

Application of Peanut shell as a low-cost adsorbent for the removal of anionic dye from aqueous solutions

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Abstract

In this study, peanut shell (PS) has been utilized as a low cost adsorbent for the removal of Eriochrome black T (EBT) dye from an aqueous solution using batch experiments. The characterization of the adsorbent was performed by using scanning electron microscope (SEM) coupled with EDX and Fourier transform infrared spectrometer (FTIR) techniques. The effect of operating parameters such as adsorbent dose, initial dye concentration, contact time, pH and temperature were studied. The adsorption kinetics data were fitted to the pseudo-first-order and pseudo-second-order models, and it is revealed that the adsorption of EBT onto peanut shell could be described by the pseudo-second-order model for all investigated initial dye concentrations. The equilibrium data was analyzed by Langmuir and Freundlich isotherm models and showed a good fit with the Langmuir isotherm ($R^2=0.999$). The maximum Langmuir monolayer adsorption capacity was $40.81\text{mg}\cdot\text{g}^{-1}$. The thermodynamic parameters including enthalpy ΔH° , entropy ΔS° and free energy ΔG° indicated that the adsorption process was feasible, spontaneous and exothermic in nature.

1. Introduction

In various industries such as cosmetic, pharmaceutical, paper, leather tanning, plastic and textile, synthetic dyes are widely used to provide color to their products.

Wastewaters produced in large volume from these industries are one of the most dangerous and considerable environmental and water pollution. Furthermore, discharging even a small amount of dye into the natural aquatic streams can affect aquatic and humans life [1], due to the toxic, carcinogenic and mutagenic effects of synthetic dyes [2]. Hence, it is necessary to accurately treat them before discharging to the environment.

Currently, various treatment technologies have been widely employed to treat dye containing wastewater which includes flocculation-coagulation [3], oxidation [4] and adsorption [5]. Most of these techniques have significant disadvantages including high reagent, energy necessity, low selectivity, high operational cost and generation of secondary wastes that are difficult to be disposed [6]. However the adsorption process still remains one of the most effective techniques because of its high efficiency, simplicity, inexpensiveness, and the availability of a wide range of adsorbents.

Activated carbon is the widely used adsorbent for dye removal from wastewater, but due to the expensive production and the difficulty of disposing the used carbon, it is considered as an uneconomical adsorbent. Therefore, there is a growing need to find available, low cost and effective adsorbent for the removal of dyes. In the past few years a number of researches have been studying the application of natural materials as economical *adsorbents* such as wood [7], clay [8], mussel shell [9], potato peels [10], etc

This present study reveal the possible use of peanut shell as a nonconventional, low-cost adsorbent for the removal of Eriochrome black T (EBT) from aqueous solutions.

The Influence of adsorption parameters such as contact time, adsorbent dose, initial dye concentration, temperature and pH were studied. The adsorption kinetic was evaluated by applying the pseudo-first-order and pseudo-second-order models. The equilibrium data were analyzed using Langmuir and Freundlich isotherm models. The thermodynamic parameters of the adsorption were also evaluated.

2. Materials and methods

2.1. Adsorbent

Peanut shells (PS) used as an adsorbent in this study, were collected from a local market in Morocco. This natural waste was first washed with water to remove any dirt and then was dried at room temperature. The dried peanut shells were grinded to fine powder, sieved to obtain particle sizes below 125 μm and stored in glass containers.

2.2. Adsorbate

Eriochrome black T (EBT) was selected as a model for evaluating the capacity of PS to remove anionic dyes from wastewaters. EBT is an anionic dye with molecular weight of $461.38\text{g}\cdot\text{mol}^{-1}$, maximum wavelength of 526nm and chemical structure presented in figure1. It was supplied from labkem and was used without further purification.

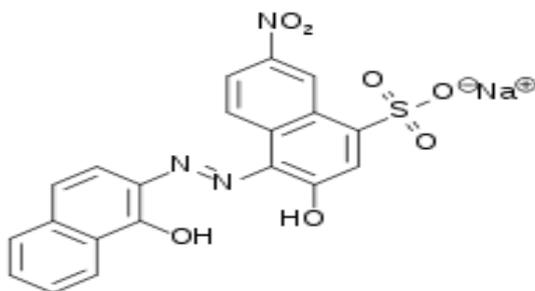


Figure 1: Chemical structure of EBT.

2.3. Adsorption experiments

The adsorption experiments were carried out using discontinuous batches by mixing in Erlenmeyer flasks $2\text{ g}\cdot\text{L}^{-1}$ of PS with 200 mL of EBT solutions in the concentration range of $50\text{-}120\text{ mg}\cdot\text{L}^{-1}$ and initial pH values varying from 2 to 12, adjusted with either HCl or NaOH at 0.1 M. The mixtures were agitated at a constant temperature for 60 minutes which was more than enough to achieve equilibrium. At predetermined time, the samples were taken from the Erlenmeyer flasks and the liquid phase was separated by filtration using $0.45\text{ }\mu\text{m}$ syringe filter (Minisart, sartoriumstedim biotech), the residual concentrations of EBT were determined by using a UV-Vis spectrophotometer (1240 SHIMADZU), all experiments were conducted in duplicate.

The amount of adsorbed dye (q_t , $\text{mg}\cdot\text{g}^{-1}$) was calculated by using the following equation:

$$q_t = \frac{(C_i - C_t)V}{m} \quad (1)$$

Where C_i ($\text{mg}\cdot\text{L}^{-1}$) and C_t ($\text{mg}\cdot\text{L}^{-1}$) are the initial concentration and the concentration at time (t) of EBT solution, V (L) is the volume of solution, m (g) is the mass of the adsorbent.

3. Results and discussion

3.1. Characterization of PS

3.1.1. Scanning Electron Microscopy (SEM)

The morphological characterization of PS was observed by Scanning electron microscopy (SEM) (Quanta 200 FEI) combined with energy dispersive X-ray (Figure2).

The SEM images revealed a fiber structure of peanut shell and showed a partial linkage among the fibers which create pores with different sizes.

3.1.2. Energy dispersive X-ray (EDX)

Elemental analysis of PS was carried out, in order to determine percentage weight of chemical compositions available on the surface, through Energy Dispersive Spectrometer (EDX) analysis (Figure 3). The results are grouped in the following table.

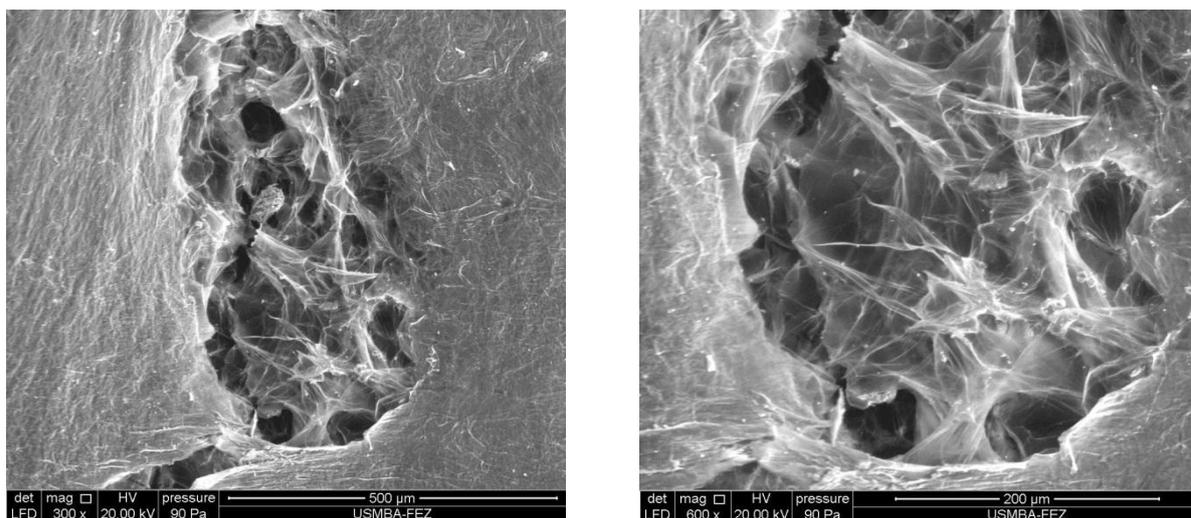


Figure 2: SEM Images of PS: (a) Magnification 300 x; (b) Magnification 600x.

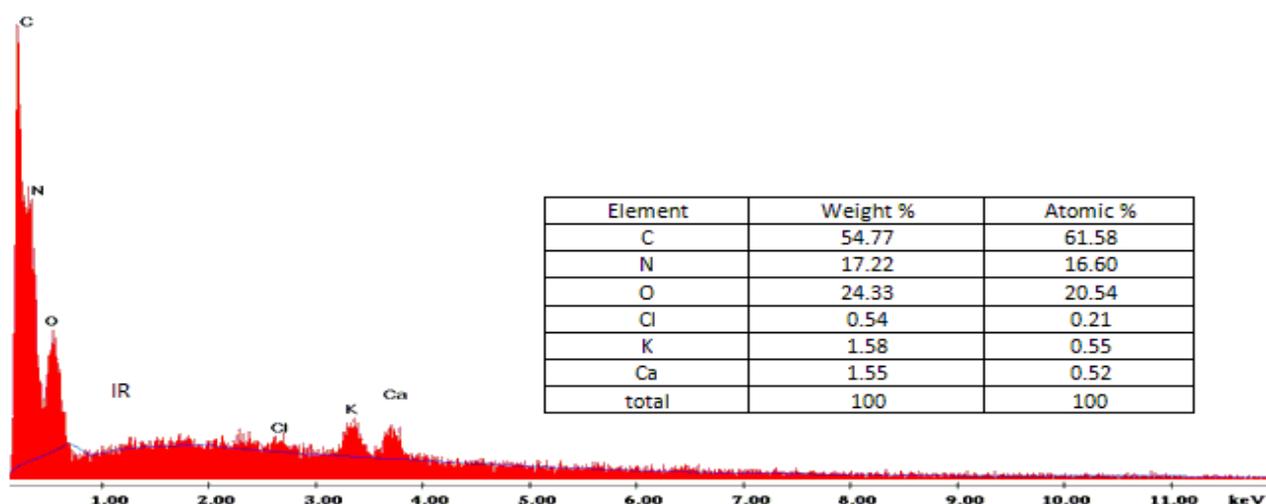


Figure 3: EDX analysis of PS

According to the table, the highest amounts corresponded to the Carbon and the Oxygen which prove the organic nature of the adsorbent.

3.1.3. Fourier transform infrared spectroscopy (FTIR)

In order to identify the major functional groups present in peanut shell, FTIR spectra was recorded in mid IR region in the range of 4000 to 400 cm^{-1} by BRUKER (Vertex70). (Figure 4).

FTIR spectra for the peanut shell displayed a number of peaks pertaining to different functional groups. The broad and intense peak around 3310 cm^{-1} corresponds to O-H stretching vibrations and a peak at 2917 cm^{-1} was attributed to C-H stretching vibrations indicated the presence of methyl and methylene groups. The peak at 1742 cm^{-1} was ascribable to C=O stretching vibrations. The peaks at 1628 cm^{-1} and 1509 correspond to C=C stretching vibration, other peak at 1260 cm^{-1} represented C-H bending vibration. The characteristic peak at 1024 cm^{-1} corresponds to the C-O stretching vibrations. [11, 12]

3.2. Effect of various parameters on removal of EBT

3.2.1. Effect of adsorbent dosage

The effect of adsorbent (PS) dose on the removal of EBT from the aqueous solution was studied by varying the dose of PS from 0.5 to 3g.L^{-1} in 200 ml of the prepared dye solution while the other parameters were kept constant. (Figure 5).

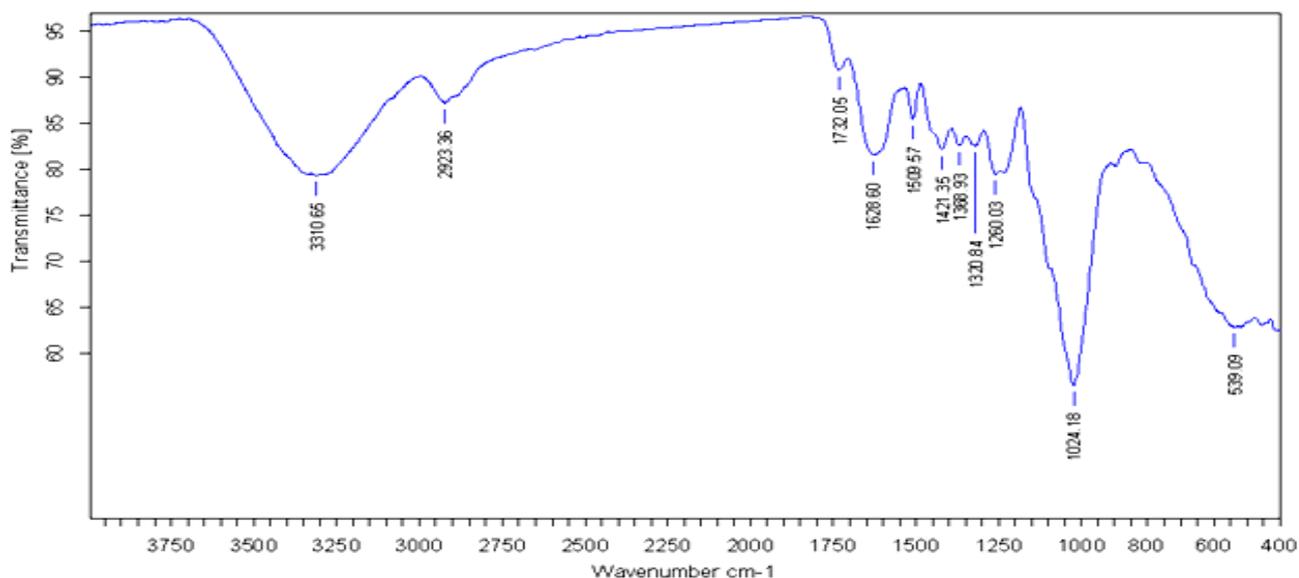


Figure 4: FTIR spectra of peanut shell.

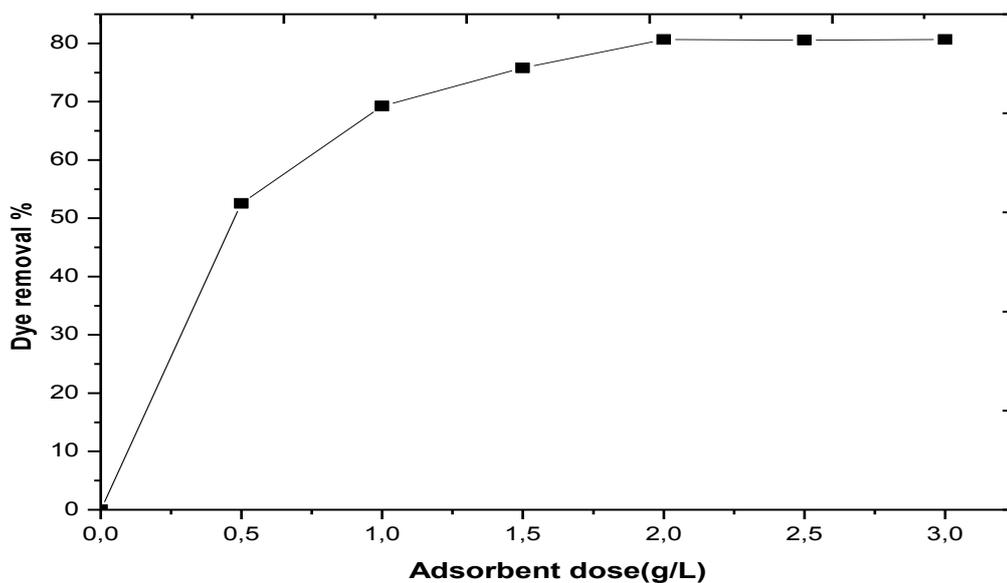


Figure 5: Effect of PS dose on EBT removal.

The results indicated that the percentage removal of EBT increased from 52% to 81% with the increase of adsorbent dose from 0.5 to 2g.L⁻¹. Beyond 2g.L⁻¹ of PS the percentage remains almost constant. Thus, the adsorbent mass was fixed at 2g.L⁻¹ for the following experiments to avoid any useless overdose.

3.2.2. Effect of contact time

The effect of contact time on the removal of EBT by the PS was evaluated for different concentration: 50; 70; 90 and 120 mg.L⁻¹. (Figure 6).

The figure showed rapid adsorption of dye in the first 5 min, thereafter, the adsorption rate slowly increases to reach equilibrium in about 60 min. This can be explained by the fact that the adsorption sites were vacant and easily accessible at the beginning so EBT molecules could easily interact with these sites.

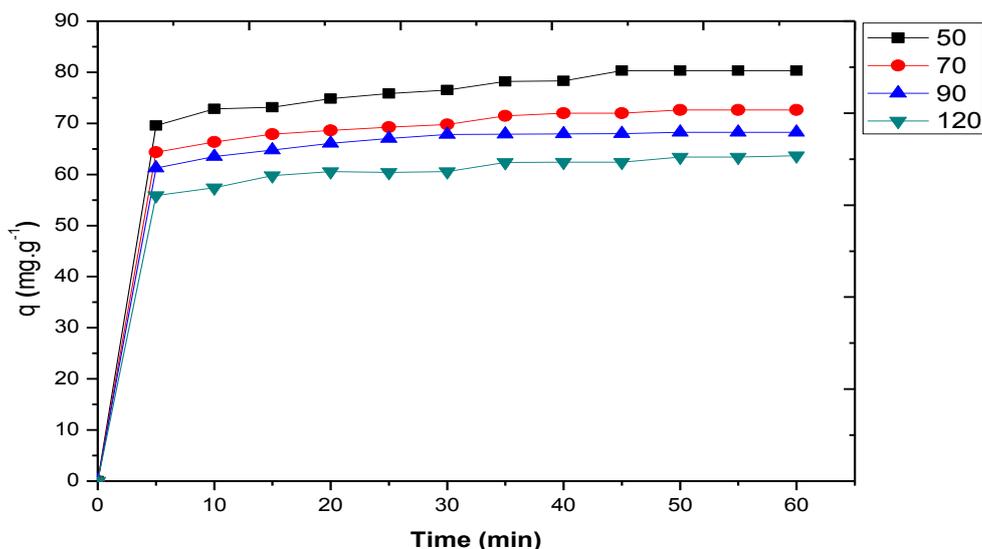


Figure 6: Effect of contact time on EBT removal

3.2.3. Effect of initial dye concentration

The effect of initial EBT concentration on the adsorption efficiency was investigated at different EBT concentrations: 50, 70, 90 and 120 mg.L⁻¹. (Figure 7)

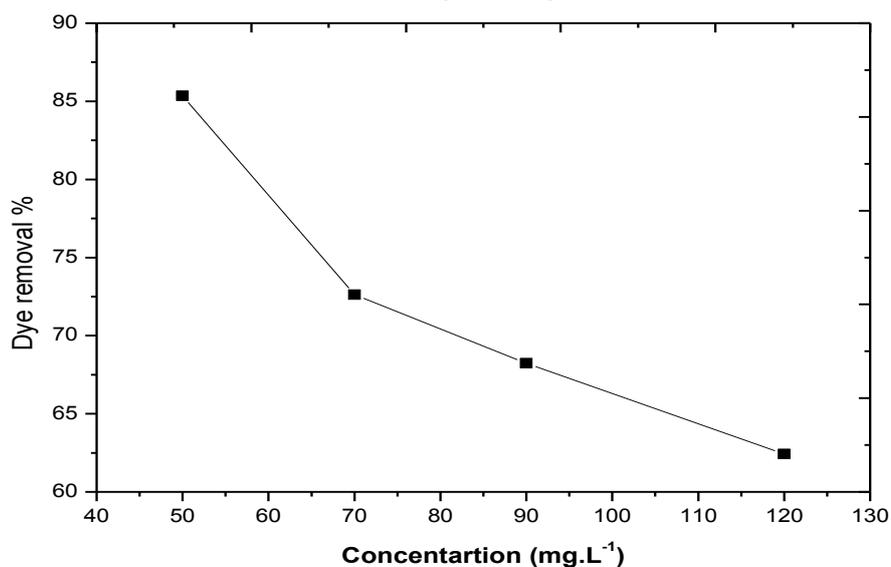


Figure 7: Effect of initial dye concentration on the EBT removal

It is obvious from the figure that the removal percentage of EBT decreased with the increase in initial dye concentration. This can be explained by the fact that the increasing in initial dye concentration intensifies the interaction between PS and EBT [13]. Thus the removal percentage was found to be 85.34% for 50 mg.L⁻¹ of initial concentration, while at 120 mg.L⁻¹ this value was 62.41%.

3.2.4. Effect of pH

The pH of the dye solution is one of the most important parameter in the removal of dyes from aqueous solution. The pH can exerts profound influence on the adsorptive uptake of EBT molecule due to its effect on the surface charges of the adsorbent. In this study the effect of pH on the removal of EBT from aqueous solution was studied by changing the initial pH of the solutions from 2 to 12, while the other operational parameters were kept constant. (Figure8)

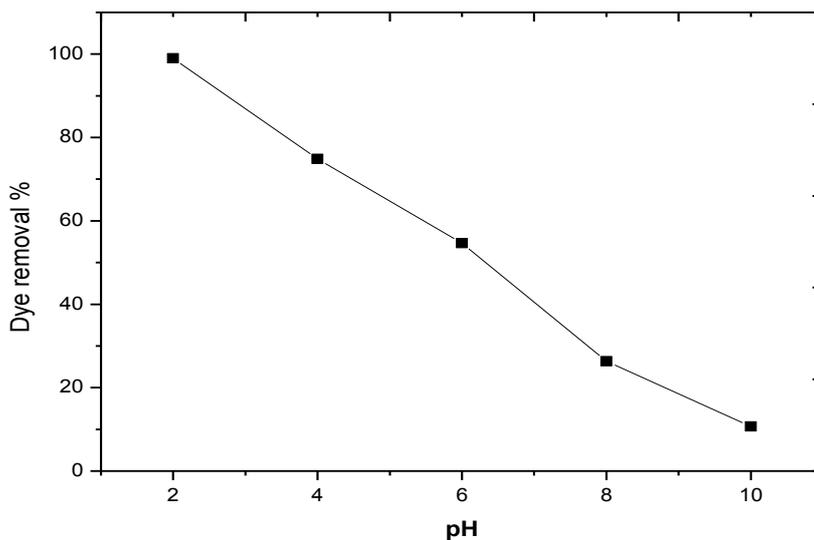


Figure 8: Effect of pH on EBT removal

From the figure, it is clear that the percentage removal of the dye decreased from 99% to 10% as the pH of the solution increased from 2 to 12.

The adsorption mechanism can be explained by determination of the point of zero charge (PZC) of the adsorbent corresponding to the pH value at which the surface exhibits a net surface charge of zero.

3.2.5. Determination of point of zero charge (PZC)

The point of zero charge of PS was determined by adding 20mL of 5.10^{-2} NaCl to a series of 100 mL of Erlenmeyer flasks and the pH_i values of each solution were adjusted, by adding either HCl or NaOH, at values from 2 to 12. The pH_i of the solutions was then accurately noted and 0.1 g of PS was added to each flask. The suspensions were then shaken for 48 hours, and the final pH values of the supernatant were measured. The difference between the initial and final pH value, ΔpH ($pH_i - pH_f$), was plotted versus pH_i and the intersection point of the resulting null ΔpH corresponds to the point of zero charge [14]. The value of PZC of PS was determined to be 6.7 (Figure 9)

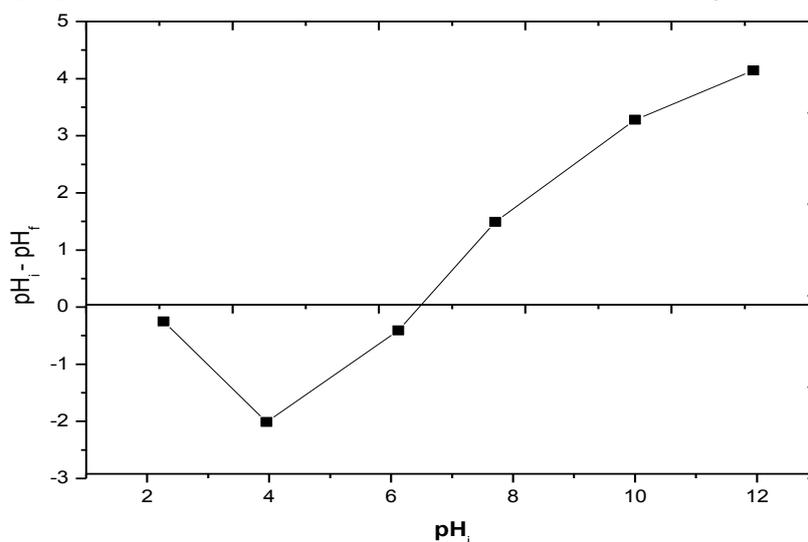


Figure 9: Point of zero charge of PS

At $pH < PZC$ the H^+ ion concentration increase in the system and the surface of the PS acquires positive charges by absorbing H^+ ions, which allow a strong electrostatic attraction between the positively charged PS surface and the negatively charged EBT molecules leading to maximum adsorption of dye at low pH .

At pH >PZC the adsorbent surface is negatively charge which disfavored the adsorption of the negatively charged EBT molecules due to the electrostatic repulsion. So, EBT adsorption onto PS is favored at pH lower than 6.7.

3.2.6. Effect of temperature

The effect of temperature on the adsorption of EBT onto PS was investigated by varying the temperature from 20 to 60 °C. (Figure 10)

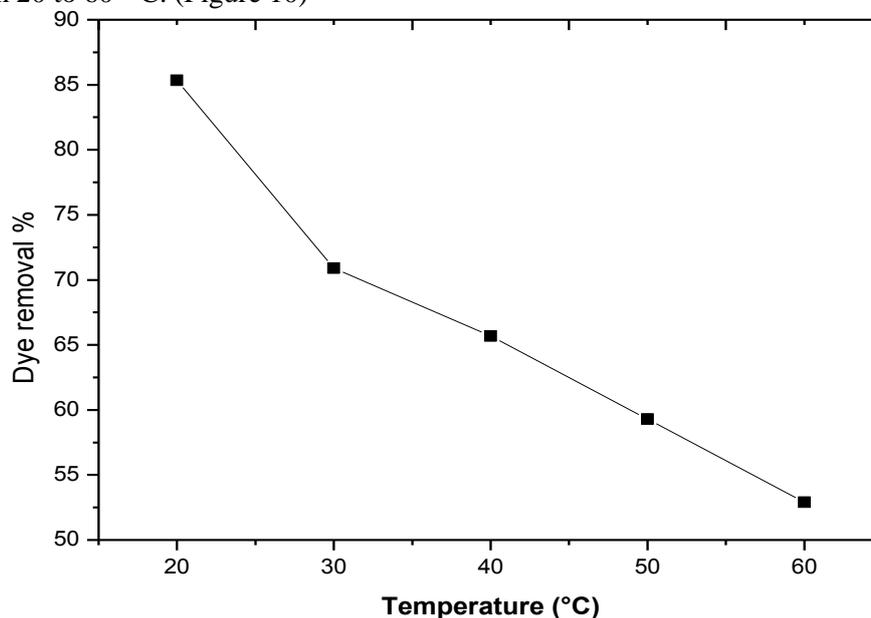


Figure 10: Effect of temperature on EBT removal

The percentage removal of EBT onto PS decreased from 86% to 51%, with the increase of temperature from 20°C to 60°C which indicated that the high *temperature* is disadvantageous to the adsorption process.

3.3. Adsorption kinetics

In order to evaluate the performance of the adsorbent for dye removal and predict the mechanism of the adsorption process, two kinetic models were used to describe the experimental data: pseudo-first-order and pseudo-second-order. The pseudo-first-order model was suggested by Lagergren [15]; it's represented by the following equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

Where q_e and q_t ($\text{mg}\cdot\text{g}^{-1}$) are the amounts of dye adsorbed at equilibrium and at time (t), respectively; and k_1 (min^{-1}) is the pseudo-first-order rate constant.

After integration by applying boundary conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$, the equation becomes:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

If the pseudo-first-order kinetic model is applicable, the plot of $\ln(q_e - q_t)$ versus t gives a straight line and the rate constant k_1 and the amounts of dye adsorbed at equilibrium q_e can be determinate from the slope and intercept.

Ho and Mckay [16] proposed a pseudo-second-order model frequently used in adsorption. This model has the following form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

Where k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) is the rate constant of the pseudo-second-order equation; q_e and q_t ($\text{mg}\cdot\text{g}^{-1}$) are the amounts of dye adsorbed at equilibrium and at time t .

After integrating equation 4 by applying the boundary conditions, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ the equation becomes the following:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \quad (5)$$

q_e and k_2 can be obtained from the slope and intercept of the linear plot of t/q_t against (t) . The experimental data of EBT adsorption onto PS were fitted using the pseudo-first-order and pseudo-second-order kinetic models. The nonlinearity plot of $\ln(q_e - q_t) = f(t)$ suggested the invalidity of the pseudo-first-order model for the adsorption kinetics of the EBT onto PS, so the process does not follow this model, while the plot of t/q_t against (t) gives a linear relationship (figure 11), which suggests that the adsorption data are well represented by pseudo-second-order kinetic model. The kinetic parameters of pseudo-second-order at different initial concentrations of EBT are given in table 1.

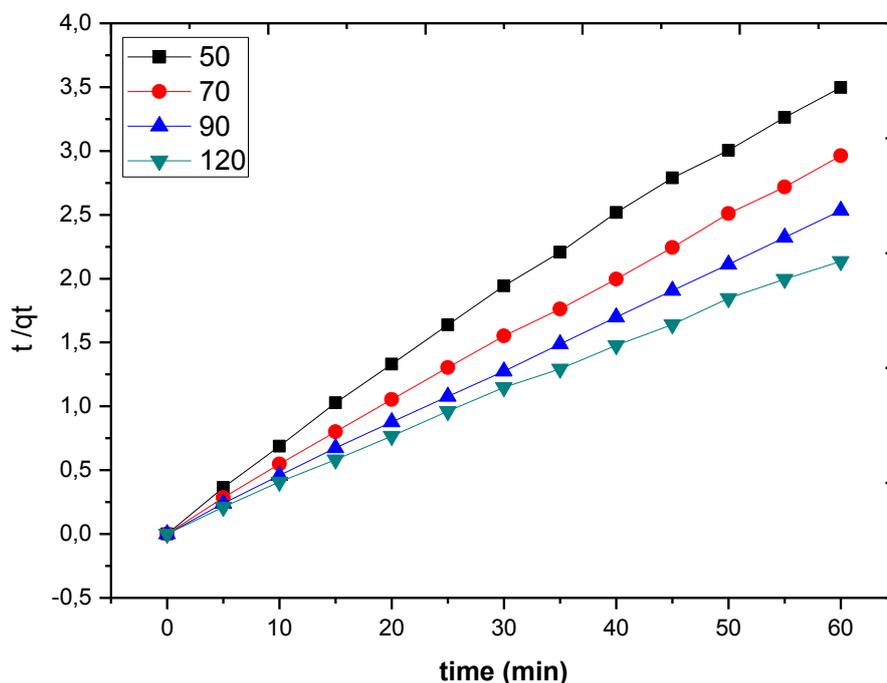


Figure 11: Kinetics adsorption of EBT onto peanut shell.

Table 1: Kinetic parameters for EBT adsorption onto PS obtained at various initial concentrations

C_i (mg.L ⁻¹)	$q_{e,exp}$ (mg.g ⁻¹)	pseudo-second-order model		
		$q_{e,cal}$ (mg.g ⁻¹)	k_2 (g.mg ⁻¹ .min ⁻¹)	R^2
50	17.15	17.82	0.0033	0.996
70	20.24	20.83	0.002	0.999
90	23.68	23.96	0.0017	0.999
120	28.094	28.089	0.0012	0.998

At all investigated initial dye concentrations, the straight lines, with nearly equal to unity correlation coefficients (> 0.996), were obtained and the calculated ($q_{e,cal}$) values were much close to the

experimental values ($q_{e \text{ exp}}$). Therefore, it can be concluded that the kinetics of EBT adsorption onto PS followed a pseudo-second-order model.

3.4 Adsorption isotherms

Adsorption isotherms describe the distribution and interaction of dye molecules within the adsorbent at equilibrium [17]. Adsorption isotherms demonstrate the relationships between the adsorption capacity and the residual concentration of the adsorbate at constant temperature.

Several isotherm models are available; two well-known models were selected for this study: Langmuir and Freundlich models, due to their simplicity and reliability.

3.4.1. Langmuir isotherm

The Langmuir isotherm assumes that the maximum adsorption exists when saturated monolayer coverage of the adsorbate is present on the adsorbent surface, the Langmuir model also assumes that adsorption occurs at specific homogeneous sites within the adsorbent and there is no important interaction among the adsorbed species.

The Langmuir isotherm model is expressed by the following equation [18]:

$$\frac{q_e}{q_m} = \frac{K_L C_e}{1 + K_L C_e} \quad (6)$$

Where C_e (mg.L^{-1}) is the dye concentration at equilibrium, q_e and q_m (mg.g^{-1}) are the amount of the dye adsorbed at equilibrium and the maximum monolayer adsorption capacity, K_L (L.mg^{-1}) is the Langmuir isotherm constant related to the heat of adsorption.

The linear expression for the Langmuir isotherm is:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \quad (7)$$

The linear plot of $1/q_e$ versus $1/C_e$ shows that adsorption obeys the Langmuir model and the constants q_m and K_L can be evaluated from the intercept ($1/q_m$) and the slope ($1/q_m K_L$) respectively.

The essential characteristic of the Langmuir isotherm could be described by a dimensionless constant R_L referred to as equilibrium parameter calculated by using the following equation [19]:

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

Where C_0 (mg L^{-1}) is the initial concentration of dye.

The value of R_L indicates the adsorption nature which is:

- Favorable adsorption if $0 < R_L < 1$
- Unfavorable adsorption if $R_L > 1$
- Linear adsorption if $R_L = 1$
- Irreversible adsorption if $R_L = 0$

3.4.2. Freundlich isotherm

The Freundlich isotherm model assumes a multilayer adsorption on heterogeneous surface with interaction between adsorbed molecules [20].

The model is expressed as follows:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (9)$$

Where K_F is a constant related to adsorption capacity and n is an empirical parameter indicates the favorability of adsorption process. The value of n should be higher than unity for favorable adsorption conditions.

The linear form of the Freundlich model is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (10)$$

The Freundlich constants K_F and n were determined from the linear plot of $\ln q_e$ vs $\ln C_e$.

The table 2 shows the obtained values of Langmuir and Freundlich parameters.

Table 2: Isotherm parameters for EBT removal by PS

Langmuir isotherm				Freundlich isotherm		
q_m ($\text{mg}\cdot\text{g}^{-1}$)	K_L ($\text{L}\cdot\text{mg}^{-1}$)	R_L	R^2	K_F ($\text{mg}/\text{g})(\text{L}/\text{mg})^{(1/n)}$	n	R^2
40,81	0,039	0,33	0.999	0.28	0.775	0.896

Based on the correlation coefficients shown in Table 2, the data were perfectly fitted with the Langmuir isotherm model with $R^2= 0.999$ and $R_L < 1$ implying that EBT molecules are adsorbed at homogenous sites without any interactions whit a maximum Langmuir monolayer adsorption capacity of $40.81 \text{ mg}\cdot\text{g}^{-1}$. (Figure 12)

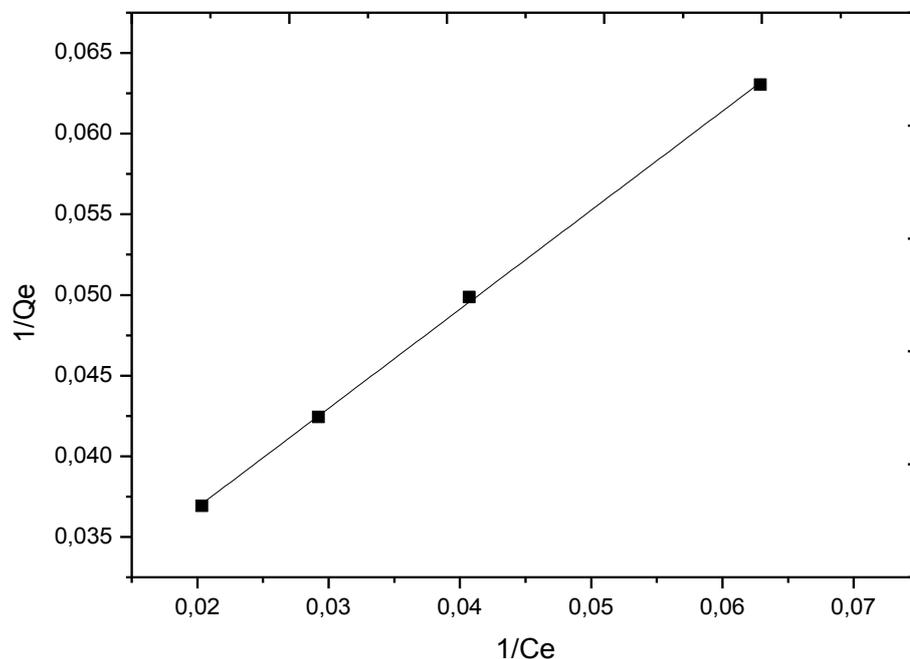


Figure12: Langmuir isotherm model of EBT adsorption onto PS

3.5. Adsorption thermodynamics

The thermodynamic parameters such as Gibbs free energy ΔG° , enthalpy ΔH° and entropy ΔS° can be calculated at different temperatures: 20, 30, 40, 50 and 60°C by using the following equations:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (12)$$

Where $K_d = q_e/C_e$ is the distribution coefficient, R is the universal gas constant and T is the temperature (K).

The values of ΔH° and ΔS° were determined from the slope and intercept of the plot of $\ln K_d$ vs $1/T$ (figure 13) then the value of ΔG° was calculated using the equation 12. (Table 3)

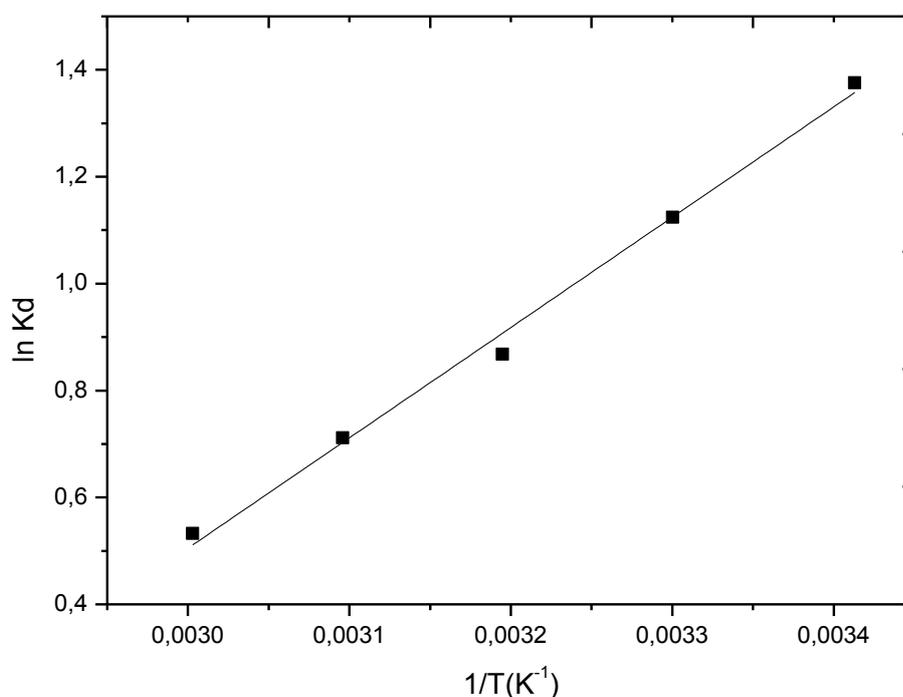


Figure 13: Plot of $\ln K_d$ vs $1/T$ for EBT adsorption onto PS.

Table 3: Thermodynamic parameters of EBT adsorption onto PS at different temperatures

Temperature (K)	ΔH° (kJ.mol ⁻¹)	ΔS° (J.mol ⁻¹ .K ⁻¹)	ΔG° (J.mol ⁻¹)	R^2
293	-17.151	- 47.25	-3307.25	0.98
303			-2834.75	
313			-2362.25	
323			-1889.75	
333			-1417.25	

The negative ΔG° value suggests that the adsorption of EBT is a spontaneous and feasible thermodynamically. With an increase of temperature from 20 to 60°C the negative ΔG° value decreased, indicating that the adsorption process is more favorable at lower temperatures. The negative ΔH° value indicates that that the adsorption phenomenon is physical exothermic process. The negative value of ΔS° suggests that the adsorption leads to the increasing order at the adsorbent–solution interface during the process of adsorption.

Conclusions

The present study showed that PS, an agricultural waste material, present amazing adsorption performance for anionic dye from aqueous solutions. The adsorption process was strongly pH dependent since the higher removal percentage of 99% was obtained at a pH=2. The effect of contact time shows a rapid adsorption of dye in the first 5 min and, thereafter, the adsorption rate slowly increases to reach equilibrium in about 60 min.

The equilibrium data have been analyzed using Langmuir and Freundlich isotherm and was best fitted with the Langmuir isotherm model based on its correlation coefficient value ($R^2=0.999$) with the monolayer adsorption capacity of PS was found to be 40.81 mg g^{-1} . The kinetic data agrees well with the pseudo-second-order model ($R^2>0.996$) for different initial EBT concentrations. The thermodynamic parameters indicated that the adsorption process was feasible, spontaneous and exothermic in nature with increasing order at the adsorbent–solution interface.

This study demonstrates that peanut shell can be successfully used as a low cost adsorbent for the removal of EBT from aqueous solutions.

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