

Kinetic Study of Adsorption Rhodamine 6G Dye from Aqueous Solutions Using Bentonite Clay

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Abstract The kinetics of adsorption of Rh6G on bentonite has been investigated in a batch adsorption process. The adsorption of Rh6G was found to be dependent on pH, initial concentration, adsorbent dose, contact time and Temperature. The result indicated that, optimum contact time was 30 minutes and the adsorbent dose was 0.2g of bentonite. The Langmuir, freundlich and Temkin isotherm models were analyzed for the equilibrium adsorption data and the various isotherm parameters were evaluated. The Rh6G on bentonite follows pseudo-second order rate kinetics.

Keywords Rh6G, Bentonite, Kinetics model adsorption

1. Introduction

Dyes are widely used in industries such as textiles, paints, rubber plastic, paper, cosmetics, etc.. The presence of dyes is most often in industrial processes and their removal may be an environmental problem[1-4]. The treatment of dyes in industrial wastewater possesses several problems since dyes are generally difficult to photodegrade and biodegradation [5]. Research is being carried out for removal dyes using chemical, physicochemical and biological treatment technologies, such as cloud point extraction, oxidation processes, coagulation flocculation, and adsorption have been used for the removal of Colored dyes from wastewater [6-9]. However, adsorption is considered more effective and less expensive than other technologies[10-12]. In the present study, detailed are carried out to remove this dye by adsorption technique using bentonite as an adsorbent. Various parameters affecting adsorption process, such as contact time, initial dye concentration, temperature and PH were investigated. In addition, kinetic parameters were also calculated to determine adsorption mechanism was fitted into adsorption isotherms in order to give the best fit correlation.

2. Materials and Methods

2.1. Preparation of Adsorbed and Characterization

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The bentonite clay was supplied from the state company for geological survey and mining – Iraq. The bentonite had the following composition with particle size less than 75 μm .

Constituent	SiO ₂	Al ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Fe ₂ O ₃	L.O.I
%Wt	56.77	15.67	4.48	3.42	0.60	1.11	5.02	12.49

The molecular formula of bentonite could be written as:

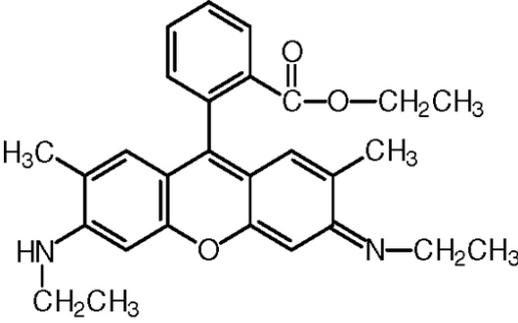


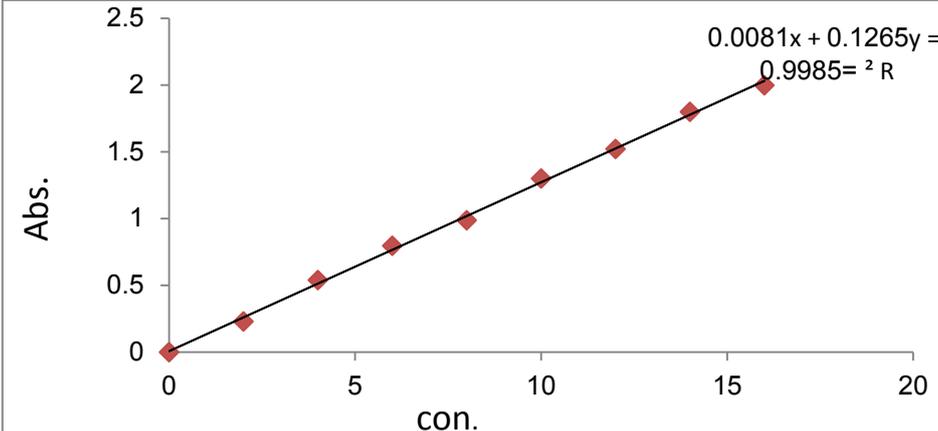
The ground adsorbent was washed thoroughly with distilled water in order to remove any dissolved impurities and then dried at 160 °C and sorted for further use.

2.2. Adsorbate

The dye used in this work was Rhodamine 6G, it was choice in this study because it has a strong adsorption onto solids and also for its high solubility in water. The characteristics and chemical structure of this dye are listed in Table 1. A stock solution of Rhodamine 6G was prepared by dissolving its 1.0 gm in 1000 mL distilled water. The stock solution was diluted accordingly to obtain fresh solutions of desired concentrations. To determine the dye concentration, a calibration curve was first obtained from a series of predetermined concentration of dye solution Fig.1. The maximum absorbance of the dye was confirmed by scanning the dye solution over the spectral range of 400-600nm by using UV-VIS spectrophotometer (UV-Visible spectrophotometer, Double beam, Shimadzu. PC 1650, Japan). The absorbance of those standard samples was measured at the corresponding maximum wavelength ($\lambda_{\text{max}}=524\text{nm}$).

Table 1. Physical properties and molecular structure of Rhodamine 6G[13]

specification		Structure of dye
Empirical formula	$C_{28}H_{31}N_2O_3Cl$	
Molar mass	479.02	
Soruce	Chem. -supply	
Class	Xanthane	 <p style="text-align: center;">Rhodamine 6G</p>


Figure 1. calibration curve of Rhodamine 6G dye at ($\lambda_{max}=524$)

2.3. Batch Adsorption Study

The adsorption isotherm have been determined by Rhodamine 6G dye solution of known, initial concentration to be mixed with accurately weight amount of bentonite in tightly closed flask at certain temperature and pH. The amount of bentonite has been 0.2 gm/50ml solution. A constant temperature and pH were achieved using a shaker water bath (JEIOTECH BS-1). The flask s were subsequently capped and placed on controlled temperature mechanical shaker at a speed of 160 rpm at desired temperature and equilibrated for 30 min .After adsorption, the solution was separated by centrifuge at 3000 rpm for 15 min and super solution was subjected to analysis using UV-VIS technique at wavelength of maximum absorbance (524 nm), the absorbance is then converted to concentration using the calibration curve. The same experiment was repeated at different initial concentration temperature and pH.

The amount of adsorbed Rh6G at any time, q_t (mg/g) was calculated using Eq.1

$$Q_e = (C_0 - C_e) V/m \quad (1)$$

Where $C_0 - C_e$ are the initial concentration of Rhodamine 6G in the solution ($mg \cdot L^{-1}$); q_e is the equilibrium adsorption

capacity per gram dry of the adsorbent, $mg \cdot g^{-1}$, V is volume of the solution (L); and m is the weight of bentonite.

The removal efficiency, R (%) of the system, is Eq.2

$$R = \frac{(C_0 - C_e)}{C_0} \cdot 100 \quad (2)$$

2.4. Effect of Adsorption Parameter

To study the effect of temperature, adsorption experiments were conducted at 25, 35 and 45 °C , respectively .The influence of the pH was investigated at values: 3, 6, 9 and 12. Rhodamine 6G solution pH was Adjusted using 0.1 M NaOH and 0.1 M HCl solution and measured using (pH-Meter-Hanna-HI-8417 / England). Adsorbent adsorbate dosage used in this study was in the range 0.2gm to 1gm.

3. Result and Discussion

3.1. Effect of Contact Time

Adsorption study was carried out by adding a known amount of bentonite (0.2gm), 50ppm of Rhodamine6G dye solution was examined at different time as shown in Fig.2. The result showed that the rate of adsorbed Rhodamine6G onto natural bentonite was rapid and then became slower near the equilibrium. Most of the maximum quantity

adsorption of Rh 6G dye was attained after about 30min of shaking time at different dye initial concentration. The results indicated that the fact that a large number of vacant surface site were available for adsorption during the initial stage. Near the equilibrium the remaining vacant surface sites were difficult to be occupied due to the slow pore diffusion of the solute molecules on the solid and the bulk phase.

3.2. Effect of pH

The pH has been considered an important parameter in adsorption studies it controls the adsorption at the adsorbent solution interface Experiments were conducted varying the solution pH from 3to 12 while the remain of the factors were kept constant. The maximum removal of Rh6G was observed at pH = 6. The adsorption mechanism on the bentonite reflect the nature of physiochemical interaction of the solution.

3.3. Effect of Adsorbent Dose

The effect of adsorbent dose is an important parameter because this determine the capacity of adsorption for aginen initial concentration. The adsorption efficiency of R6G as a function of adsorbent dose was studied. The percentage of the R6G adsorption steeply increases with the adsorbent dose loading up to (0.2gm - 1gm). This result can be explained by the fact that the adsorption sites remain unsaturated during the adsorption reaction where as the number of a sites available for adsorption site increases by increasing the adsorbent dose. The maximum adsorption (99%) was attained at adsorbent dose 0.2gm. Therefore, the optimum adsorption dose was taken as 0.2gm forfurthar experiments.

3.4. Adsorption Isotherms

The adsorption mechanism and relationship between the concentration of the adsorbate and adsorption capacity of both the adsorbent was studied using different adsorption isotherm.

3.4.1. Langmuir Adsorption Isotherm

The Langmuir isotherm describes the formation of a monolayer adsorbate on the uniform surface of the adsorbent, and after that no further adsorption takes place. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The model assumes uniform energies of adsorption on to the surface and no transmigration of the adsorbate in the plane of the surface[14].

The linear form of the Langmuir isotherm model is described as:

$$C_e/Q_e = 1/K_L q_{max} + 1/q_{max} C_e \tag{3}$$

Where

Ce = The equilibrium concentration of the adsorbate (mg/L)

qe = The amount of adsorbed per gram of the adsorbent at equilibrium (mg /g)

qmax = Maximum monolayer adsorption capacity (mg/g).

KL = Langmuir constant (mg /L) related to the energy of adsorption

The values of q max and KL were calculated from the slope and intercept of the Langmuir plot of Ce/qe versus Ce as show in Fig.3 Values of q max, KL and regression coefficient R² are listed in Table 2.The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter RL, which is a dimensionless constant referred to as separation factor or equilibrium parameter RL expressed as in the following equation

$$R_L = 1/(1 + K_L C_0)$$

Where KL is the Langmuir constant and C0 is the initial concentration.

The value of separation parameter provides important information about the nature of adsorption to be either unfavorable if RL > 1, linear it RL =1, favourable (0 < RL < 1). The RL was found to be for 25,35 and 45C⁰ respectively (0.042, 0.024 and 0.013) for concentration (50 ppm)They are in the range of (50-250 ppm) which indicates the adsorption.

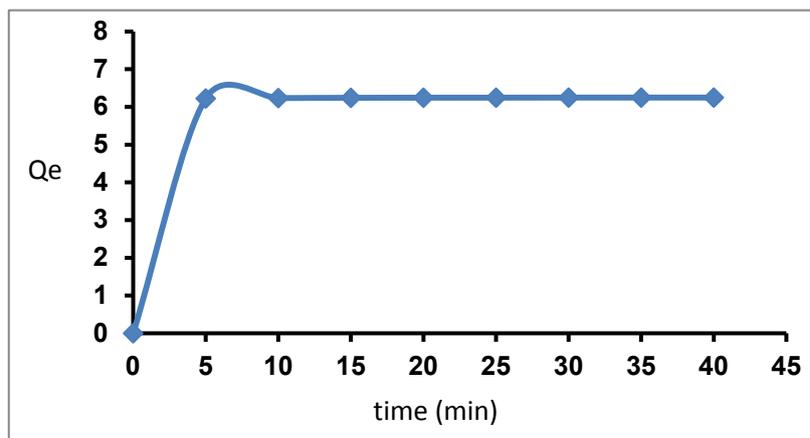
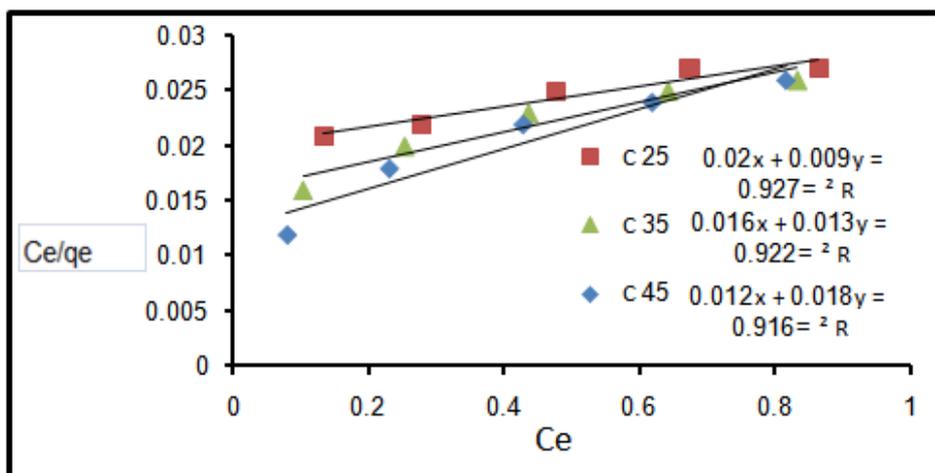


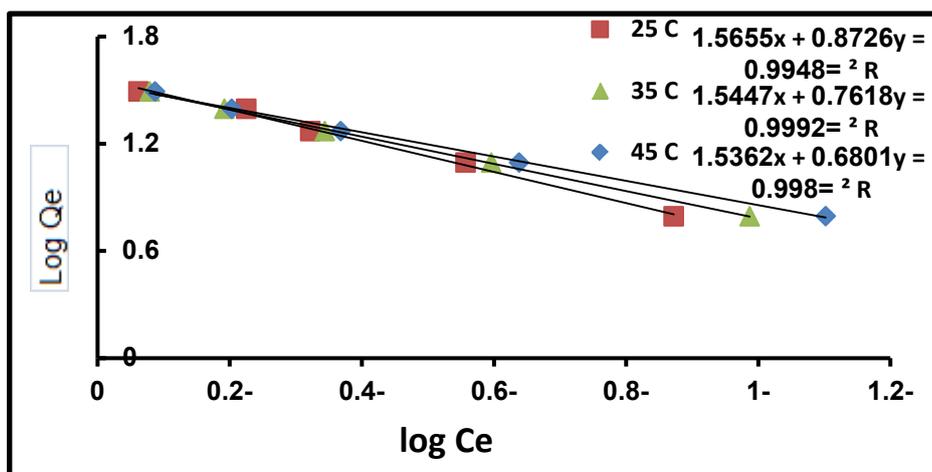
Figure 2. Effect of shaking Time on removal efficiency

Table 2. Effect of Langmuir equation at different temperature

C_0 ppm	298K		308K		318K	
	C_e (mg .L ⁻¹)	Q_e/C_e (mg.g ⁻¹)	C_e (mg .L ⁻¹)	Q_e/C_e (mg.g ⁻¹)	C_e (mg .L ⁻¹)	Q_e/C_e (mg.g ⁻¹)
50	0.134	0.021	0.103	0.016	0.079	0.012
100	0.277	0.022	0.253	0.020	0.230	0.018
150	0.476	0.025	0.436	0.023	0.428	0.022
200	0.595	0.027	0.642	0.025	0.619	0.024
250	0.865	0.027	0.833	0.026	0.817	0.026

**Figure 3.** Effect of Langmuir equation at different temperature**Table 3.** Effect of Freundlich equation at different temperature

C_0 (ppm)	298K		308K		318K	
	Log C_e	Log Q_e	Log C_e	Log Q_e	Log C_e	Log Q_e
50	-0.872	0.794	-0.987	0.794	-1.102	0.794
100	-0.557	1.095	-0.596	1.095	-0.638	1.095
150	-0.322	1.271	-0.360	1.271	-0.368	1.271
200	-0.171	1.396	-0.192	1.396	-0.203	1.396
250	-0.062	1.493	-0.079	1.493	-0.08	1.493

**Figure 4.** Effect of Freundlich equation at different temperature

3.4.2. Freundlich Isotherm

This is commonly applies to adsorption on heterogeneous surfaces. These data often fit the empirical equation proposed by Freundlich[16].

$$Q_e = K_f C_e^{1/n} \tag{4}$$

Where K_f = Frenundich constant (mg/g)

N = Adsorption intensity.

C_e = The equilibrium concentration of a dsorbate (mg/L)

Q_e = The amount of adsorbed per gram of the adsorbent at equilibrium (mg/g). linearzing equation (4)

$$\text{Log } q_e = \text{log } K_f + (1/n) \text{ log } C_e \tag{5}$$

The constant K_f is an approximate indicates of adsorption capacity, while $1/n$ is a function of strength of adsorption in the adsorption process. freundlich equilibrium constants were determined from the plot of $\text{log } q_e$ versus $\text{log } C_e$, Fig.4 on the basis of the linear of Freundlich equation (5). The n value indicates the degree of non-linearity between solution concentration and adsorption as follows.

The value $1/n$ and K_f were calculated from slope and intercept of plot $\text{log } q_e$ versus $\text{log } C_e$, respectively(Fig.4) and are given in Table 5. The n value indicates the degree of nonlinearity between the two phases as follow. if $n=1$, then adsorption is linear, if $n<1$, then adsorption is chemical process; if $n>1$, the adsorption is physical process.

3.4.3. Temkin Isotherm

This isotherm is used to describe the adsorption characteristics, the model assumes that heat of adsorption of all molecules in the large decreases linearly with coverage due to adsorbent –adsorbate interactions and that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy was carried out by plotting q_e against $\ln C_e$ and the constant were determined from the slope and intercept[15].

The model is given by the following equation (6)

$$q_e = RT/b_T \ln A_T + (RT/b_T) \ln C_e \tag{6}$$

A plot of q_e versus $\ln C_e$ shows that adsorption follows Temkin isotherm in (Fig.6).

The b_T and A_T were calculated from slope and the intercept of the linear plot. where A_T (L/g) is the equilibrium binding constant corresponding to the maximum binding energy and constant b_T is related to the heat of sorption (318K).

The Langmuir, Freundlich and Temkin constant are shown in Table 5, all the isotherms were found to be fit well to the experimental data the Freundlich isotherm is slightly better than Langmuir isotherm as indicated by higher R^2 value.

Table 4. Effect of Temkin equation at different temperature

C ₀ ppm	298K		308K		318K	
	Q _e (mg.g ⁻¹)	ln C _e	Q _e (mg.g ⁻¹)	ln C _e	Q _e (mg.g ⁻¹)	ln C _e
50	6.233	-2.009	6.237	-2.273	6.240	-2.538
100	12.465	-1.283	12.468	-1.374	12.471	-1.469
150	18.690	-0.742	18.695	-0.83	18.696	-0.848
200	24.925	-0.394	24.919	-0.443	24.922	-0.479
250	31.141	-0.145	31.145	-0.182	31.147	-0.202

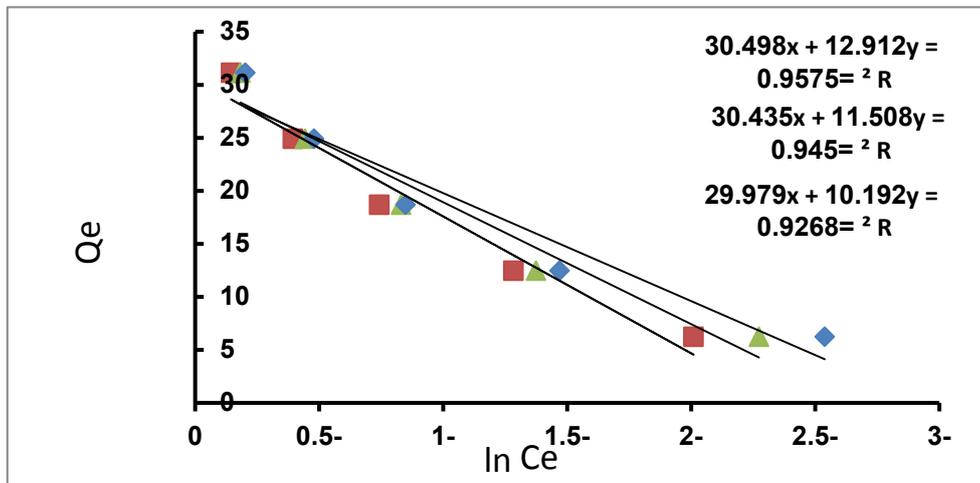


Figure 5. Effect of Temkin equation at different temperature

Table 5. Adsorption isotherm constants of R6G on bentonite

Tem. (C ⁰)	Freundlich constants			Langmuir constants				Temkin constants		
	n	K _F	R ²	K _L	q _{max}	R _L	R ²	A _T	b _T	R ²
25	1.146	36.728	0.927	0.45	111.11	0.042	0.994	0.0107	191.91	0.957
35	1.314	34.994	0.922	0.81	76.92	0.024	0.999	0.0141	222.67	0.945
45	1.470	34.355	0.916	1.5	55.55	0.013	0.998	0.0189	259.45	0.926

3.5. Adsorption Kinetics

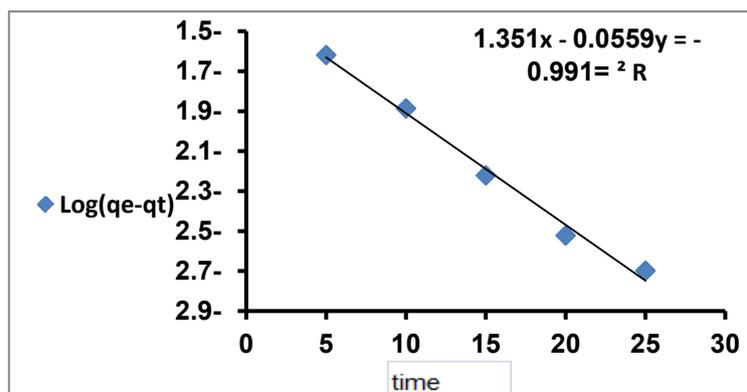
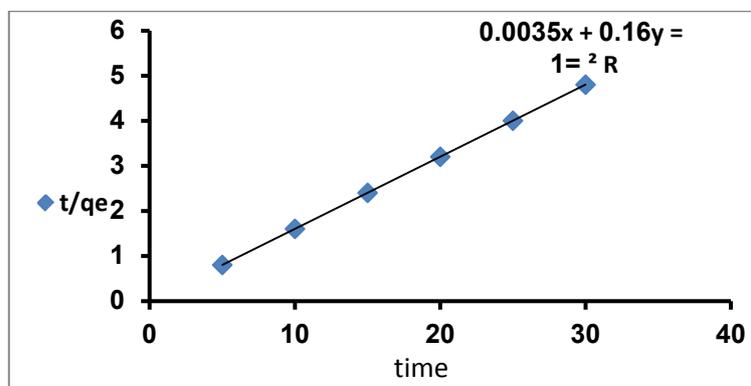
Constant from two kinetic models, pseudo first-order and pseudo second-order were fit to experimental data to examine the adsorption kinetics of R6G by bentonite.

3.5.1. Pseudo First-order Model

The pseudo-first order equation of Lagergren is given by equation.

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (7)$$

where q_e and q_t are the adsorption capacities at equilibrium and at time t , respectively (mg/g) and K_1 is the rate constant of pseudo first order adsorption, (L.min⁻¹). The slopes and intercepts of plot $\log (q_e - q_t)$ versus t Fig.6 were used to determine the pseudo first-order rate constant (K_1) and q_e . The adsorption constant with correlation coefficients for the pseudo-first order model and shown in Table 6.

**Figure 6.** The applicability of the first order kinetic model to Rh6G on bentonite clay**Figure 7.** t/q against time of adsorption of Rh6G on to bentonite clay**Table 6.** Adsorption kinetics parameters of pseudo-first and second order of Rh6G on bentonite

Pseudo-first order			Pseudo-second order		
K ₁	q _e	R ²	K ₂	q _e	R ²
0.126	0.044	0.991	8.547	6.25	1

3.5.2. Pseudo-second Order Model

The pseudo second-order model, which has been applied for analyzing adsorption kinetics rate is given by equation :-

$$\frac{t}{q_e} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

When t is the contact time (min), q_e (mg/g) and q_t (mg/g) are the amount of the solute adsorbed at equilibrium and at any time, the slope and intercept of the plot t/q_e versus t , Fig.7 are used to calculate q_e and (K_2) the adsorption constant with correlation coefficients for the pseudo-second order model are shown in table 6 the correlation coefficients for the second order kinetic model are greater than first order Fig.7.

4. Conclusions

In present study bentonite clay was selected as a local, cheap and readily available adsorbent for the removal of Rh6G from aqueous solution. Bentonite was studied by batch adsorption experiments. The adsorption of Rh6G was found to be dependent on pH, initial concentration, adsorbent dose, contact time and temperature. The Langmuir, Freundlich and Temkin isotherm models were analyzed, adsorption data and the various isotherm parameters were evaluated. The Rh6G on bentonite follows pseudo-second-order rate kinetics.

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