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An Investigation of the Surface Adsorption of Cationic Brill Red X – 5 GN on Poly (ethylene terephthalate) – Grafted – 2- Hydroxy Propyl Methacrylate

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ABSTRACT

In this study the adsorption of a cationic dye (Cationic Brill Red X- 5 GN) onto poly (ethylene terephthalate) – grafted – 2-hydroxy propyl methacrylate has been accomplished via batch technique. The effect of pH, adsorbent dose, adsorbate concentration, temperature, contact time and grafting yield were investigated. The optimum results recorded (pH=10.00, t=60min, G%=53%, adsorbent dose=0.1g, adsorbate concentration= 200mg/L). The adsorption data were best fitted by Freundlich and Intra-particle diffusion kinetic models. Thermodynamic parameters have been determined. The adsorption process is physisorption, exothermic and spontaneous.

Keywords: Adsorption, 2-Hydroxy propyl methacrylate, Isotherm models, Kinetics.

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INTRODUCTION

Dyes were manufactured in the world is annually about 7×10^5 tons. Almost 100 thousands kinds of dyes are used in different industries like textile, plastic, paint, paper, cosmetic and etc. They are usually toxic and carcinogen. Therefore, purification and removing of dyes from wastewater is necessary. For this aim, various methods like electrolysis, membrane separation, chemical coagulation, ion exchange, evaporation, reverse osmosis, chemical precipitation and adsorption have been used [1-6]. Adsorption is one of the most important methods which many researchers have been noticed it. They have been investigated various adsorbents such as perlite, fly ash, peat, wood, coir pith, rise husk, orange peel, activated carbon, carbon nanotube for removing of dyes from wastewater [7-19]. Recently, some researchers have been attended to remove of dyes and heavy metals from water and wastewater by the use of polymer fibers as adsorbent [20, 21]. This is mainly related to high kinetic adsorption and low cost of them. In our previous works, the graft copolymerization of poly (ethylene terephthalate)(PET) by 2-hydroxy propyl methacrylate (2-HPMA) in the presence of benzoyl peroxide(Bz_2O_2) and 4,4 azobis(4-cyanovaleric acid)(ACV) have been reported [22-24].

The aim of this study was to assay the useability of 2-HPMA-Grafted-PET fibers as a new adsorbent for removal of Cationic Brill Red X-5GN from aqueous solution via batch technique.

MATERIALS AND METHODS

Experimental

PET fibers (44 filaments, 167dTex) purchased by chemistry department of Amir Kabir University of Technologhy (Tehran). They were cut as small hank (0.1g) and then they were extracted by Soxhlet for 6h with acetone and finally they were dried at ambient temperature. For removal of inhibitors which exist in 2-HPMA, it was used after distillation under reduced pressure in inert atmosphere (23mmHg, T=99˚C). Bz_2O_2 (Aldrich) was recrystallized twice from the methanol-chloroform mixture and dried in vacuum desiccator and was kept in refrigerator. The Cationic Brill Red X-5GN was purchased from Institute for Color and Technology (ICST) (Iran).

Grafting procedure

Grafting procedure was achieved in a Pyrex polymerization tube containing 0.1g PET fiber, 0.5 mol/L monomer,2×10^{-3} mol/L initiator,45mL doubly distilled water at 75˚C in water bath [22-24]. For providing of various grafting yields, the operation was carried out in the range of 10-60min. The removal of undesirable homopolymers were accomplished by N,N-dimethyl formamide(DMF) and (toluene-acetone) mixture for 6 and 8h , respectively. The percent of grafting was determined according to gravimetrically [22-24].

Adsorption procedure

All of the Cationic Brill Red X-5GN solution was prepared with doubly distilled water. The pH of the solution was adjusted with 0.1 N HCl or NaOH by using a model 3C Digital pH-meter. 0.1g of grafted fiber was mixed with 20 mL dye solution in a 250 mL Erlenmeyer stirred with a rate of 150 rpm for 60 min. A constant bath was used to keep the temperature constant. At the end of the adsorption period, the solution was centrifuged for 10 min at 1000 rpm. After centrifugation, the dye concentration in the solution was analyzed using a Uv spectrophotometer (Shimadzu 1208) by monitoring the adsorbance changes at a wavelength of maximum adsorbance (513.5nm). The amounts of dye adsorbed on grafted fiber at any time, t, were calculated from the concentrations in solution before and after adsorption .At any times, the amount of dye adsorbed (mg/g) onto grafted fiber was calculated from the mass balance equation and calibration curve "**Figure 1.**"

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

Where, q is the amount of adsorbed dye on grafted fiber at any time (mg/g), $C_\circ$ and C are the initial and equilibrium liquid-phase concentrations of dye (mg/L), respectively. V is the volume of dye solution, and m is the mass of grafted fiber sample used (g).

RESULTS AND DISCUSSION

Effect of pH

pH is one of the most important parameters which affects both the surface charge of reactive fibers as adsorbent and the degree of ionization of dye in solution media. The effect of pH was determined in the range of 3-11. As seen in "**Figure 3.**"at the fixed condition of other parameters (V_{sol}=20 mL ,$C_\circ$=50 mg/L, T=303K, shaking rate= 150rpm, t=60 min, adsorbent amount= 0.1g, G%= 53%), The best pH for removing of dye was observed in 10.00. In acidic media, due to interaction of –OH groups in dye structure and H^+, and decreasing of the dye concentration, adsorption of dye into the PET chains decreases.

Effect of contact time

The effect of contact time for removal of 50 mg/L of dye concentration by reactive fibers were investigated from 10 to 70 min. The results show that dye uptake is rapid for the first 15 min and finally attains saturation within about 60 min. The equilibrium was attained at 60 min. Results have been shown in "**Figure 4.**"

Effect of adsorbent amount and grafting yield

By increasing of the modified fibers and grafting yield, the adsorption increases. This is related to excess surface area in adsorbent and more available active sites. "**Figure 5,6.**"

Effect of initial adsorbate concentration

The effect of dye concentration on the adsorption was investigated at different concentrations from 50 to 250 mg/L at the fixed condition of other variables (adsorbent = 0.1g, pH = 10.00, V_{sol}=20 mL, T=303K, G%= 53%, shaking rate= 150rpm, t=60 min). As shown in "**Figure 7.**"maximum removal has been recorded 29.60 mg/g for 200 mg/L initial dye concentration. This is related to saturating of available adsorbent surface by adsorbate.

Adsorption kinetics

By the help of three kinetic models, the kinetic of adsorption have been studied [25,7,26].

Lagergren's pseudo-first order: $\text{Ln}\,(q_e - q_t) = \text{Ln}\,q_e - K_a$

Ho's pseudo-second order: $t / q_t = 1 / K_2\,q_e^2 + t / q_e$

Intra-particle diffusion: $q = K_d \cdot t^{1/2} + I$

Results showed that the best kinetic model was intra-particle diffusion. According to this model the correlation coefficient has been determined (R^2=0.998). This value has good agreement to explain the kinetic data. "**Figure 8-10.**"

Adsorption isotherms

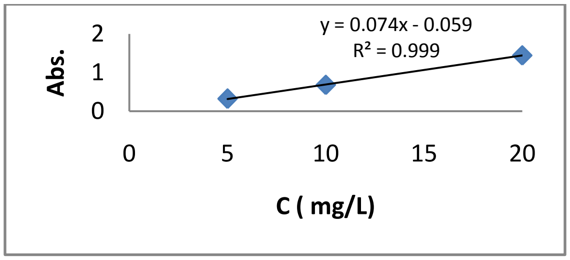
The analysis of the adsorption equilibrium accomplished by the commonly used adsorption isotherms, like Langmuir, Freundlich and Temkin [27-29]. The best isotherm model which explain the relationship between equilibrium and heterogeneous surfaces is Freundlich isotherm. It explains the assumption of adsorbent sites are distributed exponentially with respect to the heat of adsorption. "**Figure 11-15.**"

Thermodynamic parameters

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. Gibbs free energy change is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG° is a negative value. The thermodynamic parameters (ΔG°,ΔS°,ΔH°) for the adsorption processes are calculated using the following equations:

$$\Delta G^\circ = -RT\,\text{Ln}K_d \quad , \quad \text{Ln}K_d = \Delta S^\circ / R - \Delta H^\circ / RT \quad , \quad K_d = q_e / C_e$$

Where, R is the universal gas constant (8.314 J/ mol.K) and T is the absolute temperature in K. The results of $\text{Ln}K_d$ versus 1/T have been shown in "**Figure 16.**" and **Table 1**. The calculated values showed that the adsorption process was exothermic, spontaneous and by a decrease of entropy which related to the nature of adsorption and electrostatic interaction between dye and the surface of adsorbent.



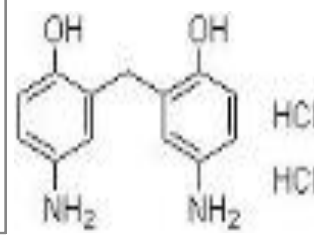
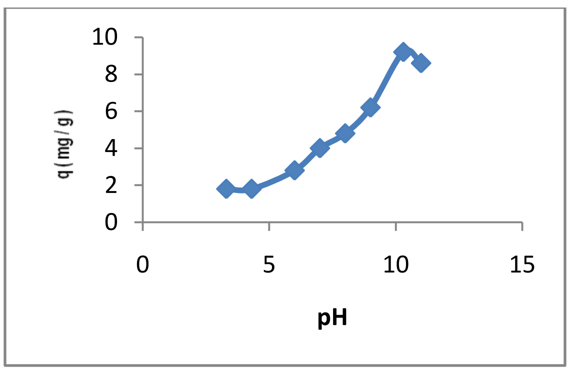


Fig1. Calibration Curve (Cationic Brill Red X -5GN 250%)

Fig 2.The Structure of Cationic Brill Red X -5GN 250%



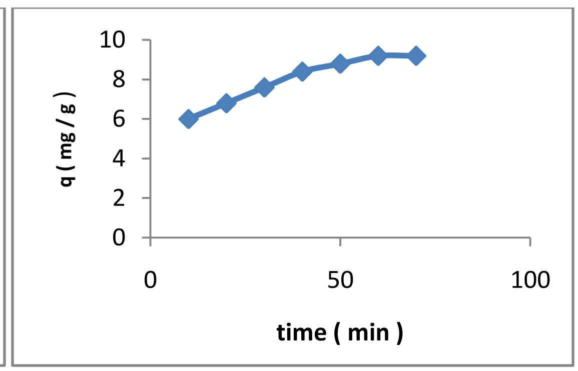
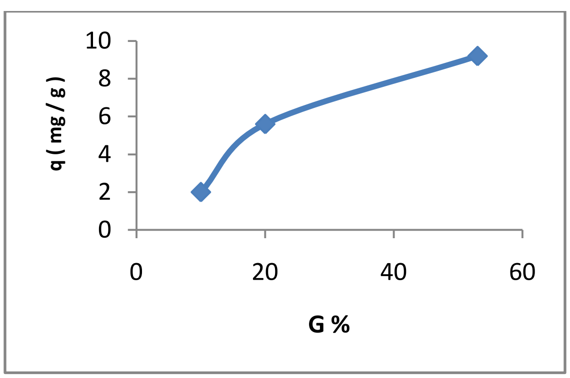


Fig3. Effect of the pH on the adsorption of dye

Fig4. Effect of time on the adsorption



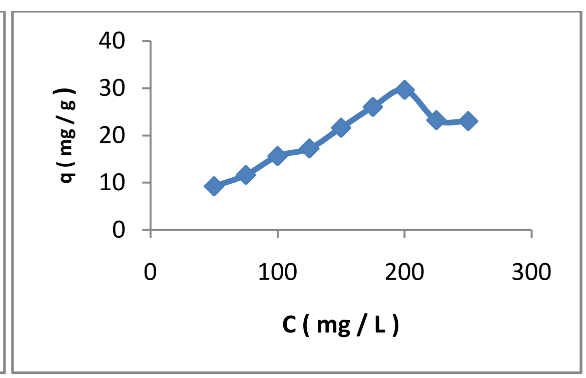


Fig5. Effect of grafting yield on the adsorption

Fig7. Effect of dye concentration on the adsorption

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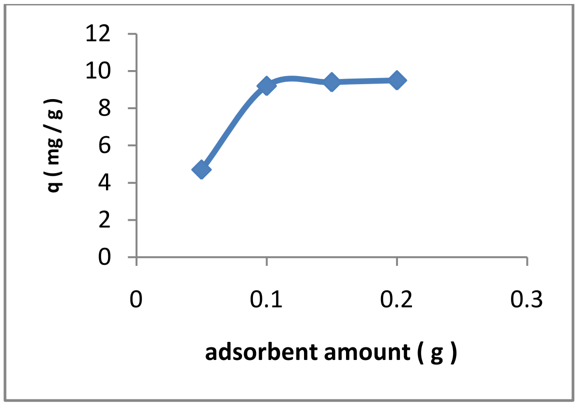


Fig6. Effect of adsorbent amount on the adsorption

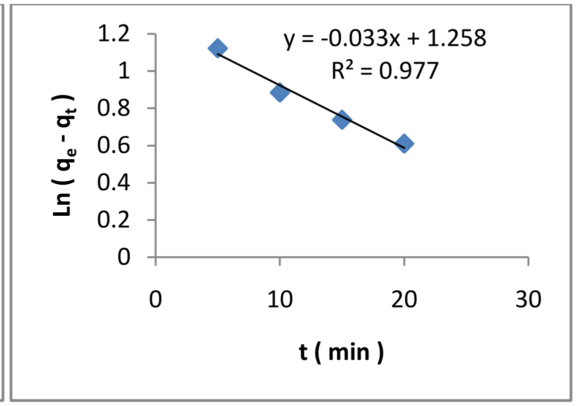


Fig8. Pseudo - first order kinetics

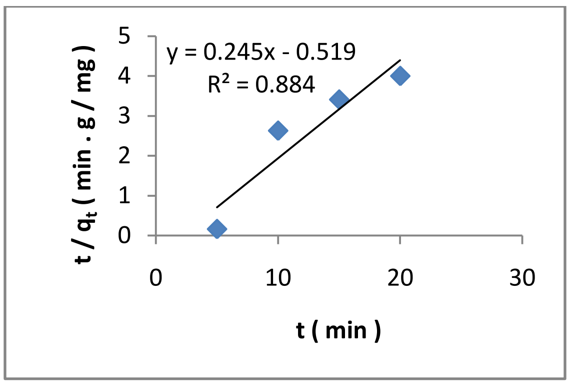


Fig9. Pseudo - second order kinetics

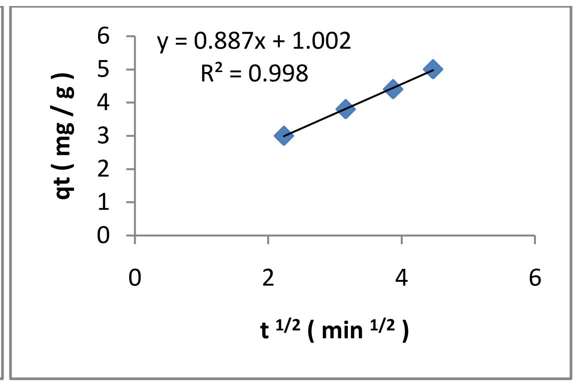


Fig10. Intra - particle diffusion kinetics

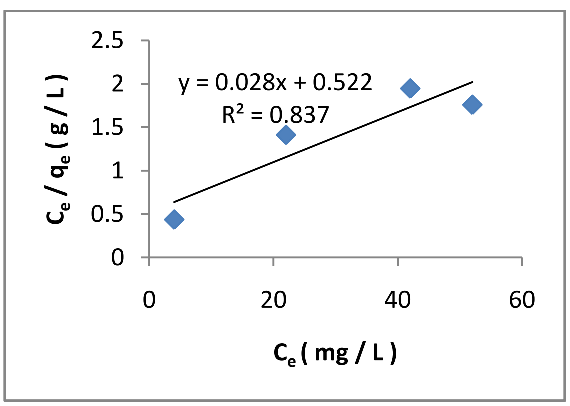


Fig11. Langmuir isotherm (T= 303 K)

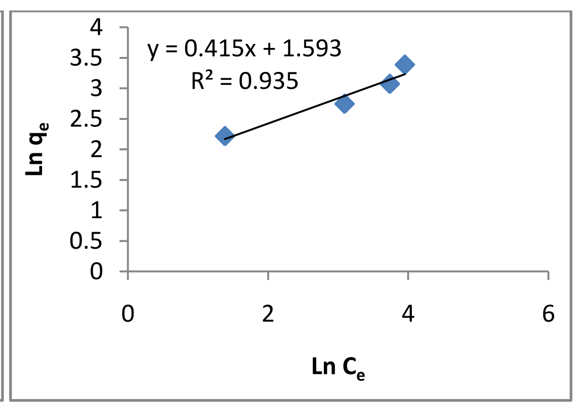
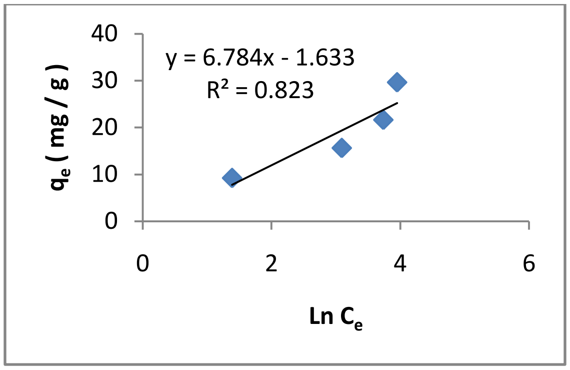


Fig12. Freundlich isotherm (T = 303 K)



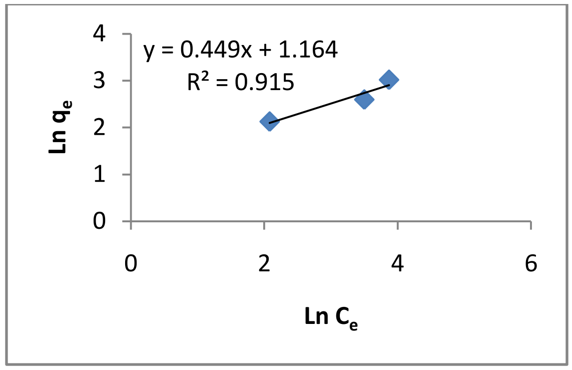
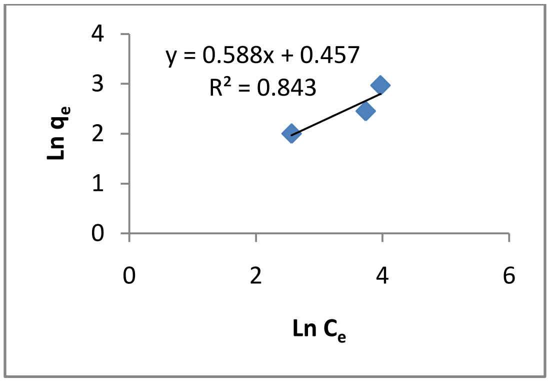


Fig13. Temkin – Pyozhev isotherm (T = 303 K)

Fig14. Freundlich isotherm (T = 318K)



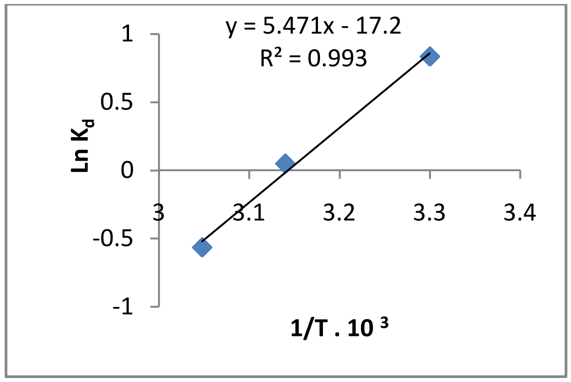


Fig15. Freundlich isotherm (T = 328K)

Fig16. Van't Hoff plot for thermodynamic parameters

Table 1 . Thermodynamic Parameters at Different Temperatures

T (K)	ΔH° (J / mol)	ΔS° (J/mol .K)	ΔG° (kJ/mol)
303	-45.480	-143.000	-2.098
318			-0.129
328			1.527

CONCLUSION

In this study, the modified fibers introduced as a new adsorbent for removal of cationic dye from aqueous solutions. The results of adsorption showed that the process has been affected by the pH, contact time, adsorbent dose, grafting yield and dye concentration. The isotherm and kinetic data showed that Freundlich and Intra-particle diffusion models explained the adsorption equilibrium, as well. Thermodynamic parameters emphasized the adsorption of dye onto reactive fibers was exothermic, spontaneous and physisorption.

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