Adsorption of Bromo Phenol Red Dye from Aqueous Solution by Iraqi Bentonite Clay

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Abstract

This studies deals with investigated the potential of a Iraqi bentonite clay for the adsorption of bromo phenol red dye from contaminated water. Impulse adsorption experiments were performed. The contact time influence of initial dye concentration, temperature, pH, ionic strength, partical size adsorbent and adsorbent dosage on bromo phenol red adsorption are investigated in a series of batch adsorption experiments. Adsorption equilibrium data were analyzed and described by the Freundlich, Langmuir and temkin isotherms equations. Thermodynamic parameters inclusive the Gibbs free energy ($\Delta G^{\bullet}$), enthalpy ($\Delta H^{\bullet}$), and entropy ($\Delta S^{\bullet}$), were also calculated. These parameters specified that adsorption of bromo phenol red onto bentonite was functional, more spontaneous and endothermic with increase of temperatures from 298.15 to 313.15 K.

Keywords: Bentonite clay, bromo phenol red dye, Langmuir, Temkin, Freundlich isotherms, thermodynamic.

Introduction

Many industries use dyes extensively in different operation such as textile, leather tanning, paper, plastic, food processing, cosmetics, printing etc. [1-3]. Numerous dyes are pestilent to some microorganisms which may cause direct consuming or inhibition of their catalytic power textile industry that use dye and pigments to color their out put. Numerous techniques have proposed by various researchers for the treatment of dye effluents [4].The adsorption use the gotten adsorbent for parquet poisoning as a gastric decontaminant.

Common environment instructive recommend low permeability soils, which naturally should contain bentonite as a stamping material in the construction and repair of Garbage dump to ensure the security of ground water from the contaminated.

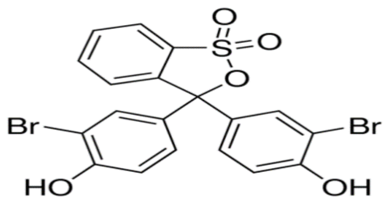
Last few years, bentonite clay was successfully used for the adsorption of metal ions and dyes as of contaminated from water [5,6].

The objective of this paper is to use Iraqi bentonite clay in removing bromo phenol red dye from wastewater under different temperatures.

Experimental

Materials

The bentonite clay used in the present work was supplied from Doakhla site in the west part of Iraq and chemically characterized in the state company of Geological survey and mining – ministry of industry using atomic absorption spectra, the chemical composition of this clay is 54.66% SiO_2, 14.65% Al_2O_3, 4.88% Fe_2O_3, 4.77% CaO, 6.00% MgO, 0.65% Na_2O, 1.20% SO_3 and 12.56% loss on Ignition . bromo phenol red [$C_{19}H_{12}Br_2O_5S$] purchase from Sigma-Aldrich, M. wt =512.17 g/mol, pH range 5.2-6.8 yellow to red. The following Figure shows the chemical structure of bromo phenol red dye.



Sckematic the chemical structure of bromo phenol red dye

The Apparatus

The following apparatus were used in this work.

1- UV- Visible Spectrophotometer double beam (Shimadzu-UV 1800).

2- Labtech Shaking water Bath, Centrifuge tubes, Hettich (EBA- 20).

3- Electronic Balance (KERN) ± 0.0001g.

4- pH meter (Bench pH Trans).

Prepare of Bentonite Clay Powder

The bentonite clay was supplied in powder form; it was washed with excessive amount of deionized water to remove the soluble materials than dried form (3 hours) at 150 $^{\circ}$C. Coal at room temperature and milled after sieved by using the available sieves of nominal size (75, 150, 250 μm).

Calibration Curve

Figure (1) the range of the concentration under study for bromo phenol red was prepared by serial dilution from the standard stock solution (100 mg/L) . Wave length of maximum absorbancy (λ_{max}) for bromo phenol red dye was selected and found (574nm) which agree with preview studies [7].

Method

The time that is sufficient for the bromo phenol red dye adsorption process by bentonite clay to reach equilibrium at certain temperature was found (90 mint) from Figure (2).
Adsorption experiments were carried out in batch system by shaking (0.2gm) bentonite samples with (10ml) of Aqueous solution of range concentrations (5-40 $mg.L^{-1}$) of dye at a certain temperature 25°C.
Constant speed (100 rpm) for the required equilibrium time, the mixtures were discreted by centrifugation at (5000 rpm) (10min), the dye equilibrium concentration was measured by using double beam spectrophotometer.
The adsorbed amounts of bromo phenol red dye were calculated from the concentration in solution before and after adsorption granting to the equation (1).

$$q_e = \frac{(C_\circ - C_e)V}{w} ---------------(1)$$

Where q_e is equilibrium dye concentration on adsorbent (mg/g), C_e and C_o are the equilibrium liquid phase concentration of dye solution (mg/L), and the initial equilibrium respectively, w is the mass of bentonite sample used (mg), and V is the volume of dye solution (L).

Results and Discussions

Effect of Contact Time

The adsorption of bromo phenol red on bentonite as function of time at fixed initial concentration (40 ppm) was studied for bromo phenol red dye at different times. Figure (1), showed that the amount of adsorption (q_e) growing with time and optimum contact times was (90) min of bromo phenol red dye. The amount of adsorbed dye was found (0.56 mg/g).

Effect of Adsorbent Dosage

Adsorption of bromo phenol red on bentonite was studied at different bentonite mass (0.01, 0.04, 0.07, 0.1, 0.17 and 0.29g). Keeping initial bromo phenol red (40 mg/L), temperature (25 $^\circ$C) and contact time (2 hour). Figure (3) showed that the percentage of dye adsorption at beginning increased with the increase of amount of bentonite, but amount of dye adsorbed per unit mass of adsorbent decreased with increase of a mount of adsorbent. The plateau value represents the amount of the adsorbent at a saturation stage, which depends on the physical properties of the clay [8]. The plateau value for bentonite was (0.2g).

Adsorption Isotherms

Freundlich, Langmuir and Temkin models were allawys studied adsorption of dye from aqueous solution onto the bentonite clay.
Freundlich be decided the following model [9]

$$q_e = K_f[Ce]^{\frac{1}{n}} ------------(2)$$

A more suitable form from over equation [10]

$$In\ q_e = InK_f + \frac{I}{n} InCe --------(3)$$

Where q_e is the quantity adsorebed in ($mg.g^{-1}$), C_e is the concentration of solute at equilibirium in the solution (mg/L), (1/n) refer to the heterogeneity factor, and K_f represents empirical Freundlich constant or capacity factor ($L.g^{-1}$). The slop $\frac{1}{n}$ and intercept of ln k. with reference to Langmuir model [11]

$$\frac{C_e}{q_e} = \frac{q_{\max}}{k_L} + \frac{C_e}{q_{\max}} -------------(4)$$

Where q_{max} ($mg.g^{-1}$) is the monolayer adsorption capacity of the adsorbent, (k_L) ($L.mg^{-1}$) is the Langmuir constant, C_e ($mg.L^{-1}$) is the equilibrium concentration of dye in solution and q_e ($mg.g^{-1}$) is the amount adsorbed per unit mass of adsorbent corresponding to complete coverage of sites. A linear plot of C_e/ q_e Vs C_e in Figure (4-b).
The Temkin isotherm consist of agent that taking into the account of adsorbent adsorbate interaction by ignoring the frequently low and high value of concentrations, the model suppose that heat of adsorption of all molecules in the layer would reduce linearly that logarithmic with coverage [12,13]. As implied in the equation its derivation is characterized by auniform distributon of binding energies. The Temkin isotherm can be qualified by equation.

$$q_e = \frac{RT}{b_T} Ink_T + \frac{RT}{b_T} InCe --------(5)$$

Where T is the absolute temperature, R is the universal gas constant (8.314 $J.k^{-1}$ mol^{-1}), k_T is equilibrium binding constant ($L.g^{-1}$) corresponding to the maximum binding energy, and b_T is related to the adsorption heat. The Temkin isotherm plot between In C_e and q_e is shown fiqure (4-c), enables the determination of the slop and intercept these results in Table (1).
Table (1) shows the account of the constant of the Freundlich isotherm at different temperatures, the values of the constant (n) in range (0-1) for all temperature suggest that the adsorption of bromo phenol red on bentonite clay is easily, The values of (k_F) and (n) increase with increase temperature and these less adsorption in high temperature , the values of (R^2 > 0.84) was not higher for all the temperarures evaluated and this indicated the Freundlich model less fitted to experimental date for not all the temperatures. Also Table (1) shows the value of the constant of the Temkin isotherm at different trumpeters. Adsorption of bromo phenol red on bentonite clay which have heat of adsorption (b_T) within (3-12) ($kJ. mol^{-1}$) that indicate that adsorption of bromo phenol red on bentonite clay favorable for the physical adsorption at all different the values of (R^2> 0.89) for Temkin model was more than R^2 for Freundlich model for all tempearures which indicated that model fitted better to experiment data for all temperatures.
As well Table (1) shows the account of the constant of the Langmuir model at various temperatures for adsorption of bromo phenol red dye on bentonite clay is not useful because the values of (R^2 = 0.20-0.46) and this model fitted to experimental data for some the temperatures[9,11].

Effect of Practical Size

The effect of particle size (surface area) of the adsorbent materials on the extent of adsorption was studied by using three different size of the studied adsorbent materials (75 µm, 150 µm and 250 µm). These experiments were performed by using a fixed concentration (40 ppm) of bromo phenol red and the same weight of the adsorbent (0.2g) at 25 °C. Figure (5) showed that there is an increase in adsorption with decreasing their particles size. It is known that the break of the large particles into smaller would lead to increase in the surface area [14].

Effect of Ionic Strength

Figure (6) show The effect of (0.01-0.02M) of NaCl solution containing concentration of dye (40) mg.L^{-1} was added to flasks each containing (0.2g) of adsorbent, ionic strength (I) (0.078, 0.088, 0.098, 0.108, and 0.128M) at 25 $^{\circ}$C the increase in ionic strength between (0.01-0.05M) has decrease the amount of adsorption between (0.487- 0.409mg.g^{-1}) this may be due to solubility of NaCl more than solubility of dye which lead to increase competition between sodium ions and dye molecules for the active sities of bentonite and these lead to decrease adsorption capacity of dye on bentoite.

It found that relationship between the ionic strength (I) and the adsorption quantity (q_e) at a fixed equilibrium concentration is linear relationship as illustrate in Figure (7) , It proposed the following empirical equation between (I), (q_e).

$$q_e=q_e^0 - AI \qquad \text{-----------------------(6)}$$

Where q_e^0 the adsorption at I=zero and A is the Empirical constant for the system according to the slope and straight line intercept for linear relation between (I), (q_e) , Figure (7) and value of R^2 indicate that the equation could be applied for the adsorption of bromo phenol red on bentonite clay surface[15].

Effect of pH

Adsorption experiments were carried out as mentioned previously as function of pH by using a fixed concentration (40 mg/L) of dye in different pH media which were adjusted by using (0.1M). NaOH and (0.1) M HCl and (0.2g) of bentonite clay at temperature 25 $^{\circ}$C, the pH of the system for adsorption was measured by using pH-meter . The premier pH rates of the dye solution effect the flatness of the adsorbent and thus the adsorption of the adsorbed of the charged dye groups on it , in universal the acidic pH system presented good adsorption behavior for the dye solution.

The adsorption of dye excess with lowering of the pH from (1 to 11). As the pH of the system diminution, the protonated flatness groups simplify the adsorption of the negatively charged dye. The number of positively charged sities growing resulting binding sities for anionic dye molecules [16], Figure (8).

Thermodynamics of Adsorption

The Effect of temperature on the adsorption of bromo phenol red on bentonite was studied at (298.15, 303.15, 308.15 and 313.15K) the results were displayed in Figure (9). The result revealed that the amount of adsorption increase from (0.4473-1.2946 mg.g^{-1})with temperatures increase from 298.15K to 313.15K. This increase in amount adsorption with temperatures indicating that the process is endothermic.

This mean the high temperature are favorite for adsorption of bromo phenol red on bentonite clay. Endothermic dye adsorption may be also interpreted as consequence of possible adsorption process. This disposal imputed to adsorption operation. Which means that adsorption process may happen escorted with adsorption process.

The study of the temperature effect on adsorption of bromo phenol on bentonite will help involution. The basic thermodynamic parameters such as Gibbs free energy (J/mol.K) ,enthalpy $\Delta H^{\bullet}$ (J/mol) and entropy ($\Delta S^{\bullet}$) (J/mol.K) of the adsorption process.

The change in free energy ($\Delta G^{\bullet}$) could be determined from the equation [17,18].

$$\Delta G^{\bullet} = -nRTlnk_{eq} \qquad \text{------------------------(7)}$$

Where T is absolute temperatures, R is universal gas constant (8.314) (J.mol^{-1}K^{-1}), and k_e is thermodynamic equilibrium constant for the adsorption process at each temperatures was from the equation.

$$k_{eq} = \frac{q_e.m}{C_e.V} -----------(8)$$

Where C_e the initial concentration of dye solution (mg/L) at equilibrium m(mg), represent the weight of clay that was used, V the volume of solution used in the adsorption process and q_e ($mg.g^{-1}$) is the quantity and adsorbed per unit mass of adsorbent corresponding to complete coverage of sities.

The heat of adsorption ($\Delta H^{\bullet}$) may be obtained from the equation [19].

$$Ink_{eq} = -\frac{\Delta H}{RT} + constant ------------(9)$$

Plotting (Ink_e) versus (I/T) should produce straight line with a slop ($-\Delta H^{\bullet}/R$) Figure (10).The entropy ($\Delta S^{\bullet}$) were also calculated using the equation

$$\Delta S^{\bullet} = \frac{\Delta H^{\bullet} - \Delta G^{\bullet}}{T} -------- 10)$$

Table (2) shows the basic thermodynamic values of bromo phenol red on bentonite. The positive value of $\Delta G^{\bullet}$ at (298,303K) assert the eventuality of operation and the unspontaneous quality of adsorption and the negative value of $\Delta G^{\bullet}$ at (308, 313K) assert the eventuality of the process and spontaneous nature of adsorption [17]. The values of $\Delta H^{\bullet} \geq 112.76$ kJ.mol were positive and indicating that adsorption reaction is endothermic [20]. The positive value of ($\Delta S^{\bullet}$) indicates that the adsorbed species are less ordered on the surfaces. The outcome could be due to the verity , that the entropy variation of the required considered adsorbed layer is always minimal than that of the dissolved solutes[17].

Conclusions

Impulse adsorption studies were managed to correct the effect of different parameters like pH, adsorbent dosage effect, contact time, and temperature on the adsorption of bromo phenol red. Approbating to outcome these conclusions were gained:

1- The quantity of dye uptake was found to increase with increase in contact time

2- The outcomes exhibited that bentonite adsorbent could potentially be applied for a low-cost substance for the adsorption of dye in aqueous solutions.

3- Adsorption isotherm of bromo phenol red dye on the flatness of bentonite obeyed Temkin and Freundlich relations.

4- Results concerning the effect of increasing temperature on the adsorption process revealed that, there was an increase of adsorption for bromo phenol red by bentonite.

5- Results concerning the effect of increasing (ionic strength,pH) of the solution on the adsorption of dye indicated that there was a decrease in the quantity of dye adsorbed on bentonite.

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Table (1) Several isotherms constants for bromo phenol red dye adsorption by bentonite clay

T/K	Freundlich isotherm		
	K_F (L/g)	n	R^2
298	0.004555	0.663218	0.903471
303	0.000842	0.450753	0.959449
308	0.002135	0.364699	0.842979
313	0.066106	0.811243	0.871086
T/K	Langmuir isotherm		
	K_L (L/mg)	a_L (mg/g)	R^2
298	-0.029	-0.263	0.262
303	-0.048	-0.073	0.469
308	-0.099	-0.071	0.340
313	-0.044	-1.496	0.201
T/K	Temkin isotherm		
	K_T (L/g)	b_T	R^2
298	0.321	12.0994	0.979
303	0.247	7.8773	0.890
308	0.325	3.0862	0.950
313	0.665	4.7964	0.894

Table (2) Values of Thermodynamic Functions For The Adsorption of bromo phenol red dye on bentonite Clay Surface at Different temperatures

T/K	bentonite			
	ΔG° (J .mol^{-1})	ΔH° (J. mol^{-1})	ΔS°(J. mol^{-1} K^{-1})	K_{eq} (g. L^{-1})
298	2831.522	112762.8	368.8968	0.319
303	1549.834	112762.8	367.0394	0.541
308	-1734.27	112762.8	371.7437	1.968
313	-2202.52	112762.8	367.3013	2.331

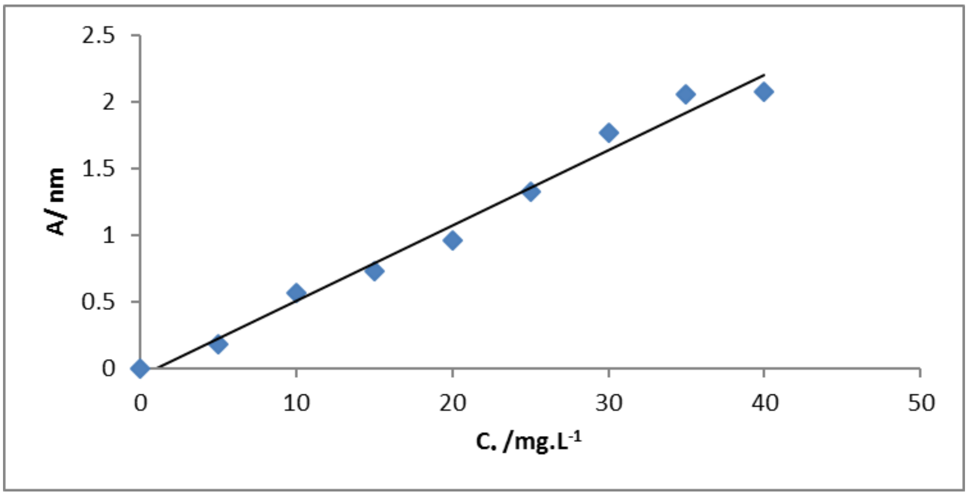

Figure (1) A calibration Curve used to follow the bromo phenol red concentration range (5-40mg/L) before and after adsorption process

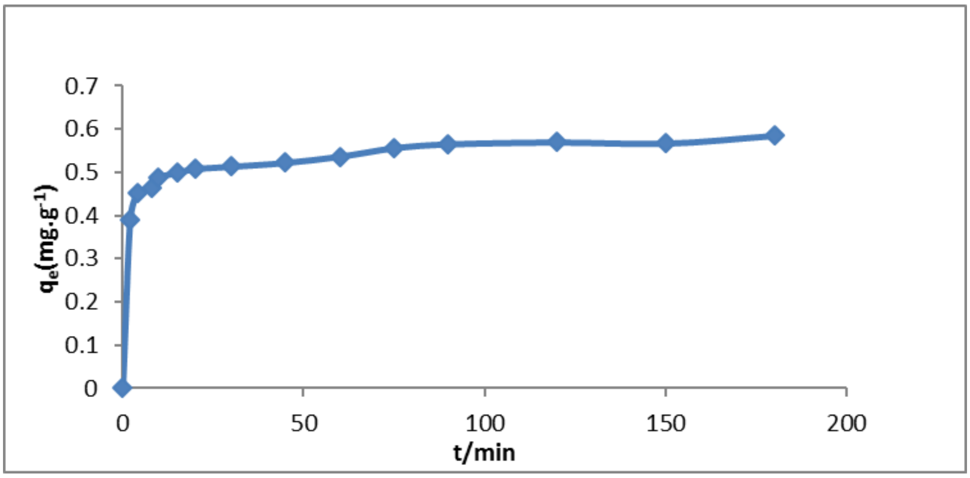

Figure (2) Effect of contact time on the adsorption of bromo phenol red by bentonite clay at certain temperature

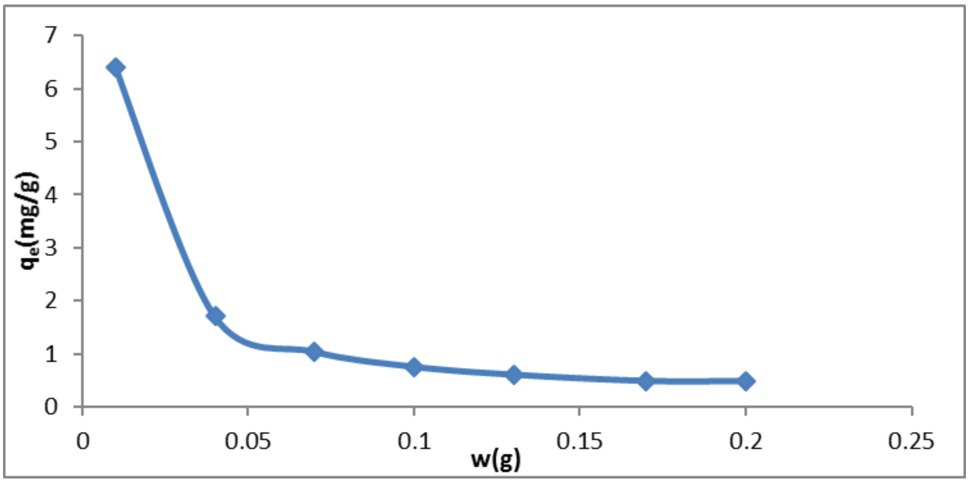

Figure (3) Effect of adsorbent weight on adsorption of bromo phenol red at 25 °C on the bentonite clay surface of different weights

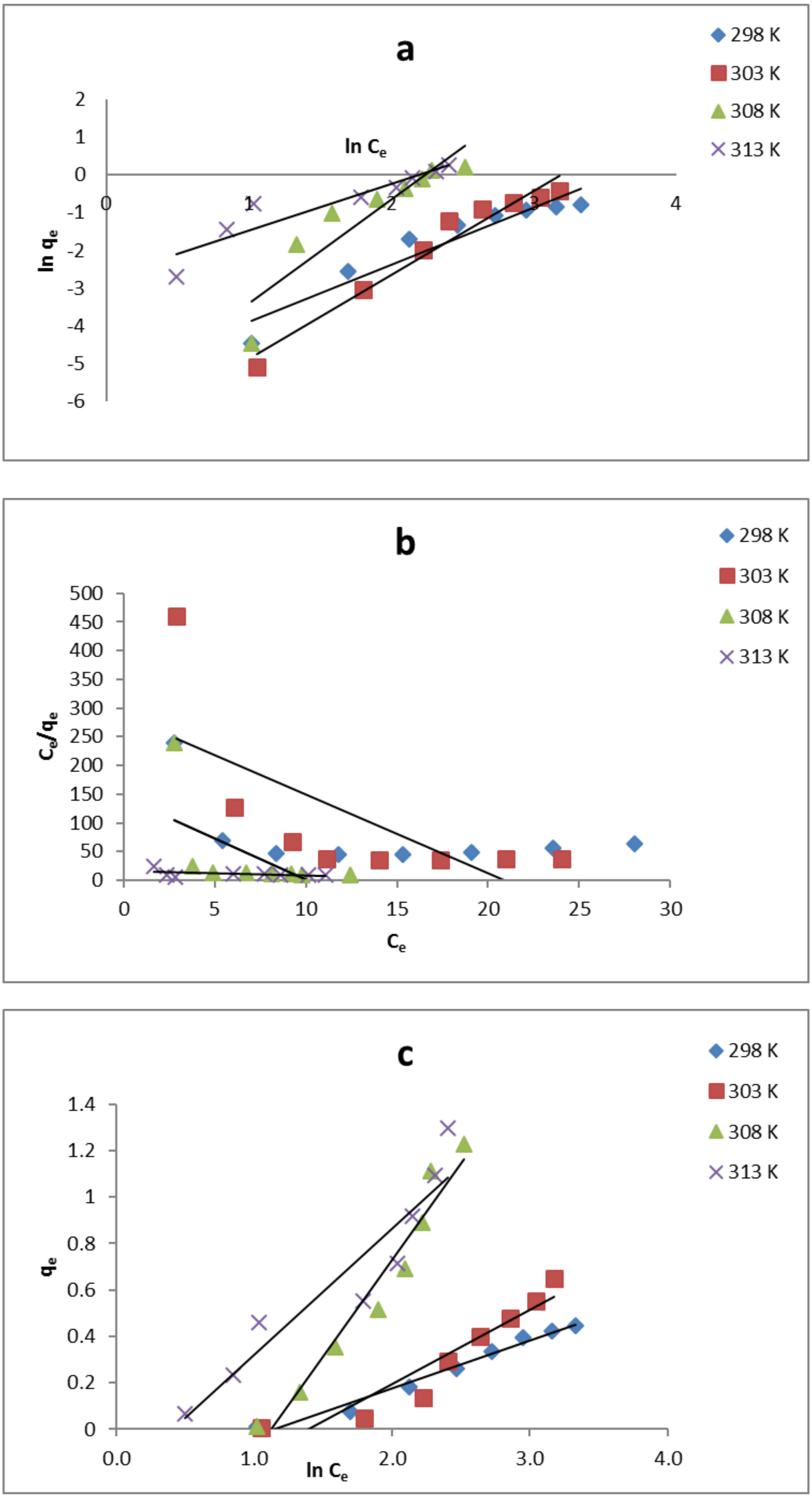

Figure (4) Adsorption isotherms models of bromo phenol red dye on bentonite clay: a- Freundlich, b- Langmuir, c- Temkin at different temperatures

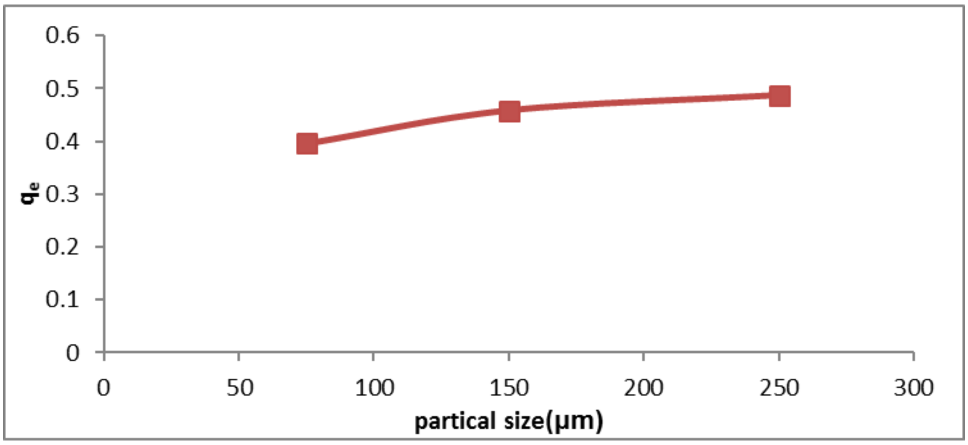

Figure (5) Effect of particle size on the adsorption of bromo phenol red on the bentonite clay surface at 25 °C

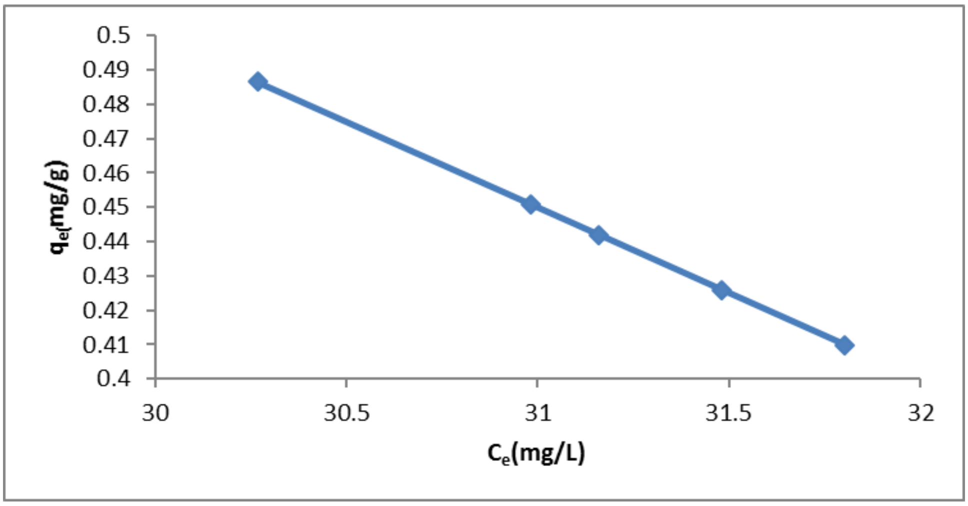

Figure (6) Adsorption isotherm of bromo phenol red dye on bentonite clay in the presence of different concentrations of (NaCl) at 25 °C

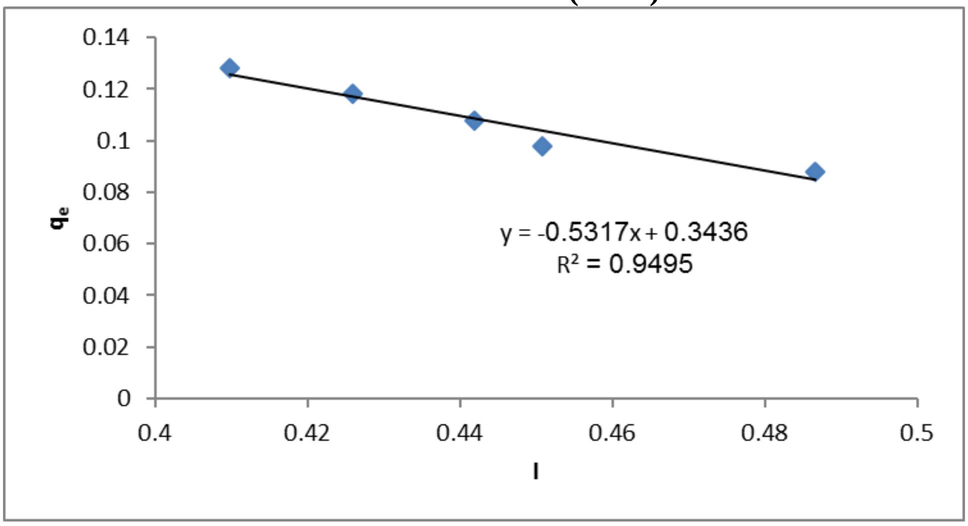

Figure (7) The relationship between the ionic strength and the adsorption quantity of bromo phenol red on the bentonite clay surfaces at 25 °C

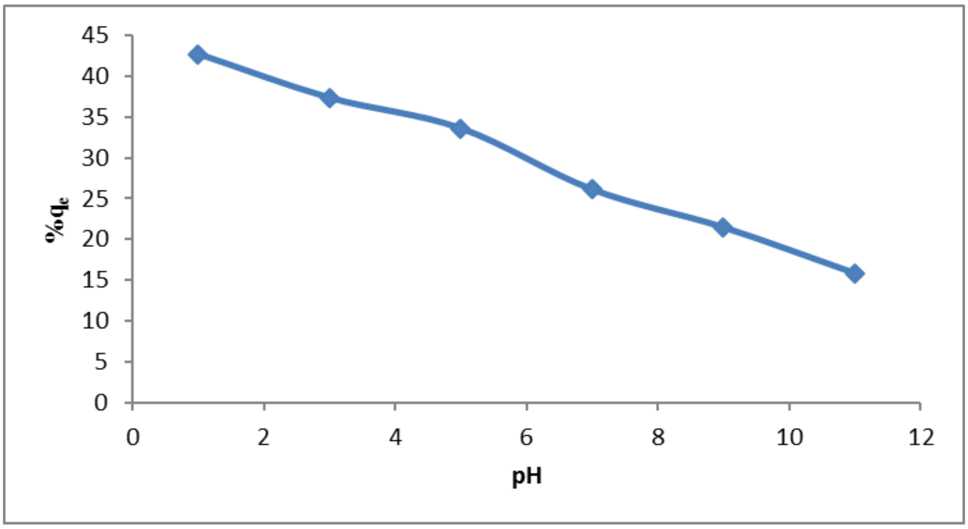

Figure (8) Effect of pH on adsorption of bromo phenol red on the bentonite clay surface at 25 °C

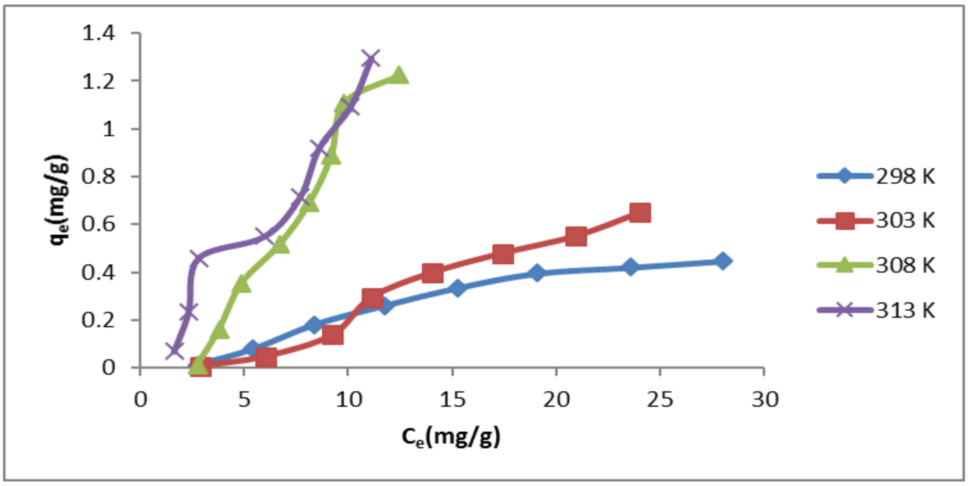

Figure (9) Adsorption isotherms of bromo phenol red dye on bentonite clay at different temperatures

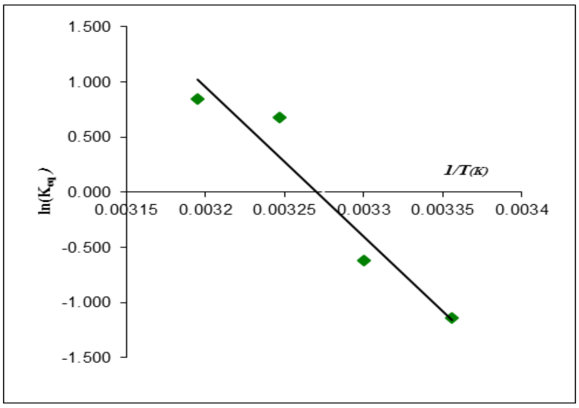

Figure (10) Plot of ln k_e against reciprocal absolute temperature for adsorption of bromo phenol red dye on bentonite clay

امتزاز صبغة برومو الفينول الاحمر من محاليلها المائية بواسطة طين البنتونايت العراقي

زينب عباس حسن الدليمي
قسم الكيمياء / كلية التربية للعلوم الصرفة /(ابن الهيثم) / جامعة بغداد

استلم في:16/اذار/ 2016 ، قبل في:12/حزيران/2016

الخلاصة

في هذه الدراسة قمنا بالتحقيق في احتمالية استعمال طين البنتونايت العراقي لامتزاز صبغة برومو الفينول الاحمر من المياه الملوثة بها ،اجريت تجارب الامتزاز بطريقة الدفعات، قمنا بالتحقيق في كلا من تاثير التركيز الابتدائي للصبغة، زمن التماس، الشدة الايونية، الدالة الحامضية، درجة الحرارة، حجم دقائق السطح الماز و جرعة السطح الماز على امتزاز صبغة برومو الفينول الاحمر لسلسة من تجارب الامتزاز بطريقة الدفعات. معلومات التوازن للامتزاز حللت ووصفت من خلال ايزوثيرمات فريندليش، لانكماير وتمكن. الدوال الثرمودیناميكية التي تتضمن طاقة كبس الحرة (ΔG°) والانثالبي (ΔH°) والانتروبي (ΔS°) حسبت، تدل هذه الدوال الثرموديناميكية على ان عملية امتزاز صبغة برومو الفينول الاحمر على سطح طين البنتونايت تكون سهلة واكثر تلقائية وماصة للحرارة مع زيادة درجة الحرارة.

الكلمات المفتاحية: طين البنتونايت، برومو فينول الاحمر، ايزوثيرمات لانكماير، تمكن، فريندليش، ثرمودانيميك.