Polymer Bulletin 55, 259–268 (2005)
DOI 10.1007/s00289-005-0440-z

Polymer Bulletin

Adsorption of hexavalent chromium from aqueous solutions using 4-vinyl pyridine grafted poly(ethylene terephthalate) fibers

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Received: 18 November 2004 / Revised version: 18 August 2005 / Accepted: 25 August 2005

Summary

Sorption of hexavalent chromium ions from aqueous solution by 4- vinyl pyridine (4-VP) grafted poly(ethylene terephthalate) (PET) fibers was studied. The Influences of adsorption time, pH of solution and Cr(VI) concentration on the adsorbed amount were investigated. 30 minutes of treatment time was found to be sufficient to reach equilibrium. pH 3.0 was found as the optimum pH value in the process. The maximum adsorption capacity of the material (k_s) was found to be 263.16 mg g^{-1}. It was found that the reactive fibers are stable and regenerable by acid or base without losing their activity.

Introduction

Chromium contamination generated from various industries, such as electroplating, leather tanning, mining, steel making, and pigments, has a significant impact on human health and other living organisms in the environment. Human toxicity includes lung cancer, liver, kidney and gastric damage and epidermal irritation [1]. Therefore, the concentration of chromium ions has to be decreased to permissible levels, which are less than 0.05 mg L^{-1} [2].

In the environment, chromium, a redox active metal element, usually exists as Cr(III) or Cr(VI) species. Cr(III) in aqueous solution is relatively insoluble and an essential micronutrient, while Cr(VI) has been reported as toxic species. Due to its high toxicity, especially in the hexavalent form, the tolerated concentration is controlled by strict norms.

Adsorption has been one of the methods used to remove chromium species from aqueous solutions with relatively low chromium concentration. There are many types of adsorbents, including activated carbon [3-6], bentonite [7], biomaterials [8-14], lignin [15], chitosan [16], maple sawdust [17], polyacrylamide grafted sawdust [18], bagasse and fly ash [19], that have been studied for the adsorption of chromium from aqueous solutions. However, some of these adsorbents do not have high adsorption capacities or need long adsorption equilibrium times while others may have difficulty for regeneration and reuse.

One of the new developments in recent years to remove heavy metal ions from water or wastewater is the use of polymer fibers as adsorbent. This is mainly attributed to the relatively large external spesific surface areas, high adsorption kinetics, and low cost of these polymer fibers [20-23].

It is therefore of practical and research interest to develop effective adsorbents from these cheep polymer fibers for the removal of chromium in water and wastewater treatment. In our previous work, the adsorption behaviour of pure PET fibers was studied toward heavy metal ions in aqueous solutions by a batch equilibration technique [24]. We have also used methacrylic acid grafted PET fibers [25] and 4-VP grafted PET fibers [26] as an adsorbent for the removal of copper (II) ions from an aqueous solution. It has been observed that within those studies the reactive fibers are stable and regenerable by acid without losing their activity.

Experimental

Materials

The PET fibers (126 denier, 28 flaments) used in these experiments were provided by SASA Co. (Adana, Turkey). The fiber samples were Soxhlet-extracted until contant weight (for 6 h) with acetone and dried in a vacuum oven at 50°C. 4-VP was purified by vacuum distillation at 2 mmHg and 65°C. Benzoyl peroxide $[(C_6H_5C0)_2O_2]$ was twice precipitated from chloroform in methanol and dried in a vacuum oven for 2 days. Other reagents were used as supplied. All reagents were Merck products.

Swelling procedure

A temperature controlled oil bath was used for heating. The fiber samples (0.3± 0.01 g) were dipped into dicloroethane (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 procedure

Polymerization was carried out in a thermostated 100 mL tubes under reflux. The mixture containing the PET fiber sample (0.3 ± 0.01g), monomer, and $(C_6H_5C0)_2O_2$ at required concentration dissolved 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 (T=50°C). At the end of the predetermined polymerization time, fibers were removed from the polymerization medium and residual solvent, monomer and homopoly (4-VP) 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 (G Y) was calculated from the weight increase in grafted fibers as follows:

$$G\ Y\ (\%) = [(w_g - w_i)/w_i] \times 100 \qquad (1)$$

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

Determination ofiIntrinsic viscosity

Intrinsic viscosity measurements were carried out for 4-VP grafted PET fibers in m-cresol, using a Ubbelohde capillary flow viscometer mounted in a water bath maintained at 25.0 ± 0.1°C.

Determination of water absorption capacity

PET fibers were immersed in distilled water at 20°C for 48 h, blotted between a filter paper, and weighed. They were then vacuum dried at 50°C for 72 h and weighed again. Water absorption capacity was determined from the weight gain of the fibers.

Differential scanning calorimetry

Thermal analyses were performed with General V4.1C Dupont 2000 Differential Scanning Calorimeter (DSC). Sample weights ranged from 3.0 to 9.0 mg. The samples were heated from 30 °C to 300 °C at a heating rate of 10 °C/min. The intercept points of slopes were taken as glass transition temperatures (T_g).

Scanning electron microscopy

SEM studies of the original and 4-(VP) grafted PET fibers, coated with gold, were performed using a JEOL Model JSM 5600 microscope.

Sorption of chromium ions on the adsorbent

Volume of 30 cm^3 of Cr(VI) ion solution (20 mg L^{-1}, pH 3) were added onto 0.10 g of 4-VP grafted PET fibers in 100 mL erlen-mayer. The contents were shaken at 125 rpm for a predetermined period of time at 25 °C using orbital shaker (Edmund Mühler TH 15). After filtration (used a Cole-Parmer micro filtration apparatus with membrane filter) of the solution the chromium ion concentration of the filtrates was measured by a GBC 933A 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 poly 4-VP grafted PET fibers were evaluated by using the following expression:

$$q=(C_o-C)V/m \tag{2}$$

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

Effect of pH on chromium sorption

To study the effect of pH on sorption, the 4-VP grafted PET fibers were incubated for 30 min. with aqueous Cr(VI) solution (20 mg L^{-1}) adjusted to required pH values a range of 2-6 using buffer solutions (glycine/HCl, acetic acid/sodium acetate, di-sodium citrate dehydrate/tri-sodium citrate dehydrate).

Effect of contac time

The time required for the solid-liquid system to achieve the equilibrium conditions was determined by placing 30 cm^3 of 20 mg.L-1 aqueous solution of Cr(VI) with 0.1 g of the 4-VP grafted PET fibers. At each time (range of 0-60 min.) the supernatant was separated and the Cr(VI) ion determined as above.

Effect of ion concentration

To obtain the maximum adsorption capacity for Cr(VI), 30 cm^3 of aqueous solution in varying the initial concentration from 10 to 500 mg L^{-1} were shaken (125 rpm) with 0.1 g of the 4-VP grafted PET fibers for 30 min. at 25 °C. After filtration of the solution the Cr(VI) ion concentration of the filtrates was determined as above.

Desorption of chromium ions

Desorption assay were carried out with the Cr(VI) loaded 4-VP grafted PET fibers at maximum capacity. Metal ion was recovered by treating with 30 mL 1M NaOH, 1 M H_2SO_4, 1M HCl for 30 minutes, than analyzed by the method mentioned above. The desorption percent was calculated using the following equations:

$$\%\ \text{Desorption} = \frac{\text{Amount of Cr(VI) (mg) desorbed}}{\text{Adsorbed amount of Cr(VI) (mg) by adsorbent}} \times 100 \qquad (3)$$

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. $(C_6H_5C0)_2O_2$ under goes thermal dissociation as

$C_6H_5COOOOCH_5C_6 \rightarrow 2C_6H_5COO\bullet$

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

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 4-VP:

$C_6H_5COO\bullet + \text{4-VP} \rightarrow \text{4-VP}\bullet$

$C_6H_5\bullet + \text{4-VP} \rightarrow \text{4-VP}\bullet$

The chain-transfer reaction between growing poly4-VP chains and PET which forms active sites upon PET is homopolyP4-VP$\bullet$ + PET → PET$\bullet$ + homopolyP4-VP

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

PET$\bullet$ + 4-VP → 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:

PET-P$\bullet$ + homopolyP4-VP → graft copolymer + homopolyP4-VP$\bullet$

PET-P$\bullet$ + 4-VP → graft copolymer + 4-VP$\bullet$

PET-P$\bullet$ + initiator → graft copolymer + initiator$\bullet$

PET-P$\bullet$ + solvent → graft copolymer + solvent$\bullet$

PET-P$\bullet$ + homopolyP4-VP$\bullet$ → graft copolymer

PET-P$\bullet$ + PET-P$\bullet$ → graft copolymer

Grafted PET fibers were characterized by thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). Intrinsic viscosity, water absorption capacity, and thermal analysis result of 4-VP grafted PET fibers are given in Table 1. which were increased with the increasing graft yield, showing an evidence of grafting. The scanning electron micrographs of ungrafted and 4-VP grafted (25%) PET fibers are shown in Figure 1. It is clear from the SEM results that, the ungrafted PET fiber surface (Fig. 1.a) has a smooth and relatively homogeneous appearance. The grafted side chain, 4-VP, seems to form microphases attached to the PET back-bone and caused a heterogeneous appearance in the graft copolymer (Fig. 1.b), and showing another proof of grafting. Maximum percent grafting has been reported as 70% [27].

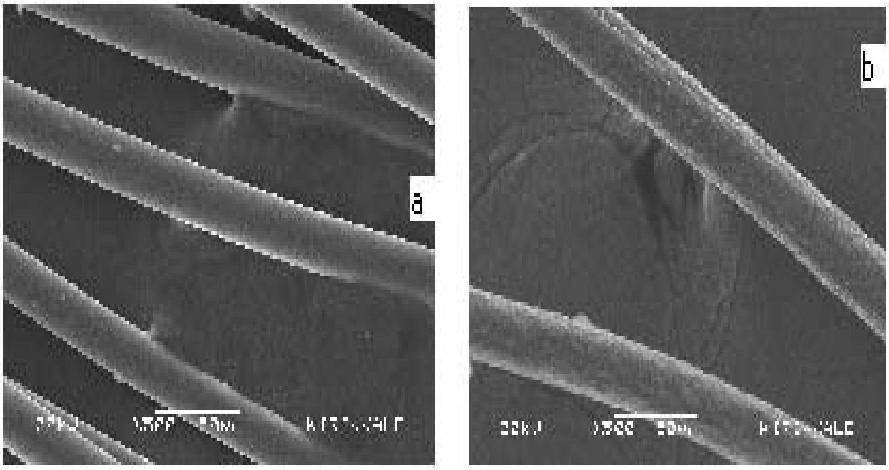


Figure 1. SEM micrographs of (a) ungrafted (500x) and (b) 4-VP grafted (500x) PET fibers.

Table 1. Variation of Intrinsic viscosity, water absorption capacity, and thermal analysis result with grafted yield.

% Graft Yield	*T_g (°C)*	*Intrinsic viscosity (dL/g)*	*Water absorption (%)*
Orijinal PET	81.05	-	2.3
9	-	0.25	14.0
26	141.26	0.56	28.0
38	-	0.70	32.6
43	145.07	0.82	35.0
50	-	0.90	36.0
60	146.80	1.50	38.0
70	-	1.70	44.0

Effect of graft yield and contact time

Preparing conditions of suitable 4-VP grafted PET fibers for the use of adsorption of Cr(VI) ions are give in Table 2 The effect of the graft yield on the adsorbed amount of Cr(VI) was investigated at 25 °C, while keeping all other conditions constant. The results are shown in Figure 2 It is seen that the adsorption takes place rapidly at first, then slows down and levels off. The similar type of curve was observed in our previous work [24-26, 28]. The adsorption equilibrium was attained within 30 minutes for all grafting levels examined. The results of the adsorption behaviour of the fibers indicated that adsorption ability of 70.0 % 4-VP grafted PET fibers is higher than that ones of others grafted fibers. The similar results were observed in the previous works [25, 26], 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. Commonly, the electrostatic interaction, surface complexation, and ion exchange mechanisms may be identified as the major adsorption mechanisms. In particular, the carboxyl and amino groups on the surface of an adsorbent have been reported to be effective in the adsorption of chromium ions [9, 29]. Thus those groups of 4-VP grafted PET fibers are responsible for the interaction of chromium ions with the fibers.

Table 2. Preparing conditions of suitable 4-VP grafted PET fibers.

Grafting Yield (%)	9	38	50	70
[4-VP]x10^{2} mol L^{-1}	11	20	40	60

$[(C_6H_5C0)_2O_2]$=2x10^{-3} mol L^{-1}; T=50°C; t=2 h

The kinetics of adsorption may be described [26,30] by using the following first-order rate expression:

$$\mathrm{Log}\frac{C_t}{C_o} = -\frac{k}{2.303}t \qquad (4)$$

Where t, is the adsorption time; k, is an adsorption rate constant; C_t, is the concentration amount of Cr(VI) ions at time t and, C_o, is the initial concentration of Cr(VI) ions. According to the adsorption equation, the experimental result of Figure 2 can be converted into the plots of log(C_t C_o^{-1}) versus t, as shown in Figure 3. which shows that the adsorption of Cr(VI) ions from aqueous solutions on 4-VP grafted PET fibers obeyed a first-order kinetic. Similar results were observed in the previous works [25,26,31,32]. Thus, the adsorption rate constants of the 4-VP grafted PET fibers calculated from the slopes of the plots are listed in Table 3. It is clearly seen that the adsorption rate constants increased with increasing percent graft yield.

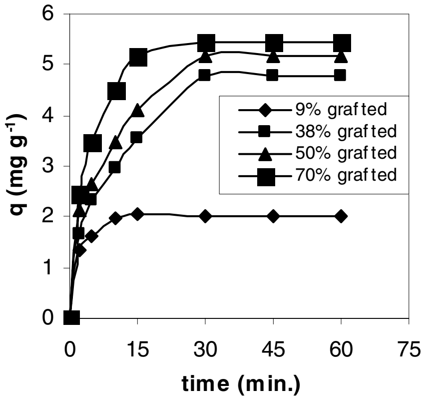


Figure 2. Relationship between adsorption time and adsorbed amount of Cr(VI) with 4-VP grafted PET fibers (Ion concentration = 20 ppm; pH=3; temperature= 298 K).

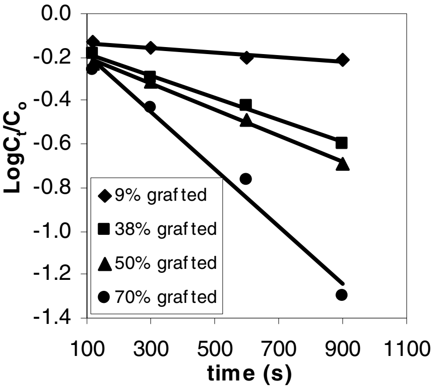


Figure 3. Plots of time versus log (C_t C_o^{-1}).

Table 3. Adsorption rate constant (k) of 4-VP grafted PET fibers.

Grafted Yield (%)	kx10^{3} (s^{-1})
9	0.230
38	1.152
50	1.382
70	2.994

Effect of pH

The uptake of Cr(VI) ions as a function of pH was examined over a pH range of 1-6. It is evident from Figure 4 that the adsorption is higher at lower pH, it is maximum at pH 3.0 and it suddenly decreases becoming almost negligible at pH 6.0. A similar type of behaviour is also reported for the adsorption of hexavalent chromium at different adsorbents [13,14,16,18,23].

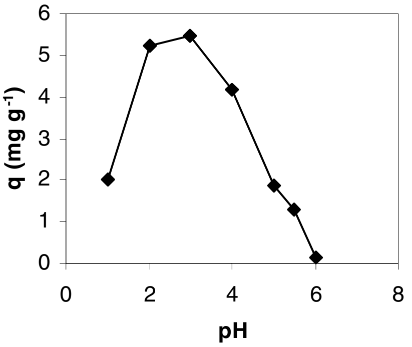
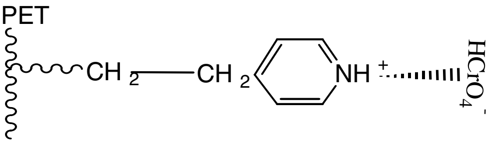


Figure 4. The pH dependence of Cr(VI) ions adsorbed by 4-VP grafted PET fibers (Ion concentration = 20 ppm; temperature= 298 K; contact time=30 min.; graft yield=70%).



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

To explain the observed behaviour of Cr(VI) adsorption with varying pH, it is necessary to examine various mechanisms such as electrostatic interaction, and ion exchange which are responsible for adsorption on sorbent surface. From the stability diagram [14,33], it is evident that the most prevalent forms of Cr(VI) in aqueous systems are acid chromates ($HCrO_4^-$), chromates (CrO_4^{-2}), dichromates ($Cr_2O_7^{-2}$), and other axyanions. From the stability diagram for the Cr(VI)-H_2O system, it is evident that at low pH, acid chromates ions ($HCrO_4^-$) are the dominant species, while chromates (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 grafted PET fibers at pH 3.0, most of the amine groups surface of the sorbent were protonated and possessed positive electric charges. The protonated amine groups can therefore attract the Cr(VI) species which carried negative electric charges in the solution through the electrostatic interaction. On the other hand, pH around 6.0, the protonation of the amine groups on the 4-VP grafted PET fibers was probably 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 [23].

Effect of ion concentration

The effect of initial Cr(VI) concentration on the adsorption efficiency by 4-VP grafted PET fibers was systematically investigated by varying the initial concentration between 10 and 500 mg L^{-1}. Figure 5 shows the percent removal and adsorbed amount of Cr(VI) ions as a function of initial concentration at pH 3.0. It was observed that 4-VP grafted PET fibers reduced from 100 to 52.60% when initial Cr(VI) concentration varied from 10 to 500 mg L^{-1} at pH 3.0. The adsorption increased with increasing initial Cr(VI) concentration. The maximum adsorption performance was achieved at 71.79 mg g^{-1} using 500 mg L^{-1} Cr(VI) solution.

The values reported varied in the range of 1.4-91 mg g^{-1} for adsorption capacities of Cr(VI) [12-15,18,23]. It has been recognized that the adsorption capacity of 4-VP grafted PET fibers is very good showing that it would be an interesting alternative and an economical industrial adsorbent.

Adsorption isotherm

The simplest adsorption isotherm is based on the assumptions that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether or not adjacent sites are occupied. The adsorption ability of an adsorbent can be described by two parameters. That is, saturation constant or monolayer capacity K_s (mg g^{-1}) and equilibrium binding constant K_b (L mg^{-1}) [24-26]. These constants can be calculated from the adsorption isotherm data according to Langmuir equation:

$$\frac{1}{q} = \frac{1}{CK_bK_s} + \frac{1}{K_s} \qquad (5)$$

Where C and q are the quantities of ions remained in the solution and adsorbed on the fibers at equilibrium, respectively. Thus a plot of q^{-1} versus C^{-1} should yield a straight line having a slope of $(K_bK_s)^{-1}$ and intercept of K_s^{-1} Therefore, the relevant experimental data were treated and it was observed that the relationship between q^{-1} and C^{-1} is linear, indicating that the adsorption behaviour follow the Langmuir adsorption isotherm (Figure 6).

The K_b and K_s values are 1.14×10^{-3} L mg^{-1} and 263.16 mg g^{-1}, respectively. The correlation coefficient was found as being 0.996.

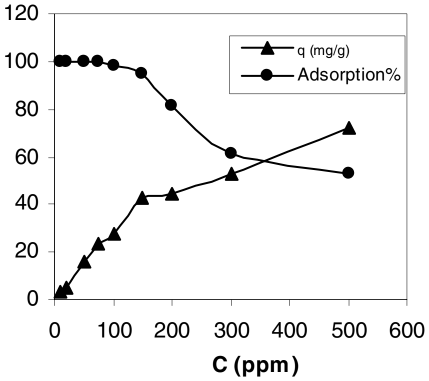


Figure 5. Effect of initial concentration of Cr(VI) on adsorption(pH =3; temperature= 298 K; contact time=30 min.).

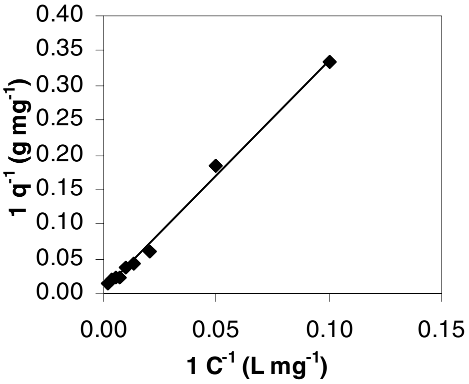


Figure 6. Langmuir plot of the removal of Cr(VI) ions on 4-VP grafted PET fibers.

Desorption studies

The study of desorption of Cr(VI) ions was carried out and the results are represented in Table 4. The Cr(VI) ions adsorbed were easily desorbed by treating the adsorbent with the different solutions mentioned in Table 4. At room temperature (T=25°C), within 30 min., the highest desorption amount, 98 %, was obtained with 1 M NaOH.

It has been recognized that 4-VP grafted PET fibers is stable and regenerable by acid and NaOH. Therefore, adsorption process should be effective for the removal of Cr(VI) ions from industrial effluents.

Table 4. Effect of solution types on desorption.

Solution type	Concentration ($mol \cdot L^{-1}$)	% Desorption
NaOH	1	98
H_2SO_4	1	75
HCl	1	68

Conclusions

PET fibers were grafted with 4-VP, and used as an adsorbent for Cr (VI) ions. The following conclusions are obtained: adsorption process was affected by the graft yield. It was observed that pH is the most important parameter and pH 3.0 was found as the optimum pH value in the process. 30 min. of treatment time was found to be sufficient to reach the adsorption equilibrium value. A Langmuir type of adsorption was observed. It was recognized that 4-VP garfted PET fibers is an excellent alternative adsorbent for removal of hexavalent chromium from aqueous medium. Thus, the material should be addressed for other heavy metals.

Acknowledgments: We are grateful to the Kırıkkale University Research Fund for the financial support of this work.

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