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RESEARCH ARTICLE

Bentonite as an Adsorption Surface for Bromothymol Blue Dye from Aqueous Solution

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Abstract

Accomplishment of Adsorption of dye from aqueous solution on the surface of bentonite was done under the following optimized conditions: temperature, initial concentration, contact time and weight surface. Via utilizing the technique of UV-Vis spectophotometry at (λ_{max}= 432 nm) the quantitative estimation of the dye adsorption has been performed. this study has demonstrated that the more increasing of adsorption with the more increasing of temperature from 25 ˚C to 45 ˚C also increasing of clay weight (0.1-1.1 g).calculating thermodynamic parameters like change in the free energy (ΔG), the enthalpy (ΔH), the entropy (ΔS). Results of adsorption isotherms obtained in this study were inconsitence with fitted with Freund lich adsorption isotherm.

Keywords: *Adsorption, Bentonite, Bromothymol blue.*

Introduction

Definition of Bentonitesis a sedimentary rock consisting of a large amount of expandable clay minerals with three-large structures (Smectites) like montmorillonites (80%), beidellite, nontroniteete with minor quantities of non-clay minerals as follows: a quartz. b. calcitec. C. dolomite d. feldspar [1].The properties of Bentonite or Smectite clays such as high cation exchange capacity are readily available and offering a low cost alternative organic compounds removal, these compounds could be produced [2].

The main essential and important application of the surface active substances is as an adsorbent for various water pollutants like metal ions [3, 4]; also different kind's industrial dyes [5-7]. Many industries used Dyes and pigments for coloring their products. Actually The effluents discharged by dye industry characterized by highly colored and represented key cause for pollution of environment [8,9]. The existence of very low concentration regarding effluents is highly visible, undesirable and considered potentially inhibiting photosynthesis. Textiles leather, printing, laundry, tannery, rubber, painting, etc. processes considered the key pollution source of colored effluents, [10].

Bromothymol blue (BTB) is a pH indicator whose chemical formula is $C_{27}H_{28}Br_2O_5S$ and molar mass 624.38 g.mol^{-1} .It's appearance either yellow or blue, respectively [11].

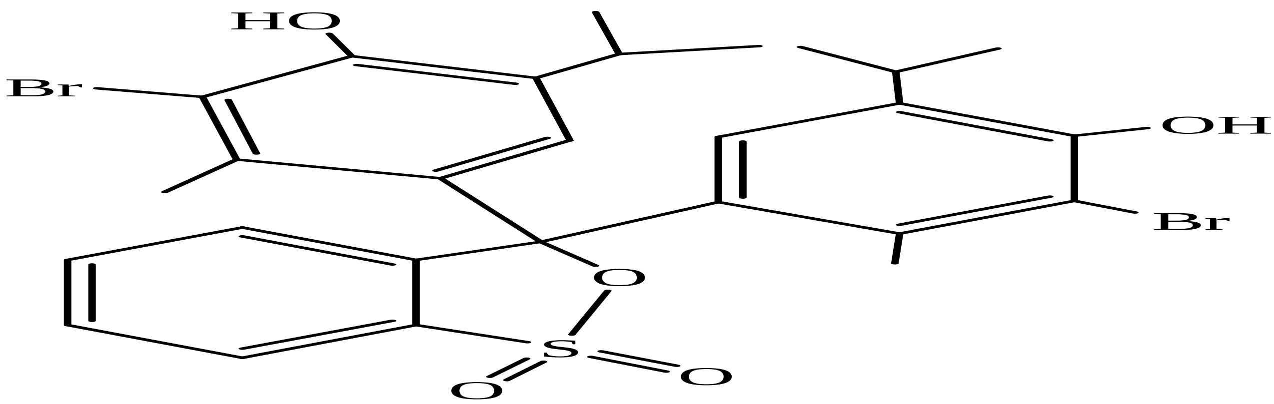

Fig. 1: Chemical structure of BTB

The objective of this paper is to use Iraqi bentonite clay in removing bromothymol blue from wastewater under different temperatures.

Experimental part

Apparatus

- UV-Vis spectrophotometer

A shimadzu double beam UV-Vis spectrophotometer "model UV-1601 Kyoto, Japan" worked at wavelength of "190-1100 nm".

- Shaker bath (Lab tech. Daihaiv. LTD).

- Digital balance.

Digital analytical-Sartorius (Bp 3015-Germany).

Materials

Adsorbents: bentonite was got from (the Geneva Company for Geological Survey and Mining)in Baghdad. Bromothymol blue (BTB) was supplied by Riedel-De Haen AG.

Preparation of Dye Solutions

Using method of dissolving (0.01 g) of dye in buffer solution and then made up to (100 ml) in a volumetric flask with same buffer the Standard stock solution of (100 mg/L) of dye. By serial dilutions for dye between (5-40 mg/L), the solution of different concentration could be prepared.

Batch Experiments

Batch experiments were performed in (100 ml) a volumetric flask included (25 ml) of dye solution with concentration (10 mg/L) and (0.5 g) of adsorbent surface.

Experiments were performed in constant temperature of 25 ˚C to determine the equilibrium concentrations and the effect of contact time on dye adsorption on bentonite. Temperature was set between 25 to 45 ˚C to understand the temperature influence on adsorption process.

Concentration in solution before and after adsorption according to the equation [12]:

$$Qe = \frac{(Co-Ce)V}{w} \quad \text{.......................................} \quad (1)$$

And the percentage of dye removal was determined using the equation:

$$\%\text{ of removal} = \frac{Co-Ce}{Co} \text{ X } 100 \quad \text{.....................} \quad (2)$$

The initial and final concentration in (mg/L), of Co and Ce, V is the solution volume in (L) and W is the clay mass clay samples that were used in gram.

Results and Discussion

Absorption Spectra

The dye of BTB giving maximum absorbance at λ_{max} = 432 nm as shown in Fig. (2):

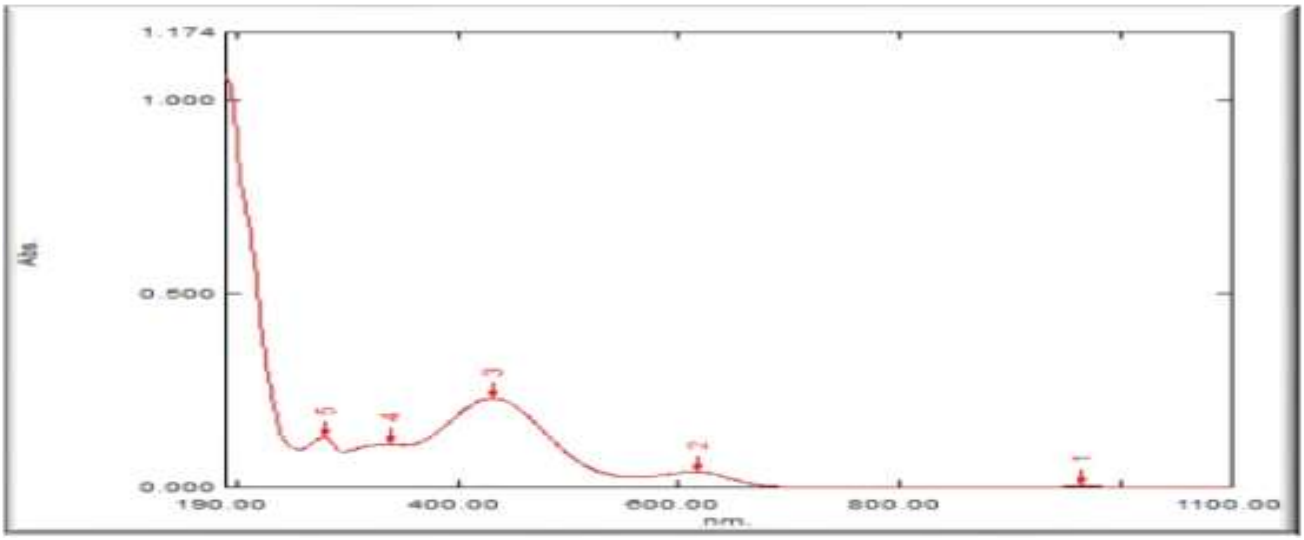

Fig. 2: Absorption spectrum of (10 mg/L) of BTB

Calibration Graph

Depending the conditions described procedure mentioned above we could obtain, a linear calibration graph for BTB is as illustrated in Fig. (3). This illustrated that, Beer´s law is followed along the concentration range of (5-40 mg/L).

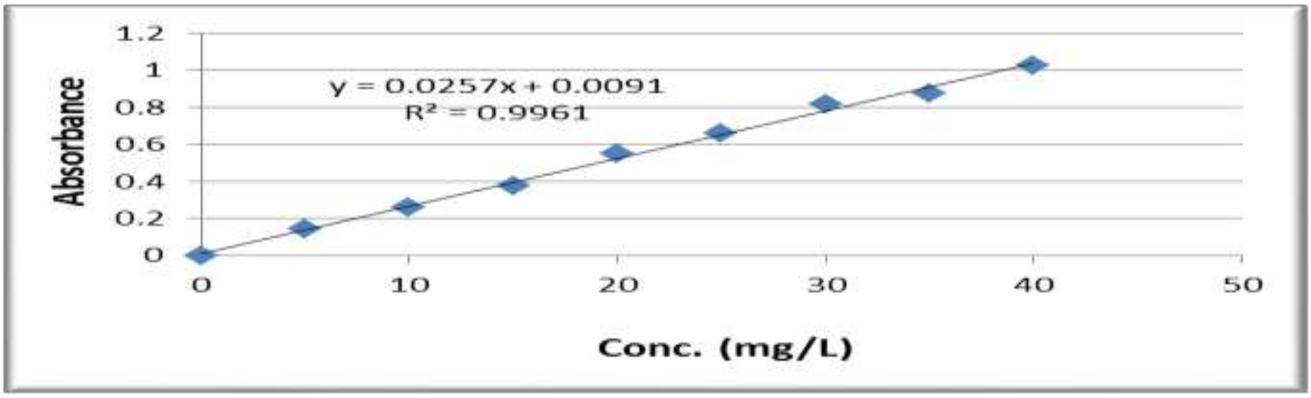

Fig. 3: Calibration graph of BTB

Factors Affecting Efficiency of BTB Adsorption on Bentonite

Effect of Contact Time

The adsorption of BTB on bentonite with time at fixed initial concentration (10 mg/L), (0.5 g), bentonite and 25 ˚C was studied at different times. Fig. (4) Showed that the adsorption increasing with time to reach for contact time (50 min.).

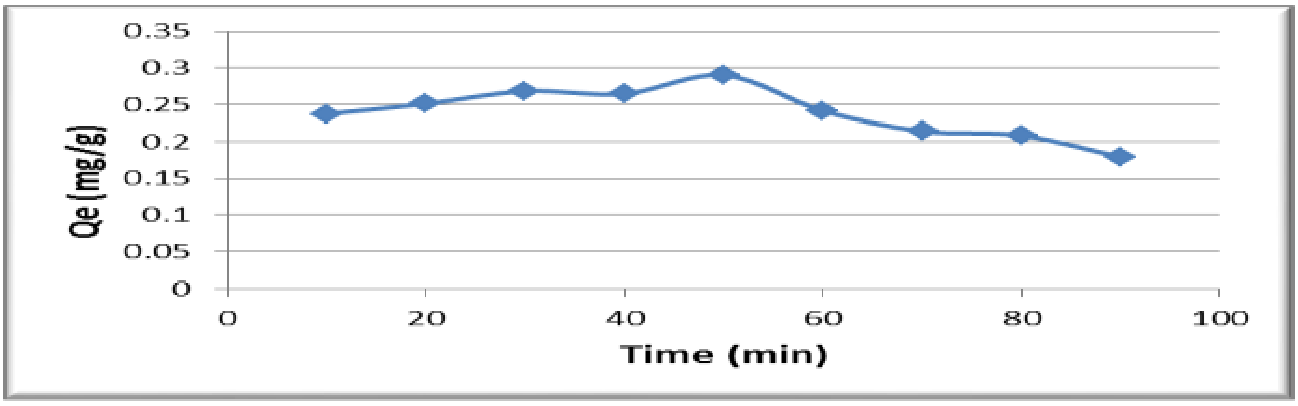

Fig. 4: presentation of contact time effect of the on the adsorption of BTB onto bentonite surface

Temperature Effect

Temperature effect on the adsorption of BTB on bentonite at three different temperatures 25, 35 and 45 ˚C was investigated. The obtained results obtained are summarized in Table (1) and Fig. (5). The equilibrium adsorption capacities slightly increase with an increase of temperature from 25 to 45 ˚C.

Table 1: Illustrates temperature effect on the adsorption of BTB on bentonite

Co	25 ˚C		35 ˚C		45 ˚C	
	Ce	Qe	Ce	Qe	Ce	Qe
5	3.4202	0.0789	2.0972	0.1451	1.0466	0.1976
10	6.6108	0.1694	6.2217	0.1889	5.1322	0.2433
15	10.3463	0.2326	9.7626	0.2618	9.3735	0.2813
20	12.6031	0.3698	12.2140	0.3893	12.1750	0.3912
25	15.9883	0.4505	15.2490	0.4875	12.3307	0.6334
30	19.0233	0.5488	18.1673	0.5916	17.3112	0.6344

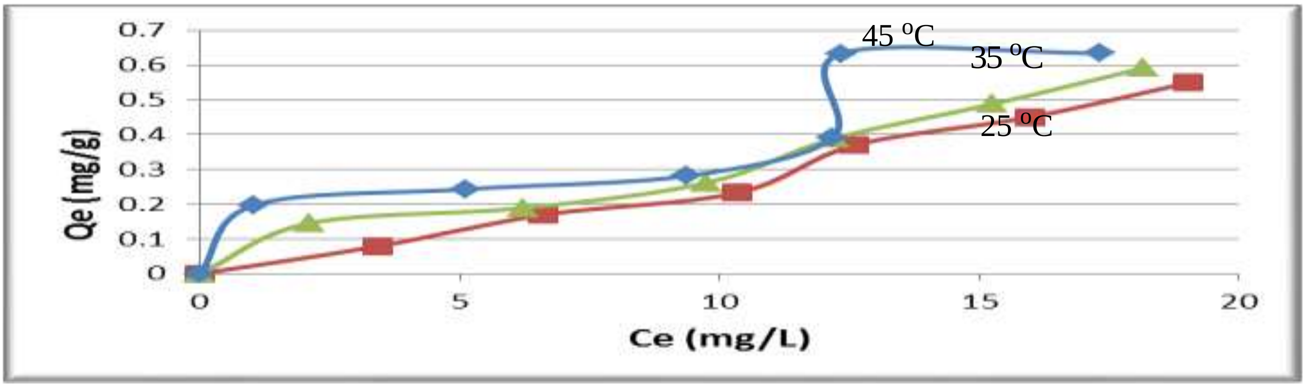

Fig. 5: Illustrates temperature effect on adsorption of BTB onto bentonite surface

Thermodynamics of Adsorption

Changes of Free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were calculated using eqs. (3-5)[13] and are given in Table (2).

$$\Delta G = -RT \ln K_{eq} \quad \text{......} \quad (3)$$

$$\text{Log } K_{eq} = \frac{-\Delta H}{2.303\,RT} + \text{Con.} \quad \text{......} \quad (4)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad \text{......} \quad (5)$$

Where R representes universal gas constant ($8.314\ J.mol^{-1}K^{-1}$), T is absolute temperature.

The positive "ΔH° value" indicates that adsorption reaction endothermic. The ΔG° is positive value enhances the process and the unspontaneous nature of adsorption feasibility. "ΔS° value "is positive because adsorption involves more disorder arrangement.

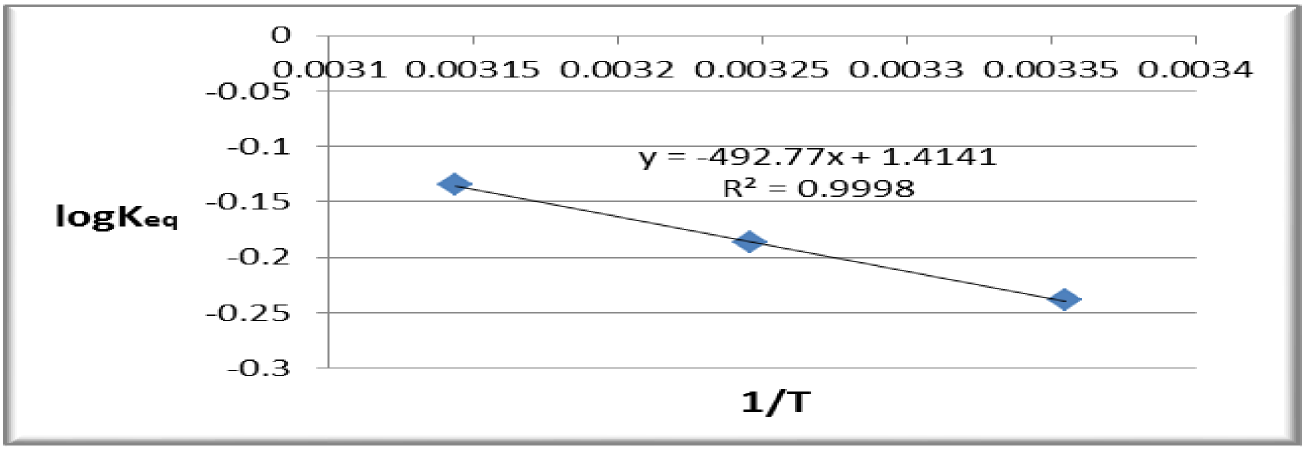

Fig.6: Relation between log K_{eq} and 1/T for adsorption dye

Table 2: Values of thermodynamic functions for the adsorption of dye onto bentonite

ΔH° ($J.mol^{-1}$)	ΔG° ($J.mol^{-1}$)	ΔS° ($J.mol^{-1}.K^{-1}$)
+9435.13	+1362.44	+27.089

Effect of Weight Surface

Dependency of BTB sorption process from different weight of bentonite (0.1-1.1 g) at temperature (25°C).

These results are shown in Fig. (7).The examination of data reveals that sorption percentage increases with increases of weight of bentonite in solution.

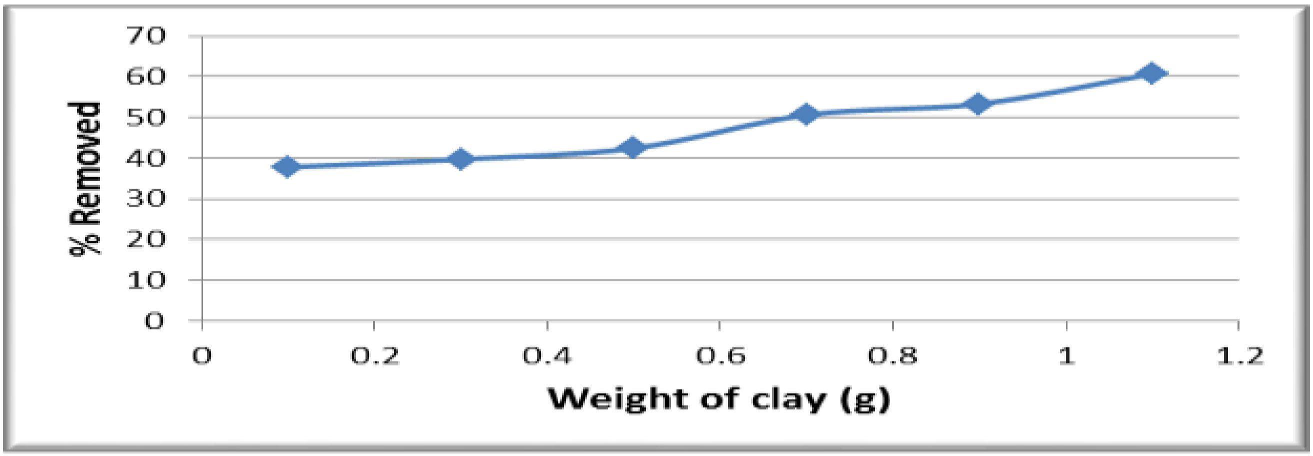

Fig. 7: Effect of weight of clay on adsorption of BTB onto bentonite surface

Adsorption Model

It is important to establish the most appropriate correlation for the equilibrium curves for optimizing the design of an adsorption system for the adsorption of adsorbents. Various isotherm equations such as Freund lich, Langmuir, and Temkin have been used to describe the equilibrium characteristics of adsorption.

Langmuir equation of the linear from can be represented as [14]:

$$\frac{Ce}{Qe} = \frac{1}{K_L q_m} + \frac{Ce}{q_m} \quad \text{......} \quad (6)$$

Where Ce ($mg.L^{-1}$) is the of dye equilibrium concentration in solution, Qe ($mg.g^{-1}$) represented the adsorbed amount per unit mass related to adsorbent, q_m ($mg.g^{-1}$) represents the adsorbent monolayer adsorption capacity and the Langmuir constant K_L.

The Freund lich isotherm is given as[15]:

Log Qe = logK_f + 1/n log Ce ………………. (7)

K_f and n represents Freund lich constant, Qe represented of absorbed adsorbed in ($mg.g^{-1}$) and Ce is the concentration of solute in the solution (mg/L).

The Temkin isotherm has been used in the following form:

Qe = RT/b ln(ACe) ………………………….. (8)

We can express the Temkin isotherm linear form as[16]:

Qe = RT/b lnA + RT/b lnCe ………………. (9)

Where R is constant of gas (8.314 J/mol/K), T is temperature (K).

Results are shown in Table (3) and Fig. (8, 9, 10).The adsorption of BTB fitted Freund lich isotherm.

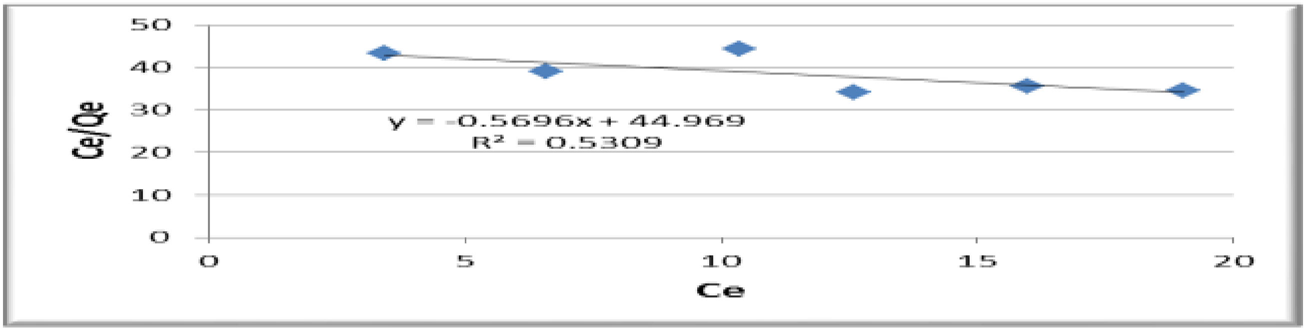

Fig. 8: Langmuir linear adsorption isotherm of BTB

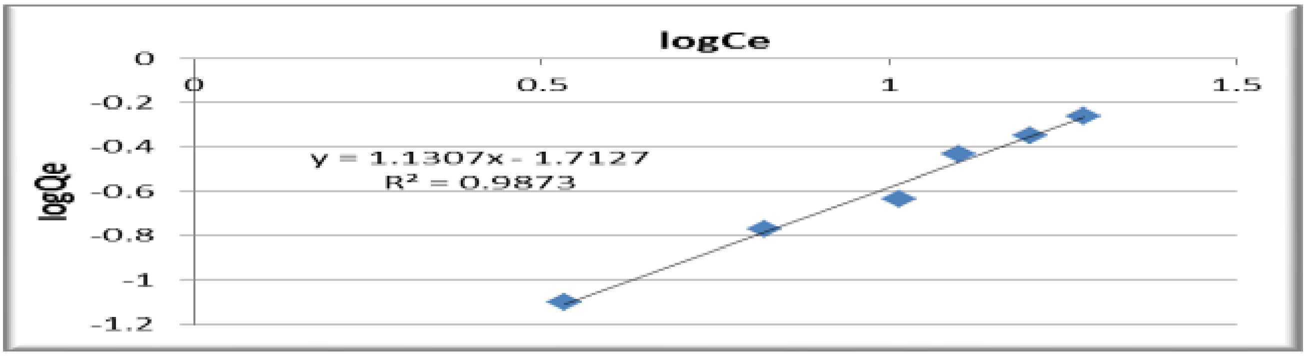

Fig. 9: Freundlich linear adsorption isotherm of BTB

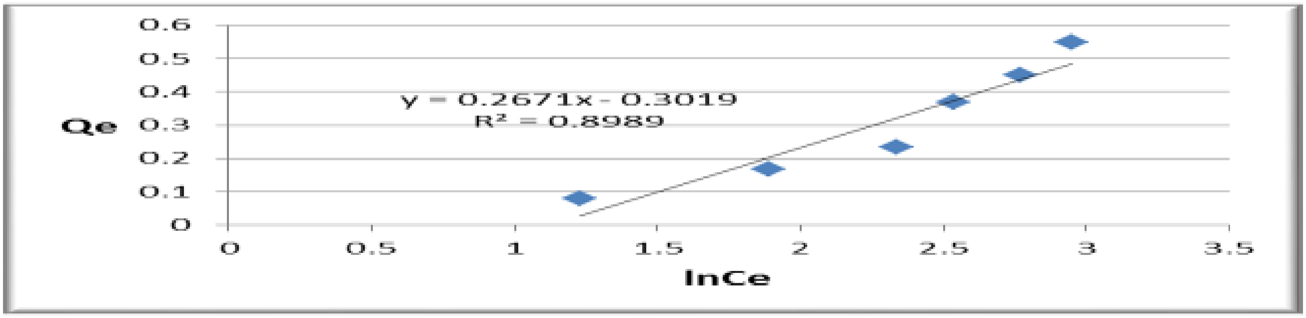

Fig.10: Temkin adsorption isotherm of BTB

Table 3: Isotherm parameters for the BTB dye adsorption by bentonite clay

Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
q_m	K_L	R^2	K_f	n	R^2	A	B	R^2
-1.757	-0.039	0.530	0.0194	0.884	0.987	0.324	0.267	0.898

Ionic Strength Effect

Ionic strength factor has been studied by different concentrations additives of sodium chloride (0.1, 0.3 and 0.5 M) to three (25 ml) solutions of BTB of constant concentration (10 ppm) and (0.5 g) of clay at 25 ˚C. Results are demonstrated in Fig. (11).The graph illustrated that the adsorption increases along with increasing of Na Cl concentration.

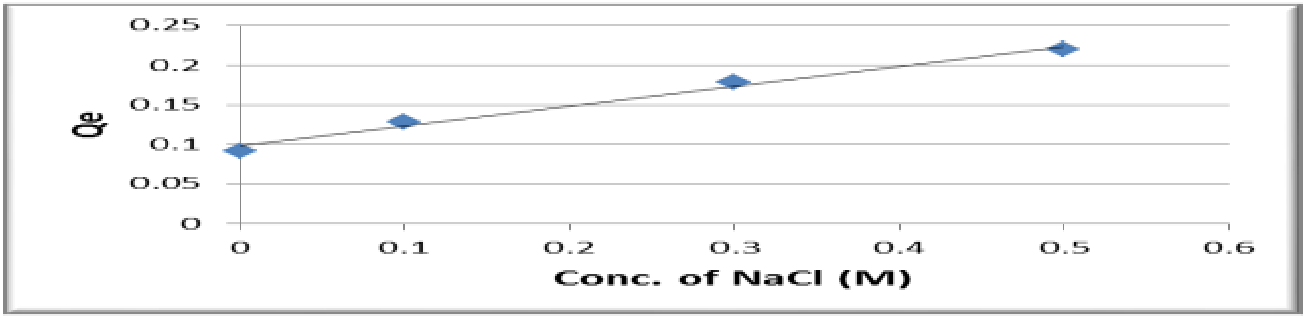

Fig.11: Presentation of ionic strength effect of on adsorption of BTB onto bentonite

Conclusion

The current study demonstrated that batch adsorption process for removal of dye onto bentonite is dependent largely on initial concentrations, contact time, weight of clay and temperature. The adsorption of dye onto bentonite follows Freund lich isotherm.

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