# Removal of Eriochrome black T dye from aqueous solutions by adsorption onto a low-cost adsorbent: pomegranate seeds wastes

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**Abstract:**

In this study, the adsorption of EBT dye from aqueous solutions onto the pomegranate seeds (PS) powder surface was investigated. The experimental design methodology has been applied to adjust the parameters, such as PS dosage, contact time, dye concentration, the temperature, and pH. Adsorption equilibrium data were analyzed by Langmuir, Freundlich, Temkin, Elovich and Harkin–Jura equations. The experimental data showed that the Freundlich and Harkin–Jura isotherms were appropriate for the EBT dye adsorption. A comparison of kinetic models was evaluated for the pseudo-first-order, pseudo-second-order, Elovich and Intrapartical diffusion kinetic models. Pseudo-second-order was found to agree will the experimental data, which indicates that physcisorption is dominant. The percentage removal was found ≈ 53% at 298 K, pH =7 of EBT dye. The thermodynamics parameters such as ΔG, ΔH, ΔS and Ea have been calculated. The results have been showed the adsorption process onto the PS surface is endothermic and nonspontaneous. The obtained results imply that PS surface powder could be employed and have moderate affinity to remove EBT from aqueous solutions.

**Keywords:** Eriochrome black T**,** pomegranate seeds surface, adsorption isotherms, kinetic study.

## 1.Introduction:

Environmental contamination of synthetic dyes in surface water and groundwater is an important environmental concern. Dye-containing waste effluents are generated by several sources such as textile, paper, printing, pulp mills, food, cosmetics and leather industries [1 -2]. Among the sources, the textile industry produces annually about $1.5 \times 10^8$ $m^3$ of discharge volume of synthetic dye and 10,000 different types of dyes [3-4], where 10‑15% of the dye is lost to the waste effluents during the dyeing process. Dyes are colored substances of synthetic origin, which are resistant to fading upon exposure to light, chemicals and water [5]. In addition, dyes have high organic content, non-biodegradable and complex aromatic structure [6]. The presence of dyes in water bodies causes environmental damage to aquatic organisms by blocking sunlight, retarding photosynthetic activity and disturbing the re-oxygenation capacity, which creates anaerobic condition that limits aquatic plan growth [7]. In addition, contaminated surface water and groundwater would make the water bodies unsuitable for other use [8] and can cause carcinogenic [9-10] and mutagenic effects [11-12].

Numerous researchers studied the development, utilization and application of low-cost adsorbents coming from both industrial and agricultural sources to remove the pollutants from the waste water [13-23]. In addition, inspections of economic and environmentally friendly materials are an important priority, pomegranate seeds(PS) were chosen in this study due to the large amount of pomegranate seeds as the by-product of juice and concentrate production plants and because of valuable pharmaceutical and nutritional compounds such as unsaturated fatty acids and phenolic compounds in the seed and their antioxidant properties, the seeds can have more beneficial applications in food industries or in commercial cosmetic products [23]. In literature, there are several studies were conducted for the removal of EBT from waste water [24-31]. In continuous to the attempt of other researches by using PS, the work is in progress to applied the PS and evaluate it capability to removal EBT from aqueous solutions.

## 2. Experimental

### 2.1 Reagents and Methods:

Pomegranate seeds (PS) were collected from shops selling juices and syrups in Al-Najaf-Al-Ashraf governorate, Iraq. the sample was thoroughly washed with tap-water and steep under stirring with boiling distilled water (100°C) over night to extract coloured of compounds from the PS, filtered and washed with distilled water until colourless, then the seeds were allowed to dry in an oven at $70^{o}$c, the dried PS samples were grinded by mechanical grinder into powdered and dried overnight in an oven at $75^{o}$c. The analytical grade EBT dye were used of chemicals and purchased from Sigma-Aldrich company (USA), while hydrochloric acid and ammonia from Merck company (Germany) were used to adjust the pH of the solutions. Stock solution of the dye was prepared by dissolving 0.1g in 1000 ml volumetric flask to make 100mg/L. Working calibration standards were prepared by serial dilution of the stock solution ranging from 5 to 50mg/l.

### 2.2 Instruments

For measuring the absorbance of dye concentration, a UV- Visible spectrophotometer (shimadzu UV 4000, Japan) was employed. HANA model (China) pH meter for applied pH measurements. A thermostat shaker water bath model GCA, Precision scientific Chicago, U.S.A, was used to stirrer the solutions at 160 rpm. The centrifuge of model Magafuge1.0, Herouse sepatech at 3000 rpm, was used to centrifugate the dyes solutions.

### 2.3 Equilibrium Adsorption Experiment:

In order to calculate the kinetic and thermodynamic parameters, batch method was used in adsorption studies by adding the best amount of PS to a series of 50 ml sealed conical flasks filled with 20 ml of initial concentration (5-50mg/l) of EBT at 298K, pH (3-11) was adjusted by using HCl and NaOH solutions. The flasks were put in a thermostat shaker water bath in speed 160 rpm at the best equilibrium time, then was removed and the solution was filtered at an appropriate time interval, centrifuged at 3000 rpm for 5 min. after that the PS and dye were separated by filtration. The filtrates were used for analysis the residual dye concentration using UV-visible spectrophotometer at the $\lambda_{max}$ corresponding to maximum absorbance 527nm. The equilibrium adsorption capacity $q_e$ ($mgg^{-1}$) and the percentage dye removal of onto PS surface were determined using the following equations: [32,33]

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (1)$$

$$\%\ \text{Dye Removal} = \frac{C_o - C_e}{C_o} \times 100 \qquad (2)$$

Where Co and Ce in ($mgL^{-1}$) are the concentrations of dye at initial and equilibrium respectively, V in (L) is the volume of the solution, and m in (g) is the weight of PS.

### 2.4 Optimization of Contact Time of Dye

To identify the required time for equilibrium sorption, the batch adsorption experiments were performed at 298K, 5ml of initial concentration 25 mg/L of EBT was put in to 25 ml stoppered conical flask and shaken with 0.2 g of PS in a thermostat shaker water bath was setting at 298K. Initial pH was adjusted at the optimum pH obtained from the first set of experiments, pH value of 7, the percentage of dye uptake was measured at time intervals from 10 minutes to 80 minutes. After each 10 min. flasks were removed from the shaker water bath, then the solution was filtered, centrifuged at 3000 rpm for 10 min. and repeats filtration again through filter paper. The EBT concentrations were analyzed using spectrophotometer Biochrom Ltd, combridge CBu at the $\lambda_{max}$ of EBT.

### 2.5 Optimization of Adsorbent Dosage

To determine the optimum PS dose for removal of the EBT from aqueous solutions, experiments were carried out using different weights of PS ranging from 0.05 to 0.40 g were put in to 25ml conical flask and adding 20ml of initial concentration 25 mg/L of EBT at pH=7 and temperature 298K, then agitated in water bath at equilibrium time. After that PS and EBT solution were separated by filtration through filter paper, centrifuged at 3000 rpm for 10 min., the concentration of EBT were determined spectrophotometry at the $\lambda_{max}$ of EBT.

## 3.Result and Discussion

### 3.1 Effect of contact time

As shown in figures 1. the time necessary to reach equilibrium for the removal of the EBT by PS from aqueous solution was established about 50 minutes with percentage removal reaching 55%, respectively.

### 3.2 Effect of Adsorbent Dosage

The results of the percentage removal of EBT with respect to PS dosage are shown in figure 2. It was observed that highest amount of EBT removal was attained to 0.1g.

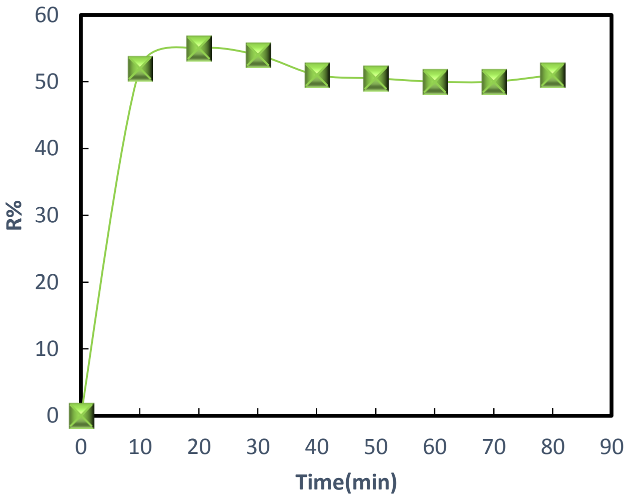

**Fig.1.**Variation of contact time on percent and removal of EBT from aqueous solution onto 0.2 g PS at temperature =298K, $C_o$ = 25mg/L and pH=7

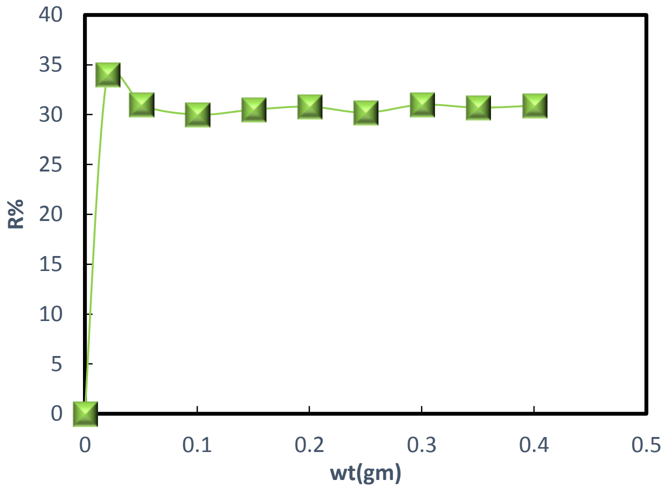

**Fig.2.** Variation of PS dosage on EBT adsorption from aqueous solution at temperature = 298K, $C_o$ = 25 mg/L and pH=7

### 3.3 Effect Initial EBT Concentration

The effect of initial EBT dye concentrations on the adsorption amount by the adsorbent (PS) was examined in the concentration range 5-50mg/L at 298K, 160 rpm agitation speed, pH 3-11 and at optimum adsorbent dosage (Figures 3). The experimental results showed that the adsorption capacity increased with increasing concentration. It was clear that the amount of adsorbed EBT dye was dependent on the concentration. Although the increase of dye concentration increased the amount of dye adsorbed, the percent color removal decreased. Similar trend was reported [34] in literature.

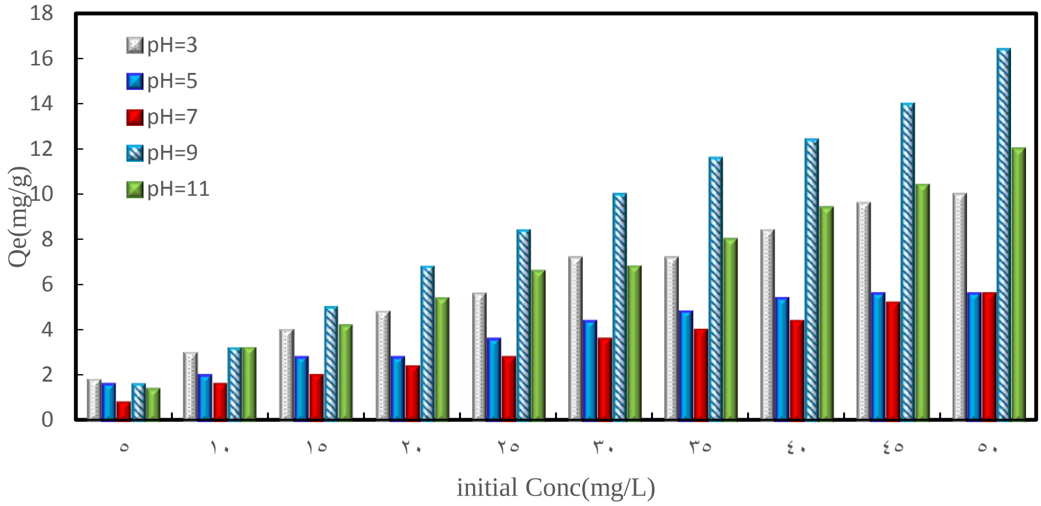

**Fig.3.** Effect of initial concertation of EBT on adsorption capacity onto the PS surface in the pH range 3-11 and at temperature 298K

### 3.4 Effect of Initial pH

The pH value of an aqueous solution is an important parameter in the adsorption study of anionic dye because of its effect on both ionization of dye molecules and surface binding sites (surface charge). The removal of EBT by PS at different pH values (3-11)was studied at initial concentrations of 50 mg/L of EBT at temperature 298K. (Figures 4) showed that the maximum dye adsorption take place of EBT at pH = 9 , it may be due to the $pH_{pzc}$(at which positive charges on the surface are equal to the negative charges) of the PS surface, it seems about 10 , below this pH, the PS surface acquires a positive charge due to protonation of functional groups and above this pH, negative charge exists on the surface of PS. The adsorption of anionic dyes are favored at $pH < pH_{pzc}$ where the surface becomes positively charged [35]. (Figure 4) shows that the pH significantly affects the extent of adsorption of EBT onto PS surface and the maximum amount adsorbed increased with an increase in pH was observed.

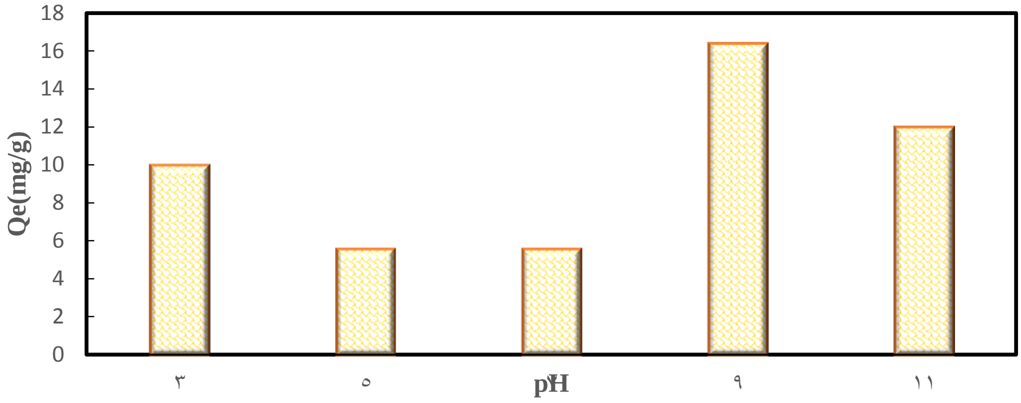

**Fig.4.** variation of pH value on EBT adsorption onto 0.05 g of PS surface, initial concentration 50 ppm, contact time =50 min, and

### 3.5 Adsorption Equilibrium studies

In order to understand the distribution of adsorbate between the liquid - solid phase at equilibrium during the adsorption process i.e., how solutes interact with an adsorbent, adsorption isotherms should be studied. In this work, Langmuir, Freundlich, Temkin, Elovich and Harkins-Jura, isotherms models [13-36] are used to describe the equilibrium between the EBT adsorbed onto PS surface and to verify which model presented the best fitting to the experimental data. The isotherm constants and correlation coefficients ($R^2$) values of these models are presented in tables 1. Figures(5,6,7,8,9) shows the linear form of these isotherms , from this table and figures, correlation coefficients of Freundlich isotherm model were the good fitting for EBT adsorption at temperature range 298-318K, that means the adsorption sites increase exponentially with adsorption and the heat of adsorption of all molecules in the layer would decrease linearly with coverage, The experimental adsorption isotherms were further analyzed using Langmuir, Temkin, Elovich and Harkins- Jura, the results indicated that these models were poor fitting with the experimental data except Harkins- Jura isotherm model at temperature 298K was the best fitting ($R^2$= 0.9846) to the experimental adsorption data.

### 3.6 Kinetics studies

The adsorption kinetic experimental data of EBT on PS surface were analyzed by Pseudo –first-order, Pseudo-second-order, Elovich and Intra-particle diffusion kinetic models. Table 2 summarizes the kinetic parameters for these models. The Pseudo-second-order kinetic model is the best fitting to the experimental data better than the other models, the high values of correlation coefficients ($R^2 \geq 0.9503$). The Pseudo-second-order kinetic model implies that two reactions, either in a series or in parallel, occur; the first one is fast and rapidly reaches the equilibrium, while the second one is a slower reaction that continues for a long period of time [37]. Figure 10 shows the plots of the adsorbed amount of the EBTversus time at temperature 328K for these models.

**Table 1**: Comparison of the isotherm equations constants and correlation coefficients for EBT adsorption onto pomegranate seeds at pH= 7, initial concentration 5-50ppm, contact time 50min., pomegranate seeds dosage 0.1 g and the temperature 298K.

| Linear equation of isotherm model | Parameters | Temperature | | | |
|---|---|---|---|---|---|
| | | 298K | 308K | 318K | 328K |
| Langmuir<br>$\frac{1}{K_L q_m} + \frac{C_e}{q_m}$ | K (L /mg) | 0.020 | 0.042 | 0.042 | 0.037 |
| | $q_m$ (mg /g) | 12.195 | 9.174 | 9.900 | 10.416 |
| | $R^2$ | 0.7309 | 0.7971 | 0.8486 | 0.6916 |
| Freundlich<br>$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e$ | N | 1.338 | 1.858 | 1.739 | 1.686 |
| | $K_f$ (L /mg) | 0.364 | 0.791 | 0.876 | 0.715 |
| | $R^2$ | 0.9841 | 0.9699 | 0.9469 | 0.9503 |
| Tempkin<br>$q_e = B\ln K_T + B\ln C_e$ | K (L /mg) | 0.083 | 0.282 | 0.215 | 0.211 |
| | B (J /mol) | 1.86 | 1.645 | 1.842 | 1.819 |
| | $R^2$ | 0.8857 | 0.8489 | 0.8719 | 0.8251 |
| Elovich<br>$\ln\frac{q_e}{c_e} = \ln K q_m - \frac{1}{q_m} q_e$ | $q_m$ (mg /g) | 9.090 | 4.048 | 5.263 | 6.329 |
| | K | 0.028 | 0.147 | 0.102 | 0.070 |
| | $R^2$ | 0.6498 | 0.7436 | 0.7188 | 0.5443 |
| Harkins-Jura<br>$\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A}\log C_e$ | A | 2.159 | 2.242 | 2.061 | 2.012 |
| | B | 1.556 | 1.641 | 1.436 | 1.452 |
| | $R^2$ | 0.9846 | 0.88 | 0.8559 | 0.8906 |

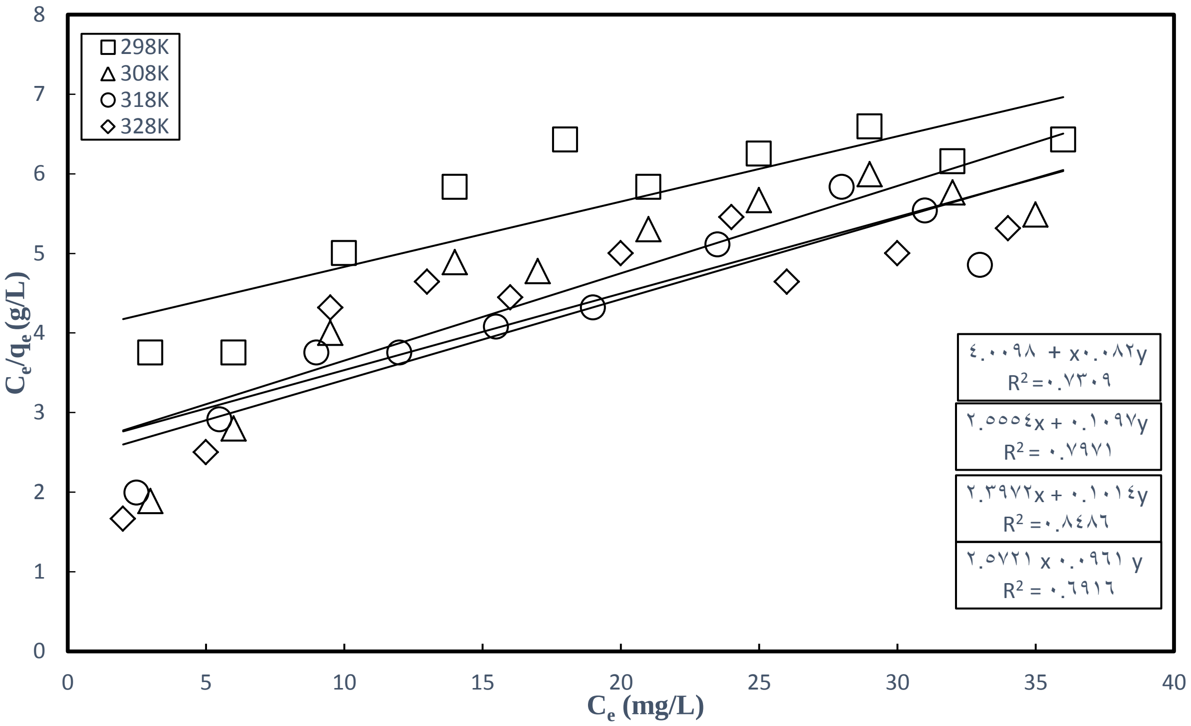

**Fig. 5.** Langmuir isotherm model plot for the adsorption of EBT onto the PS surface with optimum condition: concentration range 5- 50 mg/L, temperature (298-328K), PS wt.0.1 g/20 mL, agitation speed 160 rpm, contact time 50 min and pH=7.

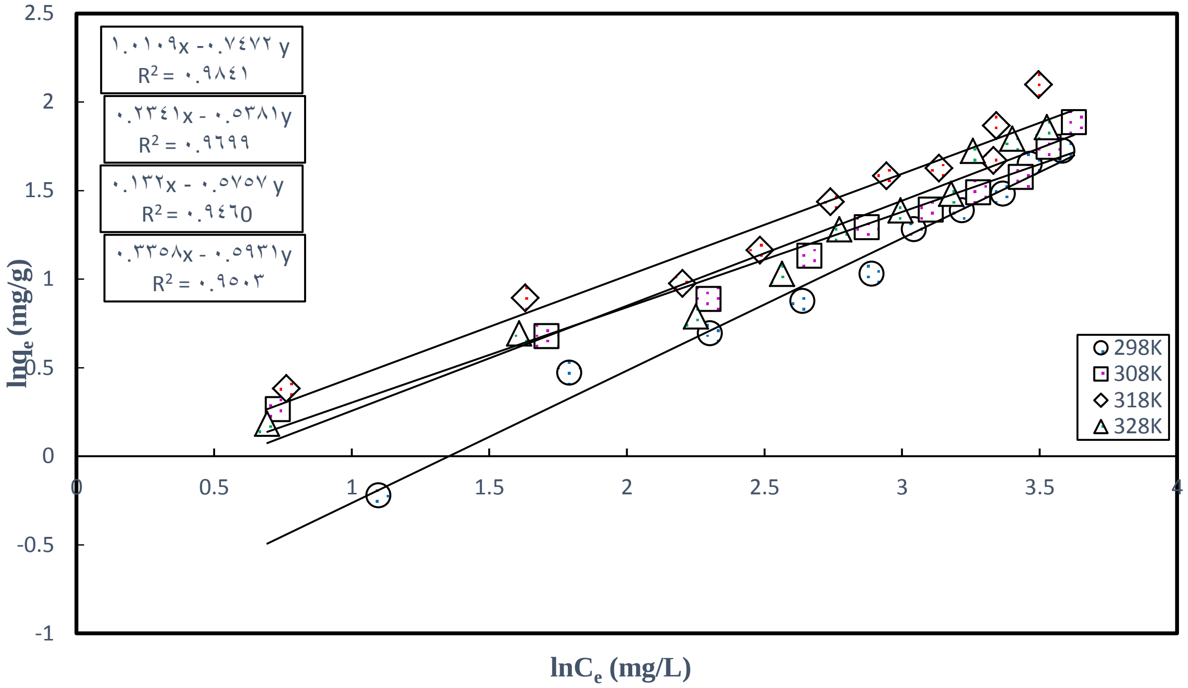

**Fig. 6.** Freundlich isotherm model plot for the adsorption of EBT onto the PS surface with optimum condition: concentration range 5- 50 mg/L, temperature(298-328K), PS wt.0.1 g/20 mL, agitation speed 160 rpm, contact time 50 min and pH=7.

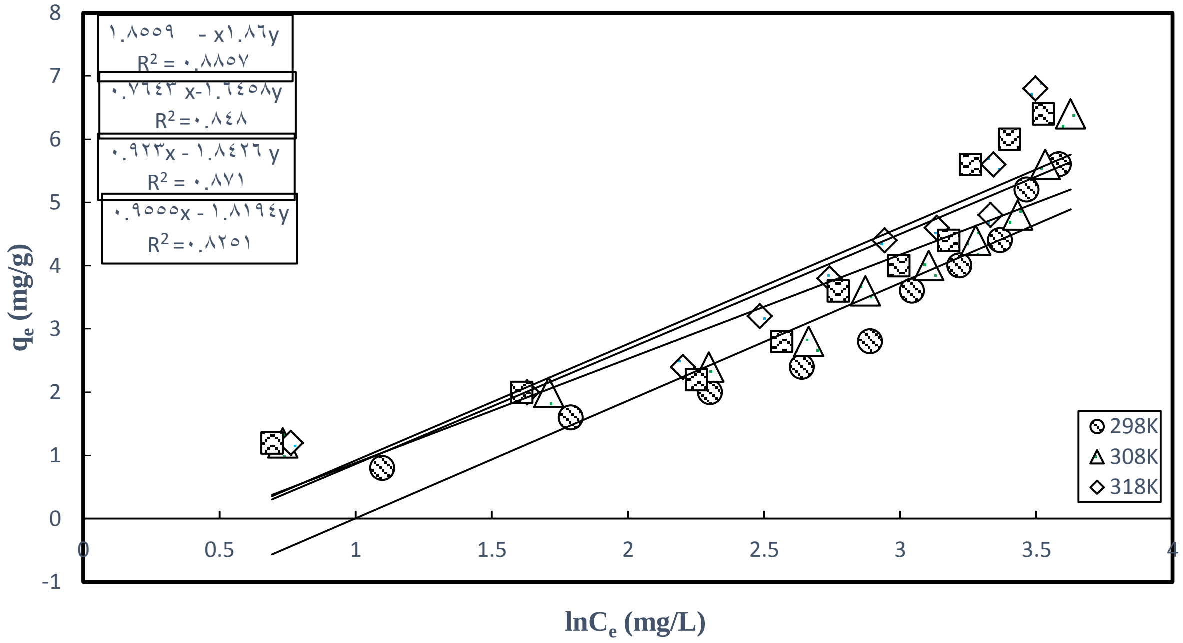

**Fig. 7.** Tempkin isotherm model plot for the adsorption of EBT onto the PS surface with optimum condition: concentration range 5- 50 mg/L, temperature (298-328K), PS wt.0.1 g/20 mL, agitation speed 160 rpm, contact time 50 min and pH=7.

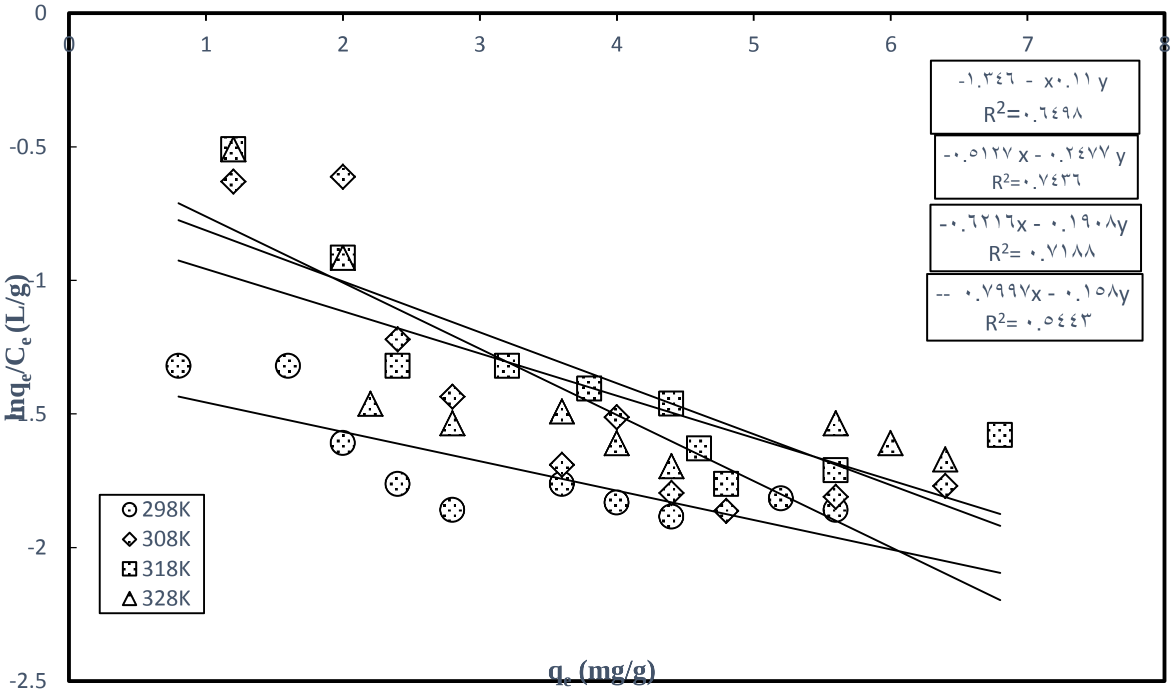

**Fig. 8.** Elovich isotherm model plot for the adsorption of EBT onto the PS surface with optimum condition: concentration range 5- 50 mg/L, temperature (298-328K), PS wt.0.1 g/20 mL, agitation speed 160 rpm, contact time 50 min and pH=7.

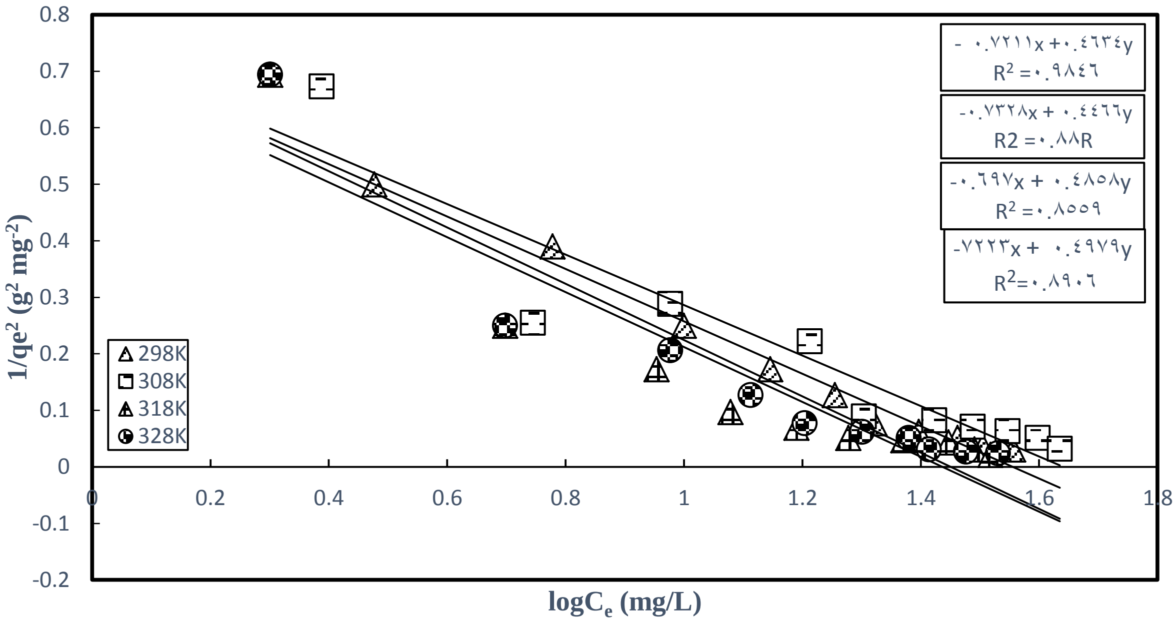

**Fig. 9.** Harkins-jura isotherm model plot for the adsorption of EBT onto the PS surface with optimum condition: concentration range 5- 50 mg/L, temperature (298-328K), PS wt.0.1 g/20 mL, agitation speed 160 rpm, contact time 50 min and pH=7.

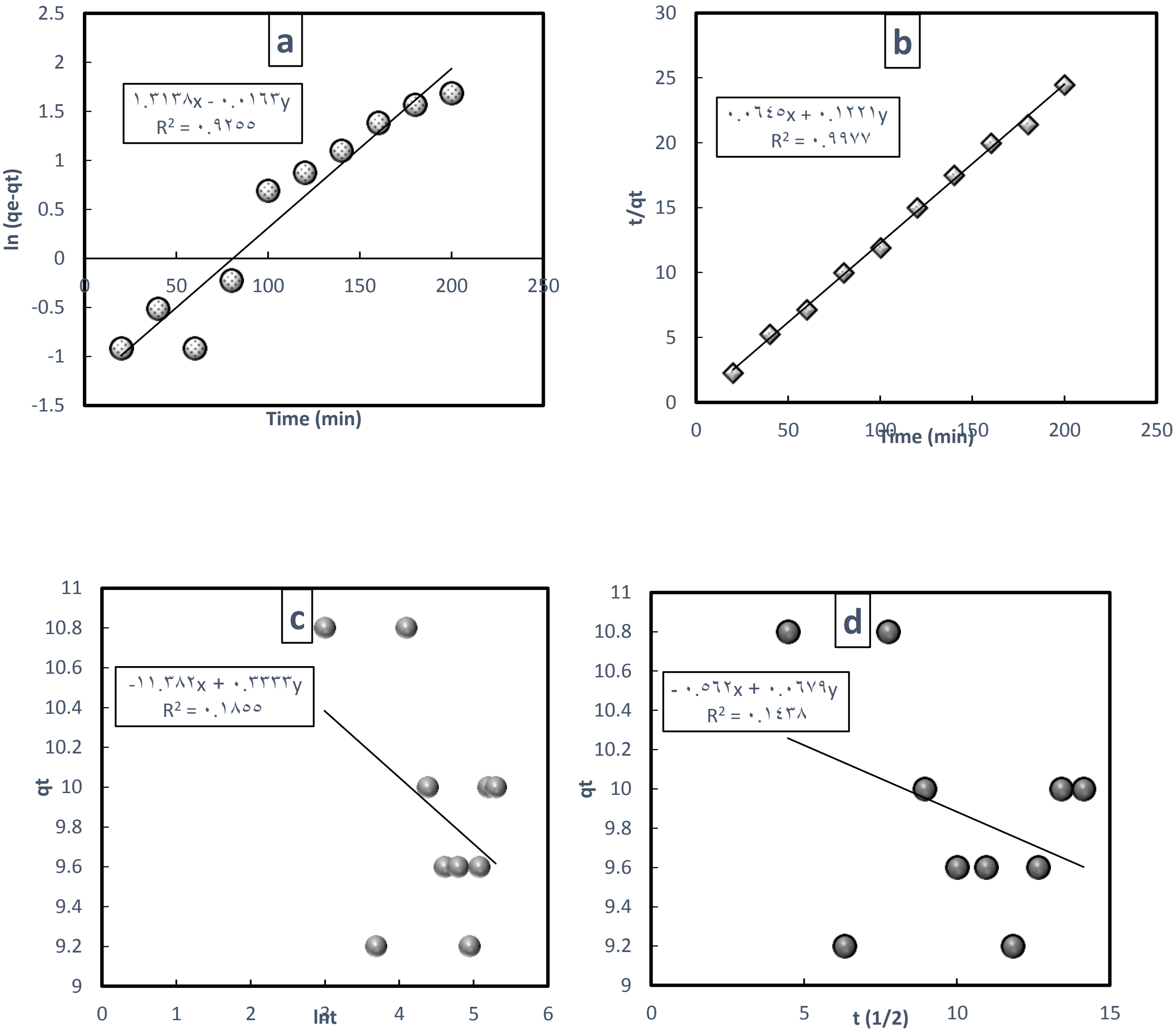

**Fig .10**. Pseudo-first -order (a), Pseudo-Second -order (b), Elovich(c)and Intrapattical diffusion kinetic models plot for the adsorption of EBT onto PS surface with optimum condition: concentration 50 mg/L, temperature 328K, PS wt.0.1 g/20 mL, agitation speed 160 rpm, contact time 50 min and pH=7.

### 3.7 Temperature dependence on dye adsorption

The adsorption of EBT dye onto PS surface from aqueous solution was studied at temperatures range 298-328K and 160 rpm agitation speed, pH 7, initial concentration 50ppm, optimum PS dosage and contact time. As shown in Figure 11 the percentage removal of EBT increase at higher temperatures which indicates that adsorption process is endothermic.

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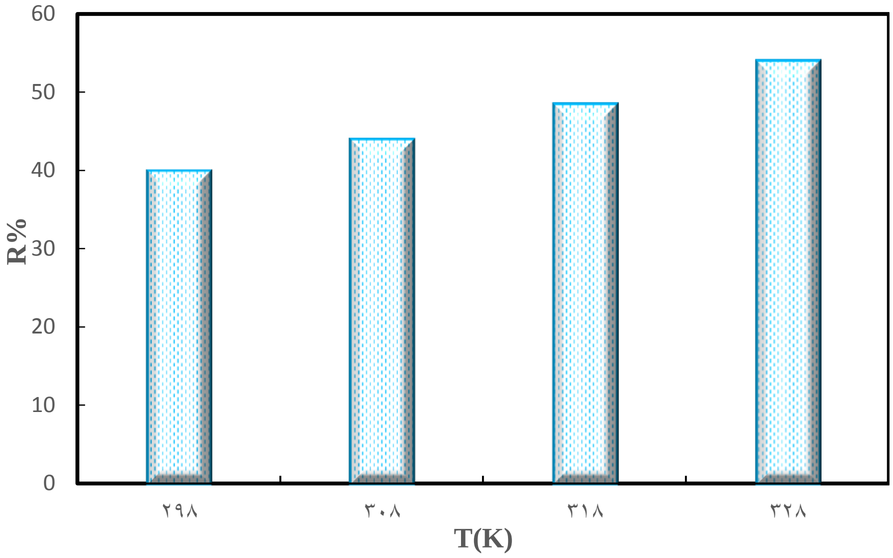

**Fig.11**. Effect of temperature on EBT removal onto PS; initial EBTconc 50ppm, adsorbent dosage 0.15 g, agitation speed160 rpm, solution pH= 7 and 50min. contact time.

### 3.8 Adsorption Thermodynamics

Adsorption Thermodynamics, the enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy change (ΔG) for adsorption of the EBT onto PS surface were determined according to the equilibrium data obtained at different temperatures, which can be calculated from the following equations [38,39]:

$$\mathrm{Keq} = \frac{\mathrm{qe}}{\mathrm{ce}} \qquad (3)$$

where $K_{eq}$ is the equilibrium constant, $q_e$ is the amount of dyes adsorbed at equilibrium and $C_e$ is the equilibrium concentrations of dyes in solution. The changes in ΔH and ΔS were calculated from the Van’t -Hoff equation :

$$\mathrm{lnKeq} = \frac{-\Delta \mathrm{H}}{\mathrm{RT}} + \frac{\Delta \mathrm{S}}{\mathrm{R}} \qquad (4)$$

A plot of $\ln K_{eq}$ vs. 1/T gives a straight line with slope -(ΔH/R) and extrapolated intercept (ΔS/R). The change in ΔG was calculated using equation:

$$\Delta \mathrm{G} = \Delta \mathrm{H} - \mathrm{T}\Delta \mathrm{S} \qquad (5)$$

The values of thermodynamic parameters at the experimental temperature range (298- 328K) are listed in Table 2. The positive values of ΔG and negative values of ΔS indicate that the adsorption process of EBT is non-spontaneous, and decreased in randominess at the solid – liquid interface during adsorption process, while the positive value of ΔH indicate that the adsorption process is endothermic in adsorption of of EBT. Also the activation energy of adsorption process was computed from the following equation [40]:

$$\mathrm{Ea} = \Delta \mathrm{H} + \mathrm{RT} \qquad (6)$$

In this study the values of activation energy (Table 2) of adsorption of EBT is less than 40 kJ/mol [41], this value confirm that the adsorption process is physisorption .

**Table 2.** Thermodynamic parameters of Eriochrome black T for dye adsorption onto PS at the temperature range 298-328K.

| Dyes | $\Delta G$ $Jmol^{-1}$ | | | | $\Delta S$ $Jmol^{-1}K^{-1}$ | $\Delta H$ $Jmol^{-1}$ | Ea $kJmol^{-1}$ |
|---|---|---|---|---|---|---|---|
| | 298K | 308K | 318K | 328K | | | |
| EBT | 2616.109 | 2702.843 | 2790.165 | 2877.495 | -8.733 | +13.071 | 2.489 |

### 3.9 FT-IR Spectroscopy Study of PS Surface

FT-IR spectroscopic study was achieved to characterize the functional groups involved in the adsorption process of the PS surface befor and after adsorption of EBT, the available active functional groups were used to determine the binding of the EBT through electrostatic interaction with the surface of the PS, it is seen from figure (12) that the spectra of PS befor adsorption displayed many absorption peaks as shown in the table (3). Figure (13) shows the FT-IR spectra analysis implied that the EBT had been adsorbed on the PS surface and could observe a slight shift in the intensity of the peaks due to the interact of EBT with the PS surface after the adsorption process and this indicates that the process of adsorption is a process of interaction between dipoles (active groups) present in the EBT and the PS surface, i.e. its physisorption occured and this is evident through the low values of the heat of adsorption.

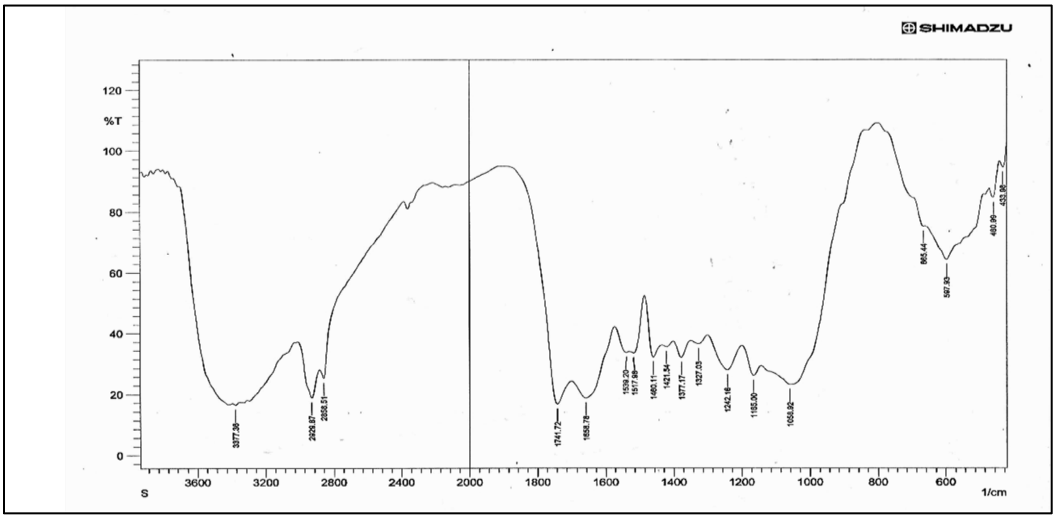

**Fig. 12**. FT-IR spectrum of pomegranate seed powder before adsorption EBT

**Table (3)**: Vibrating frequencies for FT-IR spectrum peaks for pomegranate seed surface

| Vibration frequency $cm^{-1}$ | Type of vibration |
|---|---|
| 3377 | −NH asymmetric stretching of secondary amide of proteins |
| 2929 | $CH_3$ symmetric stretching of protein and lipid |
| 2858 | C−H stretching of methyl and $-CH_2$ in carboxylic acid or ethanol |
| 2400−1800 | Not identified |
| 1741 | C=O stretching of aldehyde or ester |
| 1658 | C=C stretching of alkenes |
| 1539 | N−H bending strongly coupled with C−N stretching(amide II band) |
| 1517 | C−N stretching aromatic amine |
| 1460 | $CH_3$ asymmetric bending of protein |
| 1421 | C−C bending of aromatic |
| 1377 | C−N stretching of aromatic primary amine |
| 1327 | C− O stretching of acid group or bending of $-CH_3$ ,$-CH_2$ in carboxylic acid |
| 1242 | Ethanol |
| 1165 | C−O streching and –OH deformation of primary alcohol |
| 1085 | C−O streching and –OH deformation of secondary alcohol |
| 700−1000 | Not identified |
| 665 | C−H bending |
| 579 − 433 | Finger print |

before EBT adsorption

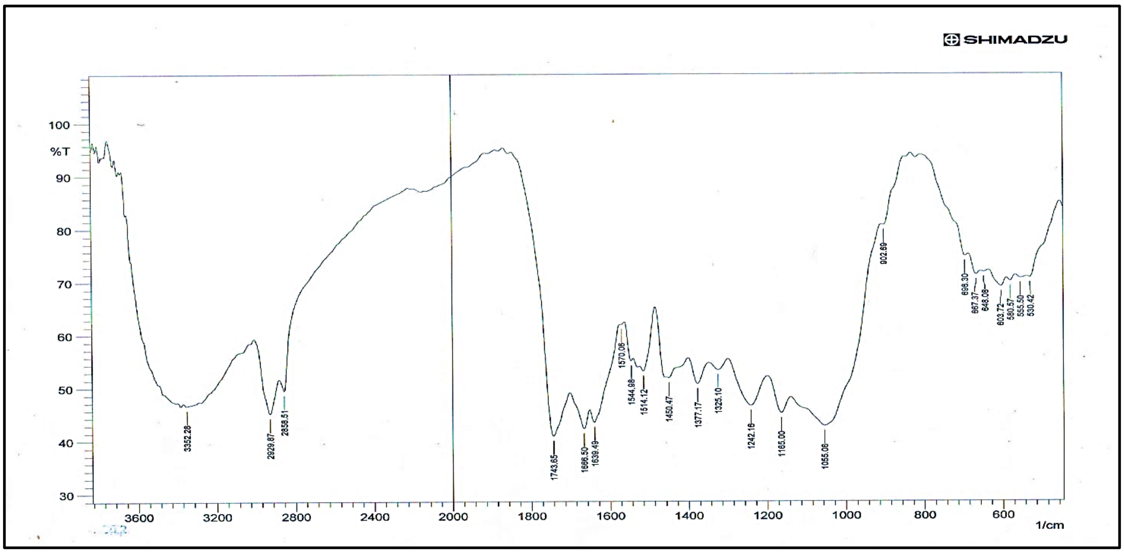

**Fig. 13**. FT-IR spectrum for EBT adsorption on PS surface

## Conclusion

The present work showed that is an effective adsorbent for removal EBT from aqueous solution. The amount of EBT adsorbed was found to vary with initial solution pH, initial concentrations, contact time, and adsorbent dose. Removal of EBT is pH dependent and the maximum removal was attained at pH= 9 and equilibrium time of adsorption is practically achieved in 50 minutes. It was also a function of adsorbate concentration and temperature of the solution. Adsorption equilibrium data fitted very well Freundlich isotherm equation at all experimental temperatures, while the adsorption equilibrium data fitted the Harkin–Jura isotherm equation at 298K. The kinetic study of EBT was performed based on pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion equations. The data indicate that the adsorption kinetics follow the pseudo-second-order rate. The determination of the thermodynamic parameters ($\Delta G$, $\Delta H$, $\Delta S$ and Ea) indicates the nonspontaneous and endothermic nature of the adsorption of EBT, and the negative sign of $\Delta S$ suggests decreased randomness at the solid / solution interface due to affinity of the PS towards EBT. The present study concludes that the PS could be employed as low-cost adsorbents for the removal of EBT from aqueous solutions.

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