## Azo Dye Adsorption onto Cobalt Oxide: Isotherm, Kinetics, and Error Analysis Studies

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**Abstract:** The current study focused on utilizing cobalt oxide to eliminate hazardous Eriochrome Black T (EBT) dye. The impact of pH (2, 4, 7, 8, and 10) and temperature (45, 50, and 55 °C) was examined for EBT removal. The results show that the maximum sorption occurred at pH = 2 and that the removal percentage increased with increasing temperature. Five non-linear regression methods were used to predict the best isotherm and kinetic models. A coefficient of non-determination, K<sup>2</sup>, was very helpful for selecting the RMSD function as a preferable error function among the five methods. Isothermal models to illustrate equilibrium sorption information, the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich models were used. The results showed that the Langmuir model (R<sup>2</sup> = 0.99) was the most favorable, indicating monolayer sorption of EBT occurred. The kinetics models were analyzed using pseudo-first-order and pseudo-second-order whereas the sorption information was well described by the pseudo-second-order model (R<sup>2</sup> = 0.99). The results of the thermodynamic study appeared that the adsorption of EBT was endothermic, feasible, spontaneous, and physical adsorption.

Keywords: Eriochrome Black T dye; adsorption; isotherm; kinetic; error analysis

## INTRODUCTION

Dyes are very recalcitrant compounds as they are stable to light, temperature, and microbial attack. Dyes are used in many vital industries and classified as one of the major causes of pollution of water resources [1]. Azo dyes are environmentally polluting dyes that are carcinogenic and very difficult to degrade even at low concentrations. They are released in massive quantities directly into water bodies impacting aquatic life and the food web [2-3]. Azo dyes are categorized as one of the most hazardous dyes due to their extreme stability in the aquatic environment, complex aromatic structure, azoic linkages, amino groups, and toxic nature; all these factors combine to make azo dyes hazardous health of living organisms [4-5]. Eriochrome Black T (EBT) is an anionic form of azo dyes. This dye is commonly used as a metallochromic indicator and employed in dyeing silk, nylon, and wool. EBT is a toxic compound whose breakdown can make a phenolic substance carcinogen [6-7]. This dye is not degraded by biological treatment and is resistant to decomposition under aerobic digestion and oxidation agents because it consists of azo groups (-N=N-) with aromatic rings and sulfonate groups [8-9]. EBT is a poison dye that causes blindness, severe eye and skin irritation, liver damage, loss of consciousness, and coma [10]. Numerous chemical, physical, and biological processes have been developed to remove dyes from water, including chemical oxidation, flotation, ion exchange, and electrochemical treatments [11-12]. Nonetheless, adsorption stands out among these approaches due to its speed. Many adsorbents are used to remove EBT dye like Cotton Waste [13], surfactant modified clay [8], Nteje Clay [2], and metal oxide [11-12]. Besides simplicity, economics, and effectiveness, reusability of adsorbent is possible. This fact made adsorption proven to be the preferable method for wastewater treatment [14-15]. Metal oxide adsorbent is low cost and efficient for the adsorption process. Metal oxides are widely used due to their ease of obtaining, limited solubility, amphoteric properties, oscillator properties, cheapness, and impedance to thermal decomposition compared to other surfaces [16-17]. Several metal oxides such as iron(III) oxide (Fe<sub>2</sub>O<sub>3</sub>), zirconium oxide (ZrO<sub>2</sub>), aluminum(III) oxide (Al<sub>2</sub>O<sub>3</sub>), and cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) have been used for this purpose [18]. In this report, EBT dye was removed Co<sub>3</sub>O<sub>4</sub> as a low cost and effective adsorbent. The impacts of some parameters like pH and temperature were studied. Four adsorption isotherms were used to find the optimum isotherm, in addition to the analyze and discuss kinematic and thermodynamic data to use Co<sub>3</sub>O<sub>4</sub> as an effective and low-cost adsorbent for EBT removal. Errol statistics were used to assess the adequacy and quality of the fitted models.

## EXPERIMENTAL SECTION

#### Materials

Eriochrome Black T(BDH),  $Co_3O_4$ , HCl, and NaOH were purchased from (BDH), the standard dye solution of 500 mg L<sup>-1</sup> was prepared and used to make different concentrations using distilled water.

#### Instrumentation

The UV-Visible scanning spectrum was taken on a (Cary 100, VARIAN CO.). A centrifuge, shaking water bath (BS-11 digital, JETO Korea, TECH) was used to shake off the samples. The pH meter (Hana) was used to measure the pH of solutions.

### Procedure

#### Adsorption experiments

Batch experiments were conducted under optimal conditions, with a 50 mL flask containing 10 mL of EBT solution (50 mg L<sup>-1</sup>), 0.1 g of Co<sub>3</sub>O<sub>4</sub> adsorbent, pH 2, and 55 °C. The flask was set on a shaking water bath and shaking at 500 rpm for 50 min. The pH of EBT solution was adjusted by 0.1 M hydrochloric acid and sodium hydroxide in the range (2, 4, 7, 8, and 10). Three temperatures (45, 50, and 55°) were used to study the impact of temperature. Adsorption isotherms are evaluated at different concentrations (30, 40, 50, and 60 mg L<sup>-1</sup>), while kinetic studies are done at various mixing times (10, 20, 30, 40, 50, and 60 min). Then the EBT was separated from the stained solution by centrifuging for 15 min (3000 rpm), and the concentration of the dye was determined at  $\lambda_{max} =$ 520 nm. The following equation is used to calculate the adsorption capacity and color removal (%):

$$q_e = C_0 - C_e \times \frac{v}{m} \tag{1}$$

Removal % = 
$$\frac{C_0 - C_e}{C_0} \times 100$$
 (2)

where v (L) is the volume of dye solution, m (mg) is the mass of  $Co_3O_4$ ,  $C_0$  and  $C_e$  (mg L<sup>-1</sup>) are EBT initial and equilibrium concentration, respectively [19].

## Isotherm and kinetic studies

Isotherm studies were used to analyzed data and estimate the applicability of the process. The Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich models were employed to describe the adsorption system. For further interpretations in favor of adsorption, a separation factor ( $R_L$ ) was used as in Eq. (3)

$$R_{L} = \frac{1}{1 + K_{L}C_{0}} \tag{3}$$

where  $K_L$  (L/mg) is the Langmuir constant.  $R_L$  implies the kind of isotherm to be irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavorable ( $R_L > 1$ ) [14].

Also, Dubinin-Radushkevich isotherm was used to identify if the adsorption is physic sorption or chemisorption from its mean (E) kJ mol<sup>-1</sup>, which supply's beneficial information on the type of mechanism of the adsorption system. (E) can defend by:

$$E = \frac{1}{\sqrt{-2\beta}}$$
(4)

If the quantity of (E) less than 8 kJ mol<sup>-1</sup>, the reaction became is physical adsorption. While, if (E) value between (8 to 16) kJ mol<sup>-1</sup>, the adsorption process is via ion exchange mechanism, and If (E) > 16 kJ mol<sup>-1</sup>, the mechanism of particle diffusion and the reaction is chemisorptions [20-21].

Kinetics was verified by examining the impact of contact time to remove the EBT dye using the pseudo-first-order and pseudo-second-order models. The most appropriate model chosen is based on  $R^2$  and error functions for both isotherm and kinetic studies. Table 1 included all equations that were used in this study.

#### Error analysis

Error analysis is an essential parameter that assessments how well the curve pronounces the experimental data. It is not sufficient to analyze the data based on the R<sup>2</sup> value to select the suitable isotherm and kinetic model, since to the empirical results R<sup>2</sup> value can be high. Therefore, it is essential to diagnose regression to analyze the outcomes [22-23]. Five error functions were studied to find the most appropriate isotherm and kinetic model, as seen in Table 2.

## RESULTS AND DISCUSSION

## **Effect of Solution pH**

pH is an essential factor that impacts the charge of the adsorbent surface and the degree of ionization of the sorbates in the solution. Thus, the pH impacts the

T (1 1 1		expressions of isothermal			D (	
Isotherm model	Equation	Linearized form	Plot	Parameters	Ref.	
Langmuir	$qe = q_m K_L C_e / (1 + K_L C_e)$	$1/q_e = (1/K_Lq_mC_e) + (1/q_m)$	$1/q_e$ vs. $1/C_e$	$q_m = (intercept)^{-1},$	[19]	
0			10	$K_L = intercept/slope$	r . 1	
Freundlich	$q_e = K_F (C_e)^{1/n}$	$lnq_e = lnK_F + n^{-1}lnC_e$	lnq <sub>e</sub> vs. lnC <sub>e</sub>	$K_F = exp(intercept),$	[19]	
Treunanen	$q_e - R_F(O_e)$	$\operatorname{III}\mathbf{q}_{e} = \operatorname{III}\mathbf{x}_{F} + \operatorname{II}^{-}\operatorname{III}\mathbf{C}_{e}$	IIIq <sub>e</sub> vs. IIIC <sub>e</sub>	1/n = slope	[19]	
Temkin	$q_e = B \ln(K_T C_e)$	$q_e = B \ln K_T + B \ln C_e$	qe vs. lnCe	B = slope,	[1]	
	were $B = RT/b$	$q_e - D III R_T + D III C_e$	qe vs. mee	$K_T = exp(intercept/slope)$		
Dubinin-	$q_e = q_{mexp}(-\beta\epsilon^2)$	$\ln q_e = \ln q_m - \beta \epsilon^2$	$\ln q_e$ vs. $\epsilon^2$	qm = exp(intercept),	[20]	
Radushkevich (D-R)	were $\varepsilon = \operatorname{RT} \ln(1 + C_e^{-1})$	liiq <sub>e</sub> – liiq <sub>m</sub> – με	iliq <sub>e</sub> vs. c	β=–slope	[20]	
Kinetics model						
Pseudo-first-order	$qt = q_e[1 - exp(-k_1t)]$	$Ln(qe - qt) = lnq_e - k_l t$	$ln(q_e - q_t)$ vs. t	$q_e = exp(intercept),$	[10]	
				$k_1 = -(slope)$		
Decude second ender	$\frac{1}{2} \frac{1}{2} \frac{1}$	$t/a = 1/k a^2 + 1/a t$	tla va t	$q_e = slope^{-1}, k_2 =$	[10]	
r seudo-second-order	$qt = k_2 q_e^2 t / (1 + q_e k_2 t)$	$t/q_t = 1/k_2 q_e^2 + 1/q_e t$	$t/q_t$ vs. t	(slope <sup>2</sup> )/intercept	[10]	

Table 1. Linear expressions of isothermal and kinetic mo
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qe, qm, qt (mg g<sup>-1</sup>) are the sorption capacity at equilibrium, saturated, and at time t; n is heterogeneity of site energies; b (J/mol) is Temkin constant; B (J/mol) is constant related to heat of adsorption;  $\varepsilon$  (J mol<sup>-1</sup>) is the Polanyi potential;  $\beta$  (mol<sup>2</sup>/kJ<sup>2</sup>) is the D-R constant; R (8.314 J/K mol) is the gas constant; T (K) is the temperature; t (min) is time; K<sub>F</sub>(mgg<sup>-1</sup>) and K<sub>T</sub> (L/g) are Freundlich and Temkin constants; K<sub>1</sub>(min<sup>-1</sup>) and K<sub>2</sub>(mg g<sup>-1</sup>) min<sup>-1</sup>) are pseudo-first order and pseudo-second order rate constants

Table 2. Error functions list	Table 2.	Error	functions	list
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Error functions	Equations	Ref.
Marquardt's is the percent standard deviation (MPSD)	$100 \sqrt{\frac{1}{n-p} \sum \left(\frac{q_{cal.} - q_{exp.}}{q_{cal.}}\right)^2}$	[11]
Sum of absolute errors (EABS)	$\sum_{i=1}^{n}  q_{cal.} - q_{exp.} $	[11]
Chi-square (X <sup>2</sup> )	$\sum_{i=1}^{n} \frac{\left(q_{cal.} - q_{exp.}\right)^2}{q_{cal.}}$	[15]
Reduced chi-square Error (X²-red)	$\frac{1}{n-p} \sum_{i=1}^{n} \frac{\left(q_{cal.} - q_{exp.}\right)^{2}}{q_{cal.}}$	[22]
Root means square error (RMSD)	$\sqrt{\frac{1}{n-1} \left(q_{cal.} - q_{exp.}\right)^2}$	[23]

 $\overline{q_{exp.}}$  and  $\overline{q_{cal.}}$  are experiment and calculated EBT concentration, p is the number of parameters (p = 2 for Langmuir and Freundlich and 3 = Temkin and D-R), n is the number of experimental data (4)

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structural stability and the color intensity of the dyes [24]. Fig. 1 shows that the highest removal ratio when the pH = 2, while increasing pH up to 10 reducing the removal percentage. The EBT removal at pH = 2 was 96.6%. This decrease in removal ratio with increasing pH is associated with an increase in the number of OH– groups in the dye that may compete with anionic ions. As a result, as the number of positively charged sites decreases, so does the removal ratio. The sites negatively charged on the surface of the adsorbent will not prefer the adsorption of dye ions because of the electrostatic repulsion of OH– groups. The sulfonic group on the EBT dye may also bind via the ion exchange [18,25]. These results are similar to previous studies for adsorption of EBT dye on other oxide surfaces such as Fe<sub>2</sub>O<sub>3</sub> [11],  $\alpha$ -Al(OH)<sub>3</sub> [25], and nanosilica [26].

## **Isotherm Studies**

Adsorption isotherm is described as the ratio between the adsorbed quantity and the remaining in solution at a constant temperature, and it gives the capacity of the adsorbent and the relationship between adsorbent and adsorbate at equilibrium; Isotherm equips fundamental physiochemical information for the valuation of the applicability of a sorption system as an operation unit [24,27]. For analyzing the mechanism of EBT sorption on the  $Co_3O_4$  surface, four isotherm equations (Langmuir, Freundlich, Temkin, and D–R) were used (Table 3).

By comparing the values of  $R^2$  and the error functions in Table 3, it was discovered that the Langmuir

isotherm is the most appropriate model to describe the study of EBT adsorption onto  $Co_3O_4$ . Modeling the equilibrium data using a Langmuir isothermal gave the highest R-value and the lowest MSPD, EABS, X<sup>2</sup>, X<sup>2</sup>-red, and RMSD values. Fig. 2(a-d) depicts the experimental Langmuir, Freundlich, Temin, and D-R models.

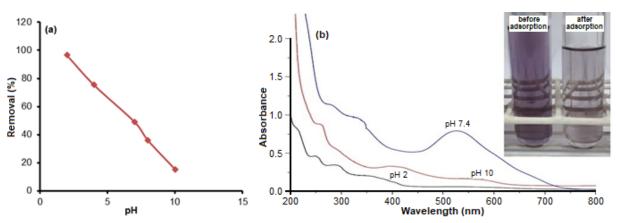
- (i) The adsorption of EBT on the surface of Co<sub>3</sub>O<sub>4</sub> is homogenous with monolayer adsorption [28].
- (ii) The value of  $R_L$  between 0 and 1 represents favorable sorption. Also, this is consistent with the findings from Freundlich model 0 < 1/n < 1, which indicates favorable sorption of dye on the adsorbent surface [28].
- (iii) Because the sorption energy B from the Temkin isotherm was positive, the adsorption is endothermic [29].
- (iv) The D-H model calculated the mean sorption energy (E) of 0.158 kJ mol<sup>-1</sup> within the range of physical adsorption (less than 8 kJ mol<sup>-1</sup>).
- (v) Base on error functions, the isothermal arrangement for the most suitable empirical data in this search was: Langmuir > Freundlich > Temkin > D-H.

To verify the error function that reduces the distribution of errors between the theoretical and experimental isotherms, the coefficient of non-determination ( $K^2$ ) was used, and it calculates from:

$${}^{2} = \frac{\text{Unexplained variance}}{\text{Total variance}}$$

$$=1 - \frac{\text{Unexplained variance}}{\text{Total variance}}$$

$$=1 - r2$$
(5)



K

**Fig 1.** (a) impact of pH on the adsorption of BET (b) UV–Visible scanning spectrum and BET photographs [at concentration of 50 mg  $L^{-1}$  and pH (2, 7, and 10)] of dye before and after adsorption

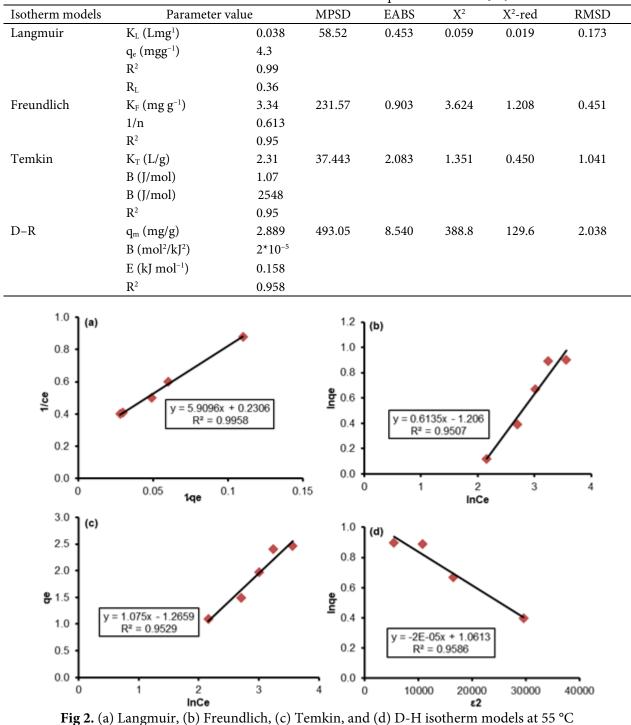


Table 3. Values of isotherm variables for sorption EBT on Co<sub>3</sub>O<sub>4</sub>

The  $K^2$  is a beneficial measurement of the linear or non-linear co-variation of two variables and to derive any inference about the range of the relationship between the Convert empirical data and the expected isotherm [22]. Fig. 3 shows the values of  $K^2$  for the isotherms expected by minimizing or maximizing the different error forms for EBT dye. Consequently, RMSD was the preferable error function used to predict the optimum isotherm due to minimal unexplained isotherm, proposing this function as the batter function to reduce the distribution of error between the empirical and expected isotherms [30]. Therefore, using RMSD functions, the arrangement for the best isotherm for EBT dye adsorption was as follows: Langmuir > Freundlich > Temkin > D-R.

# Effect of Temperature and Thermodynamics Studies

The effect of temperature is very fundamental in every transfer phenomenon like sorption due to some thermodynamics factor-like enthalpy change ( $\Delta$ H°), entropy change ( $\Delta$ S°), and Gibbs free energy change ( $\Delta$ G°). The studied thermodynamics factors help us understand the nature of the sorption process, such as endothermic or exothermic [2,31]. So, the adsorption efficiency of EBT on Co<sub>3</sub>O<sub>4</sub> was found at 45, 50, and 55 °C. Fig. 4 shows the impact of temperature on the adsorption system. It notices that with increasing temperature, the removal efficiency of the EBT dye increases, indicating the endothermic nature of the sorption process. The thermodynamics factor can be defined by the equilibrium constant Kc using the following equations:

$$K_{c} = \frac{C_{A}}{C_{e}}$$
(6)

$$\Delta G^{\circ} = -RT\ln(K_c) \tag{7}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{8}$$

$$\ln(K_c) = \frac{\Delta H^{\circ}}{RT} - \frac{\Delta S^{\circ}}{R}$$
(9)

whereas  $C_A$  and  $C_e$  (g/L) are the concentrations of EBT in the adsorbent phase and solution at equilibrium. The  $\Delta H^{\circ}$ and  $\Delta S^{\circ}$  values determined from the slope and the intercept from the plot of ln K<sub>c</sub> vs. 1/T (K-1) [21].

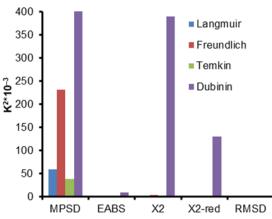
Table 4 showed as a result of thermodynamics factors, where the positive charge of  $\Delta H^{\circ}$  referred that the adsorption nature is endothermic, which is supported by the prediction from the Temkin model and the increase in EBT removal with raising the temperature from 318 K to 328 K [1,28]. Whereas, the positive values of  $\Delta S^{\circ}$  propose a raising the randomness at the solid-liquid interface, which showed that the sorption system is favorable [9]. The  $\Delta G^{\circ}$  values suggest that at low temperatures, the adsorption process is non-spontaneous, while spontaneity happens at high-temperature [32]. The energy of activation (E<sub>a</sub>) was determined based on the following relationship:

$$E_a = \Delta H^\circ + RT \tag{10}$$

In this study, the activation energy values (less than 42 kJ mol<sup>-1</sup>) indicating the adsorption processes controlled by diffusion [33].

## **Adsorption Kinetics**

Adsorption kinetics gives more information about the reaction pathways and sorption mechanisms of the



**Fig 3.** The relationship between Error function and isotherm models of EBT adsorption onto  $Co_3O_4$  surface

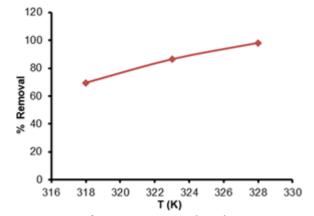


Fig 4. Impact of temperature on the adsorption system

**Table 4.** Thermodynamics factors of the sorption BET dye on the  $Co_3O_4$ 

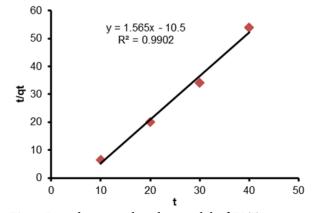
T (K)	$\Delta G^{\circ} KJ/mol$	$\Delta H^{\circ} KJ/mol$	$\Delta S^{\circ} J/mol$	A kJ mol <sup>-1</sup>
318	0.156	9.06	28.23	11.703
323	-0.058			11.74
328	-0.199			11.786

sorbate by the sorbent and helps understand system dynamics [8]. Two kinetics models were used to explain the kinetics studied of removal EBT dye on  $Co_3O_4$  surface by pseudo-first and pseudo-second-order models as shown in Table 5.

Depending on the results from the amounts of ( $R^2$ ), error function, and kinetic factors in Table 5, we noticed that the pseudo-second-order was best suited to describe the kinetics of the adsorption. The pseudo-second-order had a higher  $R^2$  (0.990) value and a smaller error function for the five models. Furthermore, the calculated  $q_e(_{cal})$ (0.638) value measured from pseudo-second-order kinetic model was analogous to the empirical  $q_e(_{exp}) = 0.6$ amounts whereas the  $q_e(_{cal})$  (0.5) for the pseudo-firstorder model was not. These results demonstrate the success of a pseudo-second-degree model in describing EBT dye uptake kinetics [34-35] (Fig. 5). For kinetic studies, RMSD functions are the preferable error function used to predict the kinetic model, as shown in Fig. 6.

#### **Comparison with Other Research**

This report included comparing the results of our study with other reports on the removal of EBT by different adsorbents, as shown in Table 6. As noticed, the





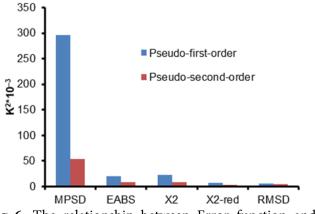


Fig 6. The relationship between Error function and kinetics models of EBT adsorption onto  $Co_3O_4$  surface

Table 5. Killette parameters for removal of LDT dye							
Kinetics models	Paramete	er value	MPSD	EABS	$X^2$	X <sup>2</sup> -red	RMSD
Pseudo-first-order	K1	0.016	295.65	19.7	22.253	7.417	6.3553
	$q_e$	0.5					
	$\mathbb{R}^2$	0.89					
Pseudo-second-order	$K_2$	0.23	53.66	8.362	7.769	2.5896	4.1809
	$q_{e(cal)}$	0.638					
	qe(exp)	0.6					
	R <sup>2</sup>	0.99					

Table 5. Kinetic parameters for removal of EBT dye

Table 6. Comparison results of removal of EBT with other adsorbents in literature
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Adsorbent	Contact time	pH/adsorption	Removal	Ref.
	(min)	nature	percentage %	
Biochar-derived date palm fronds waste	240	2/endothermic	-	[36]
Graphene/NiMgAl-layered hydroxides	180	2/exothermic	-	[24]
Cotton waste	120	2/-	83.4	[15]
Activated carbon prepared from waste rice hulls	60	2/-	93.1	[20]
H <sub>3</sub> PO <sub>4</sub> -modified berry leaves	60	-/exothermic	91.0	[9]
Nteje clay	60	2/endothermic	92.0	[2]
Surfactant modified clay	30	3/endothermic	70.0	[8]
Co <sub>3</sub> O <sub>4</sub>	50	2/endothermic	96.6	This study

contact time is lower than other adsorbents (except adsorption of dye in surfactant modified clay surface had lower time). Table 6 shows that  $Co_3O_4$  had the best equilibrium time and highest removal percentage showing  $Co_3O_4$  as a feasible adsorbent for removing EBT dye from water. The low pH of EBT absorption is preferred for various absorbents.

## CONCLUSION

In this report, the sorption of EBT dye from an aqueous solution using low-cost Co<sub>3</sub>O<sub>4</sub> surface was investigated. EBT adsorption occurred with an equilibrium time of 50 min and an optimal pH of 2, with the removal percentage of adsorption increasing with temperature. According to the isotherm study, the Langmuir isotherm is the appropriate model for the adsorption system, which confirmed the highest R<sup>2</sup> value and the smallest value of error functions, indicating that favorable monolayer adsorption was observed between EBT and Co<sub>3</sub>O<sub>4</sub>. The adsorption process was occurred via physical nature and controlled by diffusion. The sorption kinetics followed a pseudo-second-order model with the excellent agreement between experiments and calculated sorption capacity, as well as the highest R<sup>2</sup> and the smallest error function values. The adsorption of EBT was endothermic and spontaneous at high temperatures. From the K<sup>2</sup> value, the RMSD function was identified as the best function for foretelling the isotherm and kinetic models.

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