

Use of Methacrylic Acid Grafted Poly(ethylene terephthalate) Fibers for the Removal of Basic Dyes from Aqueous Solutions

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ABSTRACT: A reactive fibrous adsorbent was prepared through the grafting of a methacrylic acid monomer onto poly(ethylene terephthalate) fibers for the removal of basic dyes such as methylene blue and basic red 9 from aqueous solutions through a batch adsorption method. Effects of various parameters such as the grafting yield, pH, treatment time, initial dye concentration, and adsorption temperature on the amount of dye adsorbed onto reactive fibers were investigated. The adsorption amounts of basic dyes increased with increases in the grafting yield, pH, treatment time, initial dye concentration, and adsorption temperature. The rates of adsorption conformed to pseudo-second-order kinetics with a good correlation. The equilibrium data for methylene blue and basic red 9

adsorption fit the Langmuir equation, with maximum adsorption capacities of 200 and 250 mg/g, respectively. The adsorption rates of two basic dyes were much higher on the grafted poly(ethylene terephthalate) fiber than on the ungrafted poly(ethylene terephthalate) fiber. Within 45 min, about 99% of the cationic dyes was removed from the solutions (400 mg/L) by methacrylic acid-graft-poly(ethylene terephthalate) fibers. The highest desorption amounts for methylene blue and basic red 9 were 62 and 84%, respectively. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 30–38, 2008

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

INTRODUCTION

Basic dyes are a class of dyes, usually synthetic, that act as bases. Basic dyes constitute one of the more widely used groups. Their color base is not water-soluble but can be made so by the conversion of the base into a salt. Basic dyes possess cationic functional groups such as $-NR_3^+$ or $=NR_2^+$. Some examples of basic dyes are crystal violet, safranin, basic fuchsin, and methylene blue (MB). They are applied to wool, silk, cotton, and modified acrylic fibers. Effluents from textile industries are important sources of water pollution. Some dyes and their degradation products may be carcinogenic and toxic. Hence, the removal of dyes from strongly colored basic dye wastewater or effluents has become environmentally important. There are several methods for removing dyes from aqueous solutions, such as adsorption,¹ electrochemical methods,² ozonation,³ membrane separation,⁴ nanofiltration,⁵ and biological treatments.⁶

Because the adsorption process offers the most economical and effective treatment method for the removal of dyes, it has been one of the methods used to remove dyes from aqueous solutions. The process is often carried out in a batch mode. There are many types of adsorbents that have been studied for the adsorption of dyes from aqueous solutions, including polymers,⁷ activated carbon,⁸ wood,⁹ biomaterials,¹⁰ chitin,¹¹ chitosan,¹² rice husks,¹³ hydrogels,¹⁴ cellulose,¹⁵ activated red mud,¹⁶ and clay.¹⁷ 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 attributed to the relatively large external specific surface areas, high adsorption kinetics, and low cost of these polymer fibers.¹⁸ 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, PET fibers are hydrophobic in nature and do not contain chemically reactive groups. For these reasons, this material cannot combine with either dye cations or anions. Certain desirable properties such as improved dyeability, water absorbancy, and antistatic, mechanical, and thermal properties can be imparted to PET fibers through grafting with

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different vinyl monomers. Grafting improves the adsorption capacity and selectivity of fibers significantly by forming many reactive groups on the polymer chains.¹⁹

It is therefore of practical and research interest to develop effective adsorbents from these cheap polymer fibers for the removal of basic dyes in water and wastewater treatment. In our previous work, the adsorption behavior of pure PET fibers was studied for heavy metal ions in aqueous solutions by a batch equilibration technique.¹⁹ We also used 4-vinylpyridine-grafted PET fibers as an adsorbent for the removal of acidic dyes²⁰ and heavy metal ions²¹ from aqueous solutions. It was observed within those studies that the reactive fibers were stable and regenerable by acid without a loss of activity.

Recently, we also used 4-vinyl/2-hydroxyethyl methacrylate-g-PET as an adsorbent to remove MB from aqueous solutions.²² However, a low adsorption capacity (55.33 mg of MB/g of adsorbent) was observed. Thus, in this study, a more effective fibrous material [methacrylic acid-graft-poly(ethylene terephthalate) (MAA-g-PET)] was used for the removal of basic dyes.

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 for 6 h, and then they were dried in a vacuum oven at 50°C. Methacrylic acid (MAA) was purified by vacuum distillation. Benzoyl peroxide [(C₆H₅CO)₂O₂] 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 the treatment, the solvent on the fibers was removed through blotting with filter paper, and the fibers were put into the polymerization medium.

Polymerization procedure

Polymerization was carried out in thermostated 100-mL tubes under refluxing. As reported in the literature,²³ a mixture containing the PET fiber sample (0.3 ± 0.01 g), monomer, and (C₆H₅CO)₂O₂ 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 a water bath

adjusted to the polymerization temperature (85°C). At the end of the predetermined polymerization time, fibers were removed from the polymerization medium, and the residual solvent, monomer, and homopolymer [poly(methacrylic acid)] were removed in 4 h by a washing procedure in boiling water. Finally, the PET fibers were Soxhlet-extracted in methanol for 24 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:

$$\text{Graft yield (\%)} = [(w_g - w_i)/w_i] \times 100 \quad (1)$$

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

Scanning electron microscopy

A scanning electron microscopy study of MAA-grafted PET fibers coated with gold was performed with a JEOL model JSM 5600 microscope (Midland, ON, Canada).

Sorption of the basic dyes onto the adsorbent

A volume of 25 cm³ of each basic dye solution (30 mg/L, pH 9) was added to 0.1 g of MAA-g-PET fibers in a 50-mL Erlenmeyer flask. The contents were shaken at 130 rpm for a predetermined period of time at 30°C with an Edmund Mühler TH 15 orbital shaker (Hechingen, Germany). The loaded adsorbent was separated by filtration and washed gently. After the cationic dye concentration of the supernatant was adjusted to pH 6.8, it was measured with an ultraviolet-visible spectrophotometer [Ultrospec 2000, Pharmacia Biotech, Cambridge, England; pH = 6.8, λ = 665 nm for MB, λ = 540 nm for basic red 9 (BR9)]. Calibration curves were plotted between the absorbance and concentration of the standard dye solutions. The adsorption capacity of the MAA-g-PET fibers was evaluated with the following expression:

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

where q is the amount of dye adsorbed onto a unit of mass of the MAA-g-PET fibers (mg/g); C_0 and C are the concentrations of the dye 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 dye solution used (L); and m is the amount of MAA-g-PET fibers used (g).

Desorption of the basic dyes

Desorption assays were carried out with the dye-loaded MAA-g-PET fibers. The dye was recovered in 30 min by a treatment with 25 mL of acetic acid in

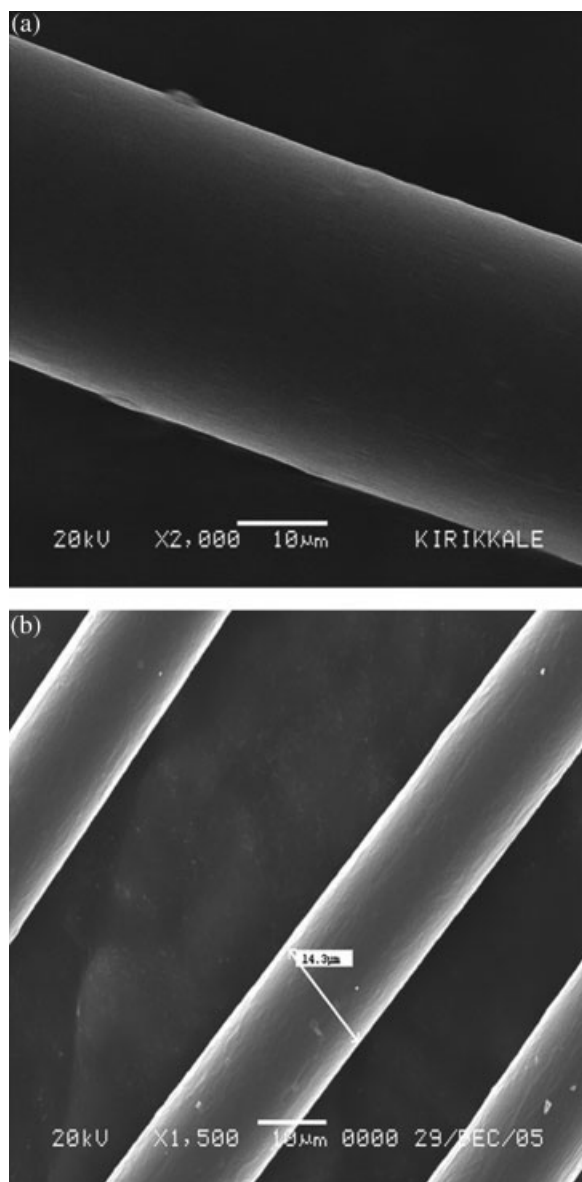


Figure 1 Scanning electron micrographs of (a) ungrafted and (b) MAA-g-PET (83%) fibers.

methanol adjusted to different concentrations and then analyzed by the method mentioned previously. The desorption percentage was calculated with the following equation:

$$\text{Desorption (\%)} = \frac{\text{Amount of basic dye desorbed (mg)}}{\text{Amount of basic dye absorbed by adsorbent (mg)}} \times 100 \quad (3)$$

RESULTS AND DISCUSSION

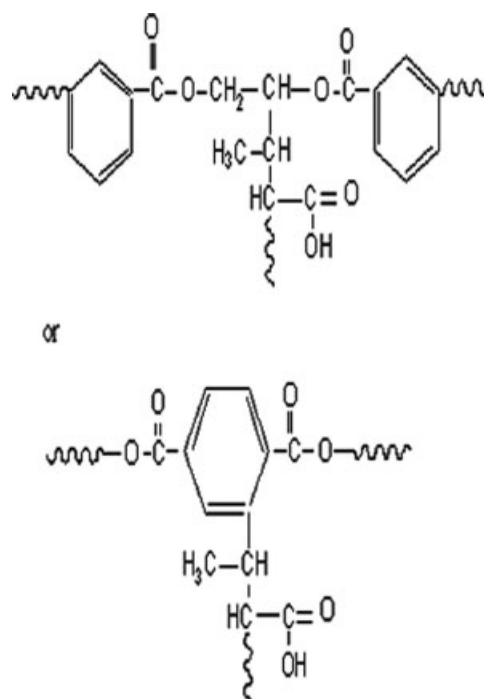
The grafting mechanism of MAA-g-PET was described and characterized by Saçak et al.²³ In addition, scanning electron micrographs of ungrafted

and MAA-g-PET fibers are shown in Figure 1. The ungrafted PET fiber [Fig. 1(a)] had a smooth and relatively homogeneous surface. At a graft yield of 83%, the grafted side chain seemed to cover the PET fibers [Fig. 1(b)], showing further proof of grafting. The suggested structures²⁴ of MAA-g-PET are illustrated in Scheme 1.

Effect of pH

The uptake of basic dyes as a function of pH was examined over a pH range of 5–12. The MAA-g-PET fibers were incubated for 60 min with aqueous basic dye solutions adjusted to required pH values in a range of 5–12 with buffer solutions (acetic acid/sodium acetate, disodium citrate dehydrate/trisodium citrate dehydrate, and sodium carbonate/sodium bicarbonate). Figure 2 shows the relationship between the pH and adsorbed amount of basic dyes. Increasing the pH value of the basic dye aqueous solution from 5 to 7 increased the adsorbed amount significantly, and it remained constant at pH 7–12. The following studies were conducted at a fixed pH of 9. Similar behavior was also reported for the adsorption of basic dyes with different adsorbents by other workers.²⁵

To explain the observed behavior of basic dye 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. At different pH values, the protonation and deprotonation



Scheme 1 Structures of MAA-g-PET.

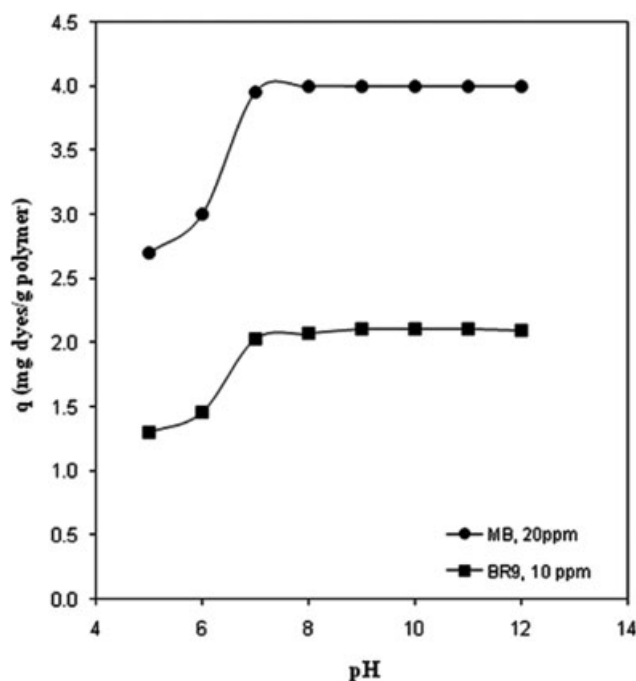
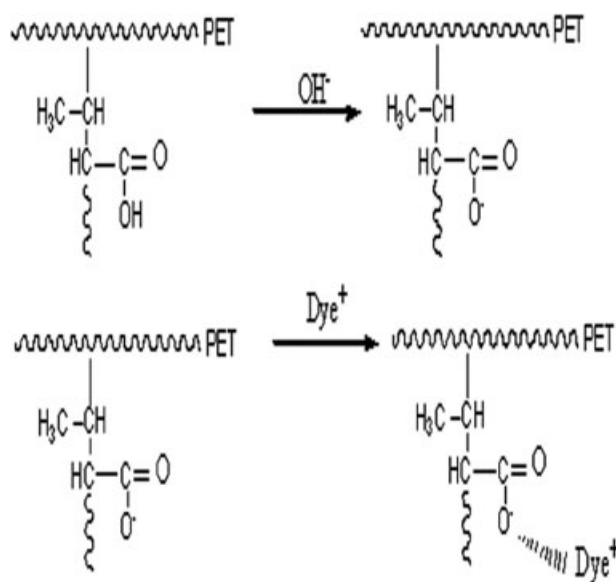


Figure 2 pH dependence of basic dyes adsorbed by MAA-g-PET fibers (temperature = 30°C, contact time = 60 min, graft yield = 83%).

influence the surface structure of MAA-g-PET fibers, and dye ions exist in different forms. At low pH values, H^+ ions are abundant on the surface, where COO^- groups and H^+ ions produce $COOH$ groups. The carboxyl groups are present in a nonionized form, and no interaction can occur between the carboxyl groups and the basic dyes molecules. When the pH increases, the carboxyl groups are ionized, and the probability of interactions between the carboxylic groups and the cationic groups of the basic dyes increases. At higher pHs, the surface of MAA-g-PET fibers will become negatively charged, with uptake of positively charged basic dyes through electrostatic forces of attraction. A similar mechanism was suggested in our previous work.²² This is illustrated in Scheme 2.

Effect of the graft yield and contact time

Figure 3 shows the effect of the graft yield on the adsorbed amount of cationic dyes, with all other conditions kept constant. The results for the adsorption behavior of the fibers indicated that PET fibers that were 83% grafted had a higher adsorption capacity than those grafted less than 83%. Increasing the graft yield increased the number of functional groups, so the MAA-g-PET fibers had many carboxyl groups that could increase the electrostatic interaction between the cationic groups of basic dyes and carboxyl groups of MAA-g-PET fibers. The increase in the adsorption of basic dyes on materials with



Scheme 2 Adsorption of cationic dyes onto MAA-g-PET fibers.

increasing graft yield could be attributed to a higher surface area and more active sites. Figure 4 shows the effect of the contact time on the adsorption of grafted PET fibers. The adsorption took place rapidly at first and then slowed down and leveled off. A similar type of curve can be observed in the literature.²⁶ The adsorption equilibrium was attained within 45 min. The relation between the nature of

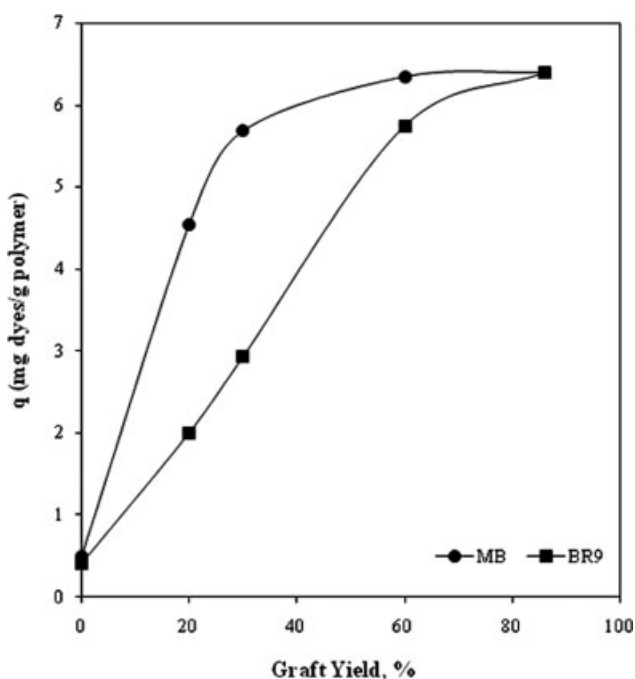


Figure 3 Effect of the graft yield on the adsorbed amount of basic dyes on MAA-g-PET fibers (dye concentration = 30 ppm, pH = 9, temperature = 30°C, contact time = 60 min).

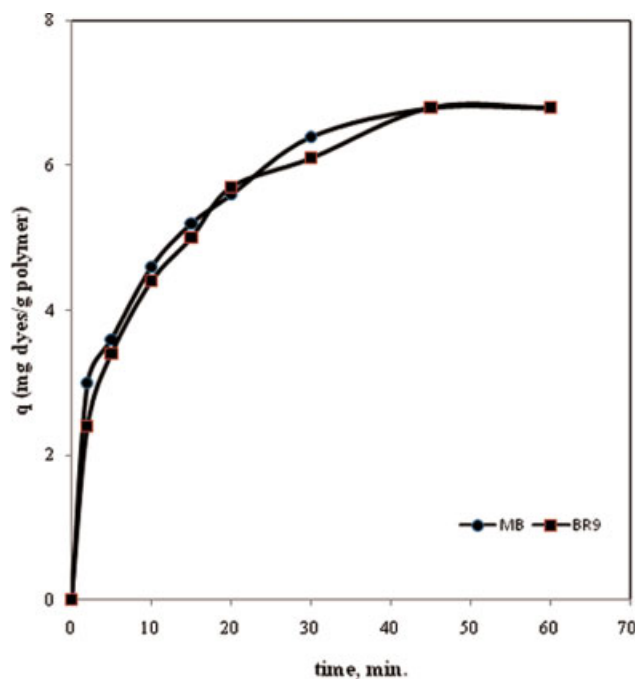


Figure 4 Relationship between the adsorption time and adsorbed amount of basic dye with MAA-g-PET fibers (dye concentration = 30 ppm, pH = 9, temperature = 30°C).

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, COOH groups (at a high pH) on the surface of an adsorbent have been reported to be effective in the adsorption of cationic dyes.²⁵ Thus, those groups of MAA-g-PET fibers are responsible for the interaction of basic dyes with the fibers. The Langergren equation, a pseudo-first-order equation, describes the kinetics of the adsorption process as follows.²⁷

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

where q_t is the amount of dye adsorbed at any time (mg/g), q_e is the amount of dye adsorbed at the equilibrium time per gram of adsorbent, k_1 is the rate constant (min^{-1}), and t is the time. 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 (not shown in the figure), as shown in Table I. Values of k_1 were calculated from the plot of $\text{log}(q_e - q_t)$ versus t . Although the correlation coefficient values are 0.98 for BR9 and 0.92 for MB, the experimental q_e values do not agree with the calculated values obtained from linear plots (Table I) of BR9 and MB. This shows that the adsorption of basic dyes onto MAA-g-PET fibers is not a first-order reaction.

The second-order kinetic model is expressed as follows:

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

where k_2 ($\text{g min}^{-1} \text{mg}^{-1}$) is the rate constant of second-order adsorption.²⁸ If second-order kinetics are applicable, a plot of t/q versus t should show a linear relationship. There is no need to know any parameter beforehand, and 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 versus t . The linear plot of t/q versus t (Fig. 5) shows good agreement between the experimental and calculated q_e values (Table I). The correlation coefficients for the second-order kinetic model are greater than 0.99, indicating the applicability of this kinetic equation and the second-order nature of the adsorption process of basic dyes on MAA-g-PET fibers. Similar phenomena have been observed in the adsorption of basic dyes on bamboo-based activated carbon.⁸

The possibility of intraparticle diffusion resistance affecting adsorption was explored with the intraparticle diffusion model as follows:²⁸

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

where k_p is the intraparticle diffusion rate constant. According to Figure 6, q_t should be linearly proportional to $t^{1/2}$, and k_p could be obtained from the slope of the relationship. k_p of the MAA-g-PET fibers was 0.852 and 0.935 $\text{mg g}^{-1} \text{min}^{-1/2}$, and the corresponding linear regression correlation coefficient

TABLE I
Comparison of k_1 and k_2 and Calculated and Experimental q_e Values

	Experimental q_e (mg/g)	k_1 (min^{-1}) or k_2 ($\text{g min}^{-1} \text{mg}^{-1}$)	Calculated q_e (mg/g)	R^2
MB				
First-order kinetic model	6.8	0.130	5.94	0.92
Second-order kinetic model	6.8	0.028	7.25	0.98
BR9				
First-order kinetic model	6.8	0.100	6.10	0.98
Second-order kinetic model	6.8	0.025	7.14	0.99

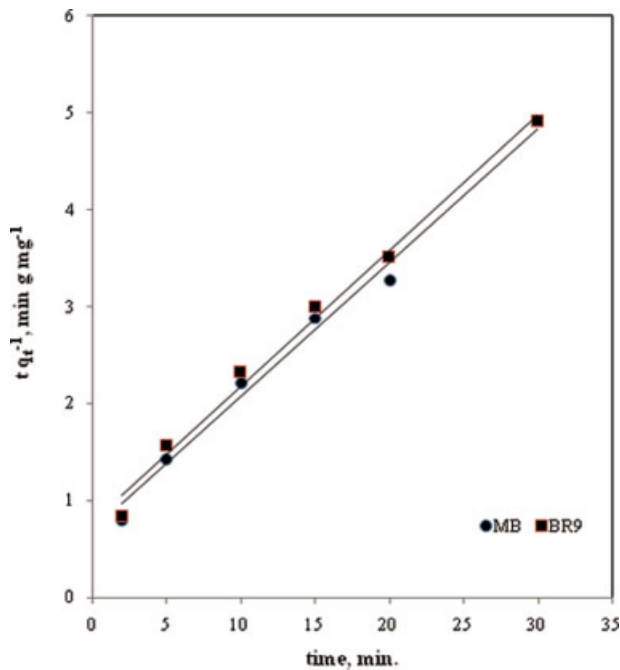


Figure 5 Plots of time versus $\log t/q_t$.

values were 0.99 and 0.98 for MB and BR9, respectively. The linearity of the plots demonstrated that intraparticle diffusion played a significant role in the uptake of the dyes by MAA-g-PET fibers. This also confirms that the adsorption of the dye on the adsorbent was a multistep process.³⁰

A dyeing process involves three continuous steps. The first step is the diffusion of the dye through the aqueous dye bath onto the fiber. The second step is the adsorption of the dye into the outer layer of the

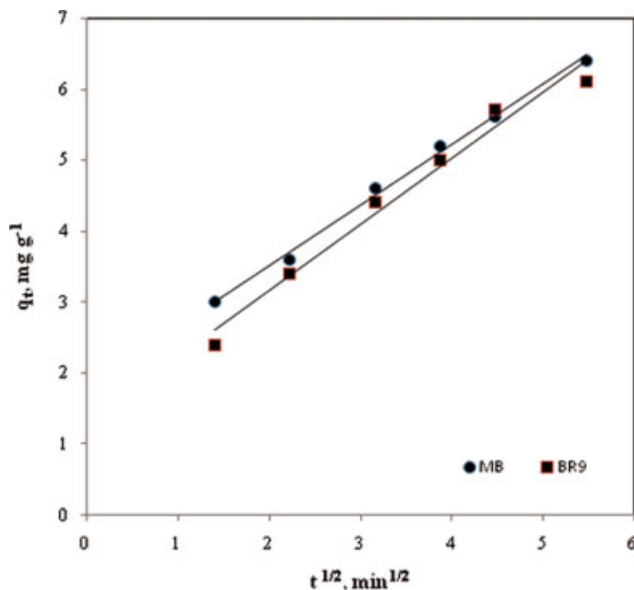


Figure 6 Test of the intraparticle diffusion model for the removal of basic dye by MAA-g-PET fibers.

fiber. The last step is the diffusion of the dye 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 dye through the aqueous solution because of the physical obstruction of dye diffusion presented by the network of fiber molecules. Figure 6 shows that the increasing uptake can be attributed to bulk diffusion.³¹

Effect of the initial dye concentration

The effect of the initial basic dye concentration on the adsorption efficiency by MAA-g-PET fibers was systematically investigated by the variation of the initial concentration between 10 and 1200 mg/L. Figure 7 shows the removal percentage and adsorbed amount of cationic ions as a function of the initial concentration at pH 9.0. The MAA-g-PET fibers were reduced from 100 to 99% when the initial basic dye concentration varied from 10 to 400 mg/L at pH 9.0. The adsorption increased with increasing initial dye concentration. The maximum adsorption performances for MB and BR9 were achieved at 169.4 and 195 mg/g with a 1200 mg/L basic dye solution, respectively. There are reported values and some data concerning the adsorption capacities of basic dyes in the literature.³² It has been recognized that the adsorption capacity of MAA-g-PET fibers is very good in comparison with those in the literature; thus, it

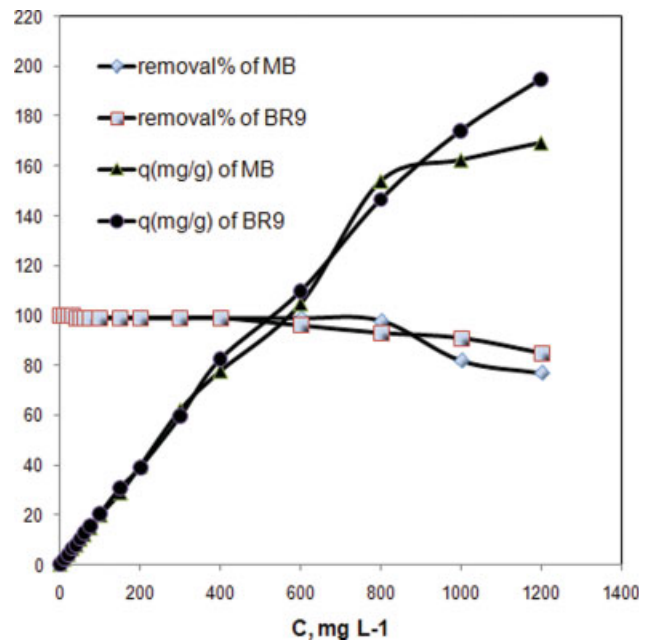


Figure 7 Effect of the initial concentration of basic dyes (C) on adsorption (pH = 9, temperature = 30°C, contact time = 45 min).

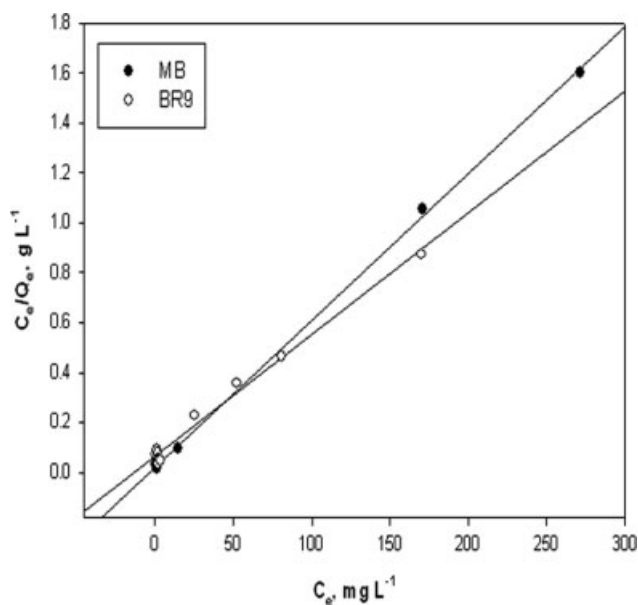


Figure 8 Langmuir plots of the removal of MB and BR9 on MAA-g-PET fibers.

seems that MAA-g-PET fibers would be an interesting alternative and economical industrial adsorbent.

The most common anionic group attached to acrylic fibers is the carboxylate group ($-\text{COO}^-$). It is this anionic property that makes acrylics suitable for dyeing with cationic dyes because there will be a strong ionic interaction between the dye and polymer. MAA-g-PET fibers under basic conditions develop a negative charge as the $-\text{COOH}$ groups are deprotonated to produce $-\text{COO}^-$. MAA-g-PET fibers have high surface areas and more active sites. Grafted PET fibers have poly(methacrylic acid) groups, which are polar and very hydrophilic. Therefore, the MAA-g-PET fibers here displayed a very high adsorption capacity.

Adsorption isotherm

The relationship between the amount of basic dyes adsorbed and the basic dye concentration remaining in the solution is described by an isotherm. The two most common isotherm types for describing this type of system are the Langmuir and Freundlich isotherms.³³

The Langmuir isotherm is given as follows:

$$Q_e = [Q_0 b C_e / (1 + b C_e)] \quad (7)$$

where Q_e is the amount of adsorption at equilibrium, Q_0 is the monolayer capacity of the adsorbent (mg/g), C_e is the concentration of the basic dye (mg/L) at equilibrium, and b is the Langmuir adsorption constant (L/mg). The constants Q_0 and b are characteris-

tics of the Langmuir equation and can be determined from a linearized form of eq. (7):

$$C_e/Q_e = 1/Q_0 b + C_e/Q_0 \quad (8)$$

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 isotherms (Fig. 8). The b and Q_0 values are presented in Table II.

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

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

where K_F is the sorption capacity (mg/g) and n is an empirical parameter. We can linearize the equation by taking the logarithm of both sides of eq. (9), and a linear form of Freundlich isotherm can be given as follows:

$$\log Q_e = \log K_F + 1/n \log C_e \quad (10)$$

Thus, a plot of $\log Q_e$ versus $\log C_e$ should give straight line having a slope of $1/n$ and an intercept of $\log K_F$. The K_F and n values are presented in Table II (figure not shown).

The results suggest that basic dyes are favorably adsorbed by MAA-g-PET fibers. The Langmuir isotherm fits quite well with the experimental data, whereas the low correlation coefficient shows poor agreement of the Freundlich isotherm with the experimental data.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the equilibrium parameter (R_L):³⁴

$$R_L = \frac{1}{1 + b C_0} \quad (11)$$

where C_0 is the initial concentration (mg/L). C_0 used in the adsorption isotherm studies was in the range of 10–1200 mg/L. R_L was found to be less than 1 and greater than 0. These results show that basic dye adsorption onto MAA-g-PET fibers is favorable.

TABLE II
Langmuir and Freundlich Isotherm Constants for MB and BR9 Basic Dyes on MAA-g-PET Fibers

	Langmuir isotherm			Freundlich isotherm		
	Q_0 (mg/g)	b (L/mg)	R^2	n	K_F (mg/g)	R^2
MB	200	0.333	0.999	2.48	29.85	0.69
BR9	250	0.063	0.988	1.88	18.32	0.84

Effects of the temperature

It has been recognized that the adsorption of basic dyes from an aqueous solution by MAA-g-PET fibers is affected by the temperature (figure not shown), such that the adsorption increases remarkably as the temperature increases. This increase in the adsorption amount of basic dyes can be attributed to an increase in the degree of swelling, so that the diffusion of the dyes into the fibers becomes much easier.

The Arrhenius plots are illustrated in Figure 9. From the slopes of Figure 9, the activation energies for adsorption were calculated to be 12.52 and 12.50 kJ/mol for MB and BR9, respectively. These low values of E_a , compared to those of a typical chemical reaction of 65–250 kJ/mol, imply that the adsorption of grafted fibers for the basic dyes was a facile procedure.³⁵ As reflected by the positive values of the activation energies for adsorption, the adsorption process was endothermic in nature.

Desorption studies

In the study, the adsorbed cationic dyes were desorbed by the treatment of the adsorbent with different acetic acid concentrations in methanol, as shown in Figure 10. At room temperature (30°C), within 30 min, as the acetic acid concentrations in methanol increased from 2 to 15%, the desorption increased from 75.5 to 83.9% for BR9 and from 47.5 to 62% for MB loaded at 100 mg/L. The desorption of dyes was very high. This was also substantiated by the significant adsorption of basic dyes at an alkaline pH,

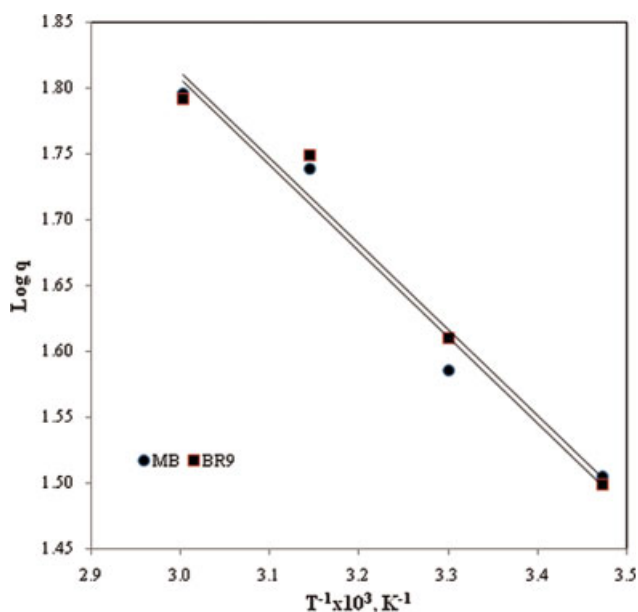


Figure 9 Plots of $\log q$ versus the reciprocal of the temperature (T^{-1}).

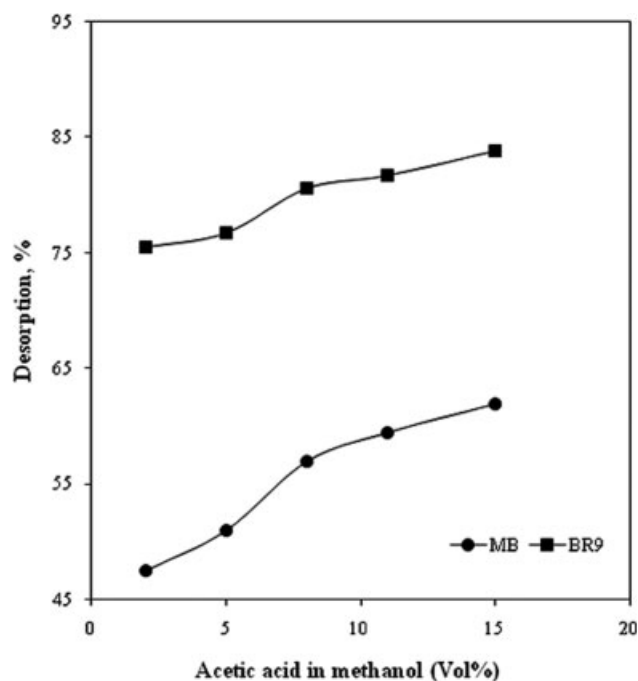


Figure 10 Effect of the acetic acid concentration in methanol on the desorption of a basic-dye-loaded adsorbent (graft yield = 83%, loaded dye amount = 100 ppm, temperature = 30°C, contact time = 30 min).

although electrostatic attraction favors adsorption. The desorption studies confirmed the mechanism of adsorption stated in the pH effect. Desorption of the basic dyes was quite fast. It has been recognized that MAA-g-PET fibers are stable and regenerable by acetic acid in methanol. Therefore, the adsorption process should be effective for the removal of basic dyes from industrial effluents.

CONCLUSIONS

PET fibers were grafted with MAA and used as an adsorbent for MB and BR9. The following conclusions were obtained. The adsorption process was affected by the graft yield. The pH was the most important parameter, and pH 7.0 was found to be the optimum pH value in the process. A treatment time of 45 min was sufficient to reach the adsorption equilibrium value. The kinetics of basic dye adsorption onto MAA-g-PET fibers followed the pseudo-second-order model. A Langmuir type of adsorption was observed. It was remarkable that the percentage of MB and BR9 removed was up to 99%. It was recognized that MAA-g-PET fibers should be used as adsorbents for basic dyes from aqueous media and examined for other cationic dyes. In the future, they could be applied in wastewater treatments, especially for textile effluents.

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