# Surface adsorption of an acidic dye (erionyl blue) on poly(ethylene terephthalate)-grafted-methyl methacrylate/acrylic Acid

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## ABSTRACT

*In the present study, graft copolymerization of methyl methacrylate (MMA), acrylic acid (AA) mixture onto poly(ethylene terephthalate) (PET) fibers was carried out in the presence of benzoyl peroxide( $Bz_2O_2$) as an initiator .The modified PET fibers was used for the removal of an acidic dye( EAR), from aqueous solutions via batch technique .The factors controlling the adsorption process were also investigated. The fibers was characterized by scanning electron microscopy (SEM) , specific surface area (BET) , cation exchange capacity (CEC) and point of zero charge ( $pH_{zpc}$). The best results for removal of dye were recorded (pH=4.0, t=30 min, adsorbate concentration=170 mg / L, adsorbent dose=0.2g).The adsorption data were fitted by Harkins-Jura isotherm and Intra-particle diffusion kinetic models, as well. On the other hand, the results of thermodynamic parameters and activation energy emphasized that the process was physisorption, endothermic and spontaneous.*

**Keywords:** Adsorption, Grafting, Equilibrium, Kinetic, Isotherm

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## INTRODUCTION

The treatment and disposal of dye-contaminated wastewater is one of the most serious environmental problems faced by the textile, dying, printing, ink and related industries. Dyes are known pollutants that not only affecting aesthetic merit but also reducing light penetration and photosynthesis and some are considered toxic and even carcinogenic for human health.[1]The removal of dyes from wastewater were reported by different methods. [2-7]Adsorption is one of the most economical method for removing of dye contaminations. [8,9] Some researchers were reported removal of water pollutants by the use of polymeric fibers. Essentially this is related to their fast kinetic adsorption, low activation energy and re generable easily.[10-20] In our previous works, the graft copolymerization of PET by the mixture of MMA/AA in the presence of $Bz_2O_2$ were reported.[21,22] The aim of this study was the evaluation of useability of MMA/AA-grafted-PET fibers for removal of an acidic dye (EAR) from aqueous solution through batch technique.

## MATERIALS AND METHODS

PET fibers (stretch ratio 2, 30 filaments, 110dTex) were purchased from Textile Department of Amir Kabir University and Technology (Tehran). They were cut as small hank (0.1±0.01 g), Soxhlet –extracted for 6h with acetone and dried at 50C in vacuum oven. MMA and AA were provided by BDH Co. of England and were used

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after purification. MMA was washed three times with 5% NaOH , dried over $CaCl_2$ , and finally distilled in vacuum at 46˚C. AA was vacuum distilled over a column filled with copper wires at 30˚C. $Bz_2O_2$ was purified twice from the ethanol-chloroform (65%vol. ethanol) mixture and dried in vacuum desiccator. The acidic dye (EAR) was purchased from Institute for Color and Technology (ICST) (Iran). All of reagents and solvents were high purity and supplied by Merck Chemical Co. and doubly distilled water used in all experiments.

**Grafting procedure:** Grafting was achieved in 100 mL Pyrex tube. The polymerization tube containing the 0.1g PET fiber, monomers (AA 30% - MMA 70% = 0.1 mol/L) , 45 mL doubly distilled water, 5 mL acetone containing $4.0 \times 10^{-3}$ mol / L $Bz_2O_2$ was added. The mixture was placed into the water bath at the fixed temperature (363K). To provide various grafting products, the operation was accomplished in the range of 20-70 min. The removal of undesirable homopolymers was done by doubly distilled water 24h water at room temperature, and toluene-acetone mixture for 6 and 8h, respectively .Then the fibers were oven dried at 323K for 48h and weighted .The percent of grafting was calculated gravimetrically:

$$G(\%) = W_g - W_0/ W_0 \times 100,$$

Where , $W_g$ and $W_0$ are the weights of the grafted and ungrafted PET fibers, respectively.

**Adsorption studies:** Adsorption experiments were accomplished using 0.1g of the grafted fibers with 20 mL dye solution (75mg/L) in the 250 mL Erlenmeyer flask at the fixed agitation speed (150 rpm). After desirable time, the solution was filtered by filter paper (Wattman No.40), and then centrifuged for 10 min at 3000 rpm. The analyzing of dye in solution was fulfilled using a Uv spectrophotometer (Shimadzu 1208) at a maximum adsorbance(628nm). The amounts of dye adsorbed (mg/g) onto grafted fibers was calculated using the following equation:

$$q = (C_\circ - C) \times V / m,$$

Where, q is the amount of adsorbed dye on grafted fiber (mg/g), $C_0$ and C are the initial and equilibrium dye concentrations (mg/L), V is the volume of the solution (L) and m is the mass of grafted fiber sample used (g).

## RESULTS AND DISCUSSION

**Characterization of adsorbent:** The specific surface area of grafted PET fiber was determined from nitrogen adsorption isotherm according to BET method using a quantochrome Autosorb instrument. It was found to be equal to $0.414m^2/g$. This value is very negligible for investigation of adsorption process according to surface area, and probably adsorption imputed to the reaction between reactive groups (-COOH, $-COOCH_3$) which attached from monomers to the PET chains and dye molecules. Cation exchange capacity (CEC) was determined according to copper ethylene diamine complex and saturating by sodium acetate methods. [23,24] The results of both methods were the same, and CEC determined (29.5 mg/g or 128.6 meq/100g). The point of zero charge ($pH_{zpc}$) of reactive fibers measured at pH 3 – 9 .As shown in Fig .1 the point of zero charge was determined 6.2.[25] Surface morphology was investigated using JEOL-JEM-100 CX II microscope. As shown in Fig 2 (a, b, c) by adsorption of dye onto PET fiber, heterogeneity was increased and the surface of fiber observed very rough.

**Effect of pH:** The effect of pH upon adsorption of dye was determined from 2.5 to 10.0. As shown in Fig .5 The optimum pH for removal of dye was found to be 4.0. At higher values of pH, insoluble dye starts precipitating from the solution. At low pH values, the hydrogen and dye on the sorption sites were competed to each other. [26]

**Effect of contact time:** The effect of contact time on adsorption was studied from 10 to 120 min at the fixation condition of other variables (pH = 4.0, solution volume = 20 mL, T = 298 K, graft percent = 75 %, adsorbent =0.1 g, adsorbate concentration= 75 mg / L, and shaking rate = 150 rpm).. As shown in Fig.6 a rapid adsorption observed at 10 min and completed at 30 min. After this time, the rate of adsorption levelled off. The maximum removal was 7.80 mg/g and it was reached in 30 min. [27]

**Effect of adsorbent:** With an increase of the reactive fibers from 0.05 g to 0.20 g, the adsorption amount (q) increased to 8.6 mg / g. This is related to the increase in adsorbent weight whereas the amount of adsorbate did not increase significantly**.** This is related to the reactive groups (-COOH, $-COOCH_3$) which attached to the PET structure after grafting of AA and MMA. [13,14] Fig.7

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**Effect of adsorbate concentration:** The effects of different concentrations of dye on adsorption were studied in this phase. For this aim, different concentrations of dye, in the range of 75-200 mg /L, were prepared and tested at pH = 4.0, solution volume = 20 mL, T = 298 K, graft yield = 75 %, adsorbent =0.10 g, and shaking rate = 150 rpm. The best result was determined to be 16.5 mg/g for 170 mg/L aqueous solution. Fig.8

**Fig.1. Determination of the point of zero charge**
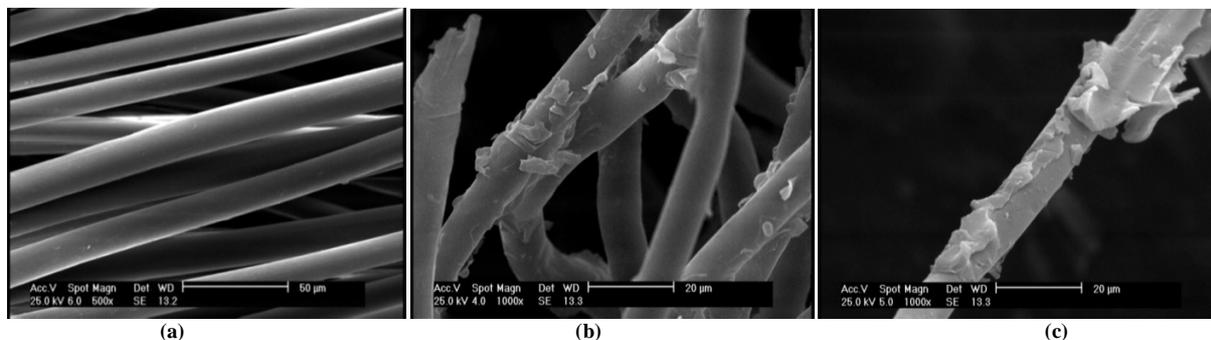


**Fig.2. SEM images of (a) ungrafted fibers (b) grafted fibers (75%) (c) grafted PET fibers containing dye at 1000× magnifications**
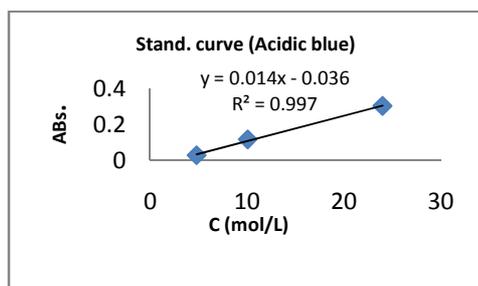


**Fig3. Calibration Curve of Erionyl Blue**             **Fig 4.The Structure of Erionyl Blue**
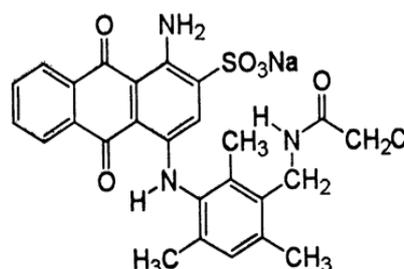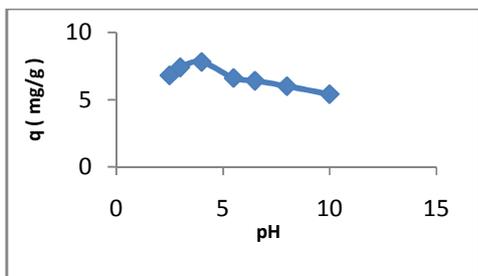


**Fig.5. Effect of the pH on the adsorption of dye onto 0.1g     Fig 6. Effect of time on the adsorption at pH=4.0
modified PET fibers ( [dye]= 75mg/L, Time =120min, agitation rate = 150 rpm, T = 298K, solution volume = 20 mL)**
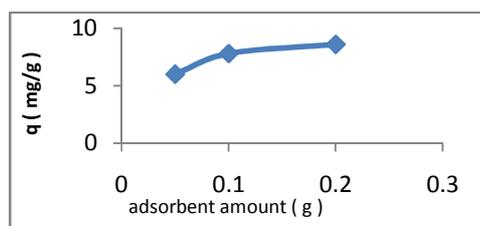


**Fig.7. Effect of adsorbent amount on the adsorption     Fig8. Effect of dye concentration on the adsorption**
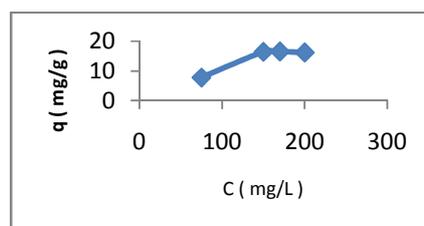
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**Adsorption kinetics**: Three models were investigated in order to exolain the adsorption kinetics of dye onto adsorbent[ 28-31]: Formula for these models are:

Lagergren's pseudo-first order: $Ln ( q_e – q_t ) = Ln\ q_e – K_a$
Ho's pseudo-second order: $t / q_t = 1 / K_2\ q_e^2 + t / q_e$
Intra-particle diffusion: $q = K_d . t^{1/2} + I$

Where $q_e$ and $q_t$ denote the amounts of metal adsorbed (mg/g) at equilibrium and at time t(min). $K_1$(1/min) and $K_2$(g/mg.min) are the rate constants of pseudo-first-order and pseudo-second-order models, respectively. I is a constant value of intra-particle-diffusion equation and identify the boundary layer thickness between adsorbate and adsorbent and $K_d$ is the rate constant.In Ho's pseudo-second-order model, initial adsorption rate is equal to h = $K_2$ . $q_e^2$. Kinetics studies were accomplished at the fixed condition of the other variables (T = 298K, [dye] = 100(mg/L), grafted fibers = 0.1g, pH= 4.0, solution volume = 20 mL, shaking rate = o.o). As shown in Fig. 9-11 and Table1.the best fitness was observed in the pseudo-second order and Intra-particle diffusion equations. Pursuant to these models the correlation coefficients were found to be very high, and can be used to describe the adsorption process. This fact may be ascribed to a chemical interaction between adsorbate with the functional groups of modified PET.
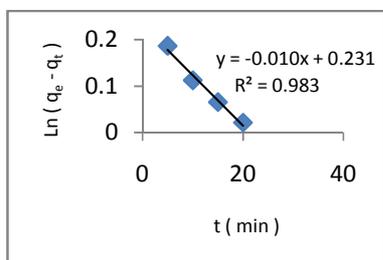


**Fig 9. Pseudo - first order kinetics**   **Fig 10. Pseudo - second order kinetics**   **Fig11. Intra - particle diffusion kinetics**
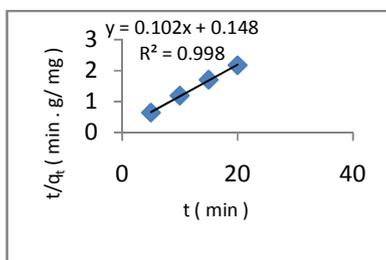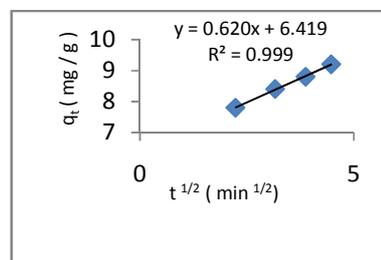
**Table 1.Adsorption kinetic parameters**

| Pseudo-first-order kinetic model | | | Pseudo-second-order kinetic model | | | Intra-particle-diffusion kinetic model | | |
|---|---|---|---|---|---|---|---|---|
| $q_e$(mg/g) | $K_1$(1/min) | $R^2$ | $q_e$(mg/g) | $K_2$(g/mg.min) | $R^2$ | $K_d$ | I | $R^2$ |
| 1.260 | 0.010 | 0.983 | 9.804 | 0.070 | 0.998 | 0.620 | 6.419 | 0.999 |

**Adsorption isotherm**:The adsorption equilibrium data were studied according to five isotherms: Langmuir, Freundlich, Temkin-Pyozhev, Dubinin – Radushkevich  and Harkins-Jura. These equations are given as follows:

Langmuir isotherm: $C_e/q_e = C_e/q_m + 1/K_a. q_m$
Freundlich isothrm : $Ln q_e = Ln K_f + 1/n\ Ln C_e$
Temkin isotherm: $q_e = a_t + B_0\ Ln\ C_e$
Dubinin – Radushkevich isotherm: $Ln\ q_e = Ln\ q_m - 2B.RT.Ln (1+1/C_e )$
Harkins –Jura isotherm: $1/q_e^2 = (B/A) – (1/A\ log\ C_e)$

As shown in Fig 12-16 and Table2.experiments were accomplished at different temperatures (298, 313 and 328 K). The $R^2$ values show that Freundlich and Harkins-Jura models fits well with experimental data. These results identify that the surfaces of reactive fibers are rough and heterogeneous and can be efficient on multilayer adsorption. [32]
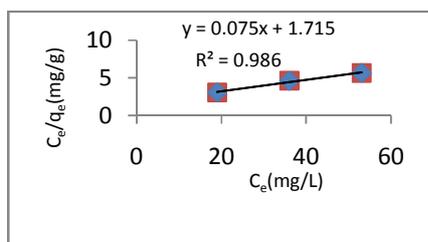


**Fig 12. Langmuir isotherm ( T= 298 K )**          **Fig 13 . Freundlich isotherm (T = 298 K)**
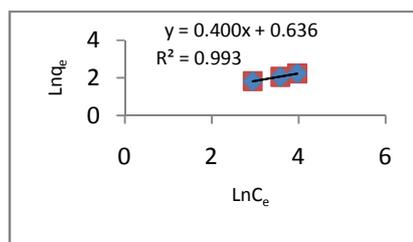
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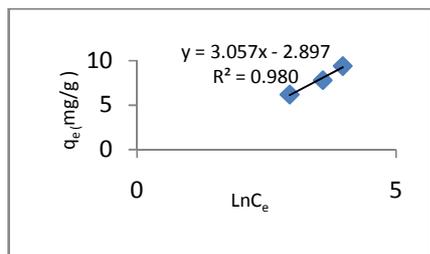


**Fig 14. Temkin – Pyozhev isotherm (T = 298 K)     Fig 15.D-R isotherm (T=298 K)            Fig 16. H-J isotherm (T=298 K)**
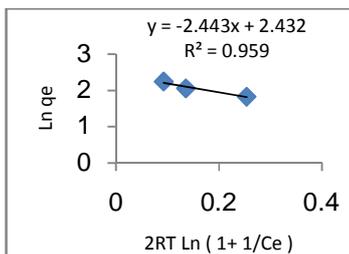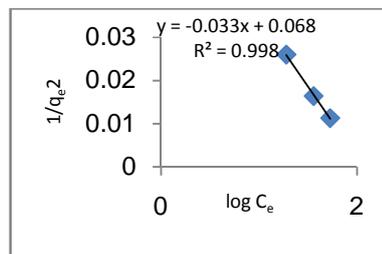
**Table 2.Adsorption isotherm constants**

| Langmuir constants | $K_a$ ( L / mg ) | $q_m$ ( mg / g ) | $R^2$ |
|---|---|---|---|
| Dye ( 298K ) | 0.043 | 13.330 | 0.986 |
| Dye ( 313K ) | 0.057 | 12.980 | 0.987 |
| Dye ( 328K) | 0.069 | 12.980 | 1.000 |
| **Freundlich constants** | $K_F$ ( mg / g ) | n ( L / mg ) | $R^2$ |
| Dye ( 298K ) | 1.890 | 2.500 | 0.993 |
| Dye ( 313K ) | 2.400 | 2.830 | 0.991 |
| Dye ( 328K ) | 2.830 | 3.120 | 0.985 |
| **D-R constants** | $q_m$ ( mg / g ) | B ( $mol^2 / kJ^2$ ) | $R^2$ |
| Dye ( 298K ) | 11.380 | 2.443 | 0.959 |
| Dye ( 313K ) | 11.450 | 1.896 | 0.953 |
| Dye ( 328K ) | 12.060 | 1.748 | 0.996 |
| **Temkin constants** | $a_t$ ( mg / g ) | $B_0$ ( L / mg ) | $R^2$ |
| Dye ( 298K ) | -2.897 | 3.057 | 0.980 |
| Dye ( 313K ) | -1.566 | 2.847 | 0.977 |
| Dye ( 328K ) | -0.683 | 2.723 | 0.996 |
| **Harkins-Jura constants** | A | B | $R^2$ |
| Dye ( 298K ) | 30.300 | 2.060 | 0.998 |
| Dye ( 313K ) | 38.460 | 2.110 | 0.999 |
| Dye ( 328K) | 47.620 | 2.190 | 0.948 |

**Thermodynamic studies**: The following equations were used to calculate the thermodynamic parameters for the adsorption process:

$K_d = q_e / C_e$
$\Delta G° = -RT \, Ln K_d$
$\Delta G° = \Delta H° - T \, \Delta S°$
$Ln K_d = - \Delta H° / RT + \Delta S° / R$

In above equations, $K_d$ is the equilibrium constant, T is the temperature (K), R is the gas constant. $\Delta H°$ and $\Delta S°$ are the change of enthalpy and entropy and by the help of Van't Hoff plots were determined. Results presented in Fig.17 and Table.3
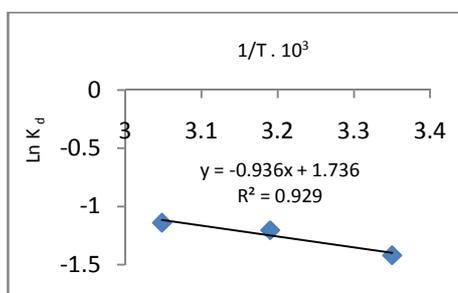


**Fig17. Van't Hoff plot for thermodynamic parameters**                **Fig18. Arrhenius plot of Ln $q_e$ – 1 / T**
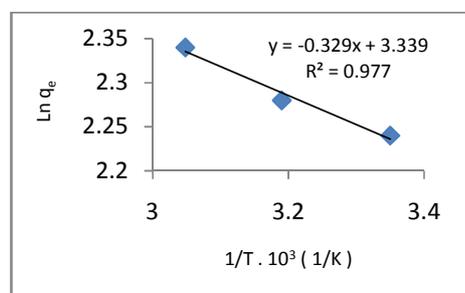
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**Table 3 . Thermodynamic Parameters at Different Temperatures**

| T ( K ) | $\Delta H^\circ$ (kJ / mol ) | $\Delta S^\circ$ ( kJ/mol .K ) | $\Delta G^\circ$ ( kJ/mol ) |
|---------|------------------------------|--------------------------------|------------------------------|
| 298     | 0.0078                       | 0.014                          | -4.291                       |
| 313     |                              |                                | -4.507                       |
| 328     |                              |                                | -4.723                       |

The low value of the $\Delta H^\circ$ demonstrates the physisorption is much more possible and the process is endothermic [33]. The $\Delta S^\circ$ identify increased disorder at the adsorbent – solution interface during the adsorption of dye. Meanwhile, during the adsorption of dye onto PET fibers the freedom degrees increase. The negative quantities of $\Delta G^\circ$, show that the adsorption process are thermodynamically favorable and spontaneous. The amounts of $\Delta G^\circ$ for physisorption were reported between -20 _ 0 kJ/mol.[34]

**Effect of temperature on adsorption:** Determination of the activation energy was computed by the Arrhenius equation. From the dependence of Ln q versus 1/T, the activation energy was determined (2.735 kJ/mol) Fig.18. The low quantity of $E_a$ emphasize the adsorption process is so easy. [15, 35] The desorption activation energy was calculated according to the following equation:

$E_d = \Delta H + E_a$   , $E_d$ computed 2.743 kJ/mol. This value is negligible and desorption process is so easy.

## CONCLUSION

The results of the present study showed that PET–g–MMA/AA is a drastic adsorbent for the removal of dye from aqueous solutions. Isotherm and kinetic studies showed that the adsorption equilibrium of dye onto modified fibers is well explained by the Harkins-Jura and Intra- particle diffusion models. The quantities of $\Delta G^\circ$, $\Delta H^\circ$ and $E_a$ purposed the adsorption of dye onto reactive PET fibers was physisorption and spontaneous

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