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RESEARCH ARTICLE
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Kinetic and thermodynamic study of adsorption of an industrial food dye using Iraqi clay

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ABSTRACT

Erythrosine was removed from its aqueous solution using the adsorption abilities of bentonite. The range for the maximum dye adsorption was shown to be between 36.68% and 44.82%. The findings of employing the Freundlich, Langmuir, and Temkin adsorption isotherms showed that the Freundlich model was followed, the Langmuir model did not match, and the Temkin model could only be partially applied at temperatures of (298,308,318) K. In addition it is physical adsorption. The results showed the applicability of the pseudo-second-order model, which was one of two kinetic models of the adsorption process tested. In this research. The process was shown to be exothermic when the thermodynamic functions were calculated using the value of the enthalpy Δ°H, which was negative and equal to (-35.6571 KJ/mol). The entropy Δ°S value, which equaled (- 129.6984 J/mole.K), was likewise negative. Gibbs free energy ΔG°was calculated and it was found that the reaction is non-spontaneous and that the reaction occurs with a lack of randomness and it is exothermic adsorption.

Keywords: *Erythrosine; Pollution; industrial food dye ; Adsorption; Bentonite.*

INTRODUCTION

One of the risks to human life is water that has been contaminated with organic dyes. Industrial dyes are regarded as potentially harmful water pollutants1. Environmental pollution is still a concern, and it gets worse when the toxins show persistence and refractory nature. The xanthene class of synthetic colors, in particular, fall within this category.

Due to the threat that water contaminants bring to the environment, researchers have been directed to develop numerous methods for treating and removing them. Adsorption is one of the most effective methods for treating pollution compared to other methods because of its high efficiency, simplicity of use, and low cost compared to other methods, as well as the availability of natural resources that can be used as suitable adsorbent surfaces for the adsorption process. As an illustration of absorbent surfaces (activated carbon, plant and animal waste, clay, etc)2.

Bentonite clay for the study used was obtained from the General Company of Geological Survey. Table1 shows below the chemical analysis of bentonite clay that was conducted in the General Company of Geological Survey using the XRF device.

TABLE 1: Chemical analysis of bentonite

Compound	SiO2	Al2O3	CaO	Fe2O3	MgO	Na2O	SO3	Loss on ignition	Total
Wt %	54.66	14.65	4.77	4.88	6.00	0.65	1.20	12.56	99.37

Erythrosine (E127) is a synthetic dye of the xanthene class that is commonly used as a food coloring3. Erythrosine is a frequent color used in many different industries, and it has a wide range of uses in industries like cosmetics, medications, and the food business, particularly for biscuits, chocolate, luncheon meat, sweets, and chewing gums4. Erythrosine exhibits good stabilities in neutral and basic solutions and is readily soluble in water (70 g/L). Fig. 1 depicts the erythrosine's chemical structure5.

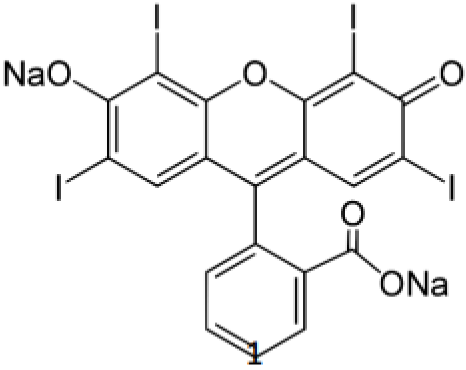

FIGURE 1: Chemical structure of Erythrosine5.

MATERIALS AND METHOD

The adsorbent Surface

The majority of chemical contaminants can be removed from aqueous solutions using clay minerals and their modified derivatives6. Adsorbents made of montmorillonite have been used to capture contaminants such dyes and heavy metal . Bentonite clay mostly consists of montmorillonite, a phyllosilicate that is a member of the smectites family7,8.

Preparation of Erythrosine stock solution

To create the standard solution, one gram of erythrosine dye was dissolved in nonionic distilled water in a glass beaker, and the resulting solution was then diluted in a 1000 ml volumetric bottle. Ranges of varied concentrations (4–60 mg/L) were created for the studies.

Preparation of Bentonite (B)

A sufficient amount of bentonite clay was taken and placed in a glass beaker for the purpose of washing, where the clay was washed with anionic distilled water 12 times to get rid of all impurities suspended in the surface. The surface was dried in a laboratory oven at 100°C for four hours. The dried surface was ground by electric grinder. Through a sieve with a granular size (≤75 µm) the bentonite is sieved. It kept in a plastic container for the purpose of the study

Determination of λmax for Erythrosine dye

A standard solution was created to measure the erythrosine's maximum wavelength (λmax). Within the range of (190-800) nm, it was being recorded in a visible and ultraviolet spectrophotometer. The dye's highest absorption is (526) nm. For the measurement, a quartz cell with a thickness of 1 cm was employed. Fig. 2. shows the absorption spectrum of erythrosine dye.

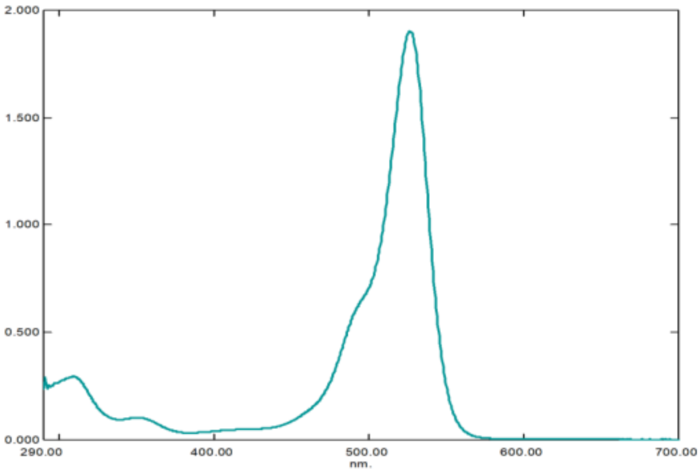

FIGURE 2: UV-visible absorption spectrum of erythrosine dye.

RESULTS AND DISCUSSION

Effect of the adsorbent weight surface (Bentonite) on the adsorption

The influence of the bentonite's weight was investigated using an initial dye concentration of 60 mg/L against a series of various weights of the adsorbent surface, 0.05-0.7g, and at 298 K, in order to identify the appropriate weight for erythrosine dye adsorption on the surface of the bentonite. From observing the results in Fig.3, it was discovered that the number of active sites prepared for adsorption of E127 increased, and that by increasing these sites the efficiency of the adsorbent surfaces are able to remove the E127 dye from its aqueous solution better . The percentage of removal (%R) increased continuously with the increase in the weight of the bentonite 0.05-0.2g, which was equal to 36.68-38.51%. The percentage of removal then starts to stabilize at the appropriate weight of 0.3g of the bentonite, which was equivalent to 44.43% 9.

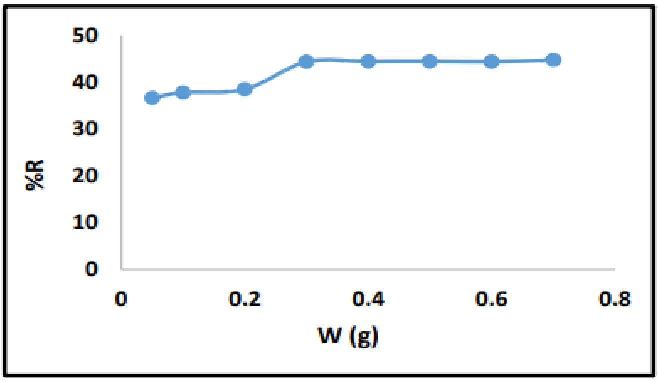

FIGURE 3: Effect of the weight of the bentonite for adsorption OF E127 dye.

Impact of the equilibrium time With an initial dye concentration of 60 mg/L and at various temperatures (298,308,313) K, granule size (≤ 75µm), and the optimal weight of bentonite 0.3g the effect of the equilibrium time of bentonite with the aqueous solution of E127 dye has been studied . Fig. 4. Shows the effect of time on the adsorption process of the adsorbent surface bentonite . The results showed that 40min is the equilibrium time required for the E127 dye adsorption process on bentonite .

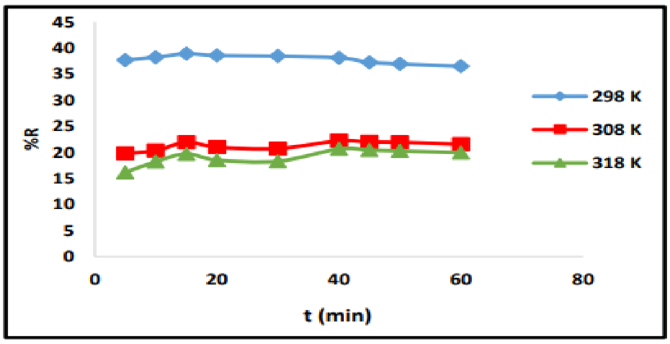

FIGURE 4: Effect of equilibrium time on the amount of E127 dye adsorbed on the surface of bentonite.

Adsorption Kinetics Models studies

Three alternative kinetic models pseudo-first-order (PFO), pseudo-second-order (PSO), and the Elovich kinetic model were used to study the adsorptive behavior of erythrosine (E127) on bentonite. The linear form of PFO is given as follows10.

$$\ln(q_{e-}q_t) = -K_1 t + \ln q_e \qquad \text{——— 1}$$

The adsorption capacity at time is represented by qt(mg/g), the adsorption capacity at equilibrium is represented by qe(mg/g), and the rate constant for adsorption (PFO). is K1(min -1). K1 is determined by the slope of the in (qe-qt) vs. time (t) linear plot, as seen in Fig. 5.

((PSO) constants determined by the formula (2)11.

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{t}{q_e} \qquad \text{——2}$$

The rate constant for the adsorption for the (PSO) process is K2 (g mg-1. min -1). K2 is calculated from the intercept of the linear plot in t/qt vs. time (t) according to Fig. 5.

Constants determined ∝ , β by the equation that are (Elovich) constants (3)12.

$$q_t = \frac{1}{\beta}\ln(\beta \propto) + \frac{1}{\beta}\ln t \qquad \text{——3}$$

∝ denotes the desorption process constant in units of (mg.g-1.tim-1) , β denotes the initial adsorption rate constant in units of , (g.mg-1). Additionally, both β and ∝ are computed from slope and intercept of plotting at versus Ln t in Fig. 5.

Table 2's findings and a study of the correlation coefficient (R2) values for each of the three Kinetic models demonstrate that the PSO is applicable to the first model since the correlation coefficient (R2) values are high and the theoretical and practical values of (qe) are converging13. Because of thevery few (R2) values and that the actual (qe) values did not approach the theoretical values, the PFO and Elovich Kinetic models could not be used14,15.

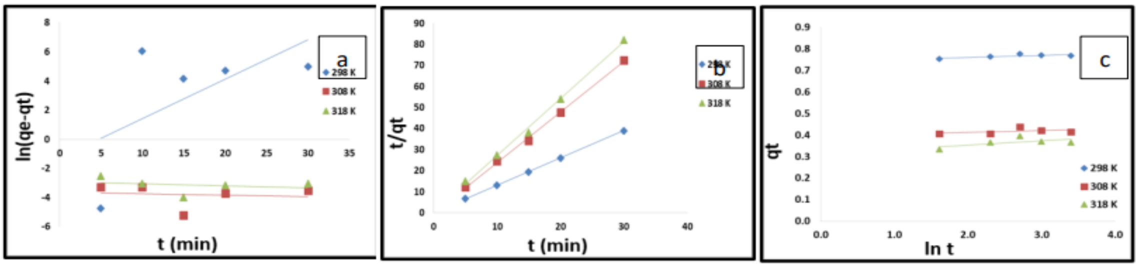

FIGURE 5: The PFO (a), PSO (b), Elovich (c) kinetic models for the adsorption of the E127 dye on the surface of the bentonite at different temperatures.

TABLE 2: The values of the kinetic constants of the adsorbent bentonite surface at different temperatures.

T (K)	First Pseudo order			Second Pseudo order			Elovich		
	K1 (min-1)	**qe (mg/g)**	**R2**	**K2 (g.mg-1.min-1)**	**qe (mg/g)**	**R2**	**β (g.mg-1)**	**∝ (mg.g-1.min-1)**	**R2**
298	-0.2714	0.2737	0.3513	24.4822	0.7722	0.9999	101.0101	3.37474*1030	0.5563
308	0.0082	0.0256	0.0097	41.2449	0.4173	0.9982	126.5822	5.34314*1019	0.1649
318	0.0142	0.0542	0.0689	39.9971	0.3712	0.9965	50.7614	169805.1	0.3873

The adsorption isotherms

The optimal adsorbent surface weight (B) (0.3 g), particle size (≤75µm), equilibrium time (40 min), and a series of varied E127 10-45 mg/L concentrations and temperatures (298,308,318)K were employed to analyze the adsorption isotherms. The Fig. 6. drawn shows the relationship between (qt (mg/g)) and (Ce (mg/L)) isotherms of adsorption of E127 dye on B at various temperatures.

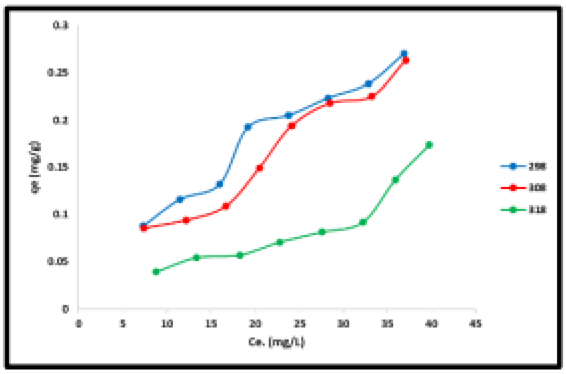

FIGURE 6: Isotherm of the adsorption process of E127 dye on B

Fig.6 shows the isotherm of dye adsorption on surface E127 of type (S3), which is based on Freundlich's principles for the adsorption process. According to Giles classification, this shows that the adsorption process takes place with various forces on the adsorbent surface. As the covered portion of the adsorbent surface increases, the amount of the adsorbent material on the surface decreases. By use of the adsorbate16. The adsorption process also takes place perpendicular to the adsorption surface, which means that the adsorbate will occupy a lesser fraction of the adsorbent surface sections. As a result, the adsorption will be high since there is an empty space on the surface17.

Calculation of activation energy

The activation energy values were studied through the values of the PSO adsorption velocity constant at different temperatures as the most applicable model among the three kinetic models, and the activation energy for surface B was calculated according to Arrhenius equation18.

$$\ln \mathrm{K}_2 = \ln A - \frac{Ea}{RT} \text{ ———————— } (4)$$

The Fig.7 shows the values calculated between (lnK2) versus (1/T) for surface B and at the temperatures used in this study (298,308,318) K.From the slope and intersection of the equation, the values of the activation energy and the Arrhenius coefficient of the surface (B) were calculated.

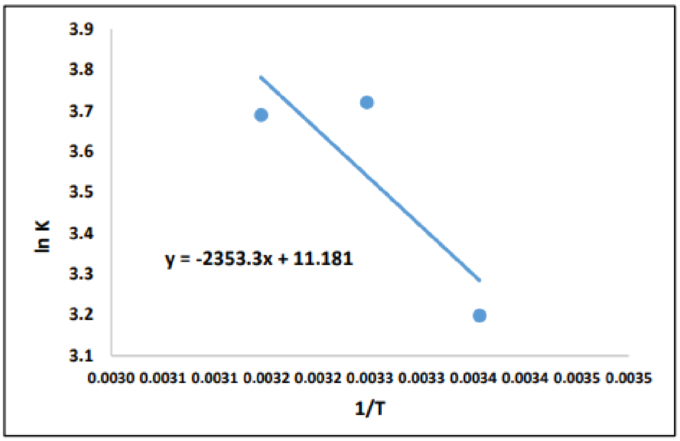

FIGURE 7: Arrhenius equation for determining the activation energy of the pseudo-second-order model for the adsorption of E127 dye on bentonite at different temperatures

From the follow-up, the value of the activation energy for the surface of bentonite is equal to (19.5653kJ/mol), and this indicates that the adsorption here is a physical adsorption19, and the interaction is weak between the surface and the dye.

Adsorption Isotherm Models

Three models of the adsorption process isotherm were applied to the obtained data, and Table 3 shows the values of the three models constants, Freundlich, Langmuir, and Temkin, as well as correlation coefficients. Fig. 8 displays the isotherm models for the adsorption procedure. Equation (5) was used to derive the Freundlich Isotherm adsorption model constants (Kf (mg/g)) and (n)20.

$$\log(q_e) = \log(K_f) + (1/n)\log(C_e) \qquad \text{———}(5)$$

The formula (6) was used to derive the qemax (mg/g) and the Langmuir constants KL(L/mg)21.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{e\,max}} + \frac{1}{q_{e\,max}K_L} \qquad \text{———}(\,6)$$

The formula (7) was used to account the Temkin constants (L/mg) and BT(J/mol)22.

$$q_e = B_T \ln K_T + B_T \ln C_e \qquad \text{———}(7)$$

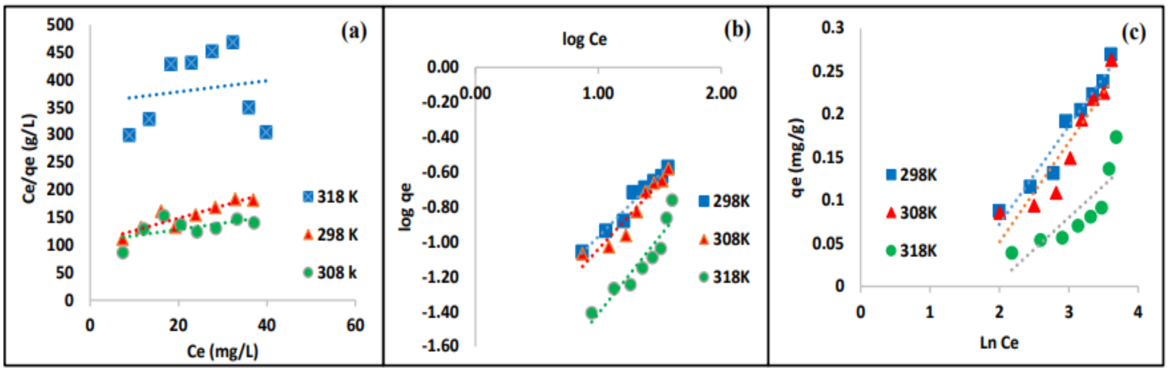

FIGURE 8: Langmuir (a), Freundlich (b), Temkin (c) isotherm for the adsorption of the E127 dye on the surface of the B at different temperatures.

TABLE 3: The values of the isotherm constants of the adsorbent surface B at different temperatures.

T (K)	Freundlich			Langmuir			Temkin		
	Kf (mg/g)	n	R2	KL (L/mg)	qemax (mg/g)	R2	KT (L/mg)	BT (J/mol)	R2
298	0.0209	1.4132	0.9687	0.0218	0.4424	0.8243	0.2558	21.7521	0.9495
308	0.0155	1.3054	0.9189	0.0109	0.8697	0.3329	0.2108	22.0751	0.8759
318	0.0051	1.1307	0.8768	0.0028	0.9942	0.0256	0.1467	35.6795	0.7174

Table 3 demonstrates that values of (n) constrained between (1-10) demonstrating that adsorption is controlled by physical forces, and Freundlich's lsotherm equation is highly relevant to the adsorption process in this experiment. Additionally, the Freundlich constant (Kf) for the adsorbent surface (B) falls as the temperature under investigation increases, supporting the exothermic nature of the adsorption process. And the adsorption process occurred on heterogeneous surfaces with a range of adsorption energy locations23.The results in Table 3 show that the Langmuir model does not fit due to the relatively weak linear correlation coefficient at the same temperatures tested24. Temkin's model is also only partially relevant since the surface correlation coefficient is less than 0.9 at all temperatures25.

Calculating thermodynamic functions

Understanding the behavior of the adsorption process and computing thermodynamic functions (such as standard enthalpy (ΔH°), Gibbs free energy (ΔG°), and standard entropy (ΔS°) depend critically on the effect of temperature on adsorption. Table 5 displays the values of the thermodynamic functions for the adsorption of an E127 dye on B26. To determine the values of the thermodynamic functions at each temperature, the equilibrium constant for the E127 dye adsorption process on the adsorbent surface (B) was calculated using equation (8)27.

$$K_{eq} = \frac{qe * w(g)}{Ce * V(L)} \quad \text{———} \quad (8)$$

Plotting Fig. 9 between lnKeq and 1/T from table 4 to according to the equation 9 for computing ΔH° and ΔS°. where the intercept is represented by ΔS°/R and the slope by (-ΔH°/R)28.

$$\text{Ln Keq} = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R} \quad \text{———} \quad (9)$$

TABLE 4: Thermodynamic values of the adsorption of E127 dye on the adsorbent surface of the ES at different temperatures.

Adsorbent	T	1/T (K-1)	Keq	Ln Keq
Bentonite	298	0.0034	0.2677	-1.3178
	308	0.0032	0.2349	-1.4488
	318	0.0031	0.1075	-2.2303

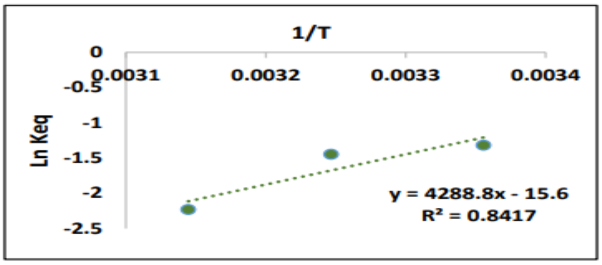

FIGURE 9: Vant Hof's equation for adsorption of E127 dye on the adsorbent surfaces of B .

Equation (10)29 is used to compute the change in the Gibbs free energy.

$$\Delta G^\circ = -RT\ln K_{eq} \quad \text{———————} \quad (10)$$

TABLE 5: values of the thermodynamic equilibrium constants for adsorption of E127 dye on the adsorbent surface of bentonite and at different temperatures.

Adsorbent	T (K)	ΔG° KJ/mole	ΔH° KJ/mole	ΔS° J/mole.k
Bentonite	298	3.2649	-35.6571	-129.6984
	308	3.7099		
	318	5.8965		

The exothermic character of the adsorption process is shown by the enthalpy of the adsorption process on the adsorption surface (B), and the enthalpy values were less than (40 KJ/mol), confirming physical adsorption30. It is evident by looking at the negative entropy values that the process of dye adsorption on the surface is regular and not random. Positive Gibbs free energy values for the E127 dye adsorption on B show that the adsorption process is non-spontaneous31.

CONCLUSIONS

Erythrosine dye was adsorbed by bentonite in this experiment. The results of the applied kinetic constants revealed that the (PSO) model was the best fit. in addition from being compatible with the Freundlich isotherm. The negative ΔH° value show up that the adsorption process is exothermic, and value less than (40 KJ/mol), indicate values of ΔH° that the adsorption process is physical, and the negative value of ΔS° indicated a decrease in randomness, in addition to the positive ΔG° values, indicating that the adsorption process is non-spontaneous.

Author's declaration

I hereby confirm that all the Figures and Tables in the manuscript are ours. Besides, the Figures and images, which are not ours, have been given permission for re-publication attached with the manuscript.

CONFLICTS OF INTEREST

None.

Ethical clearance

The project was approved by the local ethical committee in University of Baghdad.

Authors Contribution

S S.M and R A.M certify that we have participated title of MS (Kinetic and thermodynamic study of adsorption of an industrial food dye using Iraqi clay) in different roles as follows: Conception, design, acquisition of data, analysis, interpretation, drafting the MS, revision and proofreading

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