Adsorption Behavior of Congo Red from an Aqueous Solution on 4-Vinyl Pyridine Grafted Poly(ethylene terephthalate) Fibers

Metin Arslan, Mustafa Yiğitoğlu

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

ABSTRACT: In this study, a reactive fibrous adsorbent was prepared through the grafting of 4-vinyl pyridine monomer onto poly(ethylene terephthalate) (PET) fibers for the removal of Congo red (CR) dye from an aqueous solution with the batch adsorption method. Effects of various parameters such as the grafting yield, pH, treatment time, and initial dye concentration on the amount of adsorption of the dye onto the reactive fibers were investigated. The effective pH was 4.0 for adsorption on grafted PET fibers. The sufficient time to attain equilibrium was 150 min. The maximum adsorption capacity of the reactive fibers for CR was 17.3 mg/g of fiber. The rates of adsorption conformed to pseudo-second-order kinetics with good correlation. The adsorption isotherm of CR fit a Langmuir-type isotherm. The reactive fibers were stable and regenerable by acid and base without loss of activity. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2846–2853, 2008

Key words: adsorption; dyes/pigments; fibers; graft copolymers; polyesters

INTRODUCTION

Azo dye is a comprehensive term applied to a group of dyestuffs that carry the azo (—N=N—) group in the molecular structure. The group may be divided into subgroups of monoazo, diazo, and triazo dyes and further in accordance with the number of azo groups in the molecule. Congo red (CR) is a secondary diazo dye (R—N=N—R′—N=N—R), and tetrazotization of benzidine and coupling with naphthionic acid yield this very popular dye. It is used for the dyeing of cotton and as a pH indicator, despite its sensitivity to light and acids. Many industries, such as the food, cosmetic, paper, and textile industries, use dyes to color their products. CR is a benzidine-based dye, and it is expected to metabolize to benzidine, which is a known human carcinogen. Therefore, CR has to be removed from wastewater. There are several methods for removing dyes from aqueous solutions, such as several adsorption processes,[1] oxidation,[2] ozonation,[3] membrane separation,[4] and nanofiltration.[5]

Adsorption has been one of the methods used to remove dyes from aqueous solutions. There are many types of adsorbents, including activated carbon,[6] hardwood,[7] biomaterials,[8] chitin,[9] chitosan,[10] banana pith,[11] hydrogels,[12] cellulose,[13] activated red mud,[14] and zeolites,[15] that have been studied for the adsorption of dyes from aqueous solutions.

One of the new developments in recent years for removing dyes from water or wastewater is the use of polymer fibers as adsorbents. This is mainly attributable to the relatively large external specific surface areas, high adsorption kinetics, and low cost of these polymer fibers.[16,17] Poly(ethylene terephthalate) (PET) fibers are some of the most important synthetic fibers used in the textile industry and have good resistance to weak mineral acids even at the boiling temperature, most strong acids at room temperature, oxidizing agents, sunlight, and microorganisms. However, the interactive forces create inflexible tight packing among macromolecules and well-developed crystallinity, and they do not contain chemically reactive groups, showing resistance to moisture and dye anions or cations.[18,19] Certain desirable properties such as dyeability with basic, direct, and other classes of dyes and water absorbency and improvements in antistatic, mechanical, and thermal properties can be imparted to PET fibers via grafting with different vinyl monomers.

It is therefore of practical and research interest to develop effective adsorbents from these cheap polymer fibers for the removal of CR in water and wastewater treatment. In our previous work, we studied the adsorption behavior of pure PET fibers toward

heavy metal ions in aqueous solutions by a batch equilibration technique.[20] We have also used methacrylic acid grafted PET fibers[21] and 4-vinyl pyridine (4-VP) grafted PET fibers[22] as adsorbents for the removal of Cr(VI) ions from aqueous solutions. It was observed within those studies that the reactive fibers were stable and regenerable by acid without loss of activity.

EXPERIMENTAL

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 with acetone until a constant weight (for 6 h) and dried in a vacuum oven at 50°C. 4-VP was purified by vacuum distillation at 2 mmHg and 65°C. Benzoyl peroxide [$(C_6H_5CO)_2O_2$] 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 (Darmstadt, Germany).

Swelling procedure

A temperature-controlled oil bath was used for heating. The fiber samples (0.3 ± 0.01 g) were dipped into dichloroethane (50 mL) for 2 h at 90°C. After treatment, the solvent on the fibers was removed via blotting between filter paper and put into the polymerization medium.

Polymerization procedure

Polymerization was carried out in a thermostated 100-mL tube under reflux. As mentioned in our previous work,[23] the mixture containing the PET fiber sample (0.3 ± 0.01 g), monomer, and $(C_6H_5C0)_2O_2$ at the required concentration dissolved in 2 mL of acetone was made up to 20 mL with deionized water. The mixture was immediately placed into the water bath adjusted to the polymerization temperature (50°C). At the end of the predetermined polymerization time, fibers were removed from the polymerization medium, and the residual solvent, monomer, and homopolymer [poly(4-VP)] were removed by Soxhlet extraction of 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 the grafted fibers as follows:

$$\text{Graft Yield (\%)} = \left[(w_g - w_i)/w_i\right] \times 100 \qquad (1)$$

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

Scanning electron microscopy (SEM)

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

Sorption of CR on the adsorbent

A CR solution (25 cm^3, 10 mg/L, pH 4) was added to 0.1 g of 4-VP-grafted PET fibers in a 50-mL Erlenmeyer flask. The contents were shaken at 125 rpm for a predetermined period of time at 25°C with an orbital shaker (TH 15, Edmund Mühler, Hechinge, Germany). The loaded adsorbent was separated by centrifugation and washed gently. Afterward, the CR concentration of the supernatant was adjusted to pH 6.8. Then, it was measured with a UV–vis spectrophotometer (pH = 6.8, λ = 497 nm; Ultrospec 2000, Pharmacia Biotech, Cambridge, England). Calibration curves were plotted for the absorbance and concentration of the standard dye solutions. The adsorption capacity of the poly(4-VP)-grafted PET fibers was evaluated with the following expression:

$$q = (C_0 - C)V/m \qquad (2)$$

where q is the amount of dye adsorbed onto the unit of mass of the 4-VP-grafted PET fibers (mg/g); C_0 and C are the concentrations of CR in the initial solution and in the aqueous phase after the adsorption treatment for a certain period of time (mg/L), respectively; V is the volume of the CR solution used (L); and m is the amount of 4-VP-grafted PET fibers used (g).

Desorption of CR

Desorption assays were carried out with the CR-loaded 4-VP-grafted PET fibers at maximum capacity. CR was recovered by treatment with 25 mL adjusted to different pH values for 45 min and then analyzed by the method mentioned previously. The desorption percentage was calculated with the following equation:

$$\text{Desorption(\%)} = \frac{\text{Amount of CR desorbed (mg)}}{\text{Amount of CR adsorbed by the adsorbant (mg)}} \times 100 \qquad (3)$$

RESULTS AND DISCUSSION

Characterization of the polymeric adsorbent

The chemical grafting of 4-VP onto PET and the grafting mechanism were illustrated in our previous work.[23] Grafted PET fibers were also characterized

by thermogravimetric analysis and SEM. The intrinsic viscosity and water absorption capacity were illustrated in that study.

Scanning electron micrographs of ungrafted and 4-VP-grafted (90%) 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 backbone and causes a heterogeneous appearance in the graft copolymer [Fig. 1(b)], which shows proof of grafting.

Effect of pH

The uptake of CR as a function of pH was examined over a pH range of 2–6. The 4-VP-grafted PET fibers were incubated for 240 min with an aqueous CR solution (10 mg/L) adjusted to required pH values of 2–6 with buffer solutions (glycine/HCl, acetic acid/sodium acetate, and disodium citrate dehydrate/trisodium citrate dehydrate). Figure 2 shows the rela-
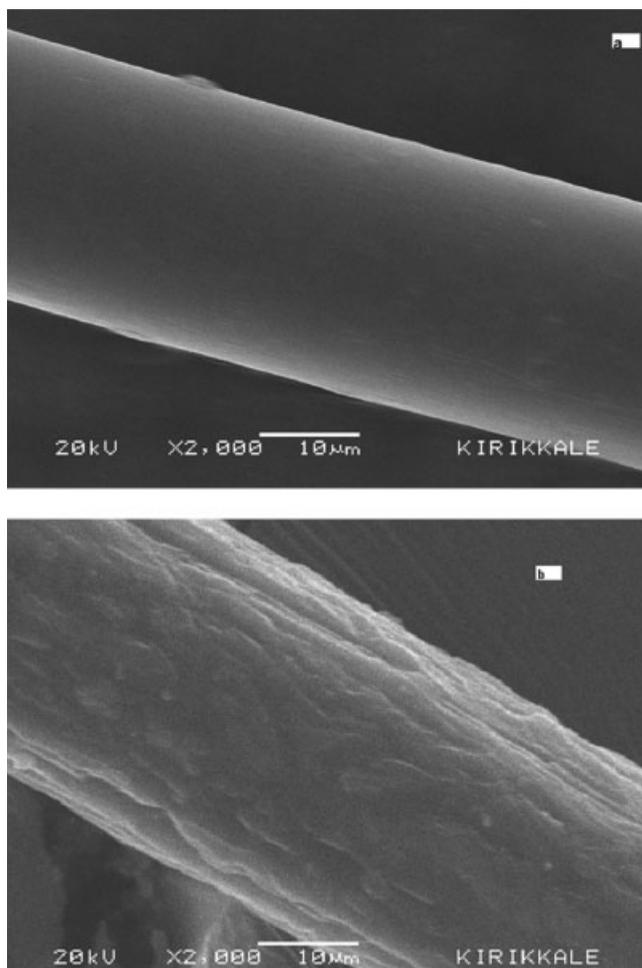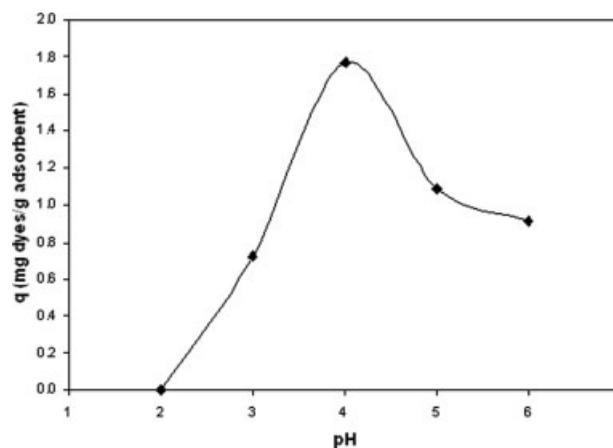
Figure 2 pH dependence of CR adsorbed by 4-VP-grafted PET fibers (dye concentration = 10 ppm, temperature = 25°C, contact time = 240 min, graft yield = 90%).

tionship between the pH and adsorbed amount of CR. It is clear from Figure 2 that with the pH value of the CR aqueous solution increasing from 2 to 4, the adsorbed amount increased significantly and reached a maximum value at pH 4; beyond that point, it decreased. In the rest of the study, experiments were carried out at pH 4. Similar behavior has also been reported for the adsorption of CR with different adsorbents by other workers.[4,24]

To explain the observed behavior of CR adsorption with various pHs, it is necessary to examine various mechanisms such as electrostatic interactions and chemical reactions that are responsible for adsorption on sorbent surfaces. The solution is acidified by hydrochloric acid, and the surface of the grafted PET of the positively charged interface will be associated with Cl^- ions. There is competition between Cl^- (at a low pH) and anionic ions of CR for positively charged adsorption sites. However, at the acidic pH, adsorption still cannot occur, and this inhibits the adsorption of CR. For the adsorption of CR onto 4-VP-grafted PET fibers at pH 4.0, most of the pyridine groups on the surface of the sorbent are protonated and possess positive electric charges. The protonated pyridine groups (pyridinium) can therefore attract the anionic dye, which carries negative electric charges in the solution through the electrostatic interaction. On the other hand, at a pH around 6.0, the protonation of the pyridine groups on the 4-VP-grafted PET fibers is probably insignificant, and the electrostatic interaction would not play an important role in the adsorption of CR on the sorbent. At an alkaline pH, the adsorption of the anionic dye on the adsorbent occurs. This suggests that chemisorption might be effective. This is illustrated in Scheme 1. Similar adsorption mechanisms of CR on activated carbon prepared from coir pith were proposed by Namasivayam and coworkers.[1,25]

Figure 1 SEM micrographs of (a) ungrafted (2000×) and (b) 4-VP-grafted (2000×) PET fibers.
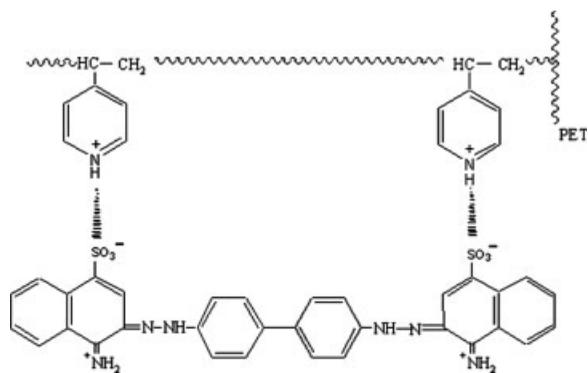
Scheme 1 Adsorption of CR on the 4-VP-grafted PET fibers.

Effect of the graft yield and contact time

The effect of the graft yield on the adsorbed amount of CR was investigated at 25°C, with all other conditions kept constant, and is illustrated in Figure 3. The results of the adsorption behavior of the fibers indicated that 90% of the grafted PET fibers had higher adsorption capacity than other grafted fibers. Similar results were observed in previous works.[21] The increase in the adsorption of CR on materials with increasing graft yield may be attributed to a higher surface area and more active sites. Figure 4 shows the effect of the contact time on the adsorption of CR by grafted PET fibers. Adsorption takes place rapidly at first and then slows down and levels off. A similar type of curve can be observed in the literature.[4,26] The adsorption equilibrium is attained within 150 min. 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. In particular, pyri-
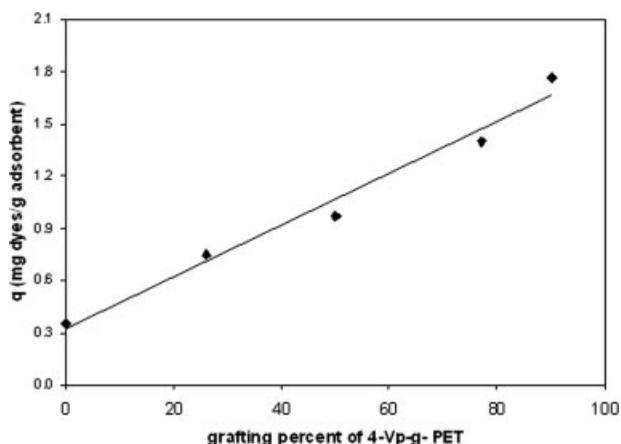

Figure 4 Relationship between the adsorption time and adsorbed amount of CR with 4-VP-grafted PET fibers (dye concentration = 10 ppm, pH = 4, temperature = 25°C).

dine groups on the surface of an adsorbent have been reported to be effective in the adsorption of anionic dye.[27] Thus, those groups of 4-VP-grafted PET fibers are responsible for the interaction of CR with the fibers. The Langergren equation, a pseudo-first-order equation, describes the kinetics of the adsorption process as follows:[28]

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

where q_t is the amount of dye adsorbed (mg/g) at any time t, q_e is the amount adsorbed per gram of adsorbent, and k_1 is the rate constant (min^{-1}). According to the adsorption equation, the experimental results of Figure 4 can be converted into plots of $\text{Log}(q_e - q_t)$ versus t, as shown in Figure 5. The value of k_1 was calculated from the plot of $\text{Log}(q_e - q_t)$ versus t. Although the correlation coefficient value is higher than 0.99, the experimental q_e value does not agree with the calculated one

Figure 3 Effect of the graft yield on the adsorbed amount of CR on 4-VP-grafted PET fibers (dye concentration = 10 ppm, pH = 4, temperature = 25°C, contact time = 240 min).
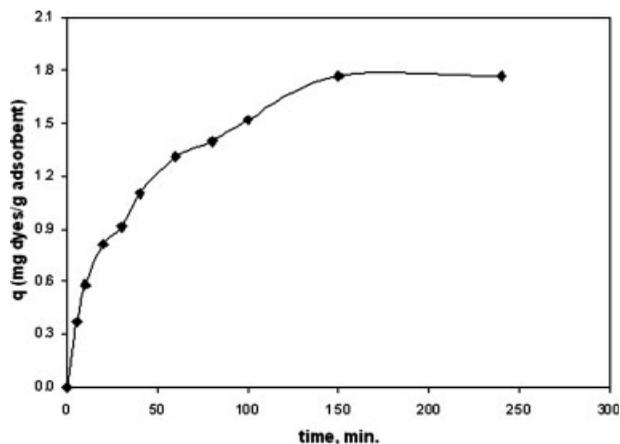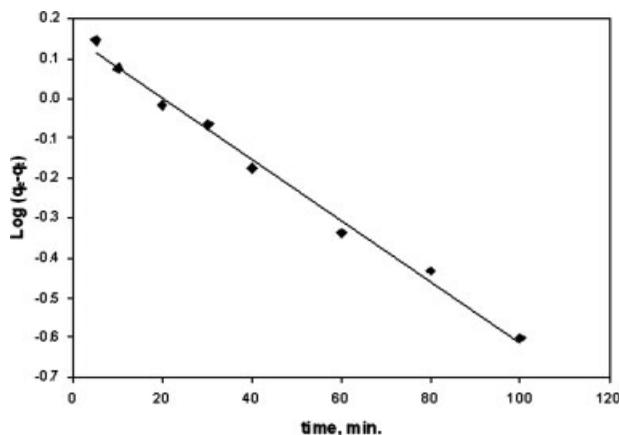

Figure 5 Plots of time versus $\text{Log}(q_e - q_t)$.

TABLE I
Comparison of the First- and Second-Order Adsorption Rate Constants and Calculated and Experimental q_e Values

	Experimental q_e (mg/g)	k_1 (min^{-1}) or k_2 (g mg^{-1} min^{-1})	Calculated q_e (mg/g)	R^2
First-order kinetic model	1.77	0.018	1.42	0.99
Second-order kinetic model	1.77	0.022	1.84	0.99

obtained from the linear plot (Table I). This shows that the adsorption of CR onto 4-VP-grafted PET fibers is not a first-order reaction.

The second-order kinetic model is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where k_2 (g min^{-1} mg^{-1}) is the rate constant of second-order adsorption.[29] If second-order kinetics are applicable, the plot of t/q_t versus t should show a linear relationship. There is no need to know any parameter beforehand, and the equilibrium adsorption capacity (q_e) can be calculated from eq. (5). Also, it is more likely to predict the behavior over the whole range of adsorption.[29] k_2 and q_e were calculated from the intercept and slope of the plot of t/q_t versus t. The linear plot of t/q_t versus t (Fig. 6) shows a good agreement between the experimental and calculated q_e values (Table I). The correlation coefficient for the second-order kinetic model is greater than 0.99, indicating the applicability of this kinetic equation and the second-order nature of the adsorption process of CR on 4-VP-grafted PET fibers. Similar phenomena were observed in the adsorption of CR on coir pith carbon.[1]

The possibility of intraparticle diffusion resistance affecting adsorption was explored with the intraparticle diffusion model:[30]
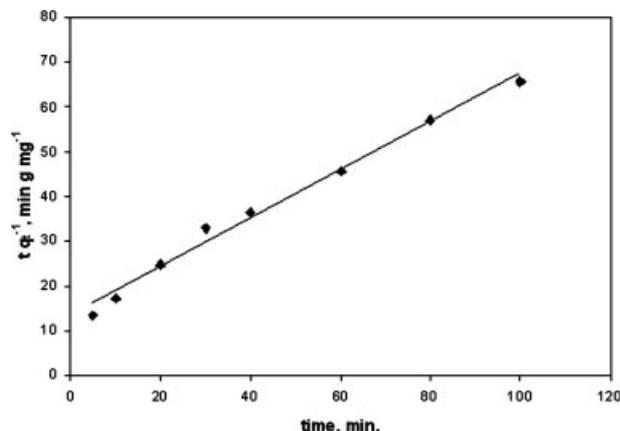
$$q_t = k_p t^{1/2} \tag{6}$$

where k_p is the intraparticle diffusion rate constant. According to Figure 7, q_t should be linearly proportional to $t^{1/2}$, and k_p can be obtained from the slope of the relationship. k_{ip} of the 4-VP-grafted PET fibers is 0.15 mg g^{-1} min$^{-1/2}$.

The dyeing process involves three continuous steps. The first step is the diffusion of dye through the aqueous dye bath onto the fiber. The second step is the adsorption of dye into the outer layer of the fiber. The last step is the diffusion of dye into the fiber 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 dye through the aqueous solution because of the physical obstruction of dye diffusion presented by the network of fiber molecules. Figure 7 shows that the increasing linearity can be attributed to the bulk diffusion.[31,32]

Effect of the initial dye concentration

The effect of the initial CR concentration on the adsorption efficiency by 4-VP-grafted PET fibers was systematically investigated by the variation of the initial dye concentration between 1 and 300 mg/L.
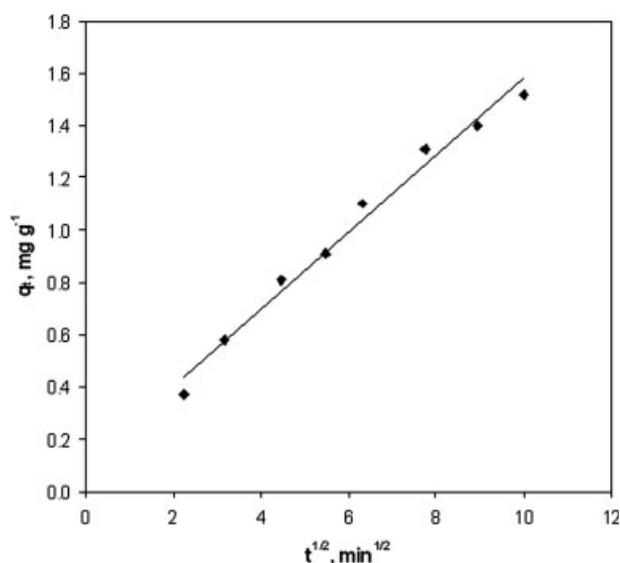

Figure 6 Plots of time versus Log t/q_t.

Figure 7 Test of the intraparticle diffusion model for the removal of CR by 4-VP-grafted PET fibers.
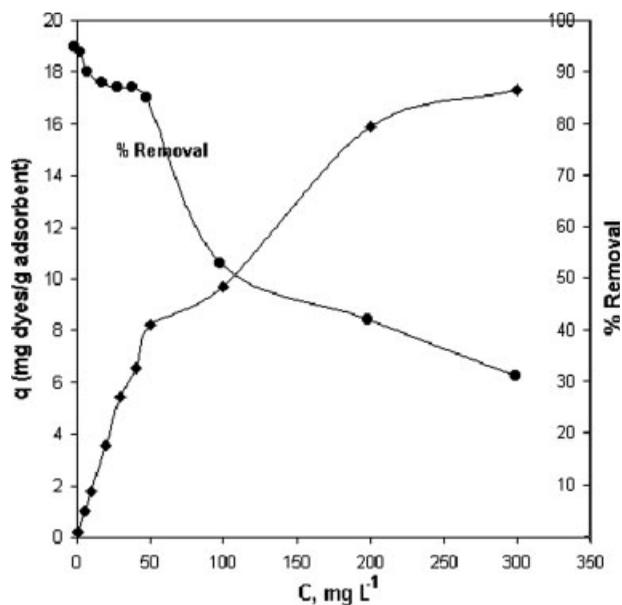
Figure 8 Effect of the initial concentration of CR on the adsorption (pH = 4, temperature = 25°C, contact time = 150 min).

Figure 8 shows the removal percentage and adsorbed amount of anionic dye as functions of the initial concentration of CR at pH 4.0. 4-VP-grafted PET fibers decreased from 100 to 31% when the initial dye concentration varied from 1 to 300 mg/L at pH 4.0. The adsorption increased with increasing initial CR concentration. The maximum adsorption performance was achieved at 17.3 mg/g with a 300 mg/L dye solution. The reported values vary in the range of 4.05–15 mg/g for the adsorption capacities of anionic dyes.[2,4,8,26] 4-VP-grafted PET fibers are polar materials and thus are more selective for polar compounds.[33] Grafted PET fiber has poly(4-VP) groups, which are polar and very hydrophilic, whereas CR is highly water-soluble and has polar amino groups and sulfonic groups in its structure. Therefore, the 4-VP-grafted PET fibers displayed a very high adsorption capacity. The increase in the adsorption capacity was mainly due to the presence of such interactions as ion exchange, hydrogen bonding between the 4-VP groups of the grafted PET and functional groups present in the anionic dye, and physical adsorption.[34] It has been recognized that the dye adsorption capacity of 4-VP-grafted PET fibers is very good, and this shows that it could be an interesting alternative and economical industrial adsorbent.

Adsorption isotherm

The relationship between the amount of CR adsorbed and the CR 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 isotherms.[35]

The Langmuir isotherm is given as follows:

$$Q_e = \frac{Q_0 b C_e}{1 + b C_e} \tag{7}$$

The constants Q_0 and b are characteristics of the Langmuir equation and can be determined from a linearized form of eq. (7):

$$\text{Langmuir:} \quad \frac{C_e}{Q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{8}$$

where C_e is the concentration of CR (mg/L) at equilibrium, Q_0 is the monolayer capacity of the adsorbent (mg/g), and b is the Langmuir adsorption constant (L/mg). Thus, a plot of C_e/Q_e versus C_e should yield a straight line having a slope of Q_0^{-1} and an 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 was linear; this indicated that the adsorption behavior followed the Langmuir adsorption isotherm (Fig. 9). The b and Q_0 values are 0.065 L/mg and 18.1 mg/g, respectively. The correlation coefficient was found to be 0.98.

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

$$Q_e = k C_e^{1/n} \tag{9}$$

We can linearize the equation by taking the logarithm of both sides of eq. (9), and the linear form of the Freundlich isotherm can be given as follows:
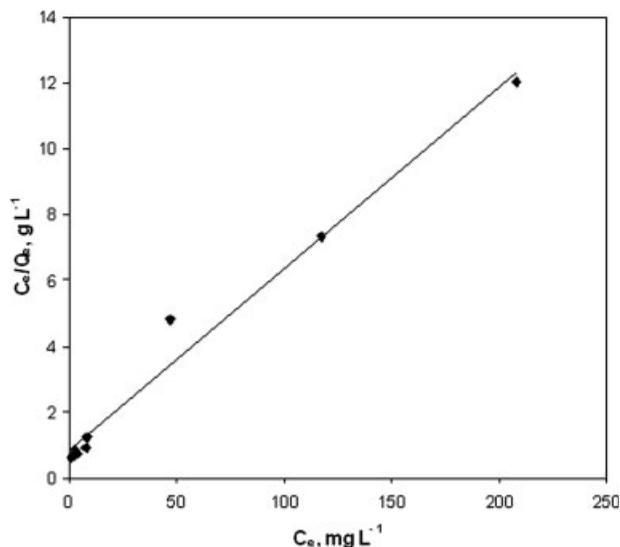

Figure 9 Langmuir plot of the removal of CR on 4-VP-grafted PET fibers.
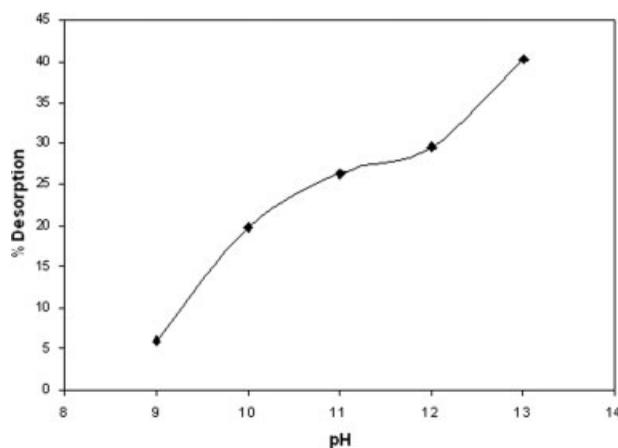
Figure 10 Effect of pH on the desorption of dye-loaded adsorbent (graft yield = 90%, dye concentration = 40 ppm, temperature = 25°C, contact time = 45 min).

$$\mathrm{Log}\, Q_e = \mathrm{Log}\, k + \frac{1}{n} \mathrm{Log}\, C_e \qquad (10)$$

where C_e is the equilibrium concentration (mg/L), k is the sorption capacity (mg/g), and n is an empirical parameter. Thus, a plot of $\mathrm{Log}\, Q_e$ versus $\mathrm{Log}\, C_e$ should give a straight line having a slope of $1/n$ and an intercept of log k. The k and n values are 1.57 mg/g and 1.87, respectively (figure not shown). The correlation coefficient was found to be 0.90. The R^2 value for the linear form of the isotherm has been presented previously. Thus, the Langmuir isotherm represents the equilibrium adsorption of CR on 4-VP-grafted PET fibers.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the equilibrium parameter (R_L),[36] which is defined as follows:

$$R_L = \frac{1}{1 + bC_0} \qquad (11)$$

where b is the Langmuir constant and C_0 is the initial concentration (mg/L). The C_0 values used in the adsorption isotherm studies were in the range of 10–300 mg/L. R_L was found to be less than 1 and greater than 0. These results show that CR adsorption onto 4-VP-grafted PET fibers is favorable.

Desorption studies

In this study, the adsorbed cationic dye was desorbed by treatment of the adsorbent with the different alkaline pHs shown in Figure 10. At room temperature (25°C), within 45 min, as the alkaline pH increased, the desorption percentage increased from 6 at pH 9 to 40.2 at pH 13 for the CR concentration

of 40 mg/L. It has been recognized that 4-VP-grafted PET fibers are stable and regenerable by NaOH. The investigation in the desorption studies confirmed the mechanism of adsorption stated in the pH effect. Therefore, an adsorption process should be effective for the removal of CR from industrial effluents.

CONCLUSIONS

PET fibers were grafted with 4-VP and used as adsorbents for an anionic dye (CR). The following conclusions were drawn. The adsorption process was affected by the graft yield. pH was the most important parameter, and pH 4.0 was found to be the optimum pH value in the process. A treatment time of 150 min was sufficient to reach the adsorption equilibrium value. A Langmuir type of adsorption was observed. It was recognized that 4-VP-grafted PET fibers could be used as adsorbents for CR dye from an aqueous medium and should be addressed for other anionic dyes.

References

1. Namasivayam, C.; Kavitha, D. Dyes Pigments 2002, 54, 47.
2. Neamtu, M.; Yediler, A.; Siminiceanu, I.; Macoveanu, M.; Kellrup, A. Dyes Pigments 2004, 60, 61.
3. Muthukumar, M.; Selvakumar, N. Dyes Pigments 2002, 62, 221.
4. Ciardelli, G.; Corsi, L.; Marucci, M. Resour Conserv Recycl 2000, 31, 189.
5. Chakraborty, S.; Purkait, M. K.; Dasgupta, S.; De, S.; Basu, J. K. Sep Purif Technol 2003, 31, 141.
6. Mall, I. D.; Srivastava, V. C.; Agarwal, N. K.; Mishra, I. M. Chemosphere 2005, 61, 492.
7. Asfour, H. M.; Fadali, O. A.; Nassar, M. M.; El-Geundi, M. S. J Chem Technol Biotechnol A 1985, 35, 21.
8. Hsueh, C. C.; Chen, B. Y. J Hazard Mater 2007, 141, 842.
9. Wang, Z.; Zhao, F.; Li, D. Colloids Surf A 2003, 16, 207.
10. Juang, R. S.; Tseng, R. L.; Wu, F. C.; Lee, S. H. J Chem Technol Biotechnol 1997, 70, 391.
11. Namasivayam, C.; Kanchana, N. Chemosphere 1992, 25, 1691.
12. Duran, S.; Şolpan, D.; Güven, O. Nucl Instrum Methods Phys Res B 1999, 151, 196.
13. Annadurai, G.; Juang, R. S.; Lee, D. J. J Hazard Mater B 2006, 92, 263.
14. Tor, A.; Çengeloğlu, Y. J Hazard Mater 2006, 138, 409.
15. Meshko, V.; Markovska, L.; Mincheva, M.; Rodrigues, A. E. Water Res 2001, 35, 3357.
16. Deng, S. B.; Bai, R. B.; Chen, J. P. J Colloid interface Sci 2003, 260, 265.
17. Deng, S.; Bai, R. Water Res 2004, 38, 2424.
18. Sakurada, I.; Ikada, Y.; Kawahara, T. J Polym Sci Part A-1: Polym Chem 1973, 11, 2329.
19. Buxbaum, L. H. Angew Chem 1968, 80, 225.
20. Yiğitoğlu, M.; Ersöz, M.; Coşkun, R.; Şanlı, O.; Ünal, H. I. J Appl Polym Sci 1998, 68, 1935.
21. Coşkun, R.; Yiğitoğlu, M.; Saçak, M. J Appl Polym Sci 2000, 75, 766.
22. Yiğitoğlu, M.; Arslan, M. Polym Bull 2005, 55, 259.
23. Arslan, M.; Yiğitoğlu, M.; Şanlı, O.; Ünal, H. İ. Polym Bull 2003, 51, 237.

24. Namasivayam, C.; Muniyasamy, N.; Gayatri, K.; Rani, M.; Renganathan, K. Bioresour Technol 1996, 57, 37.
25. Namasivayam, C.; Yamuna, R. T. J Chem Technol Biotechnol 1992, 53, 153.
26. Namasivayam, C.; Arası, D. J. S. E. Chemosphere 1997, 34, 401.
27. Kim, S. W.; Seo, K. H.; Hwang, Y. Y.; Lee, J. K. J Polym Sci Part C: Polym Lett 1988, 26, 347.
28. Namasivayam, C.; Renganathan, K. Water Res 1995, 29, 1737.
29. McKay, G.; Ho, Y. S. Process Biochem 1999, 34, 451.
30. Weber, W. J.; Morris, J. C.; San, J. Eng Div ASCE 1963, 89, 31.
31. Kim, T. K.; Son, Y. A.; Lim, Y. J. Dyes Pigments 2005, 67, 229.
32. Vickerstaff, T. The Physical Chemistry of Dyeing, 2nd ed.; Oliver and Boyd: London, 1954; p 123.
33. Li, A. M.; Long, C.; Sun, Y.; Zhang, Q. X.; Liu, F. Q.; Chen, J. L. Sep Sci Technol 2002, 37, 3211.
34. Chao, L.; Zhaoyang, L.; Aimin, L.; Wei, L.; Zhenmao, J.; Jin-long, C.; Quanxing, Z. Sep Purif Technol 2005, 44, 91.
35. Langmuir, I. J Am Chem Soc 1916, 38, 2221.
36. Weber, T. W.; Chackravorti, R. K. Am Inst Chem Eng J 1974, 20, 228.