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Thermodynamic And Kinetic Of Eriochrome Black-T Adsorption Onto Yemeni Palm-Date Stones

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Thermodynamic And Kinetic Of Eriochrome Black-T Adsorption Onto Yemeni Palm-Date Stones

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Abstract

Removal of eriochrome black-T (EB-T) dye from aqueous solutions was performed by adsorption onto Yemeni palm-date stones. The adsorption isotherm was found to follow the Langmuir model. Two simplified kinetic models including pseudo-first order and pseudo-second order equation were selected to follow the adsorption processes. Kinetic studies showed that the adsorption followed pseudo-first order kinetic model. Various thermodynamic parameters such as ΔH = -3465.3 J/mole and ΔS = -10.1 J/K/mole. ΔG was founded to be -4495.5, -2195.2, -2235.7 and -45.39 J/mole at 298, 318, 328 and 338 K respectively, the maximum adsorption capacity was equal to 142 mg/g. The results in this study indicated that the raw Yemeni palm-date stones could be employed as an effective adsorbent for the removal of eriochrome black-T from aqueous solutions.

Keywords: Date stones, eriochrome black-T, adsorption, kinetic.

Introduction:

Dyes are important hazardous substance found in textile, pharmaceutical, and plastic industries [19]. Waste water from food coloring rubber , plastics and cosmetics are polluted by dyes [6, 23]. The presence of very low concentration of dyes in these effluent (less than 1ppm for some dyes) is highly visible and undesirable [10, 24]. Some dyes are also carcinogenic and mutagenic [22]. Dyes very stable to light, temperature and microbial attack, making them recalcitrant compounds [8].The largest class of dyes are azo compounds i.e. molecules with one or several azo (N=N) bridge slinking substituted aromatic structures [15].The eriochrome black – T is an azo dye, used widely both in textile and in research and teaching laboratories primarily as metallochromic indicator in titration complexation to determine the water hardness[13,17]. A complex chemical structure of eriochrome black-T offers a greater resistance to photodegradation, water, as well as certain chemical reagents ,impairing the removal or reduction of its color during the contaminated waste water treatment [8]. This dye is hazardous as such and its degradation products like Naphtaquinone are still more carcinogenic [14].Various treatment methods for remove dyes from waste water were applied. The separation methods can be divided into physiochemical, chemical and biological methods [4, 26]. Adsorption process is one of the effective techniques that have been successfully employed for color removal from waste water. Physical characteristic of the adsorbent such as surface area, porosity, size distribution, density and surface charge have high influence in the adsorption processes [21]. Although commercial activated carbon (AC) is the most widely used adsorbent for dye removal, it is too expensive [7]. Recently agricultural waste biomass have been investigated intensively adsorbent for removal of pollutant from aqueous solution. Because of these materials are cheaper, renewable and abundantly available [2]. Consequently, numerous low-cost alternative adsorbent have been proposed including chemically modified sugarcane bagasse lignin [11], coffee husk-based activated carbon [3], rice husk [25], synthetic calcium phosphate [1], natural untreated clay [16], fruit stone [20].

Dates stone (DS) as one of the best candidate among the agricultural waste because it is cheap and quite abundant. Therefore, it is recycling or reutilization is very useful [18]. A literature survey showed that only few papers have raised the removal of EB-T[12,8]. The main objective of this work is to study and evaluate the adsorption performance of locally derived date stones for the removal of EB-T from aqueous solutions to avoid environmental pollution.

Materials And Methods:

Materials:

I. Adsorbate: Eriochrome black-T dye was chosen in this study because of its known strong adsorption onto solids, its recognized usefulness in characterizing adsorptive material [9], and is often serves as a model compound for removing azo organic contaminants and colored bodies from aqueous solutions. Eriochrome black-T is a heterocyclic aromatic chemical compound with ($C_{20}H_{12}N_3O_7SNa$) as molecular formula and a molecular weight of 461.41 g/mol. The structure of eriochrome black -T is given in Fig.(1).

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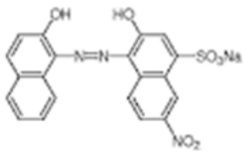


Fig.(1): Eriochrome Black -T Structure

II. Adsorbent: Yemeni palm-date stones were used as adsorbent. Stones as received were first washed several times with water to get rid of impurities, dried, crushed using disk mill and sieved. Fraction of average particle size of 250 µm was selected for the study. The content of moisture and ash were 9.5% and 2.6% respectively. The bulk density was 0.67 g/ml .

Adsorption isotherms:

The equilibrium isotherms of EB-T adsorption on date stones were determined by performing adsorption tests in 100 ml Erlenmeyer flasks where 50 ml of Eriochrome Black-T solutions with different initial concentrations (0.5, 1, 2, 5, 7, 10, 20 mmol/l) was placed in each flask. The pH of the solutions was equal to (3.92). A 0.5 g of date stones, with particle size of 250 µm, was added to each flask and placed on a magnetic stirrer with a thermostat to control the temperature to reach equilibrium. Then the samples were filtered and the residual concentrations of EB-T in the filtrate were analyzed by a UV-Visible Spectrophotometer (Jasco V-730) at maximum wave lengths of 573 nm. λmax was determined by performing a scan on a EB-T solution sample by the spectrophotometer. A calibration curve of absorptivity versus EB-T concentrations from 0.02to 0.2mmol/l in deionized water was constructed as shown in Fig.(2). The relationship is represented by straight line equation (Absorptivity = 4.320C+0.042). The correlation factor is R2= 0.996 over the studied range of concentrations.

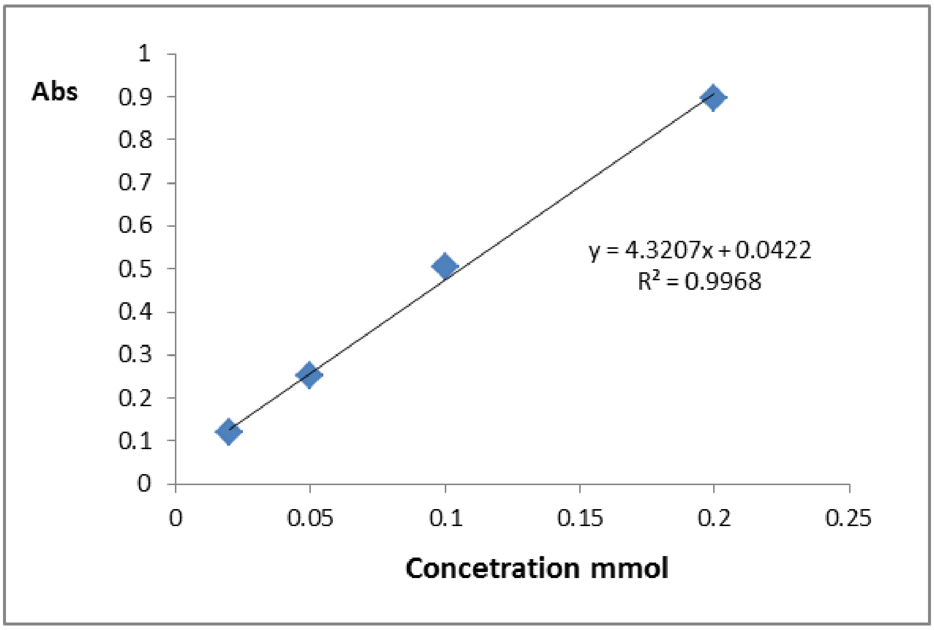


Fig.(2): Standard calibration curve

The uptake (qe) of EB-T at equilibrium was calculated by the following expression:

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

Where Co and Ce(mg/l) are the initial and equilibrium concentrations of EB-T solution, V (l) is the volume of solution, and W (g) is the weight of date stones. Two famous isotherm equations, namely the Langmuir equation (2) and Freundlich equation (3), were applied to fit the experimental isotherm data of EB-T adsorption on date stones. The equations can be written as:

$$q_e = \frac{q_L\, K_L C_e}{1 + K_L C_e} \qquad (2)$$

$$q_e = K_F\, C_e^{1/n} \qquad (3)$$

Where qL(mg/g) is the Langmuir maximum uptake of EB-T per unit mass of date stones, KL(l/mg) is the Langmuir constant related to rate of adsorption, KF [(mg/g).(l/mg)]1/n and n are Freundlich constants which give a measure of adsorption capacity and adsorption intensity, respectively, Least-squares regression program based on Hooke-Jeeves and Gauss-Newton method was used to analyze experimental data. This program gave the parameters of each equation and the agreement between experimental and calculated data in terms of correlation coefficient R2.

Adsorption kinetics:

The procedure used for kinetic tests was identical to that used for equilibrium experiments. The aqueous samples were taken at present time intervals, and the concentrations of EB-T were similarly measured. The uptake of EB-T at time t, qt (mg/g), was calculated by following expression:

$$q_t = \frac{(C_o - C_t)\, V}{W} \qquad (4)$$

Where, Ct (mg/l) is the liquid-phase concentration of EB-T solution at time t (min). Pseudo-first order model (6) and pseudo-second order model (7) were used to analyze the kinetic data. These models can be expressed as:

$$\ln(q_t - q_e) = \ln(q_e) - K_1\, t \qquad (5)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e} \qquad (6)$$

Where qe and qt(mg/g) are the uptake of EB-T at equilibrium and at time t (min), respectively, K1(1/min) is the adsorption rate constant of first-order equation, K2(g/mg.min) is the rate constant of second-order equation.

Adsorption thermodynamics:

Thermodynamic behavior of the adsorption of EB-T on date stones was evaluated by the thermodynamic parameters including the change in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS). These parameters are calculated from the following equations:

$$\text{In}\,(K_d) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (7)$$

$$\Delta G = -RT\, \text{In}\,(K_d) \qquad (8)$$

$$K_d = \frac{q_e \cdot (W/V)}{C_e} \qquad (9)$$

Where, R is the universal gas constant (8.314 J/mole.K), T is temperature (K), and
Kd is the distribution coefficient for the adsorption.

Results and discussion:

Effect of contact time on the adsorption:

The effect of contact time on adsorption of EB-T onto date stones is shown in Fig.(3). The figure presented uptakes versus contact time with different initial concentration (0.5, 1, 2, 5, 7, 10, 20 mmol/l). The results shows that the uptake of adsorbent increases rapidly with the increase of contact time at the first 30 min and remained constant after an equilibrium time was reached in about 60 minutes at lower concentrations (0.5 ,1and 2 mmol/l) and 90 minutes at higher concentrations from5 to 20 mmol/l. This is because at low concentrations the ratio of surface active sites to the total dye molecules in the solution is high and hence all dye molecules may interact with the adsorbent. The fast adsorption at the initial stage may be due to the higher driving force making fast transfer of EB-T ions to the surface of date stone particles and the availability of the uncovered surface area and the remaining active sites on the adsorbent [5]. Maximum uptakes of 425 mg/g with 20 mmol/l initial concentration of 4.98 pH and 5 g/l adsorbent dose.

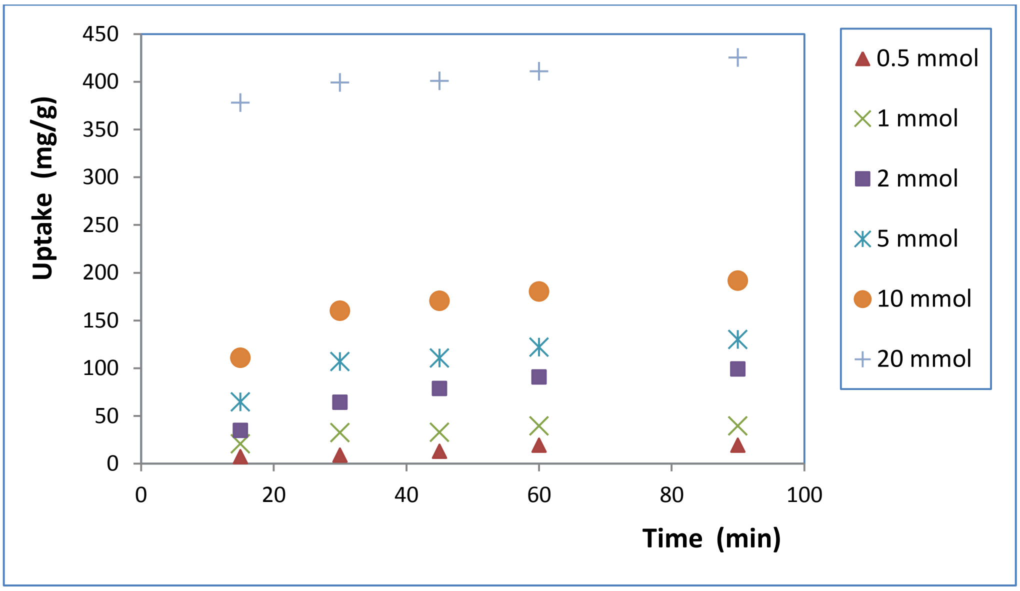


Fig.(3): Uptakes of EB-T versus time

Effect of temperature:
The effect of temperature on adsorption of EB-T onto date stones shows in Fig.(4).The figure presented uptake versus temperature (298, 318, 328 and 338 K) at fixed initial concentration (10 mmol/l) with contact time equal to two hours. It can be seen increasing in temperature from 298 to 338K leads to decrease in adsorption uptake from 198 to 116 mg/g. This indicate that the adsorption of EB-T is exothermic process in nature . It is explained that at higher temperature apart of dye leaves the solid phase and re-enters the liquid phase.

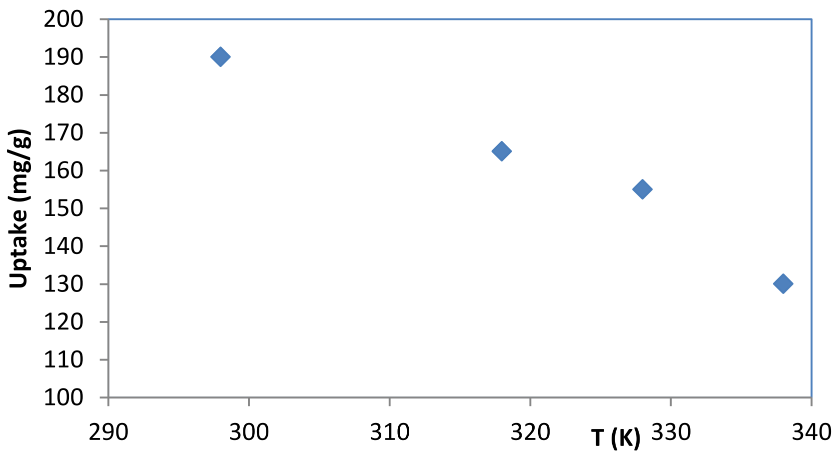


Fig.(4): Uptakes of EB-T versus temperature

Adsorption isotherms:
The experimental equilibrium data for EB-T adsorption on date stones, calculated from Eq.(1), are fitted with Langmuir Eq.(2) and Freundlich isotherms Eq.(3) . The results are represented in Fig. (5) in the form of 1/qe versus 1/Ce and in Fig (6)in the form of Log qe versus Log Ce . The comparison of correlation coefficients (*R*2) of the linearized form of both equations indicates that the Langmuir model shows higher R2 values and yields a better fit for the experimental equilibrium adsorption data than the Freundlich model of EB-T adsorption onto date stones. The maximum adsorption capacity was 142 mg/g with 10 mmol/l initial concentration of EB-T, pH equal to 4.98 and 0.5 g/l adsorbent dose.

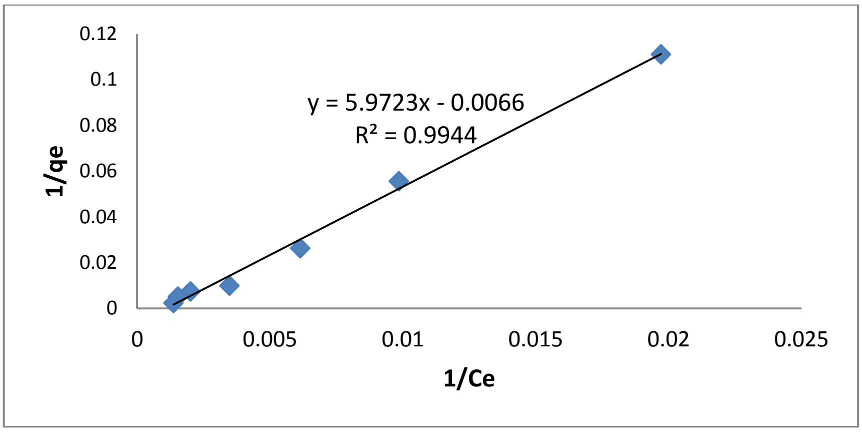
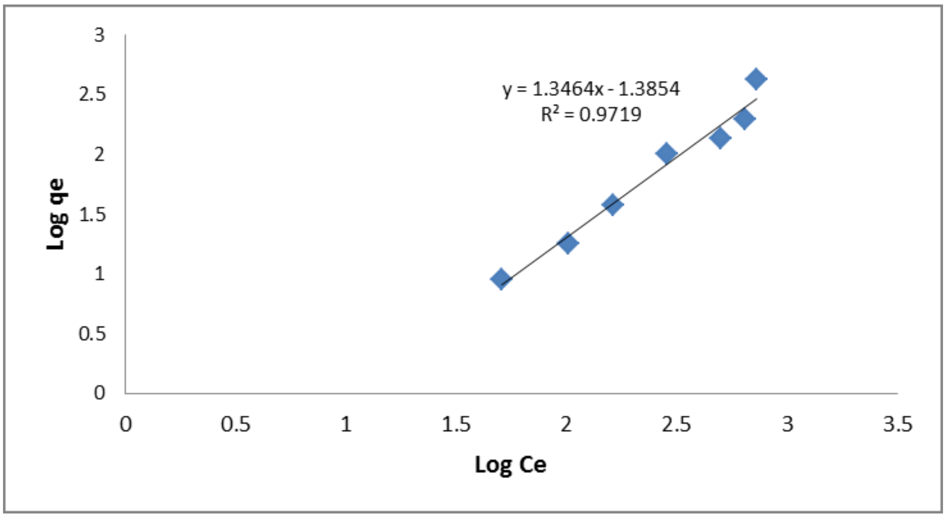


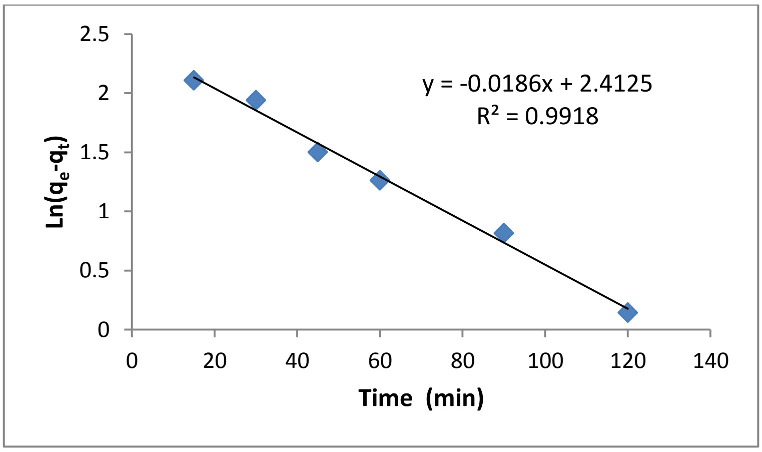
Fig.(5):Langmuir isotherm for EB-T adsorption on date stones



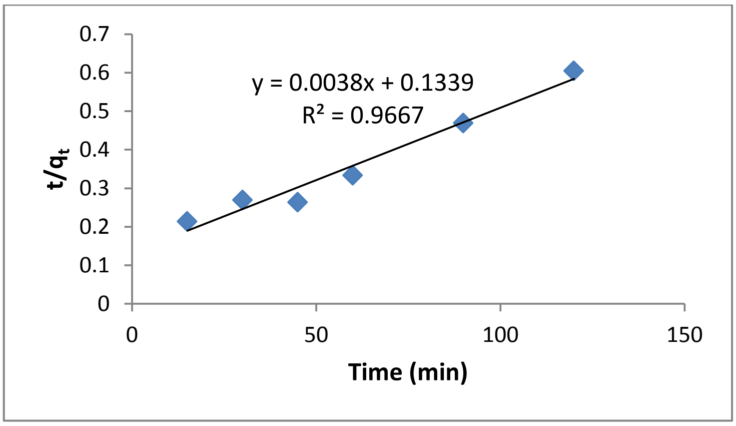
Fig(6):Freundlich isotherm for EB-T adsorption on date stones

Adsorption kinetics:

The experimental kinetic data for EB-T adsorption on date stones are fitted with pseudo-first order and pseudo-second order models Eqs.(6,7), and presented in Figs.(7,8) respectively with10 mmol/l initial adsorbate concentration and 298 K. The linear plot of ln(qe-qt) versus time for pseudo-first order equation with R2= 0.9918 as shown in Fig.(7). The linear plot of t/qt versus time for pseudo-second order equation as shown in Fig.(8). was obtained with R2=0.9667. It can be clearly seen that the adsorption of EB-T on date stones follows pseudo-first order kinetic model with higher R2 value better than pseudo-second order equation.



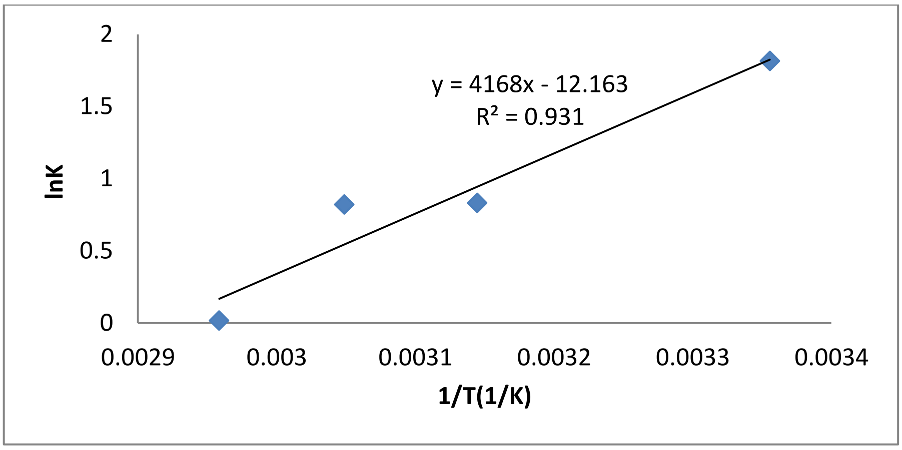
Fig(7):pseudo-first order kinetics for adsorption of EB-T at 298 K



Fig(8):pseudo-second order kinetics for adsorption of EB-T at 298 K

Adsorption thermodynamics

According to Eqs.(8,9) the ΔH and ΔS parameters for adsorption of EB-T can be calculated from the slope and intercepts of the plot of In(Kd) versus 1/T Fig.(9). The obtained values for Gibbs free energy change (ΔG) were -4495.5, -2195.2, -2235.7 and -45.39 J/mole for EB-T adsorption on date stones at 298, 318, 328 and 338 K respectively. The adsorption process is thermodynamically spontaneous nature at all temperature due to negative ΔG values obtained and show an increase in feasibility of adsorption at every temperature. The ΔH parameter was -34653 J/mole, the negative ΔH value is an indicator of exothermic nature of the adsorption. The ΔS values of adsorption was -101.1 J/mole.K, the negative ΔS value suggests an decrease in the randomness at sorbate-solution interface during the adsorption process. Thermodynamic parameters of EB-T adsorption on date stones were put in the table 1.



Fig(9):The plot of In(Kd) versus 1/T

Table 1: Thermodynamic parameters for adsorption process

T (K)	298	318	328	338
ΔG (J/mole)	-4495.5	-2195.2	-2235.7	-45.39
ΔH (J/mole)	-34653	____	____	____
ΔS (J/mole.K)	-101.1	____	____	____

Conclusions:
The adsorption of EB-T from aqueous solution onto date stones was studied. The uptake of adsorbent increases with the increase of contact time and was reached equilibrium in about 90 minutes. The equilibrium data were best described by the Langmuir isotherm model, with maximum adsorption capacity 142 mg/g. The kinetics of the adsorption process was found to follow the pseudo first-order kinetic model. On the other hand, the thermodynamic parameters indicate that the adsorption process is exothermic and spontaneous in nature at all temperature. As a result of this study, Yemeni palm-date stones can be used without any pretreatment as an effective adsorbent for the removal of eriochrome black-T from aqueous solutions.

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دراسة ترموديناميكية وحركية امتزاز الأيروكروم بلاك على نوى التمر اليمني

عبدالرحمن يوسف وحود سوسن عوض المقدي

الملخص

درست عملية إزلة الصبغة أيروكروم بلاك من المحاليل المائية بالامتزاز على نوى التمر اليمني. وجد أن أيزوثيرم الامتزاز يتبع معادلة لانجمير. أنجزت حركية الامتزاز على معادلتي الرتبة الأولى والثانية ووجد أن الحركية تتبع الرتبة الأولى. حسبت العوامل الثيرموديناميكية الأنتالبي والأنتروبي والطاقة الحرة للامتزاز. تدل نتائج الدراسة على أنه يمكن توظيف نوى التمر اليمني بشكل فعال لإزالة صبغة الأيروكروم بلاك من محاليها المائية.

الكلمات المفتاحية: نوى التمر، أيروكروم بلاك، الامتزاز، حركية.