e-Polymers **2007**, no. 055

http://www.e-polymers.org

ISSN 1618-7229

Adsorption Behaviour of Methylene Blue from Aqueous Solution on Poly(Ethylene Terephthalate)-g-4-Vinylpyridine/ 2-Hydroxyethylmethacrylate Fibers

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(Received:12 March, 2007; published: 25 May, 2007)

Abstract: In this study, a novel fibrous adsorbent obtained by grafting 4-vinyl pyridine (4-VP)/2-hydroxyethylmethacrylate (HEMA) comonomers onto poly (ethylene terephthalate) (PET) fibers was used for removal of methylene blue (MB) from aqueous solutions through a batch equilibration technique. The Influence of treatment time, pH of the solution, dye concentration, reaction temperature and percent graft yield on adsorbed amount were investigated. 300 min. of adsorption time was found sufficient to reach adsorption equilibrium for MB. It was found that the adsorption isotherm of MB fitted to Langmuir type isotherm. The highest adsorption capacity was found to be 55.33 mg MB per gram adsorbent. The adsorbed amount of MB was much higher on the comonomers grafted PET fibers than on the ungrafted PET fibers. MB was removed by 98 % while the initial dye concentration was at 5 mg L^{-1} and by 88% at 300 mg L^{-1} by monomers mixture grafted PET fibers. It was found that the reactive fibers were stable and regenerable by acid without loosing their activity.

Introduction

As the world's population and industrialization grow, environmental pollution becomes a progressively more serious problem. Water pollution is one part of the problem in both the developed and developing countries. Wastewaters from textile industries are a complex mixture of many polluting substances such as pesticides, heavy metals, pigments and dyes. The textile industries use synthetic organic dyes like direct dye, basic dye, sulfur dye, nepthol dye, and reactive dye. The textile industries are to satisfy the ever growing demands in terms of quality, variety, fastness and other technical requirements, but the use of dye stuffs has become increasingly a subject of environmental concern. Therefore, it is essential to evolve regulations designated to improve health and safety of the human and natural environment. The dyes are of special environmental concerns because of their carcinogenic nature, formation of toxic amines, persistency and recalcitrant nature [1]. MB is a heterocyclic aromatic chemical compound. It has many uses in a range of different fields, such as biology and chemistry.

Decolorations of dyes are important aspects of wastewater treatment before discharge. Dyes are not removed easily by conventional wastewater treatment processes [2], as they are fairly stable to light, heat and resist biodegradation because of their complex molecular structures [3, 4]. In recent years several physico-chemical decoloration processes have been developed [5], such as nanofiltration [6], membrane separation [7], electrochemical [8], ozone oxidation [9], biological

treatments [10, 11], etc. However, these methods are expensive and may need special infrastructure.

Adsorption has been one of the methods used to remove dyes from aqueous solutions. There are many types of adsorbents, including activated carbon [12, 13], sawdust [14], biomaterials [15], cotton waste [16], polymeric material [17, 18], rice husk [19, 20], waste Fe(II)/Cr(III) hydroxide [21], wool [22], glass fiber [23], fibrous clay [24], that have been studied for the adsorption of dyes from aqueous solutions.

One of the new developments in recent years to remove dyes from water or wastewater is the use of polymer fibers as adsorbent. This is mainly attributed to the relatively large external specific surface areas, high adsorption kinetics, and low cost of these polymer fibers [25, 26]. 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 [27, 28]. 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. 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 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. Hence this technique of graft copolymerization provides an opportunity to prepare tailor made grafted chains of desired properties by using suitable monomers [29].

It is therefore of practical and research interest to develop effective adsorbents from these cheap polymer fibers for the removal of MB in water and wastewater treatment. In our previous work, the adsorption behavior of pure PET fibers was studied toward heavy metal ions in aqueous solutions by a batch equilibration technique [30]. We have also used methacrylic acid grafted PET fibers [31] and 4-VP grafted PET fibers [32, 33] as an adsorbent for the removal of Cu (II) and Cr(VI) ions from an aqueous solution. It has been observed that within those studies the reactive fibers are stable and regenerable by acid without loosing their activity.

In the present study, a novel fibrous material 4-VP/HEMA grafted PET has been used to remove of MB from aqueous solution as an adsorbent.

Results and Discussion

Characterization of the polymeric adsorbent

The adsorbent was prepared by graft copolymerization of 4-VP/HEMA monomer mixture (50/50 mol) onto PET fiber by using benzoylperoxide as an initiator.

Grafted PET fibers were characterized by differential scanning calorimetry (DSC), scanning electron microscopy (SEM), intrinsic viscosity and water absorption capacity in our previous work [29]. The graft yield copolymerization of 4-VP in the presence of HEMA has shown a substantial increase in the graft yield in comparison

to the graft yield found with individual monomers. The HEMA has shown a synergistic effect on 4-VP, hence affinity of 4-VP for grafting onto PET fibers has increased. The polymer chains grafted onto PET fibers from the mixture of 4-VP and HEMA were random copolymeric in nature which has indicated that there was strong interaction between 4-VP and HEMA monomers responsible to prevent grafting of an individual monomer onto PET fibers [29].

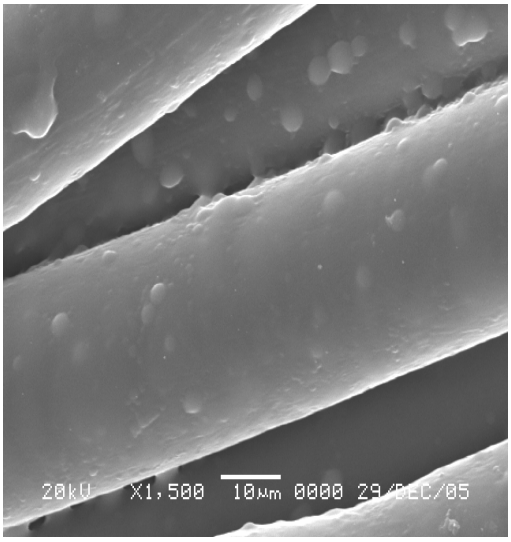


Fig. 1. SEM micrographs of 4-VP/HEMA grafted [1500x] PET fibers.

Maximum percent grafting has been reported as 280% in that study. 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 has a smooth and relatively homogeneous appearance. The grafted side chain, 4-VP/HEMA, seems to form microphases attached to the PET back-bone and to cause a heterogeneous appearance in the graft copolymer (Fig. 1), which is the evidencve of grafting [29].

Effect of pH

PET fibers do not contain suitable functional groups and thus cannot interact with dye molecules. They can only be dyed with disperse dyes and dyeability of ungrafted PET fibers with basic dyes is negligible. Dyeability of PET fibers with basic dyes 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 uptake of MB as a function of pH was examined over a pH range of 5-12. The 4-VP/HEMA grafted PET fibers were incubated for 210 min. with aqueous MB solution (20 mg L^{-1}) adjusted to required pH values of range 5-12 using buffer solutions (Briton-Robinson buffer). Fig. 2 shows the relationship between pH and adsorption amount. It is clear from the figure that increasing the pH value of the MB aqueous solution from 5 to 12, the adsorption amount increases significantly and reaches a maximum value at pH 12. In the rest of the study, experiments were carried out at pH 12. A similar type of behavior is also reported for the adsorption of MB at different adsorbents [12, 19].

To explain the observed behavior of MB adsorption with varying pH, it is necessary to examine various mechanisms such as electrostatic interaction, and chemical reaction, which are responsible for adsorption on sorbent surface. Basic dyes

possess cationic functional groups such as $-NR_3^+$ or $=NR_2^+$. 4-VP/HEMA grafted PET in basic conditions possess negative charges such as the $-C_5H_5N$, $-COO^-$ groups. Basic dyes perform poorly on natural fibers, but work very well on 4-VP/HEMA grafted PET fibers.

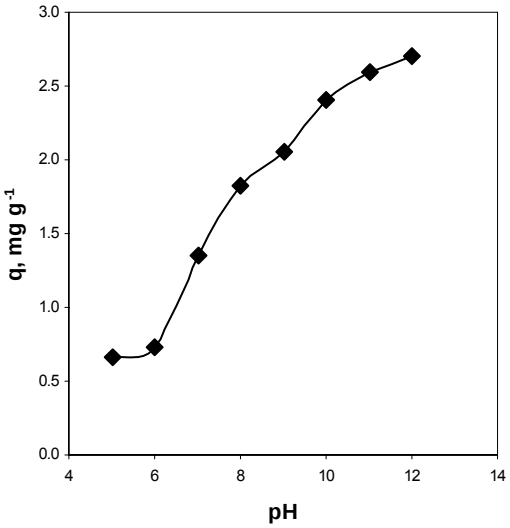
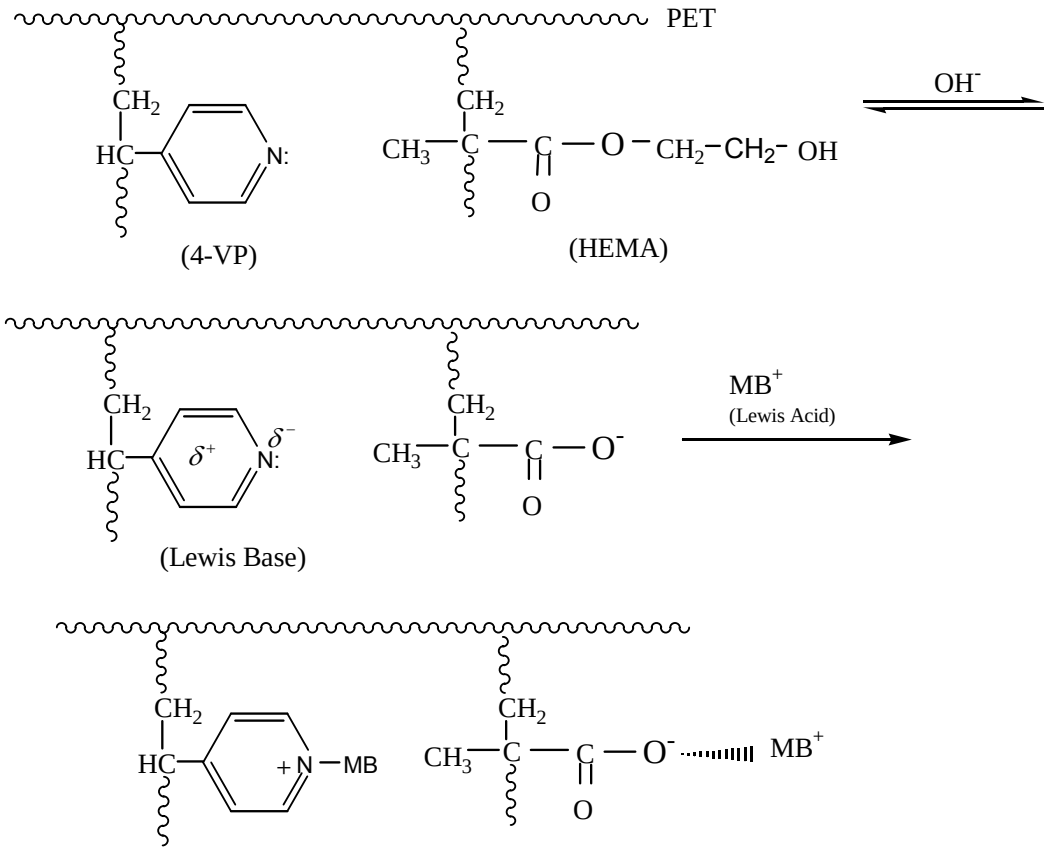


Fig. 2. The pH dependence of MB adsorbed by 4-VP/HEMA grafted PET fibers. [Dye concentration = 20 ppm, temperature 25 ^{0}C, contact time = 210 min. graft yield= 280%].



Scheme 1. Adsorption of MB on the 4-VP/HEMA grafted PET fibers.

HEMA groups of the sorbent are easily hydrolyzed by reaction with dilute alkalis, and as a result salt COO^- is formed along with ethyl alcohol. Hydrolysis by water alone is so slow as to be completely unimportant. The reaction is faster at high pH. Anionic group attached to PET is closely followed by the carboxylate group, $-COO^-$. Thus that anionic property makes grafted PET suitable for dyeing with cationic dyes since there is a strong ionic interaction between dye and polymer. For the adsorption of MB on the 4-VP/HEMA grafted PET fibers at pH 12, most of the pyridine group's surface of the sorbent was loaded negative pole. Negative pole loaded pyridine groups (Lewis base) can therefore attract the cationic dye. MB would be expected to have activity as a Lewis acid. In this way, MB interacts with grafted PET fibers, which is known as Lewis acid-base interactions. This is illustrated in scheme 1 [34].

Effect of graft yield and contact time

The effect of the grafting yield of 4-VP/HEMA grafted PET fibers on the adsorbed amount of MB was investigated, while keeping all other conditions constant. The results are shown in Fig. 3. The results of the adsorption behavior of the fibers indicate that adsorption ability of 280 % 4-VP/HEMA grafted PET fibers is higher than that ones of other grafted fibers. Increasing graft yield increases the number of functional groups and thus, increases the number of negatively charged surface of 4-VP/HEMA grafted PET fibers. The increase in the adsorption with increasing graft yield may be attributed to a higher surface area and more active sites such as 4-VP and COO^-.

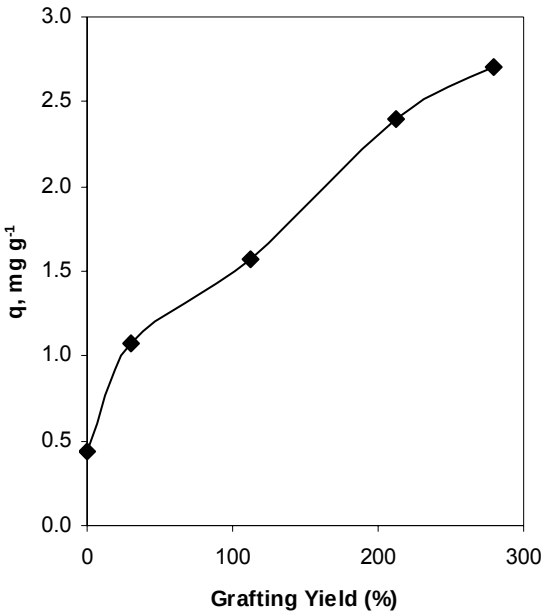


Fig. 3. Effect of the graft yield on the adsorbed amount of MB on 4-VP/HEMA grafted PET fibers. [Dye concentration = 20 ppm, pH=12, temperature= 25 ^{0}C, contact time=210 min.

Fig. 4 shows the effect of the contact time on adsorption of MB by grafted PET fibers. 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 other works as well [7]. The adsorption

equilibrium was attained within 300 minutes. During adsorption of MB, initially the dye molecules reached the boundary layer, and then had to diffuse into the surface of the grafted PET fibers, and finally, they had to diffuse into the fibrous structure of adsorbent. Therefore, this event will take a relatively longer contact time [35].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, pyridine and COO^- groups on the surface of an adsorbent have been reported to be effective in the adsorption of cationic dye [36]. Thus those groups of 4-VP/HEMA grafted PET fibers are responsible for the interaction of MB with the fibers.

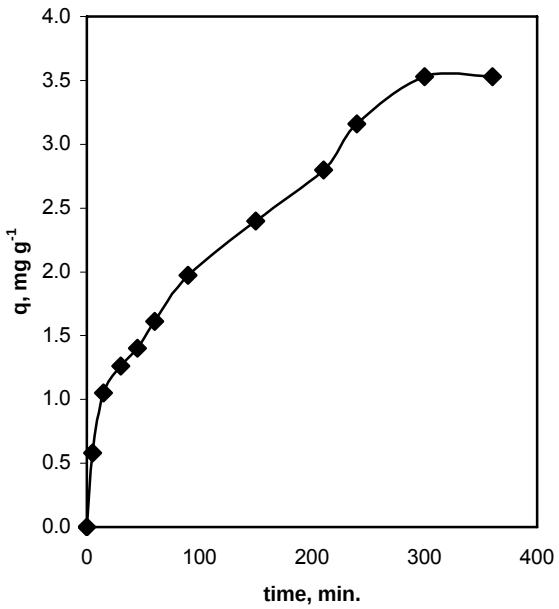


Fig. 4. Relationship between adsorption time and adsorbed amount of MB with 4-VP/HEMA grafted PET fibers. [Graft yield=280%, dye concentration = 20 ppm, pH=12, temperature= 25 ^{0}C.

The applicability of the pseudo-first-order and pseudo-second-order kinetic models was tested for the adsorption of MB onto grafted 4-VP/HEMA PET fibers. The best fit model was selected based on both linear regression correlation coefficient and the calculated q_e values. The Langergren equation, a pseudo-first-order equation, describes the kinetics of adsorption process as follows [37].

$$Log(q_e - q_t) = Logq_e - (\frac{k_1}{2.303})t \quad (1)$$

where q_t and q_e are the amount of dye adsorbed (mg g^{-1}) at any time and equilibrium time respectively, k_1 is the rate constant (min^{-1}). According to the adsorption equation, the experimental result of Fig. 4 can be converted into the plots of log (q_e-q_t) versus t, (Fig.5). Value of k_1 was calculated from the plot of Log (q_e-q_t) versus t. Although the correlation coefficient value are higher than 0.978, the experimental q_e value does not agree with the calculated one, obtained from the linear plot (Table 1). This shows

that the adsorption of MB onto 4-VP/HEMA grafted PET fiber is not a first order reaction.

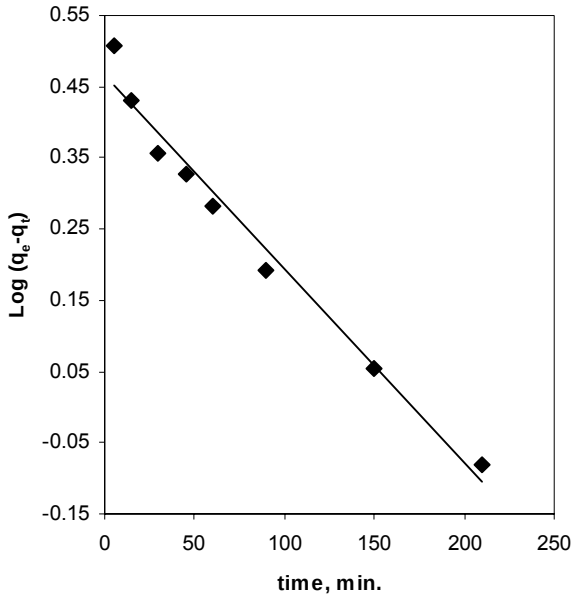


Fig. 5. Plots of time versus Log (q_e-q_t).

The second-order kinetic model [38] is expressed as:

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

where k_2 (g min^{-1} mg^{-1}) is the rate constant of second order adsorption. If second order kinetics is applicable, the plot of t q_t^{-1} versus t should show a linear relationship. 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. k_2 and q_e were calculated from the intercept and slope of the plot of t q_t^{-1} vs. t. The linear plot of t q_t^{-1} vs. t (Fig. 6) shows a good agreement between experimental and calculated q_e value (Table 1). The correlation coefficient 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 MB on 4-VP/HEMA grafted PET fibers. This suggest that the adsorption of MB onto grafted PET fibers is presumably a chemisorption process involving exchange and sharing of electrons mainly between dye cations and functional groups of the grafted PET fibers [15].

Tab. 1. Comparison of the first and second order adsorption rate constant and calculated and experimental q_e values.

	q_e (exp), mg g^{-1}	k_1, min^{-1} or k_2, g $mg^{-1}min^{-1}$	q_e (cal), mg g^{-1}	R^2
First order kinetic model	3.53	0.0062	2.91	0.97
Second order kinetic model	3.53	0.0059	3.24	0.99

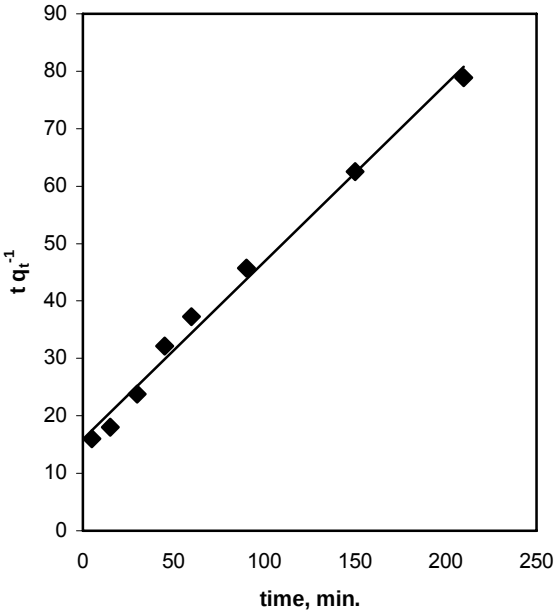


Fig. 6. Plots of time versus Log t q_t^{-1}.

The possibility of intra-particle diffusion resistance affecting adsorption was explored by using the intra-particle diffusion model as [39]:

$$q_t = k_p t^{1/2} \quad (3)$$

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 the slop of the relationship. The k_p of the 4-VP/HEMA grafted PET fibers is 0.14 mg g^{-1} min^{-1} (figure not shown).

Dyeing process involves three continuous steps. The first step is the diffusion of dye through the aqueous dye bath on to the fiber. The second step is the adsorption of dye into the outer layer of the fiber. And the last step is the diffusion of 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 due to the physical obstruction of dye diffusion presented by the network of fiber molecules. From Fig. 7, it may be seen that the increasing linear is attributed to the bulk diffusion [43, 44].

Effect of initial dye concentration

The effect of the initial MB concentration on the adsorption efficiency by 4-VP/HEMA grafted PET fibers was systematically investigated by varying the initial concentration between 5 and 300 mg L^{-1}. Fig. 7 shows the percent removal and adsorbed amount of cationic dye as a function of initial concentration at pH 12.0. It was observed that 4-VP/HEMA grafted PET fibers decreased from 98% to 88 % when the initial dye concentration varied from 5 to 300 mg L^{-1} at pH 12.0. The adsorption linear increased with increasing initial MB concentration. The maximum adsorption performance was achieved at 55.33 mg g^{-1} using 300 mg L^{-1} dye solution. 4-VP/HEMA grafted PET fibers possess higher surface area and very active sites such as 4-VP and COO^-. Therefore, 4-VP/HEMA grafted PET fibers displayed very high adsorption capacity. The increase of the adsorption capacity was mainly due to the presence of such interactions as ion exchange and chemical reaction. It has been recognized that the

adsorption capacity of 4-VP/HEMA grafted PET fibers is very good showing that it would be an interesting alternative and an economical industrial adsorbent.

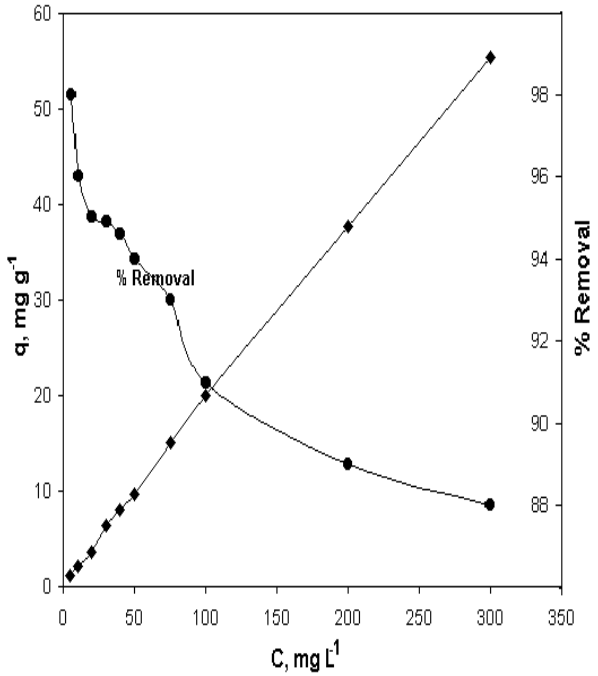


Fig. 7. Effect of initial concentration of MB on adsorption. [Graft yield=280%, pH =12; temperature= 25 ^{0}C; contact time=300 min.]

Adsorption isotherm

The relationship between the amount of MB adsorbed and the MB 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].

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}) [39]. These constants can be calculated from the adsorption isotherm data according to Langmuir equation:

$$\frac{1}{q} = \frac{1}{CK_bK_s} + \frac{1}{K_s} \quad (4)$$

where C and q are the quantities of dyes left 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 behavior follow the Langmuir adsorption isotherm (Fig. 8). The K_b and K_s values are 0.11 L mg^{-1} and 48.78 mg g^{-1}, respectively. The correlation coefficient was found to be 0.99.

However, the dye binding abilities of adsorbent could be further analyzed by Freundlich isotherm which can be described by two parameters, that is, saturation constant k, (mg g^{-1}) and equilibrium binding constant n. These constants can be calculated from the adsorption isotherm data according to Freundlich equation:

$$\text{Log } q = \text{Log } k + \frac{1}{n} \text{ Log } C_e \quad (5)$$

where C_e is the concentration (mg L^{-1}) of the dye left in the solution at equilibrium. Thus a plot of Log q versus Log C_e should give straight line having a slope of 1/n and intercept of logk. The k and n values are 4.49 mg g^{-1} and 1.37 respectively. The correlation coefficient was found as 0.98 (figure not shown). The R^2 value for linear from of isotherm are presented above. Thus Langmuir isotherm should represent the equilibrium adsorption of MB on 4-VP/HEMA grafted PET fibers.

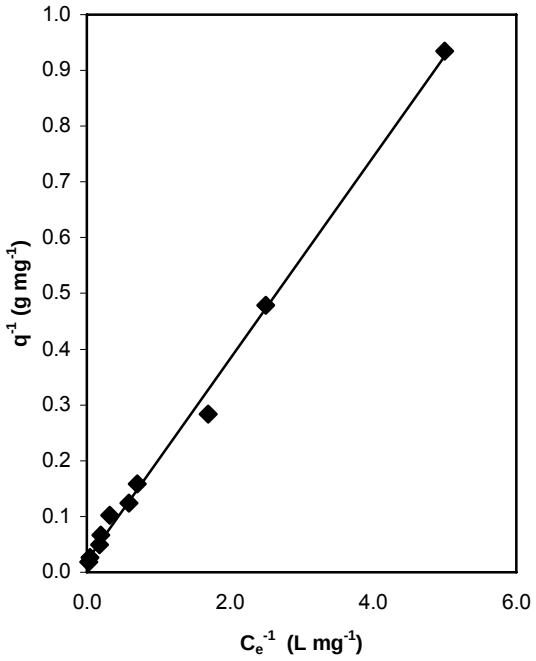


Fig. 8. Langmuir plot of the removal of MB on 4-VP/HEMA grafted PET fibers.

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant, called equilibrium parameter, R_L [41], which is defined by,

$$R_L = \frac{1}{1 + bC_0} \quad (6)$$

where b is the Langmuir constant and C_0 is the initial concentration (mg L^{-1}). C_0 used in the adsorption isotherm studies was in the range of 5-300 mg L^{-1}. R_L are found to be less than 1 and greater than 0. These results show that MB adsorption onto 4-Vp/HEMA grafted PET fibers is favorable.

Effect of temperature

It has been recognized that the adsorption of MB from an aqueous solution by 4-VP/HEMA grafted PET fiber is affected by the temperature (Fig. 9) such that the adsorption increased remarkably as the temperature increased.

The thermodynamic parameters for the adsorption process were computed from the van't Hoff equation,

$$Log\frac{q}{C_e} = -\frac{\Delta H^0}{2.303RT} + \frac{\Delta S^0}{2.303R} \quad (7)$$

where R is gas constant, T is temperature in °K, ΔS^o and ΔH^o is change in entropy and enthalpy of adsorption, respectively. According to the adsorption equation, the experimental result of Fig. 9 can be converted into the plots of log(q/C_e) versus 1/T, as shown in Fig. 10.

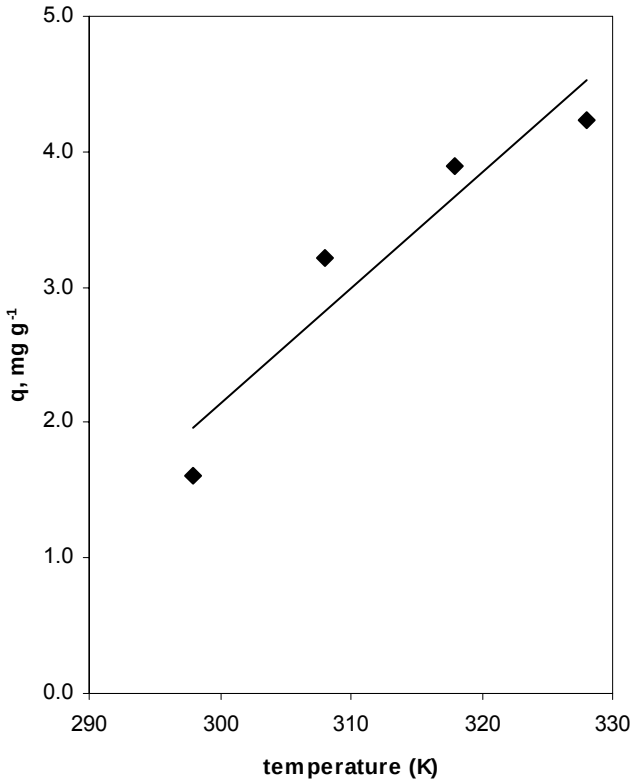


Fig. 9. Effect of temperature on adsorption of MB [Graft yield=280%, dye concentration = 20 ppm, contact time=60 min.]

Values of ΔS^o and ΔH^o were calculated from the plot of log(q/C_e) versus 1/T. This plot has a very good linearity with regression coefficient of 0.99. The entropy and enthalpy change values of adsorption were calculated as 334.65 $JK^{-1}mol^{-1}$ and 104.58 $kjmol^{-1}$ respectively. It was recognized that these values are convenient with the literature [36, 42].

As it is reflected from the positive value of the heat of adsorption, the adsorption process is endothermic and the increased temperature is responsible for the increase in adsorption. The value of the adsorption heat shows that the chemical adsorption takes place in the process. The Increasing temperature gives a speed to the hydrolysis and chemical reaction. Therefore the active sites increase in number and so does the number of negatively charged surface of 4-VP/HEMA grafted PET fibers. The big value of ΔH was compatible with the formation of strong chemical bonds between the MB and 4-VP/HEMA grafted PET.

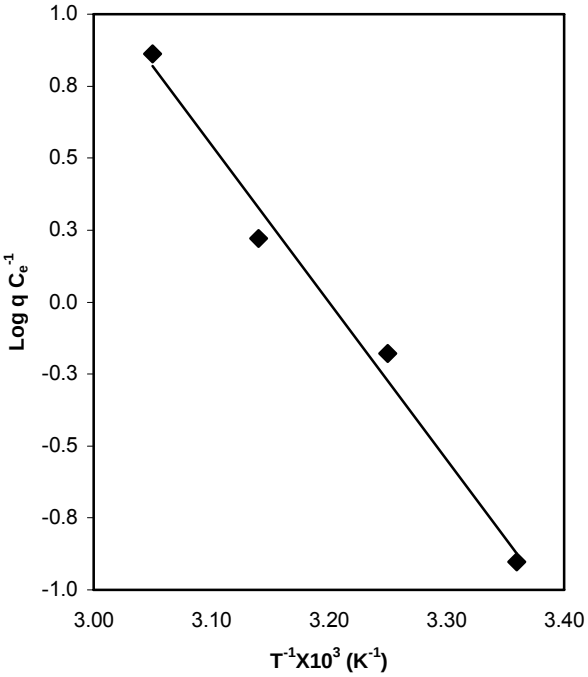


Fig. 10. Plots of Log q C_e^{-1} versus T^{-1}.

Desorption studies

The desorption studies were carried out by treating the cationic dye (40 mg L^{-1}) at different acid pH, room temperature (25 ^{0}C) and for 60 min. As seen from Fig. 11, the desorption percent increased with decreasing pH. 55 percent MB desorbed when pH was kept at 1 while only 5 percent MB desorbed at pH 5.

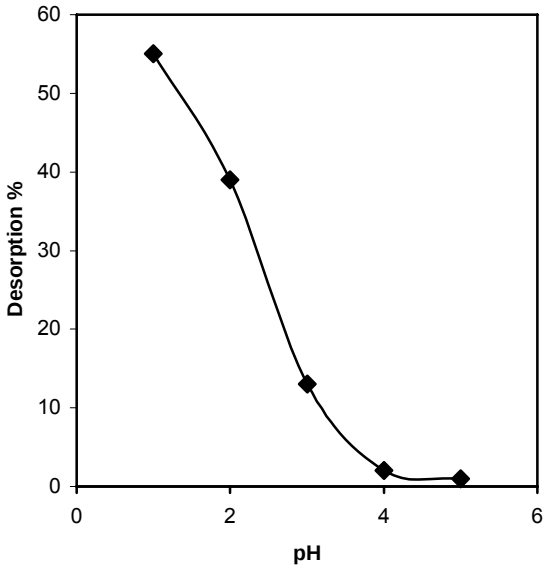


Fig. 11. Effect of pH on desorption of dye dye loaded adsorbent. [Graft yield=280%, dye concentration = 40 ppm, temperature= 25 ^{0}C, contact time=60 min.]

The high hydrogen ion concentration at the interface electrostatically repels positively charged cations dye preventing their approach to the fiber surface. It has been recognized that 4-VP/HEMA grafted PET fiber is stable and regenerable by HCl. It was showed that the desorption studies confirm the mechanism of adsorption stated in the pH effect. Therefore, adsorption process should be effective for the removal of MB from industrial effluents.

Conclusions

PET fibers were grafted with 4-VP/HEMA, and used as an adsorbent for cationic dye (MB). The following conclusions were obtained: adsorption process was affected by the graft yield. It was observed that pH is the most important parameter and pH 12.0 was found as the optimum pH value in the process. 300 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/HEMA grafted PET fibers is a cheap alternative adsorbent for methylene blue dye from aqueous medium. Thus, the material should be addressed for other cationic 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 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. Other reagents were used as supplied. All reagents were Merck products.

Polymerization 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, 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 ± 0.01g), 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, monomer and freed from the 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 ^{o}C for 72 h and weighed. The graft yield (GY) was calculated from the weight increase in grafted fibers as follows:

$$G\,Y\,(\%) = [(w_g - w_i)/w_i] \times 100 \qquad (8)$$

Where w_i and w_g denote the weights of the original (ungrafted) and grafted PET fibers, respectively [29].

Sorption of MB on the adsorbent

Volume of 25 cm^3 of MB solution (20 mg L^{-1}, pH 12) was added onto 0.1 g of 4-VP/HEMA 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 (Edmund Mühler TH 15). The loaded adsorbent was separated by centrifugation and washed gently. After supernatant was measured by using UV/Visible spectrophotometer (λ=665 nm, Pharmacia Biotech Ultrospec 2000). Calibration curves were plotted between absorbance and concentration of the standard dye solutions. The adsorption capacity of the poly 4-VP/HEMA grafted PET fibers was evaluated by using the following expression:

$$q=(C_o-C)V/m \quad (9)$$

where q is the amount of dye adsorbed onto unit mass of the 4-VP/HEMA grafted PET fibers (mg g^{-1}), C_o and C are the concentration of the MB 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 MB solution used (L); and m is the amount of 4-VP/HEMA grafted PET fibers used (g), respectively.

Desorption of MB

Desorption assay were carried out with the MB loaded 4-VP/HEMA grafted PET fibers at maximum capacity. MB was recovered by treating with 25 mL adjusted to different pH values for 60 minutes, than analyzed by the method mentioned above. The desorption percent was calculated using the following equations:

$$\% \text{ Desorption} = \frac{\text{Amount of MB (mg) desorbed}}{\text{Adsorbed amount of MB (mg) by adsorbent}} \times 100 \quad (10)$$

References

[1] Ramakrishna, K.R.; Viraraghavan, T. *Water Sci. Technol.* **1997**, 36, 189.
[2] Clarke, E.A.; Anliker, R. *The Handbook of Environmental Chemistry* **1980**, 3(A), 181.
[3] Sanghi, R.; Bhattacharya, B. *Color Technol.* **2002**, 118, 256.
[4] Baughman, G.; Perenich, T.A. *Environ. Toxicol. Chem.* **1988**, 7, 183.
[5] Robinson, T.; McMullan, G.; Marchant, R.; Nigam, P. *Bioresour. Technol.* **2001**, 77, 247.
[6] Chakraborty, S.; Purkait, M.K.; Dasgupta, S.; De, S.; Basu, J.K. *Sep. Purif. Technol.* **2003**, 31, 141.
[7] Ciardelli, G.; Corsi, L.; Marucci, M. *Resour. Conserv. Recycl.* **2000**, 31, 189.
[8] Lin, S.H.; Peng, F.C. *Water Res.* **1994**, 28, 277.
[9] Muthukumar, M.; Selvakumar, N. *Dyes Pigments* **2004**, 62, 221.
[10] Smith, B.; Koonce, T.; Hudson, S. *Am. Dyestuff. Rep*. **1993**, 82, 18.
[11] Fu, Y.; Viraraghavan, T. *Water SA.* **2003**, 29(4), 465.
[12]\Senthilkumaar, S.; Varadarajan, P.R.; Porkodi, K.; Subbhuraam, C.V. *J. Colloid and Interface Sci.* **2005**, 284, 78.
[13] Kumar, K.V. *J. Hazard. Mater.* **2006**, 137(B), 1538.
[14] Hamdaoui, O. *J. Hazard. Mater.* **2006**, 135(B), 264.
[15] Ncibi, M.C.; Mahjoub, B.; Seffen, M. *J. Hazard. Mater.* **2007**, 139, 280.
[16] Laing, I.G. *Rev. Prog. Color.* **1991**, 21, 56.
[17] Mak, S.Y.; Chen. D.H. *Dyes and Pigments* **2004**, 61, 93.

[18] Tunay, O.; Rabdasli, I.; Eremektar, G.; Orhon, D. *Water Sci. Technol.* **1996**, 34(11), 9.
[19] Vadivelan, V.; Kumar, K.V. *J. Hazard. Mater.* **2005**, 286, 90.
[20] Han, R.; Zou, W.; Yu, W.; Cheng S.; Wang, Y.; Shi, J. *J. Hazard. Mater.* **2007**, 141, 156.
[21] Namasivayam, C.; Sumithra, S. *J. Environ. Management* **2005**, 74, 207.
[22] Vashurina, I.Y.; Kalinnikov, Y.A. *Text. Chem.* **1997**, 2(11), 49.
[23] Chakrabarti, S.; Dutta, B.K. *J. Colloid Interface Sci.* **2005**, 286, 807.
[24] Hajjaji, M.; Alami, A.; El Bouadili, A. *J. Hazard. Mater.* **2006**, 135(B), 188.
[25] Deng, S.; Bai, R. *Water Res.* **2004**, 38(9), 2423.
[26] Deng, S.B.; Bai, R.B.; Chen, J.P. *J. Colloid Interface Sci.* **2003**, 260(2), 265.
[27] Sakurada, I.; Ikada, Y.; Kawahara, T. *J. Polym. Sci. A* **1973**, 11, 2329.
[28] Buxbaum, L.H. *Angew. Chem.* **1968**, 80, 225.
[29] Yiğitoğlu, M.; Arslan, M. *Polym. Bull.* In press.
[30] Yiğitoğlu, M.; Ersöz, M.; Coşkun, R.; Şanlı, O.; Ünal, H.I. *J. Appl. Polym. Sci.* **1998**, 68(12), 1935.
[31] Coşkun, R.; Yiğitoğlu, M.; Saçak, M. *J. Appl. Polym. Sci.* **2000**, 75(6), 766.
[32] Yiğitoğlu, M.; Arslan, M.; Şanlı, O.; Ünal, H.İ. *Hacettepe Journal of Biology and Chemistry* **2002**, 31, 133.
[33] Yiğitoğlu, M.; Arslan, M. *Polym. Bull.* **2005**, 55, 259.
[34] Solomons, T.W.G. *Organic Chemistry,* John Wiley and Sons, **1984**, New York.
[35] Hameed, B.H.; Ahmad, A.L.; Latif K.N.A. *Dyes Pigments*, In press.
[36] Bhattacharyya, K.G.; Sharma, A. *Dyes Pigments* **2005**, 65, 51.
[37] Namasivayam, C.; Renganathan, K. *Water Res.* **1995**, 29, 1737.
[38] McKay, G.; Ho, Y.S. *Process Biochem.* **1999**, 34, 451.
[39] Weber, W.J.; Morris, J.C.; San, J. *Eng. Div. ASCE* **1963**, 89, 31.
[40] Barrow, G.M. *Physical Chemistry*, McGraw-Hill Book Company Inc. **1961**, New York.
[42] Weber, T.W.; Chackravorti, R.K. *Amer. Inst. Chem. Eng. J.* **1974**, 20, 228.
[43] Ghosh, D.; Bhattacharyya, K.G. *Appl. Clay. Sci.* **2002**, 20, 295.
[44] Kim, T.K.; Son, Y.A. ; Lim, Y.J. *Dyes Pigments* **2005**, 67(3), 229.
[45] Vickerstaff, T. *The Physical Chemistry of Dyeing*, 2nd ed. **1954**, London.