Equilibrium and kinetic data and process design for adsorption of Congo Red onto bentonite

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Abstract

The adsorption of Congo Red onto bentonite in a batch adsorber has been studied. Four kinetic models, the pseudo first- and second-order equations, the Elovich equation and the intraparticle diffusion equation, were selected to follow the adsorption process. Kinetic parameters; rate constants, equilibrium adsorption capacities and correlation coefficients, for each kinetic equation were calculated and discussed. It was shown that the adsorption of Congo Red onto bentonite could be described by the pseudo second-order equation. The experimental isotherm data were analyzed using the Langmuir, Freundlich and Temkin equations. Adsorption of Congo Red onto bentonite followed the Langmuir isotherm. A single stage batch adsorber was designed for different adsorbent mass/treated effluent volume ratios using the Langmuir isotherm.
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1. Introduction

Colored dye wastewater arises as a direct result of the production of the dye and also as a consequence of its use in the textile and other industries. Majority of this dyes are synthetic in nature and are usually composed of aromatic rings in their structure, which makes them carcinogenic and mutagenic, inert and non-biodegradable when discharged into waste streams. Therefore, the removal of such colored agents from aqueous effluents is of significant environmental, technical, and commercial importance [1,2]. Possible methods of color removal from textile effluents include coagulation, electrocoagulation, flotation, chemical oxidation, filtration, ozonation, membrane separation, ion-exchange, aerobic and anaerobic microbial degradation. However, all of these methods suffer from one or other limitations and none of them were successful in completely removing the color from wastewater [2,3].

Adsorption of various dyes from aqueous solution has proven to be an excellent way to treat effluent also a cost effective technique. Several studies have shown that numerous low cost materials have been successfully applied in the removal of dyes from aqueous solution, some of which are coal, fly ash, wood, silica, shale oil ash, Fuller's earths, zeolite, perlite, alunite, clay materials (bentonite, montmorillonite, etc.) activated slag, and agricultural wastes (bagasse pith, maize cob, coconut shell, rice husk, sawdust, etc.) [4–7]. However, only limited application of such data has been directed towards the design of adsorption treatment systems, for example, batch adsorber design [2,5,8,9]. Clay has been accepted as one of the appropriate low cost adsorbents for removal of dyes from wastewater. Among the clays studied, bentonite has received considerable recognition as an adsorbent because of high adsorption capacity. It is hydrated alumina-silicate clay primarily composed of the smectite-class mineral montmorillonite [8,10,11]. It is well known the negative charge of clays is balanced by exchangeable cations, which are usually Na^+ and Ca^{2+} [11]. The wide usefulness of clay minerals is essentially a result of their high specific surface area, high chemical and mechanical stabilities, and a variety of surface and structural properties [12].

The present study is aimed at studying the adsorption capacity of bentonite for adsorption of Congo Red (CR) due to the fact that it is a very abundant and inexpensive material in the world

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Table 1
The chemical composition of bentonite in wt.%

Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Loss of ignition
16.3	63.2	3.0	2.1	2.4	1.3	2.0	9.7

and has excellent adsorbent properties. Equilibrium isotherms and kinetic data have been evaluated. This paper also develops a single stage batch adsorber design model. A design analysis method has been developed to predict the required amount of bentonite at various amount of effluent treated for different percentage of dye removal.

2. Materials and methods

Bentonite used in this study was obtained from Pendik Tümaylar Ticaret, Istanbul, Turkiye. The chemical composition of bentonite is given in Table 1. The bentonite was sieved to give different particle size fractions using ASTM standard sieves, and the 53–75 μm particle size was used in the experiments. The BET specific surface area was measured to be 28 m^2/g from N_2 adsorption isotherms with a sorptiometer (Quantachrome Co., NOVA 2000). It was used directly for adsorption experiments without any treatment.

As adsorbate, Congo Red (CR), an anionic disazo direct dye, contains NH_2 and SO_3 functional groups [C.I. = 22120, chemical formula = $C_{32}H_{22}N_6Na_2O_6S_2$, FW = 696.7, λ_{max} = 500 nm]. CR was supplied by the Sağlam Boya Company Istanbul, Turkiye. CR is commercial grade and was used without further purification. The chemical structure of CR is given in Fig. 1.

Batch pH studies were conducted by shaking 100 mL of each dye solution with 1 g of the bentonite for 1 h a range of pH values from 3 to 11. The pH of the solutions was adjusted with HCl or NaOH solution by using a pH meter. Blanks were run simultaneously, without any adsorbent to determine the impact of pH change on the dye solutions.

In the determination of equilibrium adsorption isotherm, 1 g bentonite and 100 mL of different concentrations (75–300 mg/L) of CR solutions were transferred in 250 mL flask, and shaken on a horizontal bench shaker (Nüve SL 250) for 2 h (the time required for equilibrium to be reached between CR adsorbed and CR in solution) at the initial pH 6.8 (natural solution pH value of CR) and at room temperature (298 ± 2 K).

The CR solutions were prepared by dissolving in distilled water at desired concentrations (75–300 mg/L). In the adsorption experiments, 1 g bentonite was added into a liter of CR solution at the initial pH 6.8 (natural solution pH value of CR) and at room temperature (298 ± 2 K). The mixture was continuously agitated by a magnetic stirrer at 500 rpm for 2 h. Three
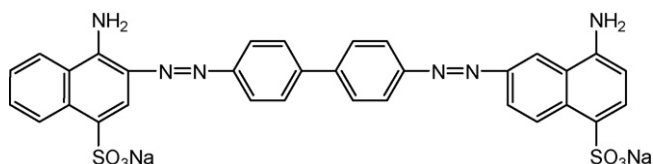

Fig. 1. Molecular structure of Congo Red.

milliliter samples were taken from the reactor at pre-determined time intervals, including equilibrium time (60 min). At the end of the adsorption period, the solution was centrifuged for 15 min at 5000 rpm. All the concentrations were measured at the wavelength corresponding to max. absorbance, λ_{max} = 500 nm, using a spectrometer (Shimadzu UV-150-02). Then the concentrations of the samples were determined by using a standard calibration graph. The amounts of CR adsorbed onto bentonite were calculated from the concentrations in solutions before and after the adsorption process.

3. Results and discussion

3.1. Adsorption equilibrium

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. Adsorption isotherm also usually describes the equilibrium relationship between adsorbent and adsorbate. Fig. 2 shows the equilibrium adsorption of CR (q_e versus C_e) onto bentonite. To optimize the design of an adsorption system to remove dyes from effluents, it is important to establish the most appropriate correlation for the equilibrium curve. Hence, the correlation of equilibrium data using either a theoretical or empirical equation is essential for the adsorption interpretation and prediction of the extent of adsorption. Therefore, the equilibrium experimental data for adsorbed data CR on bentonite were analyzed using the Langmuir, Freundlich and Temkin isotherms in the present study.

3.1.1. Langmuir isotherm

The Langmuir isotherm is most widely used for the adsorption of pollutants from liquid solutions [13,14].

The Langmuir isotherm is represented as follows:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{1}$$

where q_e (mg/g) and C_e (mg/L) are the amount of adsorbed dye per unit weight of adsorbent and unadsorbed dye concentration in solution at equilibrium, respectively. The K_L (L/g) and
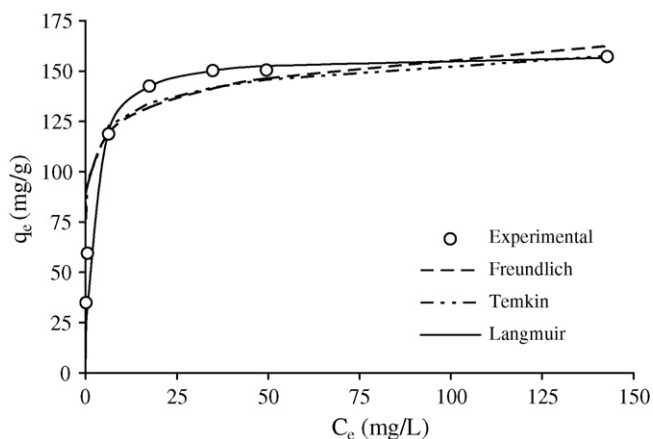

Fig. 2. Equilibrium isotherms of CR on bentonite. Conditions: 53–75 μm particle size, 1 g/L dose, 298 K temperature and pH 6.8.

Table 2
Langmuir, Freundlich and Temkin isotherm constants for CR adsorption

Langmuir						Freundlich				Temkin			
K_L (L/g)	a_L (L/mg)	Q_0 (mg/g)	R_L	r^2	S.D.	K_F (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	n (g/L)	r^2	S.D.	B	A (L/g)	r^2	S.D.
78.74	0.496	158.7	0.007–0.026	0.999	0.371	99.36	10.09	0.978	1.387	11.12	9903	0.987	1.337

a_L (L/mg) are the Langmuir isotherm constants. The Langmuir isotherm constants, K_L and a_L are evaluated through linearization of Eq. (1).

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \qquad (2)$$

The adsorption data were analyzed according to the linear form of the Langmuir isotherm (Eq. (2)). The values of the Langmuir constants K_L, a_L and Q_0 with the correlation coefficient are listed in Table 2 for the CR–bentonite system and the theoretical Langmuir isotherm is plotted in Fig. 2 together with the experimental data points.

The isotherm was found to be linear over the entire concentration range studies with a good linear correlation coefficient ($r^2 = 0.999$), showing that data correctly fit the Langmuir isotherm. The value of the correlation coefficient is higher than the other two isotherm values. In all cases, the Langmuir equation represents the best fit of experimental data than the other isotherm equation (Fig. 2). The monolayer saturation capacity of bentonite, Q_0, was found to be 158.7 mg/g.

This value was comparable to the adsorption capacities of some other adsorbent materials for CR (Table 3). The fact that Langmuir isotherm fits the experimental data very well confirms the monolayer coverage of dye onto bentonite particles and also the homogeneous distribution of active sites on the adsorbent, since the Langmuir equation assumes that the surface is homogeneous.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor (R_L, also called equilibrium parameter) which is defined by the following equation [2,13,25,26].

$$R_L = \frac{1}{1 + a_L C_0} \qquad (3)$$

where C_0 (mg/L) is the initial dye concentration and a_L (L/mg) is the Langmuir constant related to the energy of adsorption. The value of R_L indicates the shape of the isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The influence of isotherm shape on whether adsorption is favorable or unfavorable has been considered. For a Langmuir-type adsorption process, the isotherm shape can be classified by a dimensionless constant separation factor (R_L), given by Eq. (3). It was observed that the value of R_L in the range 0–1 (Table 2) confirms the favorable uptake of the CR process. The calculated R_L values as different initial CR concentrations are shown in Fig. 3. Also lower R_L values at higher initial CR concentrations showed that adsorption was more favorable at higher concentration. The degree of favorability is generally related to
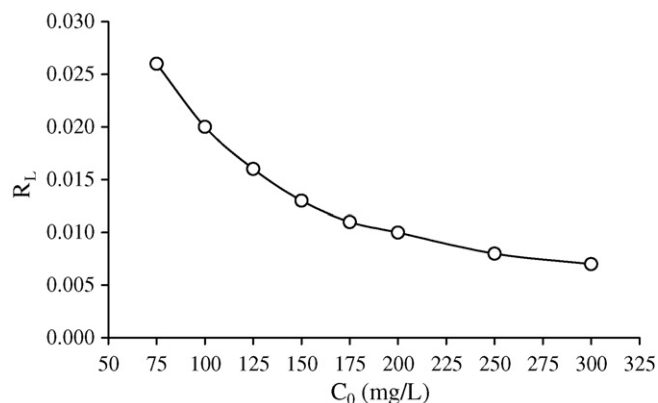

Fig. 3. Plot of separation factor versus initial Congo Red concentration.

the irreversibility of the system, giving a qualitative assessment of the bentonite–CR interactions. The degrees tended toward zero (the completely ideal irreversible case) rather than unity (which represents a completely reversible case).

Table 3
Reported maximum adsorption capacities (Q_0 in mg/g) in the literature for CR obtained on low-cost adsorbents

Adsorbent	Q_0 (mg/g)	References
Straw carbon	403.7	[15]
Rice husk carbon	237.8	[15]
Fertilizer plant waste carbon	233.9	[16]
SA/N/CaFe	189.0	[3]
Coconut shell carbon	188.4	[15]
Rice hull ash	171.0	[17]
KJA/N/CaFe	161.0	[3]
KJA/S/CaFe	159.0	[3]
Bentonite	158.7	This study
Treated sunflower stalks	155.2	[18]
Groundnut shell carbon	110.8	[15]
Bamboo dust carbon	101.9	[15]
Neem leaf powder	72.40	[19]
KJA/Ti	52.00	[3]
Waste Fe(III)/Cr(III) hydroxide	44.00	[20]
Untreated sunflower stalks	34.26	[18]
Rice hull ash/kaolinite/starch	21.00	[18]
Banana peel	18.20	[7]
Powdered activated carbon	16.81	[21]
Activated carbon	15.80	[22]
Fungal biomaass	14.16	[21]
Orange peel	14.00	[7]
Granular activated carbon	13.80	[21]
Bagasse fly ash	11.88	[4]
Activated red mud	7.080	[23]
Coir pith	6.720	[24]
Fly ash	4.125	[22]
Activated carbon (Laboratory grade)	1.875	[4]
Activated carbon (Commercial grade)	0.635	[4]

3.1.2. Freundlich isotherm

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems and is expressed by the following equation [13,27].

$$q_e = K_F C_e^{1/n} \tag{4}$$

where K_F (mg$^{1-1/n}$ L$^{1/n}$ g^{-1}) is the Freundlich constant related to the bonding energy, and n (g/L) is the heterogeneity factor. A linear form of the Freundlich isotherm can be obtained by taking logarithms of Eq. (4):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

The values of the Freundlich constants together with the correlation coefficient are presented in Table 2 and the theoretical Freundlich equation is shown in Fig. 2. The value of correlation coefficient is much lower than the other two isotherm values. In all cases, the Freundlich equation represents the poorest fit of experimental data than the other isotherm equations (Fig. 2).

3.1.3. Temkin isotherm

Temkin isotherm contains a factor that explicitly takes into the account adsorbing species–adsorbent interactions [4,14]. The Temkin isotherm is given as:

$$q_e = \frac{RT}{b} \ln(AC_e) \tag{6}$$

where

$$\frac{RT}{b} = B$$

A linear form of the Temkin isotherm can be expressed as:

$$q_e = B \ln A + B \ln C_e \tag{7}$$

A (L/mg) is the equilibrium binding constant corresponding to the maximum binding energy, b (J/mol) is Temkin isotherm constant and constant B (dimensionless) is related to the heat of adsorption. The adsorption data were analyzed according to Eq. (7). The values of the Temkin constants A and B are listed in Table 2 and the theoretical plot of this isotherm is shown in Fig. 2. The correlation coefficient is also listed in Table 2 and is higher than the Freundlich value but lower than the Langmuir value. Therefore, the Temkin isotherm represents a better fit of experimental data than the Freundlich isotherm but not in the case of Langmuir isotherm (Fig. 2).

As seen from Table 2 and Fig. 2, the Langmuir isotherm provides the best correlation for the experimental data, whereas the Temkin isotherm also fits the experimental data well. This suggests that CR adsorption is limited with monolayer coverage and the surface is relatively homogenous in terms of functional groups and there is significant interaction among the CR molecules.

It is also necessary to analyze the data set to confirm the best fit isotherm for the sorption system, a standard deviation (S.D.)

is calculated as follows [28]:

$$S.D. = \sqrt{\frac{\sum \left[(q_{t,\exp} - q_{t,\text{cal}})/q_{t,\exp} \right]^2}{(n-1)}} \tag{8}$$

where n is the number of data points. The S.D. test is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models. If data from the model are similar to experimental data, S.D. will be a small number, if they are different, S.D. will be a large number. Fig. 2 shows the Langmuir, Freundlich and Temkin curves for CR onto bentonite along with the experimental data. The curves were generated using Eqs. (1), (4) and (6). The values of S.D. for each isotherm were obtained and are given in Table 2. It was observed that, in simulation, the equilibrium data were well represented by the Langmuir isotherm equation when compared to the Freundlich and Temkin equations, with a S.D. value of 0.371, 1.387 and 1.337, respectively (Table 2). There was a good agreement between the experimental data and the calculated value from the Langmuir equation.

It can also be seen from Fig. 2, the experimental data were fitted well with Freundlich and Temkin isotherms at lower concentrations. This may be explained based on the each isotherm assumptions. The Freundlich and Temkin isotherms are used for heterogeneous surface energy systems, while the Langmuir isotherm is used for homogeneous surface sites. The Freundlich equation generally agrees quite well with Langmuir equation and experimental data over moderate ranges of concentration. Unlike the Langmuir equation, it does not agree well with the experimental data at very high concentrations, since n must reach some limit when the surface is fully covered [1]. The Freundlich isotherm assumes that there is a continuously varying energy of adsorption as the most actively energetic sites are occupied first and the surface is continually occupied until the lowest energy sites are filled at the end of the adsorption process [29]. Therefore, the Freundlich isotherm agrees quite well with experimental data at low coverage of an adsorbent surface [30]. Similarly, Temkin isotherm follows from an assumption that the heat of adsorption drops linearly with increasing surface coverage. The Freundlich and Temkin equations fit the experimental data better at low concentrations whereas those for the Langmuir expression tend to fit better at higher concentrations [1].

3.2. Adsorption kinetics

Effect of contact time and initial CR concentration on adsorption of CR by bentonite are shown in Fig. 4. The amount of CR adsorbed increased with increase in contact time and reached equilibrium after 60 min. It can be observed that the time required to attain the equilibrium was increased with increasing initial CR concentration. But in the first 20 min, the initial rate of adsorption was greater for higher initial CR concentration. Because the diffusion of CR molecules through solution to the surface of bentonite is affected by the CR concentration, since mixing speed is constant. An increase of CR concentration accel-
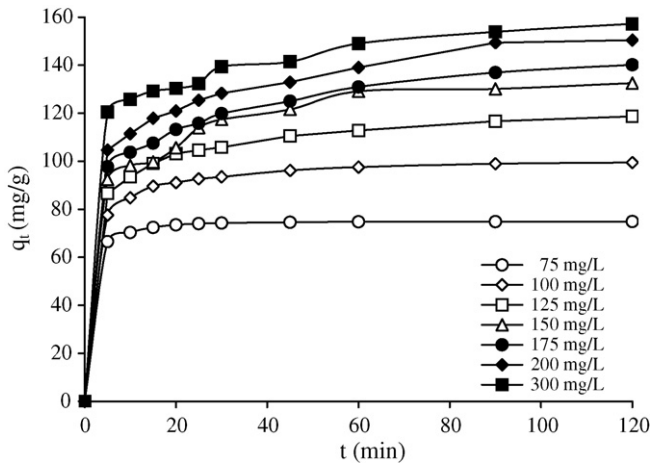
Fig. 4. Adsorption kinetics of CR on bentonite at different initial CR concentration. Conditions: 53–75 μm particle size, 1 g/L dose, 298 K temperature and pH 6.8.

erates the diffusion of CR from the solution onto bentonite due to the increase in driving force of the concentration gradients [14].

The chemical kinetic describes reaction pathways, along times to reach the equilibrium whereas chemical equilibrium gives no information about pathways and reaction rates. Adsorption kinetics show large dependence on the physical and/or chemical characteristics of the adsorbent material, and adsorbate species which also influence the adsorption mechanism [31]. In order to investigate the mechanism of adsorption such as chemical reaction, diffusion control and mass transfer, several kinetic models have been used at different experimental conditions for adsorption processes.

3.2.1. Pseudo first-order equation

The pseudo first-order equation of Lagergren [13,32] is given by

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{9}$$

where q_t and q_e are the amounts of CR adsorbed at time t and equilibrium (mg/g), respectively, and k_1 is the pseudo first-order rate constant for the adsorption process (1/min).

After integration and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = t$, the integrated form of Eq. (9) becomes

$$\ln\left(\frac{q_e}{q_e - q_t}\right) = k_1 t \tag{10}$$

Eq. (10) can be rearranged to obtain a linear form:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{11}$$

3.2.2. Pseudo second-order equation

The pseudo second-order chemisorption kinetic rate equation is expressed as [33–35]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{12}$$

where k_2 is the equilibrium rate constant of pseudo second-order equation (g/mg min). Integrating Eq. (12) for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ gives

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{13}$$

Eq. (13) can be rearranged to obtain the following linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{14}$$

3.2.3. The Elovich equation

The adsorption data may also be analyzed using the Elovich equation [6,28,36], which has the form:

$$\frac{dq_t}{dt} = \alpha\, e^{-\beta q_t} \tag{15}$$

where α is the initial adsorption rate constant (mg/g min) and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g/mg). The Elovich equation can be simplified by assuming that $\alpha\beta t \gg 1$ and the integration of the rate equation with the same boundary conditions as the pseudo first-and second-order equations becomes the Elovich equation.

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \tag{16}$$

3.2.4. Intraparticle diffusion equation

The dye adsorption is governed usually by either the liquid-phase mass transport rate or the intraparticle mass transport rate. When the diffusion (internal surface and pore diffusion) of dye molecules inside the adsorbent is the rate-limiting step, then adsorption data can be presented by the following equation [6,13,19]:

$$q_t = k_i t^{1/2} \tag{17}$$

where k_i is the intraparticle diffusion rate constant (mg/g min$^{1/2}$).

The values of the Lagergren constants, q_e and k_1, and the correlation coefficients are calculated from linear pseudo first-order equation at all concentration studied (plot not shown) and are presented in Table 4. The correlation coefficients for the pseudo first-order kinetic model obtained at all the studied concentrations were relatively high. The r^2 values for the plots were in the range 0.909–0.989 (Table 4). However, although r^2 values are reasonably high in some cases, the calculated q_e values obtained from this equation do not give reasonable values (Table 4), which are too low compared with experimental q_e values. This finding suggests that the adsorption process does not follow the pseudo first-order adsorption rate expression of Lagergren. If the intercept value does not equal $\ln q_e$, the reaction is not likely to obey a pseudo first-order kinetic model, even this plot has a high correlation coefficient with experimental data [13,33]. In addition, it was observed that, at all initial dye concentrations, the adsorption data were well represented by the Lagergren model only the first 60 min and thereafter it deviate from theory. The adsorption data were well represented only in the region where rapid adsorption took place. This confirms that it was not appropriate to use

Table 4
Kinetic parameters for the adsorption of CR onto bentonite

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	First-order kinetic equation				Second-order kinetic equation				The Elovich equation				Intraparticle diffusion equation		
		q_1 (mg/g)	k_1 (1/min) ×10²	r_1^2	S.D.	q_2 (mg/g)	k_2 [g/(mg min)] ×10³	r_2^2	S.D.	α	β	r_E^2	S.D.	k_{int} [mg/(g min$^{1/2}$)]	r_{int}^2	S.D.
75	74.90	6.514	6.43	0.964	0.983	75.19	24.6	0.999	0.009	1.509×10^{12}	0.418	0.973	0.018	2.385	0.915	0.994
100	99.48	21.15	4.11	0.989	0.899	101.0	4.83	0.999	0.026	2.173×10^{5}	0.149	0.944	0.038	4.849	0.931	0.912
125	118.7	32.57	3.04	0.989	0.873	120.5	2.39	0.999	0.062	1.073×10^{4}	0.098	0.993	0.065	6.121	0.967	0.859
150	132.5	49.20	3.64	0.957	0.783	137.0	1.56	0.999	0.084	1.470×10^{3}	0.070	0.956	0.092	7.792	0.939	0.800
175	140.2	50.12	2.86	0.982	0.817	144.9	1.34	0.998	0.097	2.322×10^{3}	0.071	0.987	0.102	6.805	0.995	0.809
200	150.5	67.35	3.94	0.909	0.675	156.3	1.23	0.998	0.147	2.453×10^{3}	0.066	0.984	0.155	7.338	0.996	0.778
300	157.2	44.84	2.80	0.982	0.871	161.3	1.54	0.999	0.094	3.456×10^{4}	0.082	0.958	0.125	5.101	0.932	0.865

the Lagergren kinetic model to predict the adsorption kinetics of CR onto bentonite for the entire adsorption period. The literature data show that the equation does not fit well with the whole range of contact time and is generally applicable over the initial stage of the adsorption process [13,19].

The pseudo second-order (and also the pseudo first-order) is based on the adsorption capacity: it only predicts the behavior over the "whole" range of studies supporting the validity, and is in agreement with chemisorption being the rate-control [13,27]. The curve-fitting plots of t/q_t versus t give a straight line for all the initial CR concentrations studied (plot not shown), while the plots of $\ln(q_e - q_t)$ versus t does not show good results for the entire adsorption period, confirming the applicability of the pseudo second-order equation. The parameters obtained for the pseudo second-order equation are presented in Table 4.

The values of r^2 and q_e also indicated that this equation produced better results (Table 4): at all concentrations, r^2 values for this kinetic model were found to be extremely high (>0.998), and the calculated q_e values also agree very well with the experimental data.

The adsorption system obeys the pseudo second-order kinetic model for the entire adsorption period and thus supports the assumption behind the model that the adsorption is due to chemisorption. The adsorption of dye takes place probably via surface exchange reactions until the surface functional sites are fully occupied; thereafter dye molecules diffuse into the bentonite layers for further interactions and/or reactions such as ion-exchange, complexation interactions [2,8,13,27]. This reaction mechanism may be partly due to complexation between the negatively charged groups (D–SO$_3^-$) in CR and positively charged Al$_2$O$_3$ groups on the bentonite surface or to ion exchange between positively charged groups (D–$^+$NH$_3$ or –$^+$NH=N–) in CR and Na$^+$ ions, initially present in the exchange position of the bentonite.

The constants of the Elovich equation for the same experimental data were obtained from the slop and intercept of the plot of q_t against $\ln t$ (plot not shown). In this case, a linear relationship was obtained between CR adsorbed, q_t, and $\ln t$ over the whole adsorption period, with correlation coefficients between 0.973 and 0.993 for all the lines (Table 4). In the case of using the Elovich equation, the correlation coefficients are lower than those of the pseudo second-order equation. The Elovich equation does not predict any definite mechanism, but it is useful in describing adsorption on highly heterogeneous adsorbents.

This situation indicates that the Elovich equation may also be used to predict the adsorption kinetics of CR onto bentonite for the entire adsorption period, since bentonite possesses heterogeneous surface active sites such as Al$_2$O$_3$ and SiO$_2$.

Intraparticle diffusion rate constants for different initial dye concentrations were obtained from the amount of dye adsorbed versus $t^{1/2}$ plots. The results showed that the plots presented a multilinearity, which indicated that two or more steps occurred in the process.

The external surface adsorption (stage 1) was not observed from q_e versus $t^{1/2}$ plots. Stage 1 is the fastest and completed before 5 min, and then the stage of intraparticle diffusion control (stage 2) is attained and continues from 5 to 30 min. Finally,
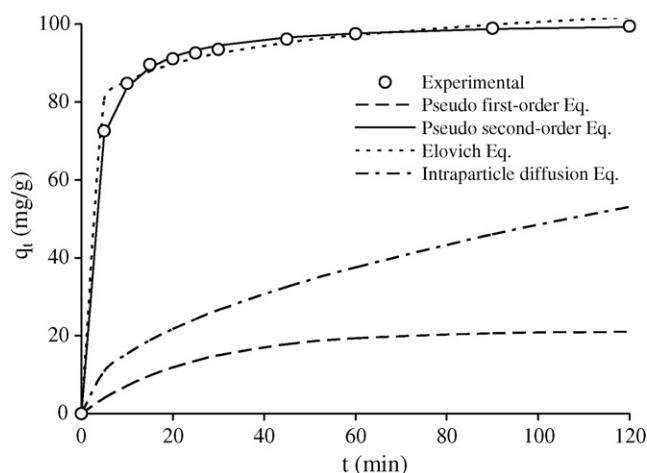
Fig. 5. Comparison between the measured and modeled time profiles for the adsorption of CR (100 mg/L initial CR concentration) on bentonite.

Fig. 6. Effect of pH on adsorption of CR by bentonite. Conditions: 100 mg/L concentration, 53–75 μm particle size, 1 g/L dose and 298 K temperature.

final equilibrium adsorption (stage 3) starts after 30 min. The slope of the first linear portion (stage 2) characterizes the rate parameter corresponding to the intraparticle diffusion, whereas the intercept of this portion is proportional to the boundary layer thickness. The k_i values for each initial concentration are given in Table 4. The r^2 values for this diffusion model are between 0.915 and 0.996 (Table 4). This indicates that the adsorption of CR onto bentonite can be followed by an intraparticle diffusion about 30 min. However, the lines do not pass through the origin (the plots have intercepts in the range 62.2–108 mg/g), indicating that intraparticle diffusion is involved in the adsorption process but it is not the only rate-limiting mechanism and that some other mechanisms such as complexation or ion exchange also play an important role.

A comparison of calculated q_t from different kinetic equations and experimental results for 100 mg/L initial dye concentration is shown in Fig. 5. The pseudo second-order equation provides the best correlation for all of the adsorption process, whereas the Elovich equation also fits the experimental data well. The pseudo first-order and intraparticle diffusion equations do not give a good fit to the experimental data for the adsorption of CR.

Four different kinetic models were used fit the experimental data. The comparison of S.D. of the kinetic models should assist in identifying the best fit equation. Since the S.D. method represents the agreement between the experimental data points and models, the S.D. value provides a numerical value to interpret the goodness of fit of a given mathematical model to the data. Table 4 presents the S.D. values calculated from each kinetic equation. From this table, the comparison of error analysis showed that the order of deviation was >intraparticle diffusion equation, >pseudo first-order equation, the Elovich equation >pseudo second-order equation, which indicated that the pseudo second-order equation was the best one in describing the adsorption kinetics of CR on bentonite. The Elovich equation follows the pseudo second-order one and also provides a good fitting to the experimental data points. This was also confirmed in Fig. 5.
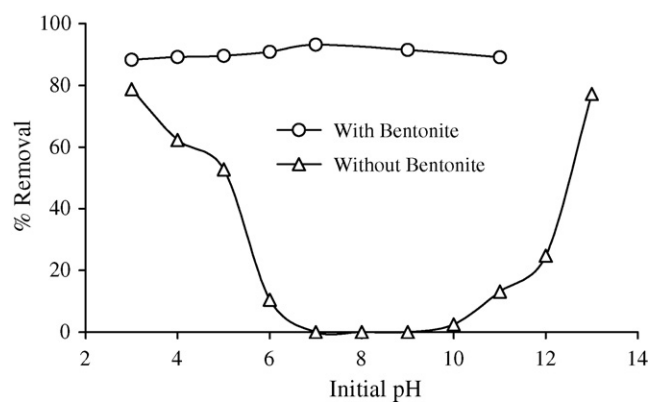
This suggests that the adsorption system studied belong to the pseudo second-order kinetic model, based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate.

3.3. Effect of pH

The initial pH values of dye solutions affect the chemistry of both a dye molecule and an adsorbent. The pH is also known to affect the structural stability of CR and, therefore, its color intensity. Hence, the effect of initial pH was studied with blank CR solutions of concentration 100 mg/L. The solution was kept for 1 h after the pH adjustment and, thereafter, the absorbance of the solution was found out. It is found that the color is stable at initial pH around 7. Fig. 6 shows the color removal without bentonite over an initial pH range of 3–13. The pH reduces the color below pH 6 and above pH 10, however, color change is negligible over a pH range of 6–10. The results indicated that the molecular form of CR in solution medium changed markedly in the pH range 3–5, and at a high pH of 12 (the color of CR changes from dark blue at pH 3–5 to red at pH 12). In addition, the red color is different from the original red in the pH range 10–12. Color and its intensity change due to pH change alone may be due to the structural changes being effected in the dye molecules.

The adsorption of organic cationic dyes by clay minerals has been investigated for many years. There is very little information on the adsorption of organic anions by clay minerals in the literature. Also, there are contradictory results about the effect of pH on the adsorption of CR by various adsorbents in the literature.

Effect of initial pH on the adsorption of CR with bentonite for 100 mg/L initial dye concentration is also shown in Fig. 6. More than 80% color removal is observed in the pH range 3–11. In spite of being an anionic dye, CR is adsorbed by clay minerals in considerably amounts. Similar result was reported for the adsorption of CR on montmorillonite [37]. This was explained based on both chemical structure and behavior of CR and bentonite in the studied conditions.

In the aqueous solution, the acid dye is first dissolved and the sulfonate groups of the acid dye (D–SO_3Na) are dissociated and

converted to anionic dye ions at natural solution pH of 6.8.

$$D - SO_3Na \xrightarrow{H_2O} D - SO_3^- + Na^+ \qquad (18)$$
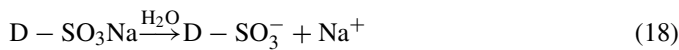
The oxides of Al, Ca and Si present in the bentonite develop charge in contact with water or dye solution. Except silica, all other oxides possess positive charge for the studied pH range of interest because zero point charge of SiO_2, Al_2O_3 and CaO are 2.2, 8.3 and 11.0, respectively [38]. Even, the negatively charged silica sites of bentonite are neutralized by H^+ ions thereby reducing hindrance to the diffusion of the anionic dye ions. For the initial pH below 7, a significantly high electrostatic attraction exists between the positively charged surface (Al_2O_3 and CaO sites) of the adsorbent and the anionic dye. As the pH of the system increased, the number of negatively charged sites increased and the number of positively charged sites decreased. A negatively charged surface site on the adsorbent did not favor the adsorption of dye anions due to electrostatic repulsion. Also, there was competition between OH^- (at high pH) and colored ions of CR for negatively charged adsorption sites. However, in the alkaline pH range 7–11, significant adsorption still occurred. This suggests that chemisorption might have been operative in this pH range. In the initial pH range 10–12, Al_2O_3 and CaO become negatively charged. Thus, electrostatic repulsion between negatively charged surface of bentonite and anionic dye causes significant reduction in the removal of dye from the solution.

CR is a dipolar molecule (H_3N^+–R–SO_3^-) at low pH [21]. Pigorsch et al. [39] suggested the presence of two protonated tautomeric species of CR zwitterion, an ammonium form, where the protons attached to the amino nitrogen and an azonium form, where they were attached to the α-azo nitrogen. Many functional N-sites are present on CR and some of the nitrogens form hydrogen bonds by accepting protons from the solution and some are protonated to form cationic species [40]. Thus, the cationic dye was adsorbed by the bentonite, probably by the mechanism of cation exchange, replacing Na^+, initially present in the exchange position of the bentonite. Based on FTIR spectroscopy study, Acemoğlu [41] reported that the interaction of CR and fly ash occurs between active sites of fly ash and SO_3^- and –N=N– groups on CR.

Fu and Viraraghavan [42] suggested that two primary amines (–NH_2) attached to the two naphthalene rings located at the two ends of the CR molecule can be protonated (–NH_3) at the initial pH of 6 and could have stronger basicity, which could result in the attraction between the protonated amine (–NH_3) and the negatively charged surface (SiO_2 sites) of the adsorbent. They also proposed that electrostatic attraction was the primary mechanism, while other mechanisms could also be involved in the biosorption of CR.

3.4. Designing batch adsorption from equilibrium data

Adsorption isotherms can be used to predict the design of single-stage batch adsorption systems [2,5,43,44]. A schematic diagram is shown in Fig. 7. Consider an effluent containing V (m^3) of solution and the dye concentration reduced from C_0
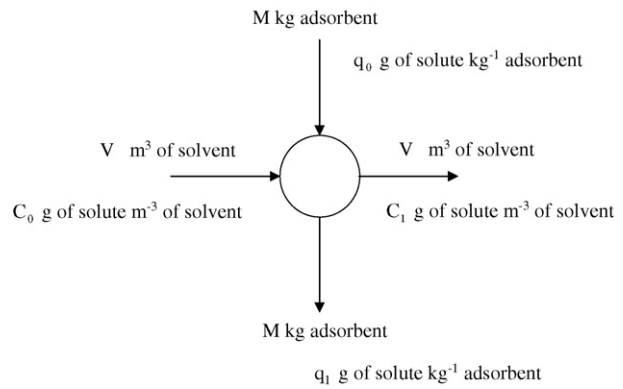

Fig. 7. Single stage contacting of a batch of fluid with a batch of adsorbent.

to C_1 (g dye/m^3) solution. The amount of adsorbent is M kg and the solute loading changes from q_0 to q_1 (g dye/kg) adsorbent. When fresh adsorbent is used, $q_0 = 0$ and the mass balance equates the dye removed from the liquid to that picked up by the solid.

$$V(C_0 - C_1) = M(q_0 - q_1) = Mq_1 \qquad (19)$$

If the system is allowed to come to equilibrium, then,

$$C_1 \rightarrow C_e \text{ and } q_1 \rightarrow q_e \qquad (20)$$

In the case of the adsorption of CR on bentonite the Langmuir isotherm gives the best fit to experimental data. Consequently, the Langmuir equation can be best substituted for q_1 in the rearranged form of Eq. (17) giving adsorbent/solution for a given change in dye concentration, $C_0 - C_e$, at this particular system.

$$\frac{M}{V} = \frac{C_0 - C_e}{q_1} = \frac{C_0 - C_e}{q_e} \equiv \frac{C_0 - C_e}{K_L C_e / (1 + a_L C_e)} \qquad (21)$$

Fig. 8 shows a series of plots derived from Eq. (19) for the adsorption of CR on bentonite. An initial dye concentration of 100 g/m^3 is assumed and Fig. 8 shows the required amount of bentonite to reduce the color content by 80–95% at various volumes of effluents. In the case of a single-stage batch adsorption system, the design procedure is now outlined. For example, 50 m^3 of solution is to be treated. The required masses of ben-
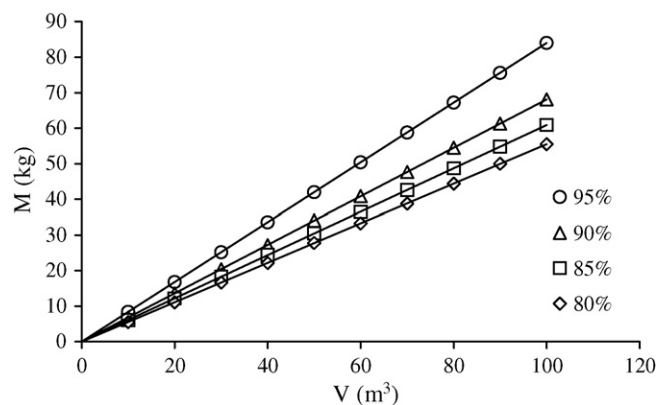

Fig. 8. Adsorbent mass (M) against volume of effluent (V) treated for various percentage of color removal at 100 g/m^3 initial CR concentration.
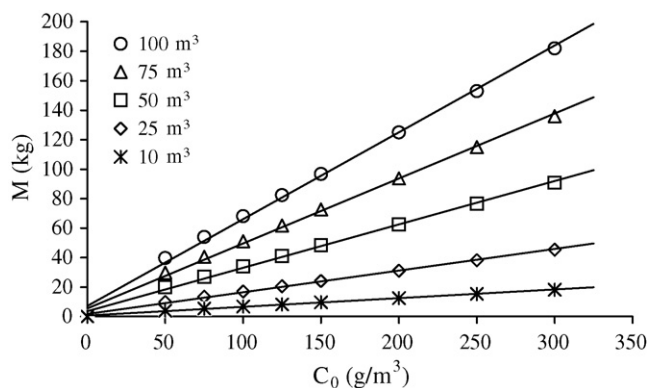
Fig. 9. Adsorbent mass (*M*) against initial CR concentration for 90% color removal at various volume of effluent (*V*) treated.

tonite are 27.8, 30.5, 34.1 and 42.0 kg for 80, 85, 90 and 95% dye removal, respectively.

Fig. 9 shows the required amount of bentonite to reduce the color content by 90% at various volumes of effluents which have different CR concentrations. For example, 50 m³ of solution is to be treated. The required amounts of bentonite to reduce the color content by 90% increased from 27.0 to 90.8 kg with increase in the initial CR concentration from 75 to 300 g/m³.

4. Conclusion

Equilibrium and kinetic studies were conducted for the adsorption of CR from aqueous solutions onto bentonite in the concentration range 75–300 mg/L at pH 6.8 and 298 K. The equilibrium data have been analyzed using Langmuir, Freundlich and Temkin isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The Langmuir isotherm was demonstrated to provide the best correlation for the adsorption of CR onto bentonite.

The adsorbed amounts of CR increased with increase in contact time and reached the equilibrium after 60 min. The equilibrium time is independent of initial CR concentration. The kinetics of adsorption of CR onto bentonite was studied by using pseudo first- and second-order equations, the Elovich equation and the Intraparticle diffusion equation. All findings presented in this study suggest that CR/bentonite system cannot be described by a first-order reaction and intraparticle diffusion model. For the examined system, the pseudo second-order kinetic model provided the best correlation of the experimental data. The adsorption of CR onto bentonite can also be successfully interpreted by the Elovich equation. This supports the heterogeneous sorption mechanism likely to be responsible for CR uptake. The reaction mechanism may be partly a result of the complexation or ion exchange between the CR molecules and the SiO_2 or Al_2O_3 groups on the bentonite surfaces.

Assuming the batch adsorption to be a single-staged equilibrium operation, the separation process can be defined mathematically using the Langmuir isotherm constants to estimate the residual concentration of CR or amount of adsorbent for desired purification.

The results of present investigation show that bentonite has considerable potential for the removal of CR from aqueous solution over a wide range of concentration. It may be concluded that bentonite may be used as a low-cost, natural and abundant source for the removal of CR and they may be an alternative to more costly materials. It may also be effective in removing as well other harmful or undesirable species such as heavy metals, dyes and other hazardous pollutants, present in the waste effluents.

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