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Adsorption and Thermodynamic Study of Direct Blue 71 Dye on to natural Flint Clay from Aqueous Solution

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Abstract

The remove of direct blue (DB71) anionic dye on flint clay in aqueous solution was investigated by using a batch system for various dye concentrations. The contact time, pH, adsorbent dose, and temperature was studied under batch adsorption technique. The data of adsorption equilibrium fit with isotherm Langmuar and Freiundlich ,when the correlation coefficient used to elucidate the best fitting isotherm model. The thermodynamic parameters such as, ΔH^o ,ΔS^o and ΔG^o. Thermodynamic analysis indicated that the sorption of the dyes onto Flint clay was endothermic and spontaneous.

Key words: adsorption, dye, Langmuir model, Freundlich model, thermodynamic, clay

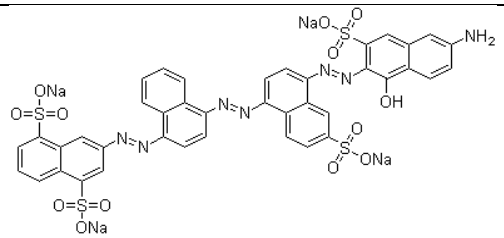
Introduction

Environmental pollution control has been a concerned issue in many countries and the most concerned environmental pollution is air pollution and wastewater pollution [1].There are much than 100,000 different synthetic dyes parameter on the market, produced in over 700,000 tons annually worldwide[2] . Wastewater pollution gives bad effects on public water supplies which can cause health problems such as diarrhea [3]. Major pollutants in textile wastewater are high acidity, heat and other soluble substances main pollution in textile wastewater came from dyeing and finishing processes[4-5].Many treatment processes included physical , chemical, and biological have been employed to treat various municipal and industrial wastewaters for example chemical [6].Biological, food[7]. Peanut hulls[8], maize bran[9]. Many researchers suggested that the potential exists for the use of highly concentrated sunlight in the removal of dyes from wastewater [10-11].Industrial facilities take clean water from nature and re-contaminated water into water sources where these industrial pollutants effect the physical properties of natural water such as the intensity , color and taste , etc. [12] , have attracted the attention of several investigations for the removal of dyes. In the present work, the ability of flint clay to remove anionic dye, by adsorption, has been considered. The effects of contact time, initial dye concentration and pH on the amount of colour removal were investigated. The equilibrium experimental data were fitted into Langmuir and Freundlich equations to determine the best isotherm correlation.

Materials and Methods :
The adsorbate

Direct Blue The anionic dye (DB71), was used without further purification, λmax = 594 nm. C.I 34140. The DB stock solution was prepared by dissolving accurately weighted dye in distilled water to the concentration of 20 mg L^{-1}. Solutions were prepared by diluting the DB71 to different initial concentrations from 2 to20 mg L^{-1}. The chemical name and their properties of this dye listed in Table 1

Table(1). The chemical name and properties of DB71

Propertie		Structure of dye
Emprical formula	$C_{40}H_{23}N_7Na_4O_{13}S_4$	 Tetrasodium 3-[[4-[[4-[(6-amino-1-hydroxy-3-sulphonato-2-naphthyl)azo]-6-sulphonato-1-naphthyl]azo]-1-naphthyl]azo]naphthalene 1,5-disulphonate
Molecular Weight	1029.87	
Class	**Azo**	

The clay

The adsorbent used in this study was Flint clay and obtained from the General Company for Geological Survey and Mining[13]. The particle size between(150-212) micrometer . This Flint clay was used in all experiments and analysis.

Table(2) The specification of flint .

Constituents	SiO_2	$Al_2 O_3$	$Fe_2 O_3$	$Ti O_2$	CaO	MgO	L.O.I
Wt %	38-45 %	35-41.5	1.4-3 %	0.5-1.96 %	0.2 %	0.1 %	13.4-15.1 %

Batch mode adsorption studies

Dye solution was prepared by dissolving in volumetetric flask an accurately weighted dye in distilled water at a concentration of (0.025) gm in 1000 ml of water to give 25ppm for dye and . The solution was prepared and diluted solutions of different concentrations of dye were prepared in concentrations, (3-15) Part per million. Dilute (0.1%) HCl or (0.1%) NaOH was used for pH adjustment in order not to increase the volume of samples too much and keep the error created by pH adjustment in a reasonable range. The different parameters such as dye concentration, clay dose, temperature and pH were studies . solution containing 100 mL day and 0.5gram , clay was taken in 250 mL capacity conical flask and agitated at 200 rpm in water bath shaker at predetermined time intervals. The adsorbate solution was centrifuge at (3000 rpm) and for (15min.). The concentration of the sample is measured by spectrophotometric determination. The amount of DB adsorbed was calculated from the following equation [14-15].

$$q_e = C_0 - C_e / m * V \quad \text{--------------} \quad (1)$$

$$R\% = (C_0 - C_t)/C_0 * 100 \quad \text{----------} \quad (2)$$

where C_0 and Ce are the initial and the equilibrium concentrations (mg/ L) of DB71 in solution, respectively. q_e is quantity of DB71 adsorbed on the adsorbent at the time of equilibrium (mg/ g), m(g) is the weight of clay , and v (L) , the solution of volume taken for experiment. The λ max (594nm) ,the spectrum for 16 mg/l DB 71 adsorption was shown in Fig.1. The calibration curve was established as a function of DB71 dye concentrate on at different pH. Figure .2

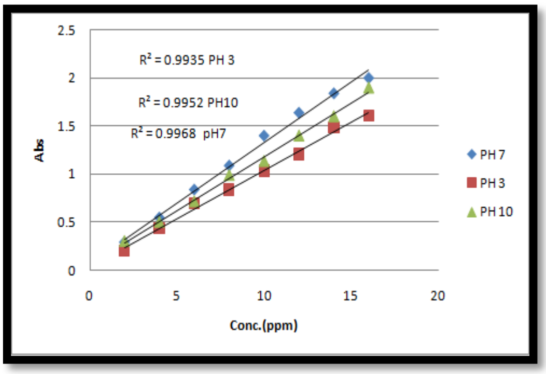


Fig (1) The scan spectrum curve of DB dye

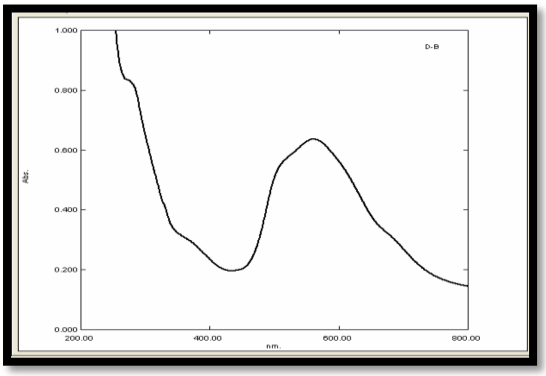


Fig (2) The calibration curve of DB71 dye at different pH

The Effect of variable parameters

The experiments were accomplishd in shaking conical flasks with 100 ml dye at constant temperature shaker .The amount of adsorbent and pH of the solution were kept constant . Sample of 10(ml) was carefully with down at every (5)minutes until the equilibrium of adsorption process has been reached. The study of adsorption was conducted from (20-40)C^0 .and take initial pH values at 3-5-7-8 and 10 . Adsorbent dosage used in this study was in the range(0.1 to1) g/ L.

Results and Discussion

The Effect of agitation time Equilibrium Time

The effect of this factor on the amount of DB71 adsorbed per unit of adsorbent was investigated at constant pH and concentration . Figure (3) and Table 3 show the results of equilibrium time for dye for 10 Part per million at 20 ºC and pH =7 .

Table(3): values of q_e with Time of 10 ppm of DB71 PH=7

Time, min	Q_e, mg g^{-1}
5	9.500
15	9.660
25	9.687
35	9.711
45	9.800
55	9.995
65	9.889
75	9.990
85	9.993
95	9.993

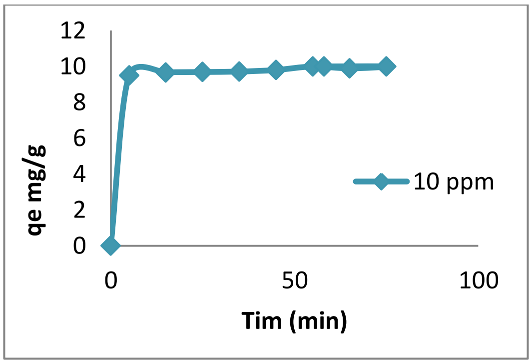


Fig. (3): The Effect of contact time

A rapid adsorption is observed at 5 minutes and thereafter a gradual increase in adsorption occurs with increasing contact time up to 55 min., After this time, the amount of dye adsorbed was not significant. Therefore, the time of55 minute is fixed as the optimum contact time [16].

The Effect of Dosage:-

The effect of adsorbent dosage on the removal of DB71 dye was studied at different amount of Flint clay, while keeping the initial dye concentration (10ppm) and contact times (55 min) are constant .The results are shown in Table(4) and Figure(4)

The removal of dye on clay was take from dosage for (0.1 -1) gram.

Table (4): The values of R %and w(g)

The quantity of adsorbent w(g)	R%
0.1	66
0.2	78
0.3	80
0.4	88
0.5	90
0.6	93
0.7	91
0.8	87
0.9	86
1	84

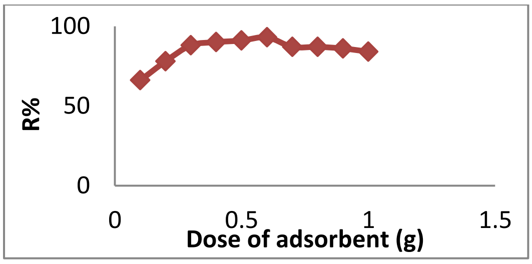


Fig. (4) The effect of adsorbent dosage

The percentage removal % of the dye increases with the increase in adsorbent dose but beyond a value of 0.6 gram. Figure (4) .This change due to the greater availability of the exchangeable sites or the increased surface area where the adsorption takes place.

The Effect of pH

Adsorption experiments were carried out at pH 3, 5, 7, 8 and 10. The acidic and alkaline pH of the media was maintained by adding the required amounts of dilute hydrochloric acid and sodium hydroxide solutions. The kept of constant parameters such as dosage of the adsorbent and temperature. While carrying out the experiments. Figure (5) and Table (5) show the result obtained in the effect of pH on dye removal.

Table (5): The R % and pH for 10 (ppm)

pH	R%
3	45%
4	44%
5	44.7%
6	45.4%
7	89%
8	72%
9	75%
10	87%

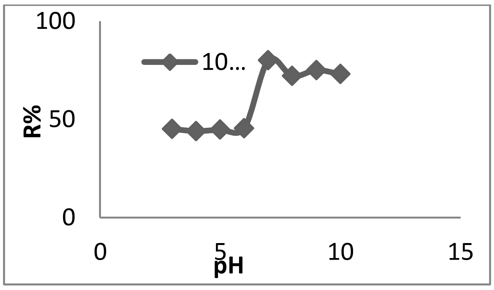


Fig. (5) The effect of pH at 10 ppm ,0.6g, 20 C °

It can be observed that the removal of dye was maximum at pH 7. Therefore, for pH value 7, the adsorption could be explained by hydrogen bond, and high affinity of DB71 from attach with SiO_2,AL_2O_3 [17-19].

Thermodynamic Analysis

The experiments were carried out at four different temperatures (20, 25, 30,35and 40C°) to observe the effect of temperature on the adsorption of DB71 by flint clay. The calculated of thermodynamic parameters such as, enthalpy change, ΔH° entropy change ΔS° and Gibbs free energy change ΔG°.ΔH°, according to Van't Hoff equation (equation (3)) ,the equilibrium constant has been calculated of the equation $K_{eq} = \frac{qe}{Ce}$ against the temperature [20] .The result show in Figure (6).

$$\ln K_{eq} = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad \text{--------(3)}$$

$$\Delta G^\circ = -RT \ln K_{eq} \quad \text{------------(4)}$$

where R is the gas constant, K_{eq} is adsorption equilibrium constant. The plot of ln K_{eq} against 1/T (in Kelvin) should be linear. The slope of the Van't Hoff plot is equal to $\frac{-\Delta H^o}{RT}$, and its intercept is equal to $\frac{\Delta S^o}{R}$. ΔH° and ΔS° obtained are given in table (6). The adsorption efficiency increase with increasing temperature. This observation is quite common, and suggest that the adsorption is endothermic. There for, enthalpy was found positive values .The positive values of entropy suggest the increased randomness, the negative Gibbs free energy value indicated the spontaneous nature of the adsorption model[21]

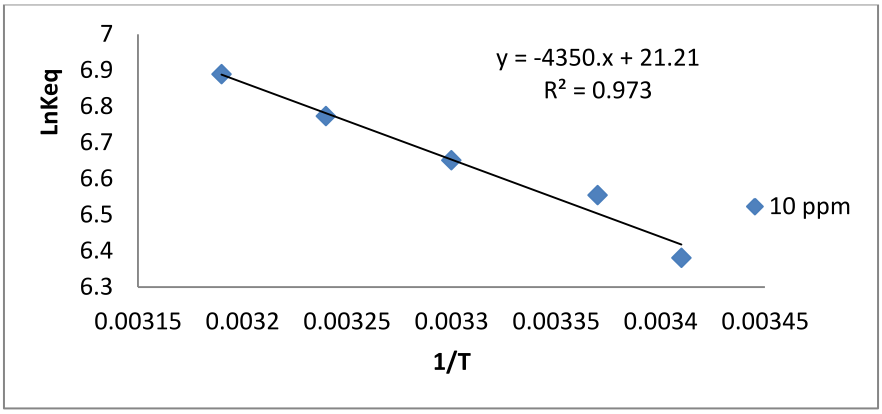


Fig. (6): The Van't Hoff plot of DB71 adsorption

Table (6) Thermodynamic parameters of DB71 adsorption on clay at 10 ppm , pH 7, and 0.6g

ΔH° KJ.mol⁻¹	ΔS° J.mol⁻¹ k⁻¹	Δ G°		KJ.mol⁻¹		
		20 C°	25C°	30C°	35C°	40C°
36	176.3	-15.4	-16.2	-17.1	-18.6	-19.02

Adsorption isotherm

The adsorption isotherm is the most important information ,which indicates how molecules are distributed between the liquid phase and solid phase when the adsorption reaches equilibrium . Two most common isotherm equations namely ,Langmuir and Freundlich, was tested in this work . Table (7) shown the data, and Figure(7) shown the adsorption isotherm take the shape at the one of the five types I to V of the classification originally proposed by Brunauer , Deming , Deming .is S-type ,indicating that the adsorbent is possibly mesoporous or is not porous and has a high energy of adsorption[22-23] .

Table (7): The values of q_e mg/g and C_0(ppm)

C_0 (ppm)	Qe mg/g
2	0.257
4	0.603
6	0.989
8	1.333
10	1.691
12	1.967
14	2.275
16	2.631

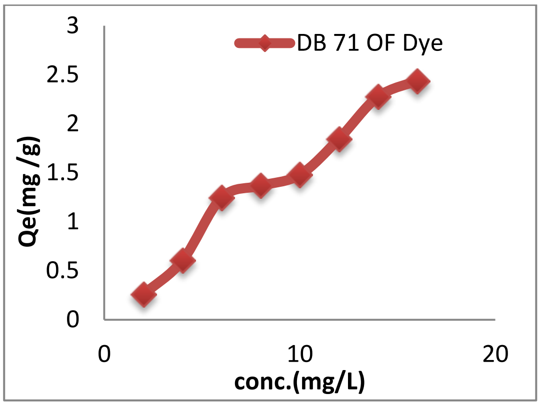


Fig.(7): The adsorption isotherms of dye

The experimental data obtained [Table 8] are also analyzed according to the linear form of Freundlich equation [(equation 5]. The linear plots of log q_e versus log Ce are shown in Figure. (7), which suggest the applicability of the Freundlich isotherm. The values of $\frac{1}{n}$ and K_f are determined from the slope and intercept of the plots and are presented in Table(8) [24] .

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad \text{--------(5)}$$

where Q*e* is solid phase concentration at equilibrium (mgg^{-1}), C_e is the equilibrium of dye in solution (mgL^{-1}), $\frac{1}{n}$ is constants incorporating the factors affecting the adsorption capacity and K_f is the intensity of adsorption.

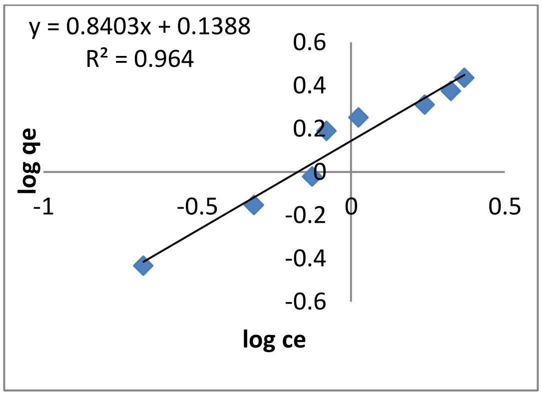


Fig. (8): The Freundliech model of linear plot

The Langmuir model has found successful application to many real monolayer sorption processes. It is expressed by the following relation equation [equation (6)].

$$\frac{Ce}{Qe} = \frac{1}{Qm\,kL} + \frac{Ce}{Qm} \quad \text{---------(6)}$$

The Q_m and $\mathbf{k_L}$ are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively(31). The linear plots of $\frac{Ce}{Qe}$ versus Ce suggest the applicability of the Langmuir isotherms (Figure(9). The values of Q_m and k_L were determined from slope and intercepts and are presented in table (8) .

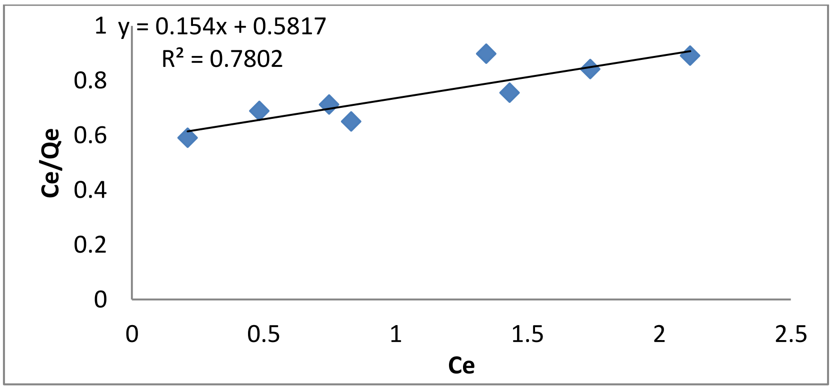


Fig. (9) The linear plot of Langmuir isotherm.

R_L, called separation factor .An essential characteristic of Langmuir isotherm can be expressed by a dimensionless constant, is calculated by using the [equation (7)]

$R_L = 1/1+K_L C_0$ ---------------(7).

R_L values indicate that the type of isotherm is irreversible (R =0) , favorable (0 < R_L< 1) , liner (R_L=1) or unfavorable (R_L> 1. values of n > 1 indicate favourable adsorption conditions[25] .The R_L value is found to be between 0 and 1 and confirm that the ongoing adsorption process is favourable . The R^2 coefficient were high (> 0.9) for Freundlich isotherm indicating the useful values of its constants . Freundlich isotherm model was explained better by the present system [26]

Table (8): The Freundlich and Langmuir equation parameters for the adsorption

Freundlich parameter	T (C°)	1/n	K_F	R^2	
	20	0.616	0.517	0.9652	
Langmuir parameter	T (C°)	q_L	K_L	RL	R^2
	20	0.716	0.5 21	0.355	0.765

Conclusions:

The main conclusions that can be drawn from the foregoing results and discussion may be formulated as in the following paragraphs :

1) The optimum pH for favorable adsorption was 7 for DB17.
2) The adsorption system could be explained by the (physical adsorption)
3) Thermodynamic analysis indicated that the adsorption of the dye onto flint clay was endothermic and spontaneous This confirmed by the values obtained of ΔH° and ΔG°. For equilibrium adsorption ,
4) DB71dye was best fitted to the Freundlich isotherm

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دراسة الامتزاز والثرموديناميك لصبغه الازرق المباشر 71 على سطح طين الفلنت الطبيعي من محلولها المائي

ازل شاكر وهيب

جامعة المثنى –كلية العلوم- قسم الكيمياء ،العراق

الخلاصة:

تم ازالة صبغة الازرق المباشر السالبة على طين الفلنت في محلولها المائي بأستخدام نظام الوجبة السريعة لمختلف تراكيز الاصباغ. تم دراسة كمية الامتزاز كدالة لزمن التماس، pH ، وزن المادة ودرجة الحرارة باستخدام طريقة الوجبة وبعد تحليل النتائج بأستخدام ايزوثيرمات لنكماير وفرندلش وعن طريق اعطاء افضل R^2 حيث تم الحصول على افضل ايزوثير. الدوال الثرموداينميكية مثلΔG^o ، ΔS^o و ΔH^o تم حسابها عن طريق المعادلات حيث اعطت الدوال افضل امتزاز على سطح الفلنت هي تفاعلات ماصة للحرارة بطبيعتها.

الكلمات المفتاحية : الامتزاز، الاصباغ ، لنكماير، فرندلش ، اطيان .