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Examination of isotherms and kinetics of surfactant adsorption with modified poly (ethylene terephthalate) fibers

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ABSTRACT: In this research, the graft copolymerization of 2-hydroxy propyl methacrylate-acrylic acid mixture onto poly (ethylene terephthalate) fibers, in the presence of benzoyl peroxide as an initiator was accomplished. The Modified fibers were used as a new adsorbent for removal of cetyl pyridinum bromide from aqueous solution. The adsorption data were best fitted by Freundlich isotherm and pseudo first order kinetic models, as well. Thermodynamic parameters like enthalpy, entropy and Gibbs free energy have been determined. The results were emphasized that, the adsorption process was unspontaneous and feasible.

Keywords: *Acrylic acid, Adsorption, 2-Hydroxy propyl methacrylate, Isotherm, Kinetic.*

INTRODUCTION

The most common method for the determination of the adsorption is the depletion method, where the change in surfactant concentration (depletion) after contact with adsorbents is measured and assumed to be adsorbed. The results from the adsorption experiment are generally expressed in the form of adsorption isotherms, where the amount adsorbed is plotted as a function of equilibrium concentrations. Adsorption isotherms are measured by keeping solution environment conditions, such as temperature, pH and ionic strength constant. Kinetics and equilibrium adsorption of surfactants at the solid-liquid interface depend on the nature of surfactants and the nature of the solid surface [1]. The adsorption of anionic-nonionic surfactant mixtures on natural soils was studied by zhou and co-workers [2, 3]. The study showed that the adsorption isotherm of TX100 from single surfactant solution was nonlinear and typical S-shape curves, reaching a plateau in adsorption amount at surfactant equilibrium concentration around the CMC. The addition of 10 mol% SDS to TX100 resulted in a 25% decrease in the maximum adsorption amount for TX100. Thus, the higher the mole fraction of SDS in mixed surfactant solutions,

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(*) Corresponding Author - e-mail: fazizinejad@iauvaramin.ac.ir the greater the decrease in the maximum adsorption amount for TX100. These results showed that, when SDS was mixed together with TX100, the sorption of nonionic surfactant onto soil was severely restricted and a higher mole fraction of SDS in surfactant solution meant that a lower plateau adsorption can be reached with a smaller TX100 concentration in surfactant solution. In this research, the isotherms and kinetics of the adsorption of cationic surfactant by the modified fibers were investigated.

MATERIALS AND METHODS

PET fibers (stretch ratio 2, 30 filaments, 110 dTex) were provided from Amir Kabir University and Technology (Tehran). 2-hydroxy propyl methacrylate and acrylic acid and were bought from merck co. of Germany and after purification were used in all experiments. Benzoyl peroxide after recrystallization was used in grafting procedure [4]. Cetyl pyridinium bromide and all reagents and solvents were analytical grade and supplied by merck and doubly distilled water used in experiments.

Grafting Procedure

Grafting of monomers inside PET fibers was performed in a water bath and inside 100 ml Pyrex tubes. For this purpose, 0.4 g of fibers, 0.006 M benzoyl peroxide (Bz_2O_2) dissolved in 5 ml of acetone, 1 M of a mixture of monomers (2-hydroxypropyl methacrylate 80%, acrylic acid 20%) and 45 ml doubly distilled water was added.The total volume was 50 ml and the temperature recorded at 85°C. To obtain a product with a high degree of grafting, the reaction was performed at 60 min. After the required time, the fibers are carefully removed from the tube, firstly washed with continuous rinsing with distilled water to remove acrylic acid homopolymers for 24 hours and then to remove 2-hydroxypropyl methacrylate homopolymers by mixture of toluene- acetone and dimethyl formamide for 8 and 6 hours in the soxhlet, respectively [5,6]. After drying the fibers, the grafting yield was computed gravimetrically:

$$G(\%) = (W_g - W_0) / W_0 \times 100 \qquad (1)$$

In this equation, W_0 and W_g are the primary and grafted fibers, respectively.

Adsorption Isotherms and Kinetics

Surface adsorption experiments were done using 0.1g of the grafted fibers with 20 mL surfactant solution (CPB) (100 mg/L) in the 250ml Erlenmeyer flask at the constant stirrer speed (150 rpm). After the specified time, the solution was filtered by filter paper (Wattman No.40), and then centrifuged for 10 min at 3000 rpm. The analyzing of surfactant in solution was fulfilled using a UV spectrophotometer (Shimadzu, 1208) at a maximum adsorbance (260 nm). The surfactant quantity adsorbed (mg/g) onto grafted fibers was calculated according to this equation:

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

Where, q is the amount of adsorbed CPB on grafted fiber (mg/g), C_0 and C are the initial and equilibrium CPB concentrations (mg/L), V is the volume of the solution (L) and m is the mass of grafted fiber sample used (g). Adsorption isotherms were performed in the presence of 0.1g fibers at 298, 308, 318 and 328K in a total volume of 20 mL, constant stirrer speed (150 rpm), constant pH 6.0 and optimal time of 90 minutes. The results of the UV spectroscopy were evaluated according to the isothermal models of Langmuir, Freundlich and Temkin [7-9]. Kinetics studies were investigated at the fixed condition of the other variables (T = 298K, [CPB] = 100(mg/L), fibers = 0.1g, pH= 6.0, solution volume = 20 mL, shaking rate = 0.0) at different times 10, 20, 30, 40, 60, 80 min. Kinetics data have been investigated by the using of Lagergren pseudo-first-order, Ho's pseudo-second-order and Intra-particle-diffusion [10-12].

RESULTS AND DISCUSSION

The results of the isotherm experiments were evaluated using three well-known isothermal models, Langmuir, Freundlich & Temkin:

$$C_e/q_e = C_e/q_m + 1/K_a.q_m \qquad (3)$$

$$\ln q_e = \ln K_f + \frac{1}{n}.\ln C \tag{4}$$

$$q_e = a_t + B_0 \ln C_e \tag{5}$$

In the above equations, C_e(mg/L) is the equilibrium concentration, q_e(mg/g) is the amount adsorbed in equilibrium, qm and Ka are the constants of Langmuir equations and determine the efficiency of the process. Kf indicates the adsorption capacity and n determines the absorption intensity, and a_t(mg/g) and B_0(mg/L) can be determined based on experimental results and after drawing the q_e-lnC_e diagram. The most compatible isothermal model was found based on the correlation coefficient obtained in the Freundlich model. Therefore, the obtained results confirm the uptake of homogenic and single-layer adsorption of CPB onto fibers (Fig. 1-12).

The kinetic results of adsorption were analyzed and evaluated based on three kinetic models:

Lagergren pseudo-first-order

$$\ln(q_e - q_t) = \ln q_e - k_a t \tag{6}$$

Ho's pseudo-second-order

$$\frac{t}{q_t} = \frac{1}{K_2.q_e^2} + \frac{t}{q_e} \tag{7}$$

Intra-particle-diffusion

$$q = K_d.t^{1/2} + I \tag{8}$$

Figs. 13-15 show that the pseudo-first-order model has the best compatibility in the kinetic justification of CPB adsorption. Here C_0 was 100 mg/L.

The effect of temperature on determining thermodynamic parameters (ΔG^0, ΔH^0, ΔS^0) in the temperature range of 298 to 328 K, under the following constant conditions was investigated.

(Fibers = 0.1g, V = 20 ml, 100 mg/L = [CPB], Shaker rate = 150 rpm, pH = 6, t =90 min).

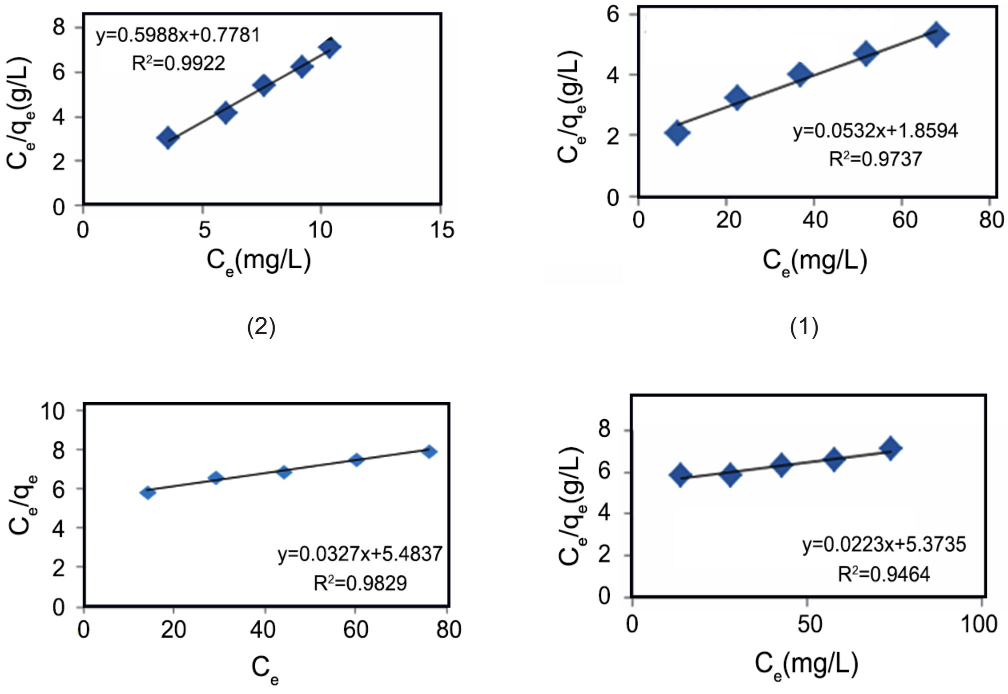
The equations used to determine the above parameters are:

$$\Delta G° = -RTLn\ K_d \tag{9}$$

$$Ln\ K_d = \Delta S°/R - \Delta H°/RT \tag{10}$$

$$K_d = q_e / C_e \tag{11}$$

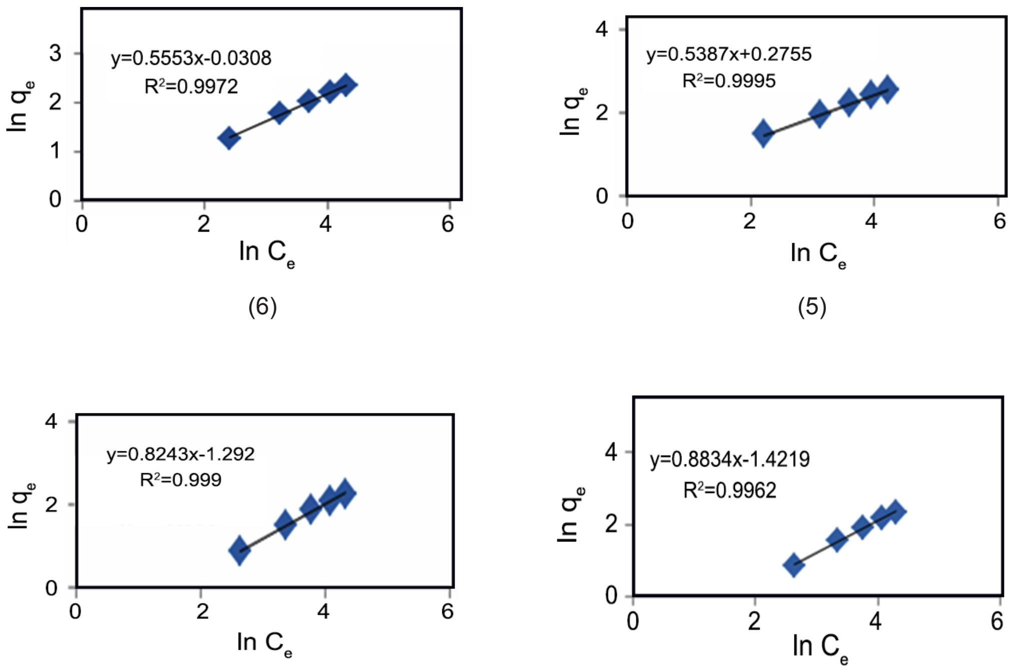
The results are shown in Table 1 and Fig. 16. The



(2) (1)

(4) (3)

Figs. 1-4. Langmuir isotherms: 1)298K 2) 308K 3)318K 4) 328K.

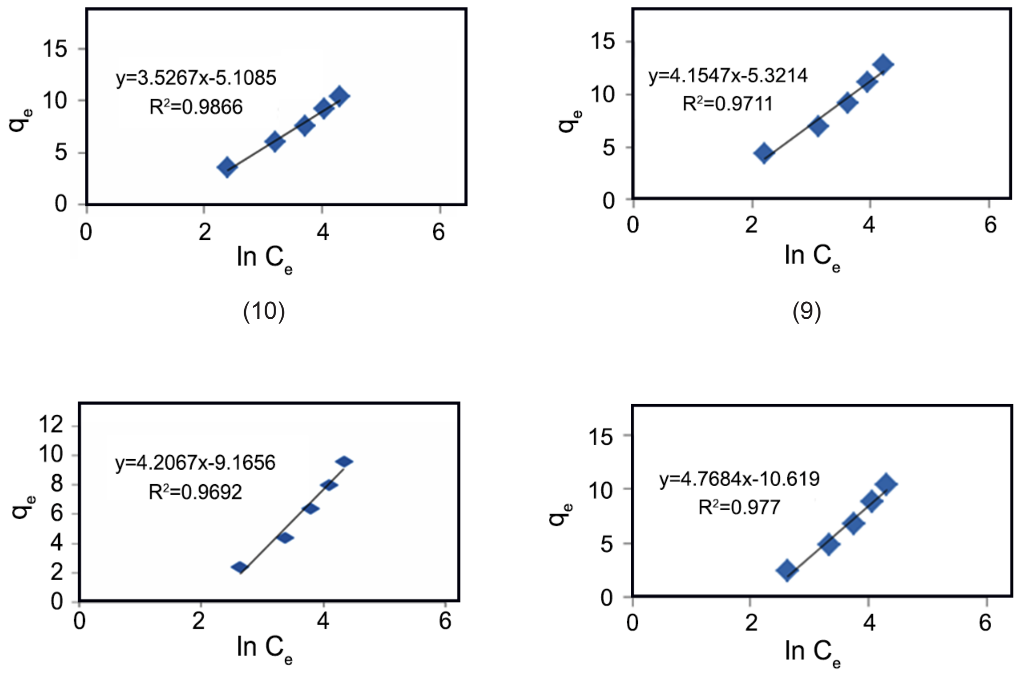


(6) (5)

(8) (7)

Figs. 5-8. Freundlich isotherms: 5)298K 6) 308K 7)318K 8) 328K.

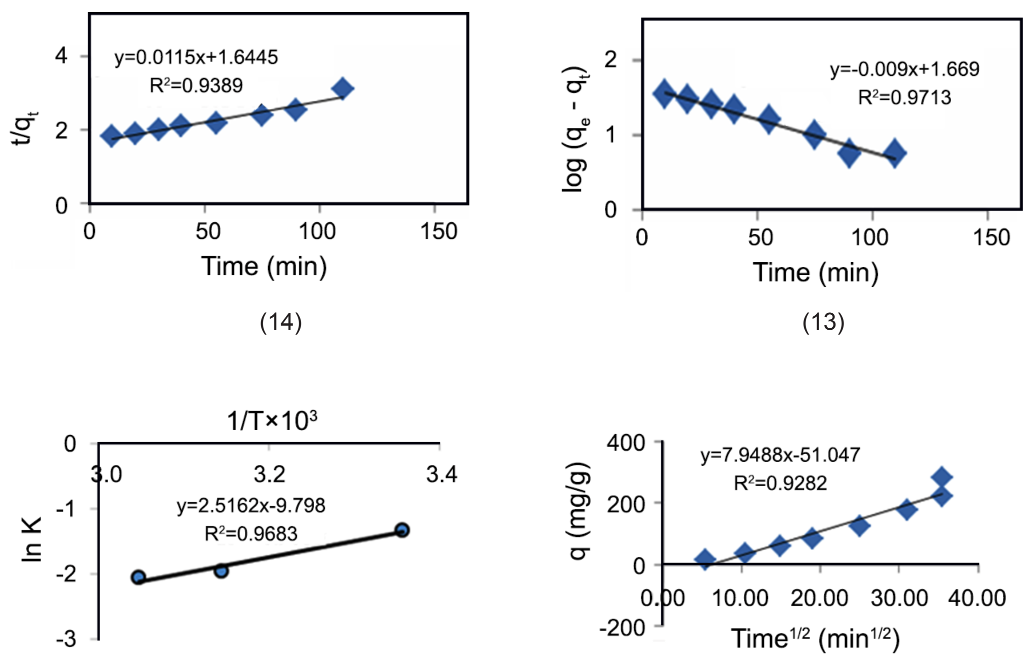
positivity of ΔG° indicates that at high concentrations the reaction is non-spontaneous and on the other hand the reaction is exothermic and the negativity of entropy confirms that the interaction between the adsorbent and the adsorbate is not appropriate.



(10) (9)

(12) (11)

Figs. 9-12. Temkin isotherms: 9)298K 10) 308K 11)318K 12) 328K.



(14) (13)

(16) (15)

Figs. 13-16. Kinetic models: 13) Pseudo - first order, 14) Pseudo - second order, 15) Intra - particle diffusion, 16) Vant Hoff plot for thermodynamic.

Table 1. Thermodynamic parameters at different temperature.

T(K)	q_e (mg/g)	1/T*10^3	ΔH° (kJ/mol)	ΔS° (kJ/mol.k)	ΔG° (kJ/mol)
298	12.8	3.356	7.624	29.688	8839.40
318	10.4	3.145			9433.16
328	9.6	3.049			9730.04

CONCLUSIONS

In this study, the negative values of ΔH° showed that the adsorption of CPB onto PET fiber was exothermic. The negativity of entropy confirms that the interaction between the adsorbent and the adsorbate is not appropriat. The quantities of ΔG°purposed the adsorption of CPB onto modified PET fibers was physisorption and nonspontaneous. The best isotherm and kinetic models were Freundlich and pseudo-first-order models, respectively.

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