Faculty of Science and Art, Department of Chemistry, Yahşihan, 71450 Kırıkkale, Turkey

### ARTICLE INFO

#### Article history:

Received 10 March 2008  
Received in revised form  
12 November 2008  
Accepted 17 November 2008  
Available online 30 November 2008

#### Keywords:

Selectivity  
Graft copolymerization  
Poly(ethylene terephthalate) fibers  
Metal removal

### ABSTRACT

In this study, a new reactively fibrous adsorbent was prepared by grafting 4-vinyl pyridine (4-VP) and 2-hydroxyethylmethacrylate (HEMA) monomer mixture onto poly(ethylene terephthalate) (PET) fibers for removal of Cr(VI), Cu(II) and Cd(II) metal ions from aqueous solution by using batch adsorption method. The influence of various parameters such as graft yield (GY), pH, adsorption time, initial ion concentration and adsorption temperature was investigated. The selectivity of the reactive fiber was also examined. The results show that the adsorbed amount of metal ions followed as given in the order Cr(VI) > Cd(II) > Cu(II). At pH 3, Cr(VI) was removed by 99% while the initial concentration of ions was at 5 mg L<sup>-1</sup> and by 94% at 400 mg L<sup>-1</sup>. It was found that the grafted fiber is more selective for Cr(VI) ions in the mixed solution of Cr(VI)–Cu(II), Cr(VI)–Cd(II) and Cr(VI)–Cu(II)–Cd(II) at pH 3 and it was observed that the grafted fibers are stable and regenerable by acid and base without losing their activity.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

Many industries such as painting, textile, metal coating, pulp and paper, printing, rubber and leather use heavy metals in their process. Heavy metals are very toxic elements and are not biologically degraded like many organic pollutants. The discharge of wastewater with heavy metals into natural waters from these industries causes detrimental effects on human health and environment. Therefore heavy metals have to be removed from wastewater.

Many processes have been used for the removal of heavy metals from industrial effluents such as chemical precipitation, membrane filtration, ion change and adsorption. Adsorption process is one of most frequently used methods to remove heavy metals from aqueous solutions as it offers the most economical and effective treatment. There are many types of adsorbents that have been studied for the adsorption of ions from aqueous solutions including activated carbon [1], sawdust [2], sporopollenin [3,4], chitosan [5], peat [6], cellulose [7], chelating resins [8], chelating fibers [9], clay mineral [10].

Most water contaminated with heavy metals contains more than one heavy metal ion and it is necessary to determine the binding ability of the adsorbent with multi-metal solutions. Therefore, some research studies the effect of competition for multi-metal binding by different adsorbents [1,11].

Increasing interest has been focused on the chelating fibers recently because they are used for enriching and separating heavy metal ions from aqueous solutions. Chelating fibers are very useful since they have higher selectivity and larger adsorption capacities than other adsorbents and they are also easy to regenerate. This is mainly attributed to the relatively large external specific surface areas, high adsorption kinetics, introduction of suitable functional groups and low cost of these polymer fibers [12,13].

Poly(ethylene terephthalate) (PET) fibers are one of the most important synthetic fibers used in the textile industry and have good resistance to weak mineral acids, even at boiling temperature, and to most strong acids at room temperature, oxidizing agents, sunlight and micro organisms. However, PET fibers do not contain chemically reactive groups, showing resistance to moisture, dye anions or cations. Certain desirable properties such as dye ability with basic, direct, and other classes of dyes, water absorbency, and improvement in antistatic, mechanical and thermal properties can be imparted to PET fiber by grafting with different vinyl monomers such as 4-vinyl pyridine (4-VP) [14], 2-hydroxyethylmethacrylate (HEMA) [15], acrylic acid [16], methacrylic acid [17], acrylamide [18], and acrylonitrile [19]. Graft copolymerization of vinyl monomers from their binary mixtures is of special importance to obtain polymers having properties of both monomers in comparison to graft copolymers obtained by the grafting of individual monomers. The grafting from binary mixture of monomers has the advantage of introducing grafted chains with tailor made properties for specific applications. The mutual effect of monomers in the reaction mixture controls the fraction of

\* Corresponding author. Tel.: +90 318 357 42 42x1580; fax: +90 318 3572461.  
E-mail address: [mustafa.yigitoglu@mynet.com](mailto:mustafa.yigitoglu@mynet.com) (M. Yiğitoğlu).

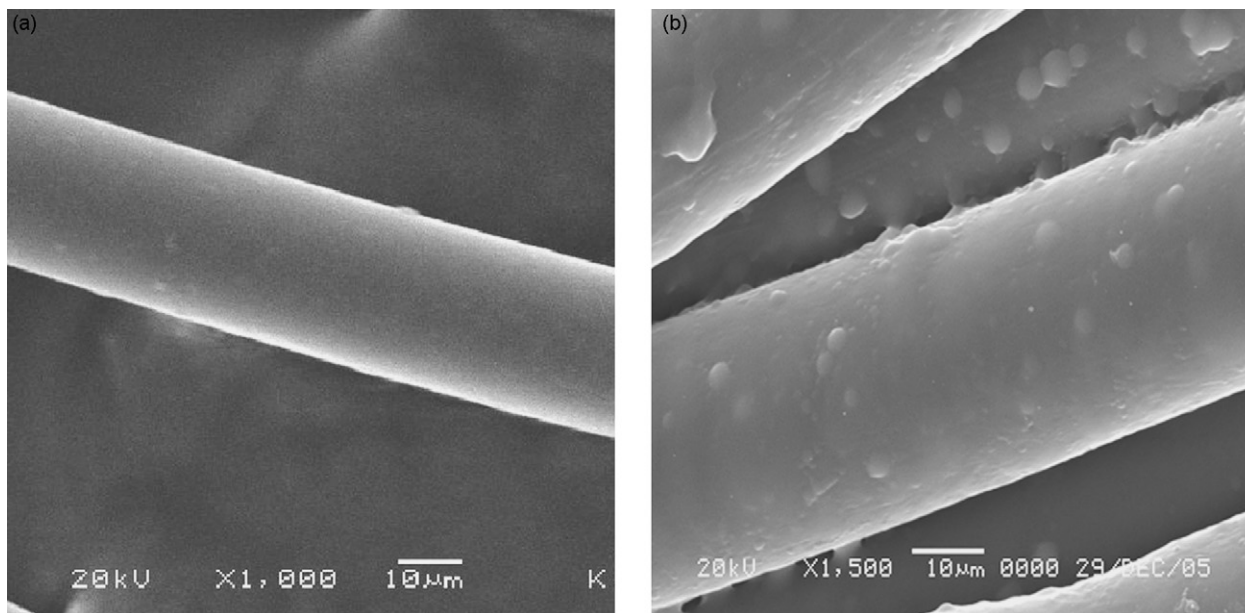


Fig. 1. (a) SEM micrograph of ungrafted PET fibers. (b) SEM micrograph of 4-VP/HEMA (180%, 50/50 mol) grafted PET fibers.

individual monomer in the grafted chains and overall yield of grafting. This synergistic effect of comonomer enhances the fraction of monomer in the graft yield (GY). Hence this technique of graft copolymerization provides an opportunity to prepare tailor made grafted chains of desired properties by using suitable monomers [20].

Recently a novel fibrous adsorbent has been obtained in our laboratory by grafting 4-VP/HEMA comonomers onto PET fibers and used as an adsorbent for acidic and basic dyes. In the present study, that material is used as an adsorbent for selective removal of Cr(VI), Cu(II) and Cd(II) from aqueous solution by a batch equilibration technique.

## 2. Experimental

### 2.1. Materials

The PET fibers (122 dTex, middle drawing) used in these experiments were provided by SASA Co. (Adana, Turkey). The fiber samples were Soxhlet-extracted until constant weight (for 6 h) with acetone and dried in a vacuum oven at 50 °C. 4-VP and HEMA were purified by vacuum distillation. Benzoyl peroxide ( $Bz_2O_2$ ) was twice precipitated from chloroform in methanol and dried in a vacuum oven for 2 days. Analytical grade reagent of potassium dichromate ( $K_2Cr_2O_7$ ), copper standard solution and cadmium standard solution were used without purification. pH values were adjusted with buffer solution of glycine–glycine HCl (pH 1–3),  $CH_3COOH-CH_3COONa$  (pH 4–5) and  $KH_2PO_4-K_2HPO_4$  (pH 6–8). Other reagents were used as supplied. All reagents were Merck products.

### 2.2. Polymerization procedure

A temperature controlled oil bath was used for heating. The fiber samples ( $0.3 \pm 0.01$  g) were dipped into dichloroethane (50 mL) for 2 h at 90 °C. After treatment, solvent on the fibers was removed by blotting between a filter paper and put into the polymerization medium. Polymerization was carried out in a thermostated 50 mL tube under reflux. The mixture containing the PET fiber sample ( $0.3 \pm 0.01$  g), appropriate amount of 4-VP/HEMA mixture and  $Bz_2O_2$  at required concentration in 2 mL acetone was made

up to 20 mL with deionized water. The mixture was immediately placed into the water bath adjusted to the polymerization temperature. At the end of the predetermined polymerization time, the grafted fibers were taken out. Residual solvent, monomers and free homopolymers or copolymers were removed by Soxhlet-extracting the PET fibers in methanol for 96 h. The grafted fibers were then vacuum-dried at 50 °C for 72 h and weighed. The graft yield was calculated from the weight increase in grafted fibers as follows:

$$GY(\%) = \left( \frac{w_g - w_i}{w_i} \right) \times 100 \quad (1)$$

where  $w_i$  and  $w_g$  denote the weights of the original (ungrafted) and grafted PET fibers, respectively.

### 2.3. Scanning electron microscopy

SEM studies of the original and 4-VP/HEMA mixture grafted PET fibers coated with gold were performed using a JOEL Model JSM 5600 microscope.

### 2.4. FTIR spectrum

A Fourier transforms infrared (FTIR) spectrophotometer from Jasco FTIR 420 plus was used to analyze the chemical and/or physical interactions in the wave number range 400–4000  $cm^{-1}$ .

### 2.5. Adsorption procedure

Twenty-five cubic centimeter from each metal ion solution ( $5 \text{ mg L}^{-1}$ ), adjusted to desired pH, was added onto 0.1 g of 4-VP/HEMA mixture grafted PET fibers in 50 mL Erlenmeyer. The contents were shaken at 125 rpm for a predetermined period of time at 25 °C using orbital shaker (Medline BS-21). After filtration of the solution the metal ion concentration of the filtrates was measured by a PerkinElmer AAnalyst 400 model flame atomic absorption spectrometer equipped with deuterium lamp background correction, hollow cathode lamps (HCL) and air-acetylene burner was used for the determination of the metals. The instrumental parameters were those recommended by the manufacturer. The adsorption capacity of the 4-VP/HEMA grafted PET fibers was

evaluated by using the following expression:

$$q = \frac{(C_0 - C)V}{m} \quad (2)$$

where  $q$  is the amount of ion adsorbed onto unit mass of the 4-VP/HEMA grafted PET fiber ( $\text{mg g}^{-1}$ ),  $C_0$  and  $C$  are the concentration of the ion in the initial solution and in aqueous phase after treatment for a certain period of time ( $\text{mg L}^{-1}$ );  $V$  is the volume of the aqueous phase (L); and  $m$  is the amount of 4-VP/HEMA grafted PET fiber used (g), respectively.

### 2.6. Desorption of metal ions

Desorption assays were carried out with the metal ion loaded 4-VP/HEMA grafted PET fibers. Cr(VI) was recovered by treating with 25 mL 1 M KOH solution. Cu(II) and Cd(II) were recovered by treating with 1 M HNO<sub>3</sub> solution and then analyzed by the method mentioned above. The desorption percent was calculated using the following equations:

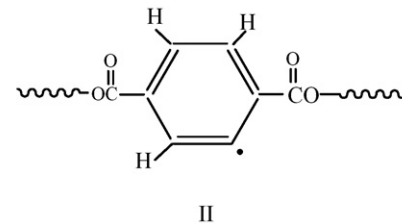
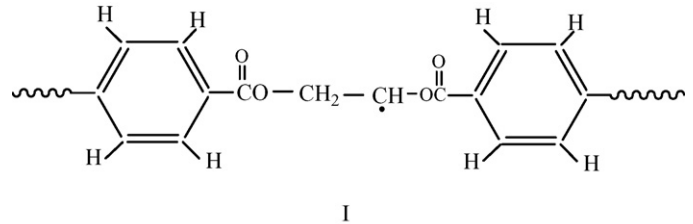
$$\% \text{Desorption} = \frac{\text{Amount of ions (mg) desorbed}}{\text{Adsorbed amount of ions (mg) by adsorbant}} \times 100 \quad (3)$$

## 3. Result and discussion

Grafted PET fibers were prepared and characterized as mentioned in our previous work [20].

The electron spin resonance (ESR) carried out on PET revealed that two types of radicals were formed there. Their structures are given below [21,22]. These radicals' sites can be created either by the direct interaction of the initiator with the fiber or by the transfer reactions between the active homopoly (4-VP), or homopoly (HEMA) or copoly (4-VP/HEMA) chains and PET fiber [9]. Type II PET radicals are known to be predominant [23]. Graft copolymerization was carried out on these active radicals of PET fibers to add

4-VP, HEMA and 4-VP/HEMA mixed comonomers.



The scanning electron micrograph of 4-VP/HEMA grafted (180%) PET fibers are shown in Fig. 1. It is clear from the SEM results that the ungrafted PET fiber surface (Fig. 1a) has a smooth and relatively homogeneous appearance. The grafted side chain 4-VP/HEMA seems to form microphages attached to the PET back-bone and causes a heterogeneous appearance in the graft copolymer (Fig. 1b), showing proof of grafting.

The FTIR spectra of ungrafted, 180% 4-VP/HEMA grafted PET fibers are given in Fig. 2. It is seen that the peaks of the ungrafted PET (Fig. 2a) can be assigned as follows:  $3428 \text{ cm}^{-1}$  (OH),  $2945 \text{ cm}^{-1}$  and  $2906 \text{ cm}^{-1}$  (C–H asymmetric and symmetric in CH, CH<sub>2</sub> groups),  $1711 \text{ cm}^{-1}$  (C=O),  $1410 \text{ cm}^{-1}$  (CH<sub>2</sub>). After the grafting with 4-VP/HEMA, the spectrum of the 4-VP/HEMA grafted PET fibers changed greatly. The absorption band at  $3428 \text{ cm}^{-1}$  shifted to  $3292 \text{ cm}^{-1}$ , with the intensity and the width of the peak increased and broadened significantly. Since this band corresponds to the stretching vibration of the OH groups of HEMA, the change indicates

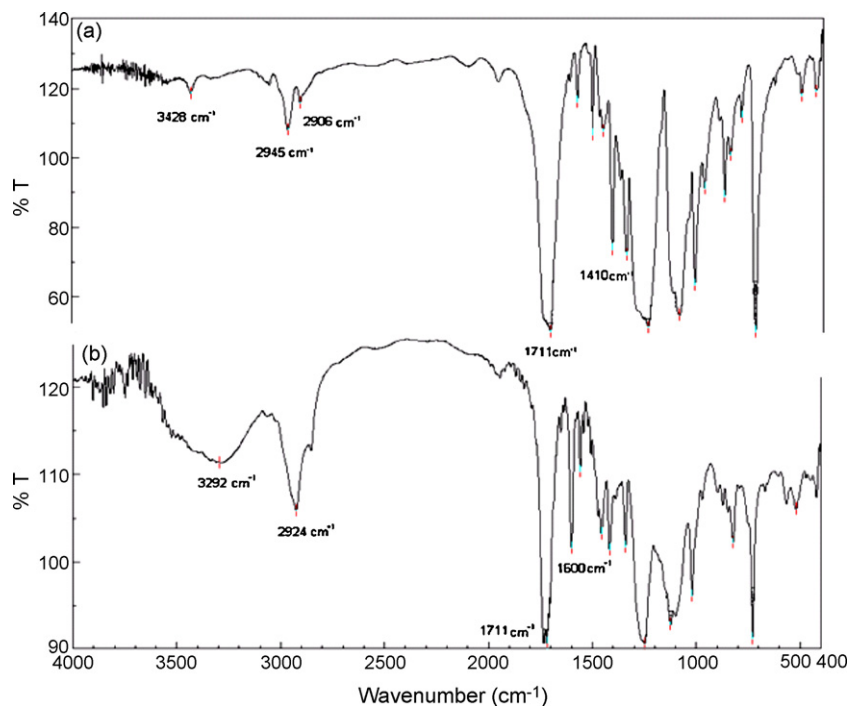
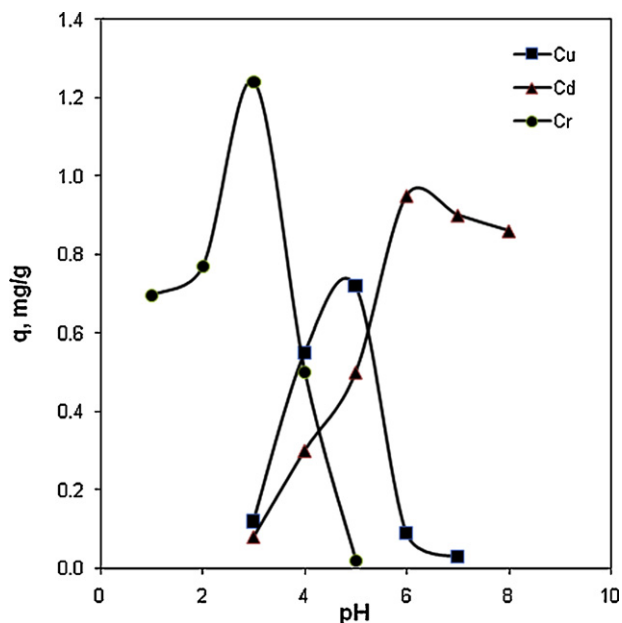


Fig. 2. FTIR spectra of: (a) ungrafted, (b) 180% 4-VP/HEMA monomers mixture grafted PET fibers.



**Fig. 3.** The pH dependence of metal ions adsorbed by 4-VP/HEMA grafted PET fibers. [Ions concentration = 5 ppm; temperature = 25 °C; contact time = 150 min; graft yield = 90%.]

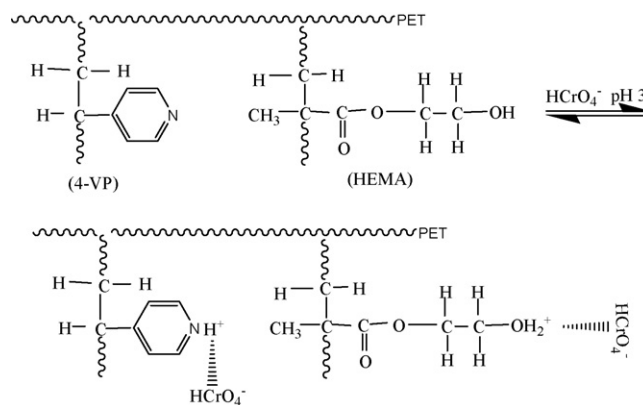
the introduction of the OH groups onto the 4-VP/HEMA grafted PET fibers. The new peak at 1600  $\text{cm}^{-1}$  in the spectrum is due to the resonance peak of the 4-VP groups. Hence these results provided strong proof for the grafting of both monomers onto PET fibers.

### 3.1. Effects of pH on adsorption

Because the pH value influences the surface structure of grafted PET fiber, pH is one of the most important factors influencing the adsorption behaviour of metal ions on the adsorbent. The uptake of ions as function of pH was examined over a pH range of 1–8. Fig. 3 shows that the pH value had a strong influence on Cr(VI), Cu(II) and Cd(II). The grafted PET fibers showed a high adsorption ability for Cr(VI) at pH 3. Cu(II) and Cd(II) ions could be adsorbed from solution at pH 5 and pH 6, respectively.

To explain the observed behaviour of the adsorption of heavy metal ions with varying pH, it is necessary to examine various mechanisms such as electrostatic interactions and chemical reactions which are responsible for adsorption on sorbent surface. In low acidic conditions, the 4-VP and OH of HEMA groups are fully protonated; thus the adsorbent is not active for the uptake of Cu(II) and Cd(II) ions. The high hydrogen ion concentration at the interface electrostatically repels positively charged Cu(II) and Cd(II) ions, preventing their approach to the fiber surface. The low adsorption values are in line with expectations. At optimum pH for Cu(II) and Cd(II) ions, there is a negative charge on the surface of grafted PET fiber; thus uptake of metal cations increases. Pyridine and OH groups (Lewis base) loaded negative poles can therefore attract Cu(II) and Cd(II) ions. The ions would be expected to have activity as a Lewis acid. Lewis acids prefer to complex with Lewis bases. In this way, these ions interact with grafted PET fibers, which is known as Lewis acid–base interactions. On the other hand beyond the optimum pH, Lewis acid–Lewis base interaction would not play an important role in the adsorption process of Cu(II) and Cd(II) ions.

From the stability diagram [24,25], it is evident that the most prevalent forms of Cr(VI) in aqueous systems are acid chromates ( $\text{HCrO}_4^-$ ), chromates ( $\text{CrO}_4^{2-}$ ), dichromates ( $\text{Cr}_2\text{O}_7^{2-}$ ), and other oxyanions. From the stability diagram for the Cr(VI)– $\text{H}_2\text{O}$  system, it is evident that at low pH, acid chromates ions ( $\text{HCrO}_4^-$ ) are



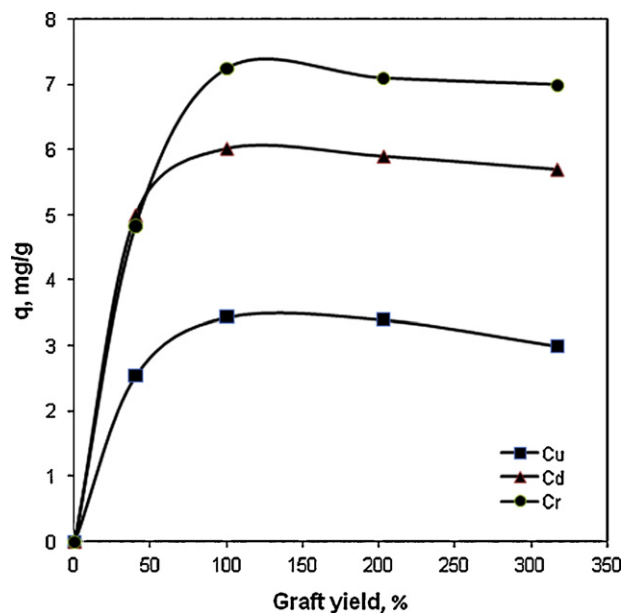
**Scheme 1.** Adsorption of Cr(VI) ions on the 4-VP/HEMA grafted PET fibers.

the dominant species, while chromates ( $\text{CrO}_4^{2-}$ ) became the main species in solution at pH 7.0 and above. For the adsorption of Cr(VI) species on the 4-VP/HEMA grafted PET fibers at pH 3.0, most of the 4-VP and OH groups on surface of the sorbent were protonated and possessed positive electric charges. The protonated groups can therefore attract the Cr(VI) species which carried negative electric charges in the solution through the electrostatic interaction. On the other hand, at pH around 6.0, the protonation of the these groups on the 4-VP/HEMA grafted PET fibers was relatively insignificant and the electrostatic interaction would not play an important role in the adsorption of Cr(VI) on the sorbent. This may be illustrated as in Scheme 1. The similar adsorption mechanisms of hexavalent chromium species on aminated polyacrylonitrile fibers was proposed by Deng and Bai [26].

These results suggested that the optimum pH for quantitative and selective separation of Cr(VI) ion from Cu(II) and Cd(II) ions is 3.

### 3.2. Effect of graft yield and contact time on adsorption

The effect of the graft yield on the adsorbed amount of metal ions was investigated at 25 °C, while keeping all other conditions constant. The results are shown in Fig. 4. The amount of ions adsorbed



**Fig. 4.** Effect of the graft yield on the adsorbed amount of metal ions on 4-VP/HEMA grafted PET fibers. [Ions concentration = 30 ppm; Cr(VI) pH 3, Cu(II) pH 5, Cd(II) pH 6; temperature = 25 °C; contact time = 150 min.]



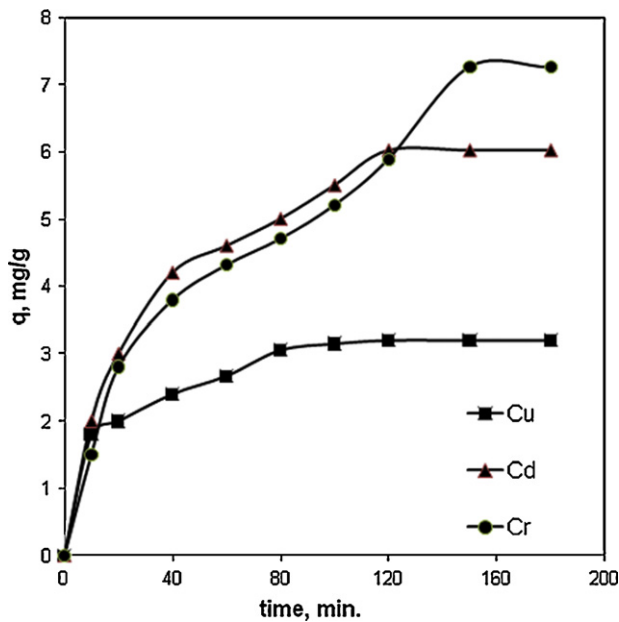


Fig. 5. Relationship between adsorption time and adsorbed amount of metal ions with 4-VP/HEMA grafted PET fibers. [Ions concentration = 30 ppm; Cr(VI) pH 3, Cu(II) pH 5, Cd(II) pH 6; temperature = 25 °C; graft yield = 90%.]

increased till the grafting yield reached 90% and beyond that point the results levelled off. Ungrafted PET fibers do not contain suitable functional groups and thus cannot interact with heavy metal ions. Adsorption amount of PET fiber is increased by grafting of PET fibers with 4-VP/HEMA monomer mixtures inserting into the fibers structure of the functional groups of 4-VP and HEMA. The increase in the adsorption with increasing graft yield may be attributed to a higher surface area and more active sites. The leveling off of adsorption may be attributed to the saturation of active sites on the grafted fibers by ions.

Fig. 5 shows the effect of contact time on adsorption of metal ions by 4-VP/HEMA grafted PET fibers. It is seen that the adsorption takes place rapidly at first, and then levels off. The similar types of curve were observed in our previous work [27–29]. The adsorption equilibrium of Cr(VI), Cu(II) and Cd(II) ions was attained within 150, 80 and 120 min, respectively. During the adsorption of metal ions, initially the ions reached the boundary layer and then had to diffuse into the grafted PET fibers surface and finally they had to diffuse into the fibrous structure of the adsorbent. Therefore, this event will take a relatively longer contact time. The relation between the nature of the polymer and sorption rate is generally complicated by many possible interactions on the surface. Generally the electrostatic interaction surface binding and chemical reaction may be identified as the major adsorption mechanisms. Thus those groups of 4-VP/HEMA grafted PET fibers are responsible for the interaction of ions with the fibers.

The applicability of the pseudo-first-order and pseudo-second-order kinetic models was tested for the adsorption of heavy metal ions onto 4-VP/HEMA grafted PET fibers. The best fit model was selected based on both linear regression correlation coefficient

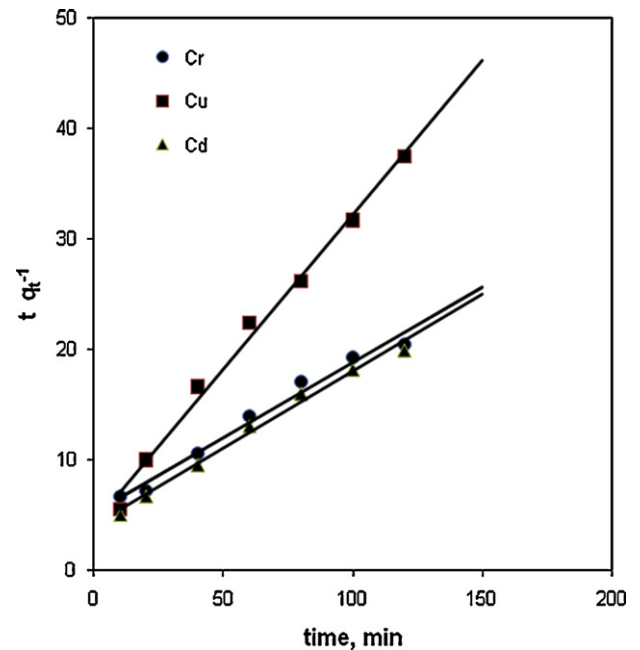


Fig. 6. Pseudo-second-order plots for metal ions on 4-VP/HEMA grafted PET fibers.

and the calculated  $q_e$  values. The Lagergren equation a pseudo-first-order equation describes the kinetics of adsorption process as follows [30].

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \quad (4)$$

where  $q_t$  and  $q_e$  are the amount of ions adsorbed ( $\text{mg g}^{-1}$ ) at any time and equilibrium time, respectively,  $k_1$  is the rate constant ( $\text{min}^{-1}$ ). According to the adsorption equation, the experimental result of Fig. 5 can be converted into the plots of  $\log(q_e - q_t)$  versus  $t$ . Value of  $k_1$  was calculated from the linear plot of  $\log(q_e - q_t)$  versus  $t$ . Experimental and theoretically calculated  $q_e$  values and coefficients related to Lagergren's plots are given in Table 1. As it can be seen from the results that the linear correlation coefficients of the plots are not good and experimental and calculated  $q_e$  values are not in agreement with each other. So, these results suggest that the adsorption of Cr(VI), Cu(II) and Cd(II) metal ions on grafted PET fiber is not a first-order reaction.

The second-order kinetic model [31] is expressed as:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \frac{t}{q_e} \quad (5)$$

where  $k_2$  ( $\text{g min}^{-1} \text{mg}^{-1}$ ) is the rate constant of second-order adsorption. If second-order kinetic is applicable, the plot of  $t/q_t$  versus  $t$  should show a linear relationship. The equilibrium adsorption capacity  $q_e$  can be calculated from Eq. (5).  $k_2$  and  $q_e$  were calculated from the intercept and slope of the plot of  $t/q_t$  versus  $t$ . The graphical interpretation of the data for the second-order-kinetic model is given in Fig. 6. The rate constants ( $k_2$ ), correlation coefficients of the plots together with the experimental and theoretical  $q_e$  values are given in Table 1. It is clear from these results

Table 1  
First-order, second-order and intra-particle diffusion rate constants.

Metal	$q_e$ (exp.) ( $\text{mg g}^{-1}$ )	First-order rate constants		Second-order rate constants			Intra-particle diff. Rate constants		
		$k_1$ ( $\text{min}^{-1}$ )	$q_e$ (theor.) ( $\text{mg g}^{-1}$ )	$R^2$	$k_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$q_e$ (theor.) ( $\text{mg g}^{-1}$ )	$R^2$	$k_{id}$ ( $\text{mg g}^{-1} \text{min}^{-1/2}$ )	$R^2$
Cr(VI)	7.25	0.0161	5.68	0.95	0.0349	7.41	0.98	0.171	0.98
Cu(II)	3.20	0.0299	2.25	0.91	0.0182	3.58	0.99	0.194	0.98
Cd(II)	6.02	0.0207	4.74	0.98	0.0048	7.19	0.99	0.485	0.98

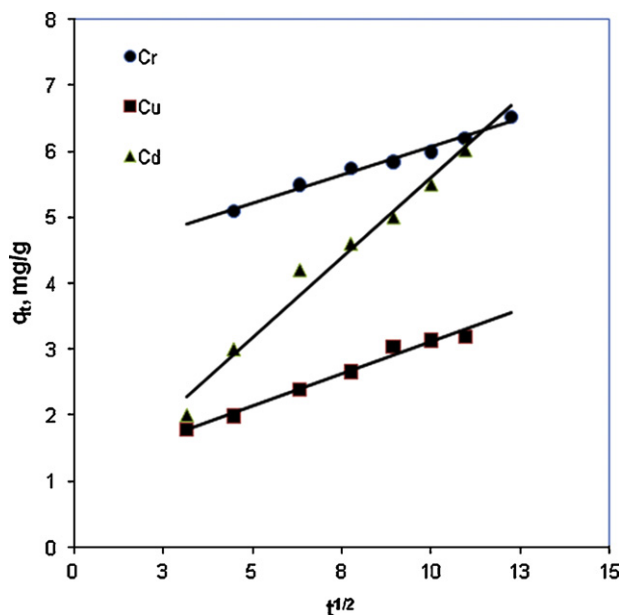


Fig. 7. Test of intra-particle diffusion model for the removal of metal ions by 4-VP/HEMA grafted PET fibers.

that the correlation coefficients are very high and experimental and theoretical  $q_e$  values are in accordance with each other. This shows that the adsorption of metal ions [Cr(VI), Cu(II) and Cd(II)] onto 4-VP/HEMA grafted PET fiber follows the second-order reaction. This result can be expected because the ordinary type of exchange processes are more rapid and controlled mainly by diffusion, whereas, those in a chelating exchange are slower and controlled either by particle diffusion mechanism or by a second-order reaction.

The possibility of intra-particle diffusion resistance affecting adsorption was explored by using the intra-particle diffusion model as [32]:

$$q_t = k_p t^{1/2} \quad (6)$$

where  $k_p$  is the intra-particle diffusion rate constant. The  $q_t$  should be linearly proportional to the  $t^{1/2}$  and  $k_p$  could be obtained from

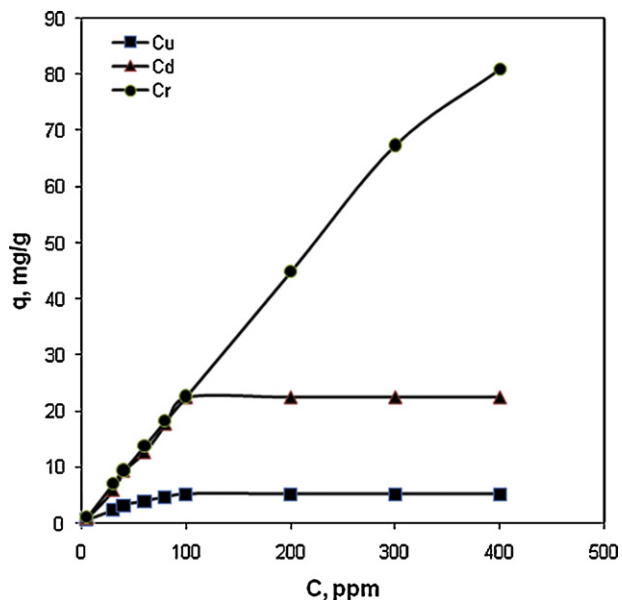


Fig. 8. Effect of initial concentration of metal ions on adsorption. [Cr(VI) pH 3, Cu(II) pH 5, Cd(II) pH 6; temperature = 25 °C; contact time = 150 min; graft yield = 90%.]

Table 2  
Langmuir and Freundlich isotherm constants.

Metal	Langmuir isotherm parameters			Freundlich isotherm parameters		
	$Q_0$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	$R^2$	$K_F$ ( $\text{mg g}^{-1}$ )	$n$	$R^2$
Cr(VI)	4.93	25.35	0.698	6.840	1.63	0.987
Cu(II)	0.23	29.99	0.956	0.442	1.74	0.994
Cd(II)	0.73	17.12	0.933	0.706	0.75	0.982

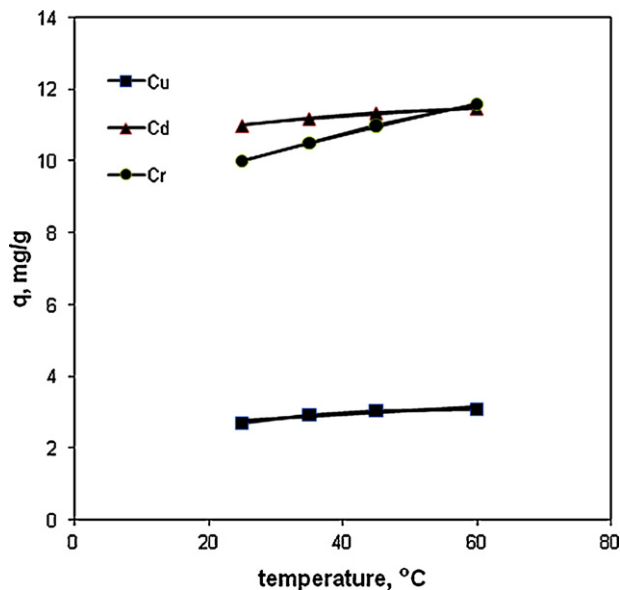


Fig. 9. Effect of temperature on the adsorption amount of metal ions. [Ions concentration = 50 ppm; Cr(VI) pH 3, Cu(II) pH 5, Cd(II) pH 6; graft yield = 90%.]

the slope of the relationship (Fig. 7). The intra-particle diffusion constants were calculated from the slope of the linear curves and given in Table 1. Bulk diffusion is observed as can be seen from Fig. 7 [33].

Adsorption process involves three continuous steps. The first step is the diffusion of ions through the aqueous solution on to the fiber. The second step is the adsorption of ions into the outer

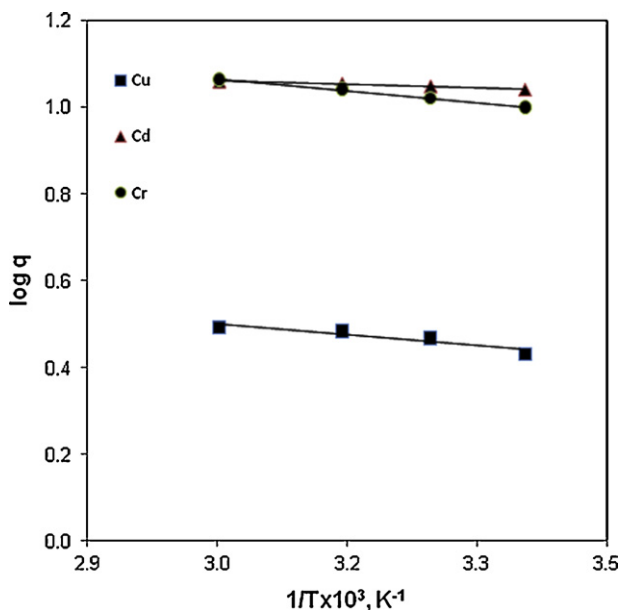


Fig. 10.  $\log q$  versus  $T^{-1}$  of metal ions.

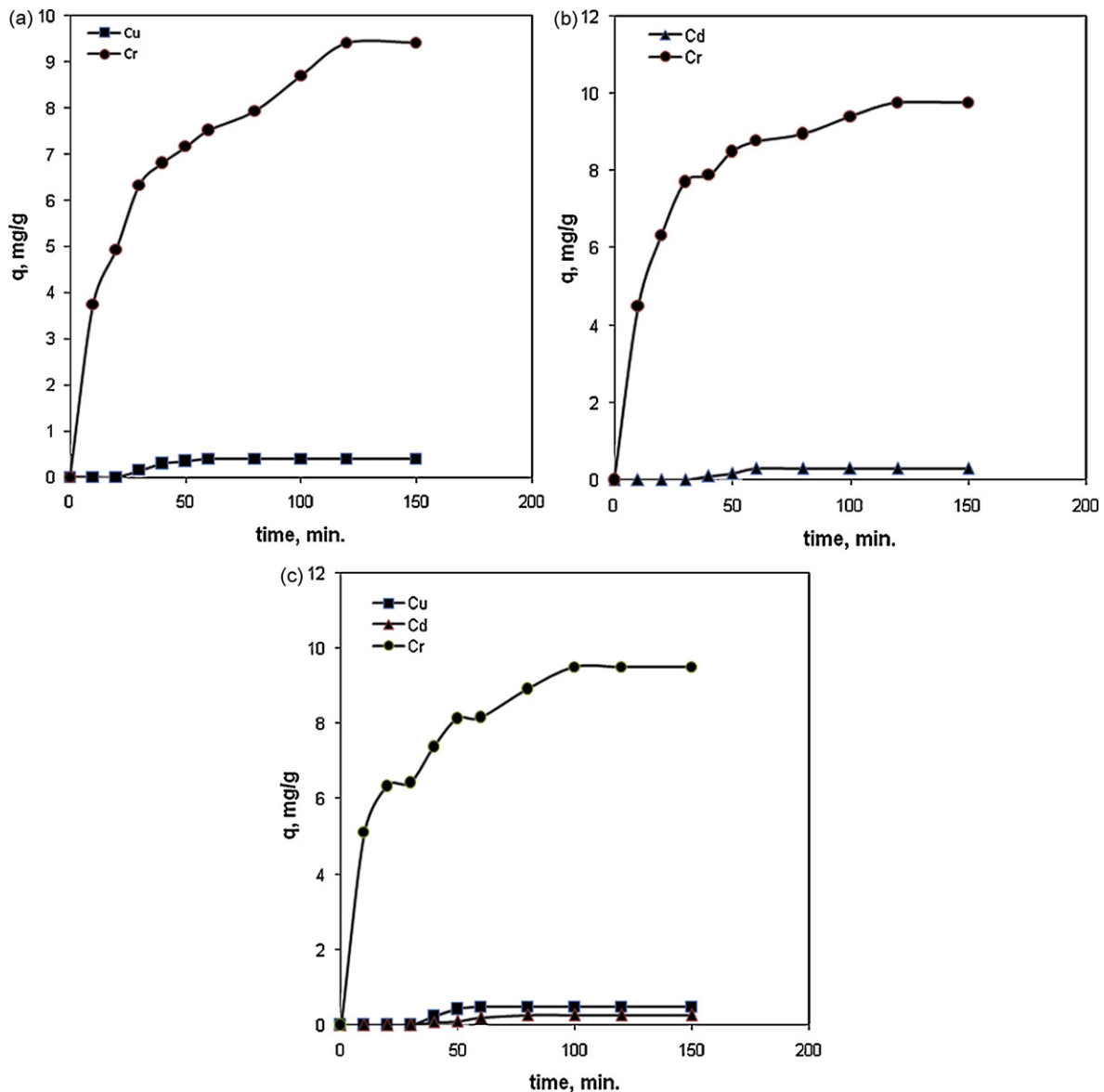
layer of the fiber. And the last step is the diffusion of ions into the fiber inside from the adsorbed surface. The second step the actual adsorption process is generally assumed to be much more rapid than either of the other diffusion steps. Of the two diffusion steps the diffusion into the inner layer is much slower than the movement of ions through the aqueous solution due to the physical obstruction of ions diffusion presented by the network of fiber molecules [34].

### 3.3. Effect of ion concentration on adsorption

The effect of initial metal ion concentration on the adsorption efficiency by 4-VP/HEMA grafted PET fibers was systematically investigated by varying the initial concentration between 5 and 400 mg L<sup>-1</sup>. Fig. 8 shows the adsorbed amount of ions as a function of initial concentration at optimum pH. It is clear from the figure that as the concentration of the ions increased, adsorption increased rapidly, then levelled off for Cu(II) and Cd(II). The adsorption amount increased as the initial Cr(VI) concentration was increased. The maximum adsorption performances for Cr(VI),

Cu(II) and Cd(II) were achieved at 81, 5.2 and 22.6 mg g<sup>-1</sup> using 400 mg L<sup>-1</sup> metal ions solution, respectively. The results suggest that the affinity of Cr(VI) for grafted PET fibers was higher than that of Cu(II) and Cd(II). It was observed that 4-VP/HEMA grafted PET fibers reduced from 99 to 94% when initial Cr(VI) concentration varied from 5 to 400 mg L<sup>-1</sup> at pH 3.0. The relation between the nature of the polymer and sorption rate is generally complicated by many possible interactions on the surface. Commonly, the electrostatic interaction, surface complexation, and ion exchange mechanisms may be identified as the major adsorption mechanisms. In particular, the 4-VP and OH of HEMA groups on the surface of an adsorbent have been reported to be effective in the adsorption of Cr(VI) ions [34,35]. Thus those groups of 4-VP/HEMA grafted PET fibers are responsible for the interaction of ions with the fiber. Grafted PET fiber has these groups, which are polar and very hydrophilic. Therefore, 4-VP/HEMA grafted PET fibers displayed very high adsorption capacity.

The values reported varied in the range of 1.4–91 mg g<sup>-1</sup> for adsorption capacities of Cr(VI) [24,26,36–39]. It has been recognized that the adsorption capacity of 4-VP/HEMA grafted PET fibers



**Fig. 11.** Competitive adsorption of ions onto 4-VP/HEMA grafted PET fibers. [(a) Cr(VI)–Cu(II); (b) Cr(VI)–Cd(II); (c) Cr(VI)–Cu(II)–Cd(II); pH 3; ions concentration = 50 ppm; contact time = 150 min; temperature = 25 °C; graft yield = 90%.]

is very good in comparison with the values in this range; thus it seems that the 4-VP/HEMA grafted PET fibers could be an interesting alternative and economical industrial adsorbent.

### 3.3.1. Adsorption isotherm

The relationship between the amount of metal ions adsorbed and the metal ions concentration remaining in solution is described by an isotherm. The two most common isotherm types for describing this type of system are the Langmuir and Freundlich [40,41]. The Langmuir isotherm is given as:

$$Q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (7)$$

The constant  $Q_0$  and  $b$  are characteristics of the Langmuir equation and can be determined from a linearized form of Eq. (7).

$$\frac{C_e}{Q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (8)$$

where  $C_e$  is the concentration of basic dye ( $\text{mg L}^{-1}$ ) at equilibrium,  $Q_0$  the monolayer capacity of adsorbent ( $\text{mg g}^{-1}$ ),  $Q_e$  is the amount of adsorption at equilibrium and  $b$  Langmuir adsorption constant ( $\text{L mg}^{-1}$ ). Thus a plot of  $C_e/Q_e$  versus  $C_e$  should yield a straight line having a slope of  $Q_0^{-1}$  and intercept of  $(Q_0 b)^{-1}$ . Therefore, the relevant experimental data were treated and it was observed that the relationship between  $C_e/Q_e$  and  $C_e$  is linear, indicating that the adsorption behaviour follows the Langmuir adsorption isotherms. The  $b$ ,  $Q_0$  and correlation coefficients ( $R^2$ ) values are presented in Table 2.

The Freundlich isotherm is derived to model the multilayer adsorption. The Freundlich model is formulated as:

$$Q_e = K_F C_e^{1/n} \quad (9)$$

The equation may be linearized by taking the logarithm of both sides of Eq. (9) and linear form of Freundlich isotherm can be given as:

$$\log Q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (10)$$

where  $C_e$  is equilibrium concentration ( $\text{mg L}^{-1}$ ),  $K_F$  the sorption capacity ( $\text{mg g}^{-1}$ ) and  $n$  is an empirical parameter. Thus a plot of  $\log Q_e$  versus  $\log C_e$  should give a straight line having a slope of  $1/n$  and intercept of  $L$ . The  $K_F$ ,  $n$  and correlation coefficients ( $R^2$ ) values are presented in Table 2.

On the comparison of the  $R^2$  values given in Table 2, we can conclude that in all cases for the adsorption of target heavy metal ions to the 4-VP/HEMA grafted PET fibers, Freundlich equation represents a better fit to the experimental data than the Langmuir equation. The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface whereas in the Langmuir theory, the basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. This result also predicts the heterogeneity of the adsorption sites on grafted PET fibers (see Fig. 1b).

### 3.4. Effects of temperature on adsorption

It has been recognized that the adsorption of heavy metal ions from an aqueous solution by 4-VP/HEMA grafted PET fiber is affected by the temperature (Fig. 9) such that the adsorption increases slowly as the temperature increases. As the temperature rises, the diffusion of the ions becomes much easier into the fibers because of the increase in the degree of swelling, so the adsorption amount of metal ions increases as well.

Fig. 10 was obtained using the data of Fig. 9 and from the Arrhenius plot of  $\log q$  versus  $T^{-1}$ . From the slopes of Fig. 9, the activation energies for adsorption were calculated as 0.380, 0.120

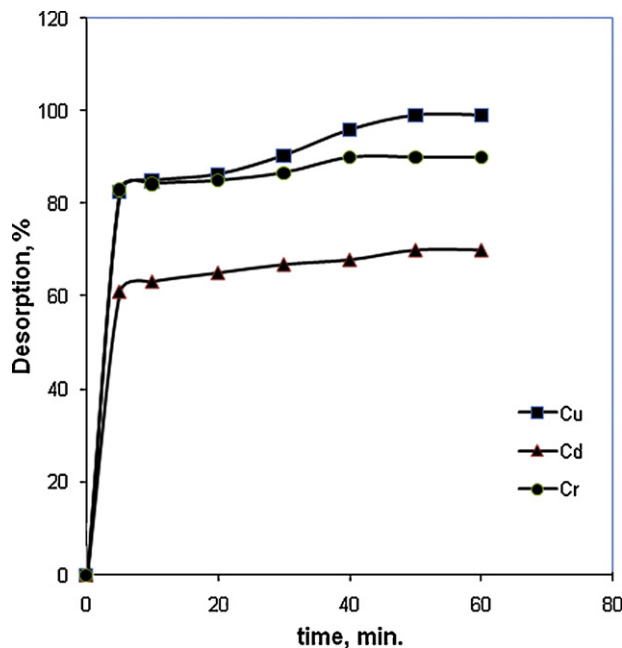


Fig. 12. Desorption profile of metal ion adsorbed PET fibers. [Graft yield = 90%; ion concentration = 50 ppm; temperature = 25 °C; contact time = 60 min.]

and  $0.421 \text{ kJ mol}^{-1}$  for Cu(II), Cd(II) and Cr(VI), respectively. These low values of  $E_a$ , compared to those of typical chemical reaction of  $65\text{--}250 \text{ kJ mol}^{-1}$ , imply that the adsorptions of grafted fibers for the metal ions are facile procedures [25].

### 3.5. Selective adsorption of metals ions

4-VP/HEMA grafted PET fiber can be used to selective separate Cr(VI) ion from binary and ternary mixed solution of metal ions. Fig. 11 shows the results of removal of metal ions by grafted fiber from an equimolar solution of Cr(VI), Cu(II) and Cd(II) ions at pH 3. Cr(VI) showed the higher affinity to 4-VP/HEMA grafted PET fiber and its uptake was not significantly affected by the presence of Cu(II) and Cd(II) ions in the solution. In the Cr(VI)–Cu(II), Cr(VI)–Cd(II) and Cr(VI)–Cu(II)–Cd(II) systems, the adsorption selectivity exceeds 97% for Cr(VI). Adsorption selectivity for Cr(VI) at pH 3 was excellent in these binary and ternary systems. It can be applied to the quantitative and selective separation of Cr(VI) ion in aqueous systems containing Cu(II) and Cd(II) ions.

### 3.6. Desorption studies

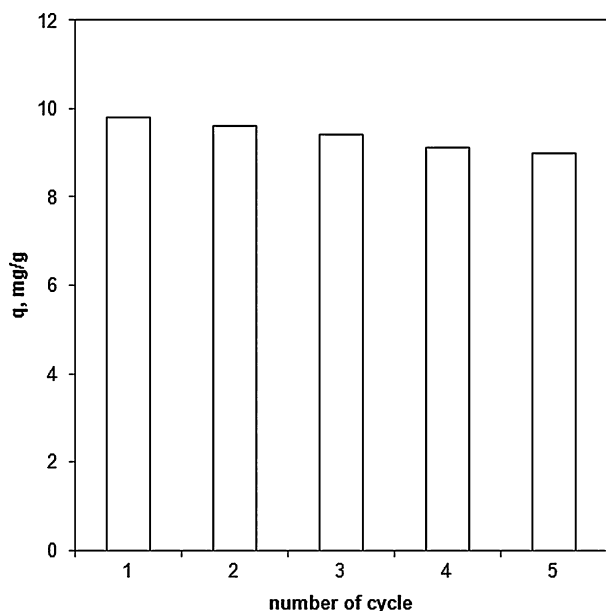
The study of desorption of metal ions was carried out and represented in Fig. 12. The Cr(VI) and Cu(II), Cd(II) adsorbed were easily desorbed by treating with 1 M KOH and 1 M HNO<sub>3</sub> at room temperature, respectively, within 50 min as seen from Fig. 12. The highest desorption percentages were found as 90, 99 and 70% for Cr(VI), Cu(II) and Cd(II), respectively.

The investigation in the desorption studies confirms the mechanism of adsorption stated in the pH effect. Desorption of heavy metal ions was quite fast. It has been recognized that 4-VP/HEMA mixture grafted PET fiber is stable and regenerable by acid and base. Therefore, adsorption process should be effective for the removal of heavy metal from industrial effluents.

### 3.7. Reusability

The adsorption/desorption cycles (Fig. 13) were repeated for five cycles using 0.1 g of the grafted fiber. It is observed that the adsorp-





**Fig. 13.** Adsorption/desorption and repeated adsorption of grafted fibers. [Graft yield = 90%; pH 3; Cr(VI) ions concentration = 50 ppm; temperature = 25 °C; contact time = 150 min.]

tion capacity of grafted PET fiber showed a slight decrease for Cr(VI) ions. The desorbed 4-VP/HEMA mixture grafted PET fibers were highly effective for the re-adsorption of Cr(VI) ions.

#### 4. Conclusions

In this study, adsorbent was prepared by grafting 4-VP/HEMA comonomer mixtures onto PET fiber. Effects of various parameters such as grafting yield, pH, adsorption time, initial ion concentration and adsorption temperature on the adsorption amount of ions onto reactive fibers were investigated. As results, the following conclusions were obtained:

- (1) The adsorption amount of metal ions increased with the increase of grafting yield and reached a plateau value around 90% grafting yield.
- (2) The optimum pH for quantitative and selective separation of Cr(VI) ion from Cu(II) and Cd(II) ions is 3.
- (3) Adsorption kinetic data follows pseudo-second-order kinetic model.
- (4) Adsorption onto 4-VP/HEMA grafted PET fiber can be expressed better with Freundlich type adsorption isotherm which shows the heterogeneous characteristics of the adsorption sites on grafted PET fibers.
- (5) Adsorption selectivity for Cr(VI) at pH 3 was excellent in these binary and ternary systems.
- (6) It can be applied to the quantitative and selective separation of Cr(VI) ion in aqueous systems containing Cu(II) and Cd(II) ions.

#### Acknowledgement

We are grateful to The Scientific and Technological Research Council of Turkey (TUBITAK, grant number 107T225) for the financial support for this work.

#### References

- [1] R.L. Ramos, L.A.B. Jacome, R.M.G. Coronado, L.F. Rubio, Competitive adsorption of Cd(II) and Zn(II) from aqueous solution onto activated carbon, *Sep. Sci. Technol.* 36 (16) (2001) 3673–3687.

- [2] M. Sciban, M. Klasnja, B. Skrbic, Modified softwood sawdust as adsorbent of heavy metal ions from water, *J. Hazard. Mater. B* 136 (2006) 266–271.
- [3] N. Ünlü, M. Ersöz, Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions, *J. Hazard. Mater. B* 136 (2006) 272–280.
- [4] M. Arslan, Z. Temoçin, M. Yiğitoğlu, Removal of cadmium(II) from aqueous solutions using sporopollenin, *Fresenius Environ. Bull.* 13 (7) (2004) 1–4.
- [5] R. Schmuhl, H.M. Krieg, K. Keizer, Adsorption of Cu(II) and Cr(VI) ions by chitosan: kinetics and equilibrium studies, *Water SA* 27 (2001) 1–7.
- [6] Y.S. Ho, J.C.Y. Ng, G. McKay, Removal of Lead(II) from effluents by sorption on peat using second-order kinetics, *Sep. Sci. Technol.* 36 (2) (2001) 241–261.
- [7] S.R. Shukla, V.D. Sakhardande, Column studies on metal ions removal by dyed cellulosic materials, *J. Appl. Polym. Sci.* 44 (1992) 903–910.
- [8] A. Lezzi, S. Cobianco, Chelating resins supporting dithiocarbamate and methylthiourea groups in adsorption of heavy metal ions, *J. Appl. Polym. Sci.* 54 (1994) 889–897.
- [9] R. Coşkun, C. Soykan, M. Saçak, Adsorption of copper(II), nickel(II) and cobalt(II) ions from aqueous solution by methacrylic acid/acrylamide monomer mixture grafted poly(ethylene terephthalate) fiber, *Sep. Purif. Technol.* 49 (2006) 107–114.
- [10] Y.S. Al-Degs, M.I. El-Barghouthi, A.A. Issa, M.A. Khraisheh, G.M. Walker, Sorption of Zn(II), Pb(II), and Co(II) using natural sorbent: equilibrium and kinetic studies, *Water Res.* 40 (2006) 2645–2658.
- [11] B.H. Jeon, B.A. Dempsey, W.D. Burgos, R.A. Royer, Sorption kinetics of Fe(II), Zn(II), Co(II), Ni(II), Cd(II) and Fe(II)/Mn(II) onto hematite, *Water Res.* 37 (2003) 4135–4142.
- [12] S.B. Deng, R.B. Bai, J.P. Chen, Behaviors and mechanisms of copper adsorption on hydrolyzed polyacrylonitrile fibers, *J. Colloid Interface Sci.* 260 (2) (2003) 265–272.
- [13] S. Deng, R. Bai, Removal of trivalent and hexavalent chromium with aminated polyacrylonitrile fibers: performance and mechanisms, *Water Res.* 38 (9) (2004) 2423–2431.
- [14] M. Arslan, M. Yiğitoğlu, O. Şanlı, H.İ. Ünal, Kinetics of swelling grafting of 4-vinyl pyridine onto poly(ethylene terephthalate) fibers using a benzoyl peroxide initiator, *Polym. Bull.* 51 (2003) 237–244.
- [15] E.M. Abdel-Bary, A.A. Sarhan, H.H. Abdel-Razik, Effect of graft copolymerization of 2-hydroxyethyl methacrylate on the properties of polyester fibers and fabric, *J. Appl. Polym. Sci.* 35 (1988) 439–448.
- [16] M. Saçak, F. Oflaz, Benzoyl peroxide initiated graft copolymerization of poly(ethylene terephthalate) fibers with acrylic acid, *J. Appl. Polym. Sci.* 50 (1993) 1909–1916.
- [17] S. Mishra, P.L. Nayak, G. Sahu, Graft copolymerization of Methyl methacrylate onto poly(ethylene terephthalate) fibers using thallium(III) ions as initiator, *J. Appl. Polym. Sci.* 50 (1993) 1909–1916.
- [18] O. Sanlı, S. Aytemiz, H.İ. Ünal, Graft copolymerization of acrylamide on swollen poly(ethylene terephthalate) fibers using cerium ammonium nitrite initiator, *J. Macromol. Sci., Pure Appl. Chem.* A34 (1997) 1003–1015.
- [19] K.N. Rao, M.H. Rao, H.T. Lokhande, N.R. Mody, A.G. Jog, Grafting onto polyester fibers. II. Kinetics of grafting of acrylic acid, acrylonitrile and vinyl acetate onto polyester fibers, *J. Appl. Polym. Sci.* 9 (1979) 1911–1919.
- [20] M. Yiğitoğlu, M. Arslan, 4-Vinylpyridine and 2-hydroxyethylmethacrylate monomer mixture graft copolymerization onto poly(ethylene terephthalate) fibers using benzoyl peroxide, *Polym. Bull.* 58 (2007) 785–798.
- [21] D. Campbell, K. Araki, T. Turner, ESR study of free radicals formed X-irradiation of poly(ethylene terephthalate), *J. Polym. Sci., Part A* 19 (1966) 461–480.
- [22] D. Campbell, T. Turner, ESR study of radicals trapped in amorphous and crystalline samples of poly(ethylene terephthalate), *J. Polym. Sci., Part A* 5 (1967) 2199–2201.
- [23] D. Campbell, L.K. Monteith, T. Turner, Post-irradiation free radical reactions in poly(ethylene terephthalate), *J. Polym. Sci., Part A-1* 8 (1970) 2703–2711.
- [24] J. Paradhan, S.N. Das, R.S. Thakur, Adsorption of hexavalent chromium from aqueous solution by using activated red mud, *J. Colloid Interface Sci.* 217 (1999) 137–141.
- [25] L.D. Benefield, J.P. Judkins, B.L. Wend, *Process Chemistry for Water and Wastewater Treatment*, Prentice Hall, Englewood Cliffs, NJ, 1982.
- [26] S. Deng, R. Bai, Removal of trivalent and hexavalent chromium with aminated polyacrylonitrile fibers: performance and mechanisms, *Water Res.* 38 (2004) 2424–2431.
- [27] M. Yiğitoğlu, M. Ersöz, R. Coşkun, O. Şanlı, H.İ. Ünal, Adsorption of Cu(II), Co(II) and Fe(III) ions from aqueous solutions on poly(ethylene terephthalate) fibers, *J. Appl. Polym. Sci.* 68 (12) (1998) 1935–1942.
- [28] R. Coşkun, M. Yiğitoğlu, M. Saçak, Adsorption behaviour of copper(II) ion from aqueous solution on methacrylic acid grafted poly(ethylene terephthalate) fibers, *J. Appl. Polym. Sci.* 75 (6) (2000) 766–772.
- [29] M. Yiğitoğlu, M. Arslan, O. Şanlı, H.İ. Ünal, Adsorption behaviour of copper(II) ion from aqueous solution on 4-vinyl pyridine grafted poly(ethylene terephthalate) fibers, *Hacetatepe J. Biol. Chem.* 31 (2002) 133–143.
- [30] G. Ciardelli, L. Corsi, M. Marucci, Membrane separation for wastewater reuse in the textile industry, *Resour. Conserv. Recycl.* 31 (2000) 189–197.
- [31] C. Namasivayam, D.J.S.E. Arasi, Removal of congo red from wastewater by adsorption onto waste red mud, *Chemosphere* 34 (1997) 401–417.
- [32] C. Namasivayam, K. Renganathan, Removal of Cd(II) from wastewater by adsorption on waste Fe(III)/Cr(III) hydroxide, *Water Res.* 29 (1995) 1737–1744.
- [33] G. McKay, Y.S. Ho, Pseudo-second order model for sorption processes, *Process Biochem.* 34 (1999) 451–465.

- [34] R.S. Bai, T.E. Abraham, Studies on enhancement of Cr(VI). Biosorption by chemically modified biomass of *Rhizopus nigricans*, *Water Res.* 36 (5) (2002) 1224–1236.
- [35] D. Rai, L.E. Eary, J.M. Zachara, Environmental chemistry of chromium, *Sci. Total Environ.* 86 (1989) 15–23.
- [36] R.S. Bai, T.E. Abraham, Studies on chromium(VI) adsorption–desorption using immobilized fungal biomass, *Bioresour. Technol.* 87 (2003) 17–26.
- [37] Z. Aksu, Ü. Açikel, E. Kabasakal, S. Teze, Equilibrium modelling of individual and simultaneous biosorption of chromium(VI) and nickel(II) onto dried activated sludge, *Water Res.* 36 (2002) 3063–3073.
- [38] A. Çelik, K. Dost, H. Sezer, An investigation of chromium(VI) ion removal from wastewaters by adsorption on residual lignin, *Fresenius Environ. Bull.* 13 (2) (2004) 124–127.
- [39] C. Raji, T.S. Anirudhan, Batch Cr(VI) removal by polyacrylamide-grafted sawdust: kinetics and thermodynamics, *Water Res.* 32 (12) (1998) 3772–3780.
- [40] I. Langmuir, The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.* 38 (11) (1916) 2221–2295.
- [41] H.M.F. Freundlich, Über die adsorption in losungen, *Z. Phys. Chem. A* 57 (1906) 385–470.