Adsorption of Congo, Red Rhodamine B and Disperse Blue Dyes From Aqueous Solution onto Raw Flint Clay

Sameer H. Kareem*   *Enaas ABD-Al-Hussien**

Abstract:

Removal of Congo red, Rhodamine B, and Dispers Blue dyes from water solution have been achieved using Flint Clay as an adsorbent. The adsorption was studied as a function of contact time, adsorbent dose, pH, and temperature under batch adsorption technique. The equilibrium data fit with Langmuir, Freundlich and Toth models of adsorption and the linear regression coefficient R^2 was used to elucidate the best fitting isotherm model. Different thermodynamic parameters, namely Gibb's free energy, enthalpy and entropy of the on-going adsorption process have also been evaluated. Batch technique has been employed for the kinetic measurements and the adsorption of the three dyes follows a second order rate kinetics. The kinetic investigations also reveal that intraparticle diffusion mechanism was operative.

Key words ; Adsorption , Rhodamine –B , Congo red . Disperse blue ,Langmuir model.

Introduction:

The pollution of the wastewaters with dyes is becoming a major environmental problem due to the growing use of a variety of dyes. Many industries use a wide variety of dyes to color their products and discharge large amount of effluents including dyes which are very toxic and could cause serious ecological problems. Therefore, dye pollution water stream is a major environmental problem. It is known that wastewaters containing dyes are very difficult to treat , since the dyes persist to aerobic digestion and are stable to oxidizing agents[1] Currently, various chemical, physical and biological treatment methods are used to remove dyes[2-4]. Among all these methods the cheapest and simplest is the physical – chemical adsorption. Activated carbon is regarded as the most effective material for removal the dyes[5]'but due to its high cost and 10 – 15 % loss during regeneration, unconventional adsorbents like, wood[6]'silica[7]'clay and activated clay[8-9],agricultural residues[10] etc. have attracted the attention of several investigations for the removal of dyes .

The focus of this research was to evaluate the adsorption potential of the crude Flint clay in removing Congo red (RC), Rhodamine B (RB) and Dispers Blue (DB) dyes from aqueous solutions through batch method. Different adsorption isotherms such as Langmiur, Freundlich , and Toth models have been applied to the adsorption data. The thermodynamics and kinetics sudiesfor the removal of these dyes onto Flint clay have been investigated.

Materials and Methods:

The adsorbate:

Three different industrial dyes (cationic, anionic and non-ionic) have been used in the experiments. The chemical names and their properties of

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these dyes are listed in Table -1.Furthermore, the chemical structure
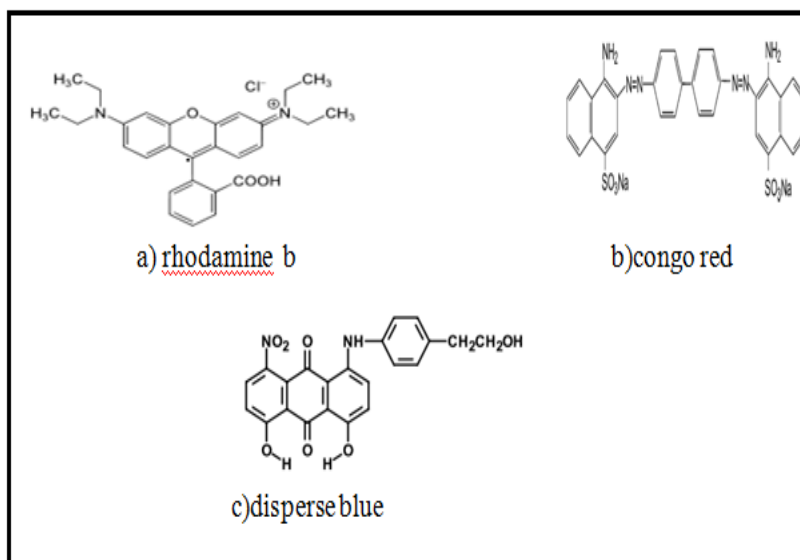are exhibited in Fig. 1.

Fig.(1) The Chemical Structure Of The Three Dyes

Table (1) The chemical names and the λ_{max} of the three dyes

Dye	Chemical formula	molecular weight,g mol^{-1}	$\lambda_{max/nm}$
CR	1-napthalenesulfonic acid, 3,3-(4, 4biph -enylenebis (azo)) bis (4-aminodisodium) salt.	696	497
RB	[9-(2-carboxyphenyl)-6-iethylamino-3-xanthenylidene]-diethylammonium chloride.	469.5	554
DB	1,8-Dihydroxy　　　　　　　　　-4-nitro-5-(N-(p-phenethylalcohol)amino)anthraquinone	420	575

The Adsorbent :

Flint clay was used as an adsorbent throughout this study. This clay was obtained from the general company of geological Survey and Mining, ministry of Industry and minerals. The Flint rock was ground and sieved to the required particle size between (106-212)micrometer. The sieved samples were washed with distilled water and subsequently dried at (120˚C) for (24h) .This Flint clay was used in all experiments and analysis. Information and analysis for the surface were supplied by the same company and described below in Table (2).

Batch mode adsorption studies :

Batch mode adsorption studies for individual dyes have been carried out to investigate the effect of different parameters such as adsorbate concentration, adsorbent dose, temperature and pH. Solution containing 100 ml adsorbate and 0.5g adsorbent 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 centrifuged at (3000 rpm) for (15 minutes). The concentration of the sample is measured by spectrophotometric determination .The amount of CR, RB

and DB adsorbed was calculated using the equation

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

Constituents	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	TiO$_2$	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 %

Where q_e is the amount of dye adsorbed per unit weight of Flint clay (mg/g); C_0 the initial concentration of dyes (ppm); C_e the concentration of dyes in solution at equilibrium time (ppm); V the solution volume (L); W is the Flint clay dosage (g). The percentage of dye removed from solution was calculated using the following equation:

$$Removal\ percentage = \frac{(C_\circ - C_e)}{C_\circ} \times 100 - - - - - (2)$$

X-ray and Texture Analysis :

The x-ray powder diffraction patterns were recorded on a SHIMADZU diffractometer using Cu kα radiation (1.5406 Å). The diffractograms were recorded in the 2θ range of 10 to 60degrees. Adsorption-desorption isotherms of the Flint clay sample were measured at 77 K on a micromeritics model ASAP 2020 to determine surface area and porosity.

Results and Discussion:

Characterization of Flint Clay Figure (2) shows the adsorption isotherm of nitrogen for Flint clay powder .It is type IV according to classification developed by Brunauer, Deming, Deming and Teller (BDDT)[11]. This type of isotherm is characteristic of a material which contains mesoporosity. This isotherm contains hysteresis loop type H$_3$ according to IUPAC committee classification which indicates a slit-

like pores. The BET surface area and total pore volume were found 18.56m^2/g and 0.10m^3/g respectively. Fig(3.)shows the XRD patterns of Flint clay. The predominate peaks found in the Flint Clay were 7.16Å, 4.44Åand 3.57Åwhich correspond to mineral phase of Kaolinite and also (4-26 Å) which corresponds to mineral phase of quartz.
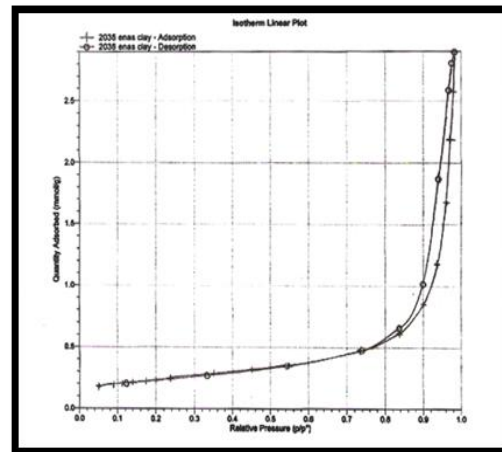

Fig. (2) N$_2$ adsorption – desorption isotherm of Flint clay
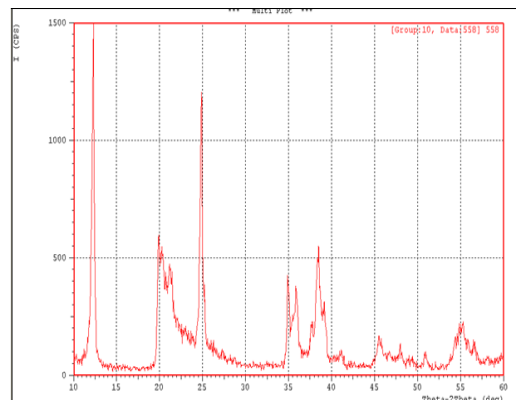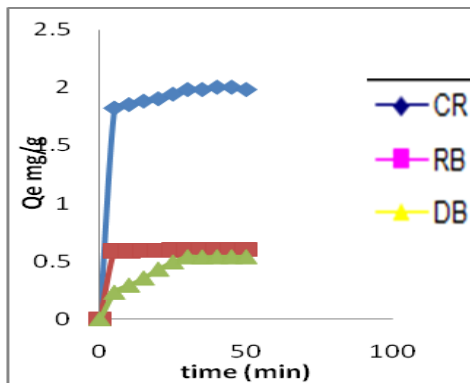

Fig. (3) XRD patterns of Flint clay

Effect of various parameters on adsorption:

The amount of the three dyes adsorbed indicates that the adsorption of dye from solution increases with the time and finally attains equilibrium in 30 minutes Fig(-4). The percentage of adsorption increases with increasing in dosage of adsorbent and reached an equilibrium value after certain sorbent dosage (0.5 g/100ml), Figure(5). As amount of adsorbent increases, number of active sides available for adsorption also increases hence % removal also increases. The results of change in pH on the extent of adsorption of dyes from an aqueous solution are depicted in Figure (6). We observed that the removal of dyes can be carried out at pH (7) for CR and pH (4) for RB and DB.
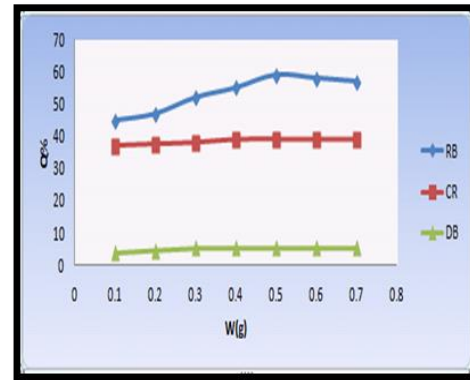

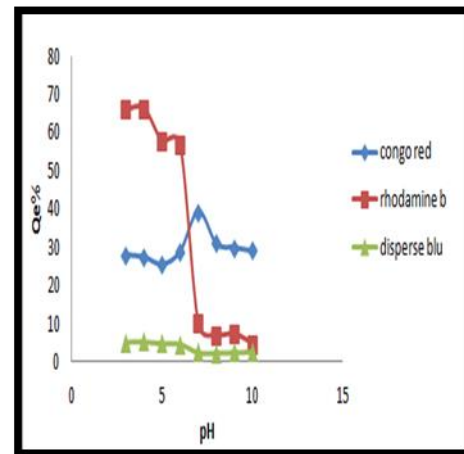**Fig .(5) Effect of adsorbent dos.**

Fig. (6) Effect of pH

The adsorption amount (q_e) of the three dyes for typical temperature are listed in Table (3), while the adsorption isotherms at temperature range (20-40 ºC are depicted in Fig. (7).

Fig(4) Effect of contact time

Table (3). The values of C_e and q_e for the adsorption of the three dyes at 25ºC

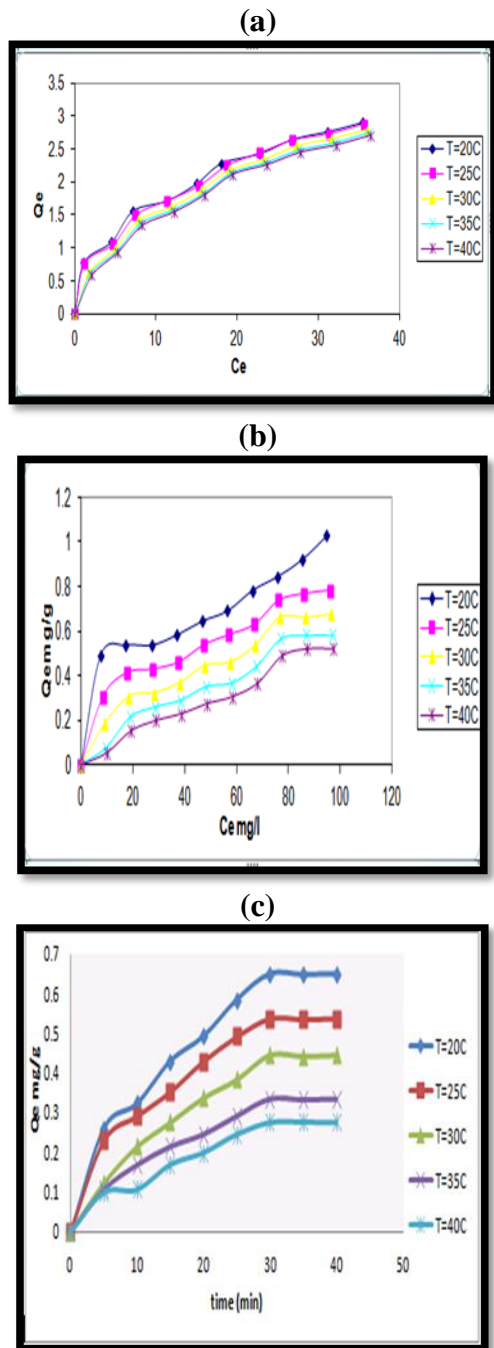| Congo red			Rhodamine b			Dispers blue		
C_0 mg/L	C_e mg/L	q_e mg/g	C_0 mg/L	C_e mg/L	q_e mg/g	C_0 mg/L	$C_{e\ mg/L}$	q_e mg/g
5	1.187	0.76	1	0.058	0.188	10	8.461	0.307
10	4.72	1.05	3	0.652	0.469	20	17.923	0.415
15	7.5	1.50	5	1.994	0.601	30	27.846	0.430
20	11.4	1.72	7	3.005	0.798	40	37.692	0.461
25	15.30	1.94	9	4.694	0.861	50	47.307	0.538
30	18.76	2.24	11	5.876	1.024	60	57.076	0.584
35	22.8	2.44	13	7.447	1.110	70	66.840	0.630
40	26.84	2.63	15	8.229	1.354	80	76.307	0.738
45	31.35	2.72				90	86.153	0.769
50	35.62	2.87				100	96.076	0.784

(a)

(b)

(c)

Fig. (7) –Adsorption isotherms of a) congo red ; b) rhodamine b; c) disperse blue

The percent adsorption amount of these dyes onto the adsorbent decreases with temperature rise of the dye solution from (20-40) ℃ .The observed decrease in the adsorption with increase in temperature is indicative of the fact that the adsorption process is exothermic in

nature. The increase in temperature of the system affects the solubility and particularly the chemical potential of the adsorbate dyes which is known to be a controlling factor in the adsorption process [12-13]

Thermodynamics Analysis

The equilibrium constant, K_{eq} has been calculated with the help of the equation [12], $K_{eq} = q_e / C_e$, where q_e is solid phase concentration at equilibrium (mg/kg) and C_e is equilibrium concentration of dye in solution (mg/L). The calculated free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) parameters at different temperatures are presented in Table (4). These parameters are calculated using the following equations:

$$\Delta G° = - RT \ln K_{eq} \text{ ----------------- (3)}$$
$$\ln K_{eq} = - \Delta H° /RT + \Delta S° / R \text{ -------(4)}$$

The $\Delta H°$and $\Delta S°$ values are calculated from the slope and intercept of the linear plots of ln K_{eq} vs 1/T, respectively (Fig.8).
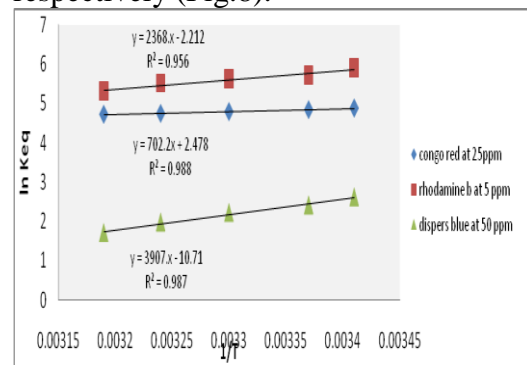

Fig. (8) Va'nt Hof plot of three dyes adsorption .

The negative values of $\Delta G°$ indicate that the adsorption of dyes onto the Flint clay is a spontaneous process. The higher negative value reflects a more energetically favorable adsorption. Enthalpy changes at different temperatures are also negative which further confirms that the process is exothermic. The negative values of $\Delta S°$ for RB and DB indicate that the degree of freedom decreased at the

solid-liquid interface during adsorption of the dyes onto Flint clay, while the positive value of ΔS° for CR indicate the increase of degree of freedom at solid –liquid interface. The values of entropy reflect affinity of both the RB and DB towards Flint clay.

Adsorption isotherms

The data obtained on the adsorption of the dyes have been analyzed on the basis of the Langmiur, Freundlich and Toth isotherms. These models are:

$$q_e = \frac{q_m . k_L . C_e}{1 + k_L . C_e} \quad ----------------(5)$$

$$q_e = K_F . (Ce)^{1/n} \quad ----------------(6)$$

$$q_e = \frac{q_T . C_e . K_T}{(1 + (K_T C_e)^t)^{\frac{1}{t}}} \quad - - - - - - - -(7)$$

Where q_m is Langmiur constant related to the capacity and K_L is related to the energy of adsorption, 1/n and K_f are Freundlich constants related to the intensity of adsorption and adsorption capacity respectively q_t and K_t are Toth constants related to the capacity and energy of adsorption, respectively.

These isotherms are fitted employing the non- linear fitting method using the software called (STATISTICA Module Switcher). Fig. (9) Presents how well the three equations fit experimental data for CR, RB, and DB – Flint clay systems at (25°C).
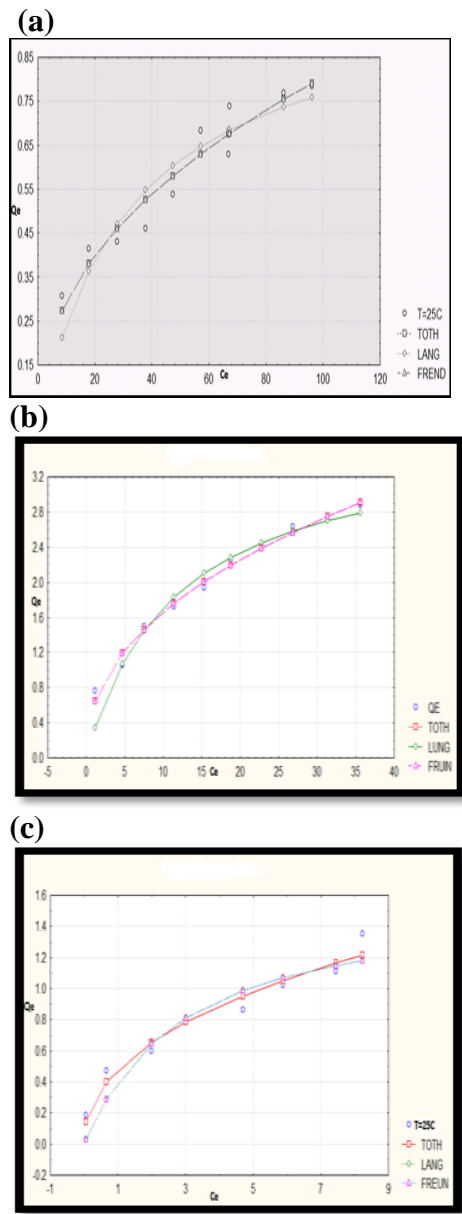
(a)

(b)

(c)

Fig.(9) Adsorption isotherm analysis of ; a) CR ; b) RB ; C) DB at 25 ºC

Table (4). The Thermodynamic parameters of the three dyes adsorption on Flint clay.

Congo red	ΔH° kJ. mol^{-1}	ΔS° JK.mol	Δ G°			° kJ.mol^{-1}	
			20 °C	25°C	30°C	35°C	40°C
At 25ppm	-5.8 38	20.602	-11.88	-11.99	-12.07	-12.15	-12.29
Rhodamin b	ΔH° kJ. mol^{-1}	ΔS° JK^{1-}.mol^{-1}	Δ G° kJ.mol^{-1}				
			20 °C	25°C	30°C	35°C	40°C
At 5ppm	-19.6	-18.393	-14.36	-14.14	-14.13	-14.11	- 13.82
Dispers blue	ΔH° KJmol^{-1}	ΔS° JK^{-1}.mol^{-1}	Δ G° kJ.mol^{-1}				
			20 °C	25°C	30°C	35°C	40°C
At 50ppm	-32.48	-89. 04	-6.37	-5.98	5.59	-5.07	-4.4

Table (5) The values of the constants of the three isotherms for the adsorption of dyes.

Dye	Freundlish			Langmuir			Toth			
	K_f	1/n	R^2	q_m	K_L	R^2	q_t	m_t	K_t	R^2
CR	0.732	0.414	0.977	0.40	8.62	0.957	0.119	0.558	0.749	0.993
RB	0.755	0.276	0.990	1.488	1.103	0.935	0.00313	0.507	0.178	0.935
DB	0.407	0.358	0.946	1.179	0.022	0.807	0.00205	0.562	1.535	0.922

As seen from the fig (9) , and the results of correlation coefficient (R^2) Table (5), indicate that the Toth model yields a better fit for CR adsorption and the Frendlich model yields a better fit for RB and DB adsorption.

Kinetics Study:

In order to determine the adsorption kinetics of the three dyes, the Pseudo-first-order, pseudo-second order and intrapartical diffution kinetics models were tested. The pseudo-first order kinetic model of Lagergren is routinely used in the linearized form [14]:

$\log(q_e - q_t) = \log q_e - k_1 t$

where q_t is the amount of adsorbed dye onto the adsorbent at time t and k_1 is the rate constant of first-order adsorption.

The pseudo-second-order kinetic mode in its integrated linear form is [15]

$t / q_t = 1 / q_e^2 k_2 + 1 / q_e t$

Where k_2 is the rate constant of second -order adsorption.

The intra-particle diffusion kinetic model based on the equation proposed by Weber and Morris is [16]

$q_t = k_D t^{1/2} + C$

where k_D is the rate of diffusion and C is the intercept.

Kinetic parameters obtained after subjecting experimental data to the three kinetic models are shown in table (6), while the linear plots of the above three equations are shown in Fig. (10).

(a)

(b)

(c)
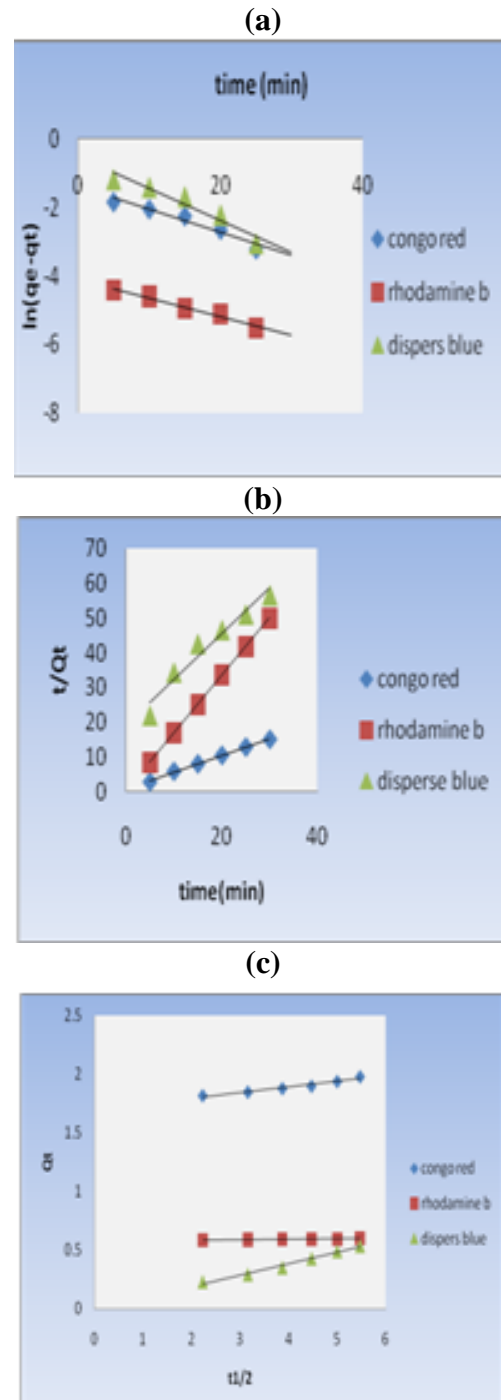
Fig(10) . The linear kinetics plots for the dyes adsorption ;a)pseudo –First order ;b) pseudo –second order ; c) Intraparticle diffusion

Table (6) The parameters of three model of kinetic for CR =25ppm, RB=5ppm, DB=50ppm

Dye	q_e (exp.)	pseudo-first -order			pseudo-second –order				Intrapartical diffusion	
		q_e(calc.)	k_1	R^2	q_e(calc.)	k_2	h	R^2	k_D	R^2
CR	1.938	0.436	1.38	0.948	1.818	0.748	2.048	0.997	0.047	0.958
R B	0.601	0.949	4.11	0.980	0.602	11.6	4.211	0.9999	0.0035	0.9486
DB	0.538	0.936	0.522	0.927	0.765	0.088	0.051	0.950	0.098	0.986

According to the values of correlation coefficient and (q_e(calc.)) , the 2nd order model is found to be more suitable to describe the adsorption kinetic data than the 1st order model for all the adsorbates. On the basis of this evidence, it has been confirmed that the adsorption process follows pseudo-second order kinetic behavior. Similar behavior has also been reported in the literature [17-18]. Although the regression of intraparticle diffusion was linear, the plot didn't pass through the origin, suggesting that adsorption involved intraparticle but wasn't the only rate-controlling step[19] The values of k_D , which are less than k_2, have also been confirmed that the intraparticle diffusion was rate-controlling step.

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امتزاز صبغات الكونكو الاحمر،والرودامين b و المنتشرة الزرقاء على طين الفلنت الخام   من محاليلها المائية

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الخلاصة :

تم في هذا البحث استخدام طين الفلنت كمادة مازة لازالة صبغات الكونكو الاحمر –الرودامين b والمنتشرة الزرقاء من محاليلها المائية . و تم دراسة كمية الامتزاز كدالة لزمن التماس وكمية المادة المازة ودرجة الحرارة باستخدام طريقة الوجبة . وبعدها تم تحليل نتائج الامتزاز باستخدام ايزوثيرمات لنكماير ،فرندلش وتوث . وحسبت كل من الدوال الثرموديناميكية °ΔH، °ΔS و °ΔG لعملية الامتزاز . وكذلك استخدمت ثلاث معادلات حركية هي معادلة الدرجه الاولى و الثانية و Intraparticle diffusion واشارت النتائج الى ان عملية الامتزاز تتبع معادلة من الدرجة الثانية ، وكانت الخطوة المحددة للتفاعل هي خطوة الانتشار الدقيق .