



## Adsorption of Congo red from aqueous solutions onto Ca-bentonite

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### ABSTRACT

The ability of Ca-bentonite to remove Congo red dye from aqueous solutions has been carried out as a function of contact time, temperature (20–50 °C), pH (5–10) and concentration (50–200 mg L<sup>-1</sup>). An amount of 0.2 g of Ca-bentonite could remove more than 90.0% of the dye from 100 mg L<sup>-1</sup> Congo red dye solution for the temperature range studied here. The amount of dye adsorbed per unit weight of Ca-bentonite increased from 23.25 to 85.29 mg g<sup>-1</sup> with increasing concentration from 50 to 200 mg L<sup>-1</sup>, but it had a little change with temperature and decreased slightly with increasing pH. The kinetics of adsorption in view of three kinetic models, i.e., the pseudo-first-order Lagergren model, the pseudo-second-order model and the intraparticle diffusion model, was discussed. The pseudo-second-order kinetic model described the adsorption of Congo red on Ca-bentonite very well. Analysis of adsorption results obtained at 20 °C showed that the adsorption pattern on Ca-bentonite followed the Freundlich isotherms. It was indicative of the heterogeneity of the adsorption sites on the clay particles. From thermodynamic studies, it was seen that the adsorption was spontaneous and endothermic.

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### 1. Introduction

Industrial effluents are one of the major causes of environmental pollution because effluents discharged from dyeing industries are highly colored with a large amount of suspended organic solid [1]. Untreated disposal of this colored water into the receiving water body either causes damage to aquatic life or to human beings by mutagenic and carcinogenic effect. As a matter of fact, the discharge of such effluents is worrying for both toxicological and environmental reasons [2,3].

Conventional wastewater treatment methods for removing dyes include physicochemical, chemical and biological methods, such as coagulation and flocculation [4], adsorption [5], ozonation [6], electrochemical techniques [7], and fungal decolorization [8]. Among these methods adsorption has gained favour in recent years due to proven efficiency in the removal of pollutants from effluents to stable forms for the above treatment methods [1]. Activated carbon, as an adsorbent has been widely investigated for the adsorption of dyes [9], but its high cost limits its commercial application. In recent years, there has been growing interest in finding inexpensive and effective alternatives to carbon, such as clay minerals [10], fly ash [11], peat [12], wood powder [13], coir pith [14,15], and lignin [16].

There are many types of naturally occurring clays such as bentonite that have shown promises in adsorption applications [17]. The wide usefulness of this kind of clay is a result of its high specific surface area, its high chemical and mechanical stability, and a variety of surface and structural properties. Bentonite is characterized by one Al octahedral sheet placed between two Si tetrahedral sheets. It has permanent negative charges that arise due to the isomorphous substitution of Al<sup>3+</sup> for Si<sup>4+</sup> in the tetrahedral layer and Mg<sup>2+</sup> for Al<sup>3+</sup> in the octahedral layer. This charge imbalance is offset by exchangeable cations (Na<sup>+</sup> and Ca<sup>2+</sup>, etc.) at the bentonite surface [18]. Moreover, the world bentonite resource is abundant. Its ultimate reserve is approximately 2.5 billion tons, more than 80% of which is Ca-bentonite [19]. Consequently, how to make full use of Ca-bentonite is of vital significance.

Na-bentonite and modified bentonite showed higher sorption capacities for the removal of most kinds of dyes from aqueous solution, and a number of studies have been carried out. For example, Tahir and Naseem have studied the removal of a cationic dye by Na-bentonite [20]. Safa Özcan and Özcan have investigated the adsorption of acid dyes from aqueous solutions onto acid-activated bentonite [21]. In another work, Baskaralingam has used organobentonite to decolorize Acid Red 151 from aqueous solution [2]. To our best knowledge, the adsorption of Congo red dye on Ca-bentonite has not been reported. Ca-bentonite is a good adsorbent for Congo red according to the experiment we conducted. Therefore, the objectives of the present investigation are to understand the way the Congo red interacts with Ca-bentonite and to study the adsorption mechanism of Congo red onto Ca-bentonite.

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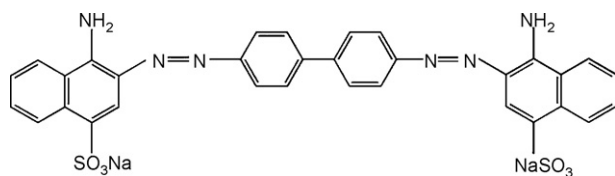


Fig. 1. Molecular structure of Congo red dyestuff.

## 2. Materials and methods

### 2.1. Adsorbent and Congo red dye

The adsorbent used in this study is provided by a local industry in Jilin, China. It was crushed, ground, and sieved through a 100-mesh and dried at 120 °C in an oven for 2 h prior to use. Bentonite cation exchange capacity (CEC) characterized by the methylene blue method [22] was 552.0 mmol kg<sup>-1</sup>. Congo red dye was purchased from Aldrich Chemical Company, and used without purification. The structure of this dye is shown in Fig. 1.

### 2.2. Experimental set-up

To study the effect of important parameters like the contact time, pH and initial dye concentration on the adsorptive removal of Congo red, adsorption experiments have been carried out by taking known doses of adsorbents with 100 mL of dye solution of various initial concentrations in 250 mL conical glass flasks in a shaking thermostat with a constant speed of 150 rpm. Samples were withdrawn at appropriate time intervals and centrifuged using Research Centrifuge at 3500 rpm for 5 min and the absorbance of the supernatant was measured colorimetrically using a spectrophotometer (UNICO WFJ2000) at 497 nm. The experiments were conducted at 20, 30, 40, and 50 °C to study the effect of temperature on the adsorption time and to evaluate the sorption thermodynamic parameter. The pH (5–10) of dye solution was adjusted with 0.1 N NaOH and HNO<sub>3</sub> solutions using a pH meter (Mettler–Toledo DTLTA320). The adsorption tests were carried out without buffer addition to avoid an influence of the additional ions on the process. To verify the concentration effect on the adsorption, 100 mL dye solution with different concentrations was contacted with 0.2 g Ca-bentonite. The values of the parameters studied in each experimental analysis are listed in Table 1. Kinetics of adsorption was determined by analyzing adsorptive uptake of the dye from aqueous solution at different time intervals. For adsorption isotherms determination, dye solutions of different concentrations were agitated with known amount of adsorbents till the equilibrium was achieved at 20 °C.

## 3. Results and discussion

### 3.1. Effect of contact time on adsorption

The effect of contact time on the percentage of color removal at various temperatures (Fig. 2) was examined at the 100 mg L<sup>-1</sup>

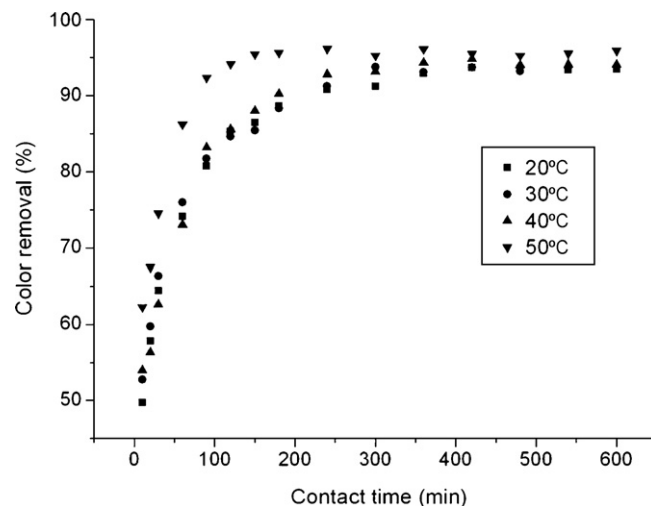


Fig. 2. Effect of agitation time and temperatures on the extent of adsorption.

concentration of Congo red. As can be seen from Fig. 2, the removal efficiency of Congo red onto Ca-bentonite by adsorption is rapid initially and then slows down gradually until it attains equilibrium. As also shown in Fig. 2, contact time need for Congo red is 480 min when the temperatures are between 20 and 40 °C. However, the uptake is very rapid and it attains equilibrium at 180 min at 50 °C. It is observed that >90% of dye removal is achieved, and maximum percent removal by Ca-bentonite is 95.92% at 50 °C. The fact that uptake of Congo red by Ca-bentonite increased with an increase in temperature implied that the enthalpy change had positive values, and the adsorption process was endothermic. Similar results have been reported for the adsorption of Reactive Red MF-3B onto organo-clay [23], and for the adsorption of reactive dye onto chemical cross-linked chitosan beads [24].

### 3.2. Effect of pH on adsorption

Congo red is an example of diazo dye, and the initial pH influences the molecular form of Congo red in the aqueous solution [25]. It was reported that the dye solution changed its color from red to dark blue when pH was adjusted to 2, and the red color was different from the original red in the pH range 10–12 [26,27]. Therefore, in this section, the pH of the solution was kept between 5 and 10.

Fig. 3 illustrates the effect of initial pH of dye solution on the adsorption of Congo red for initial dye concentration of 100 mg L<sup>-1</sup> at 20 °C. As shown in Fig. 3, the color removal efficiency (%) values are 94.59, 93.02, 92.53, 93.36, 92.53 and 92.00 in the pH range 5–10; maximum color removal takes place at pH 5, and the amount of dye adsorbed onto Ca-bentonite does not change significantly in the pH range 6–10. Furthermore, the initial pH of Congo red solution is 5.02, 6.02, 7.00, 7.93, 9.02 and 9.98, and the final pH is 6.38, 6.72, 6.97, 7.19, 7.21 and 7.25. That Ca-bentonite could neutralize H<sup>+</sup> or OH<sup>-</sup> in acidic or alkaline media and made the solution tend to neutral is because of its special structural properties. On one hand, bentonite

Table 1

The values of parameters in each experimental analysis

Experimental	pH	t (min)	T (°C)	C <sub>0</sub> (mg L <sup>-1</sup> )
Effect of contact time on adsorption	6.92 (nature pH)	0–600	20	100
Effect of pH on adsorption	5–10	0–600	20	100
Effect of temperature on adsorption	6.92	0–600	20–50	100
Effect of concentration on adsorption	6.92	0–600	20	50–200

t, contact time; T, temperature; C<sub>0</sub>, initial concentration.

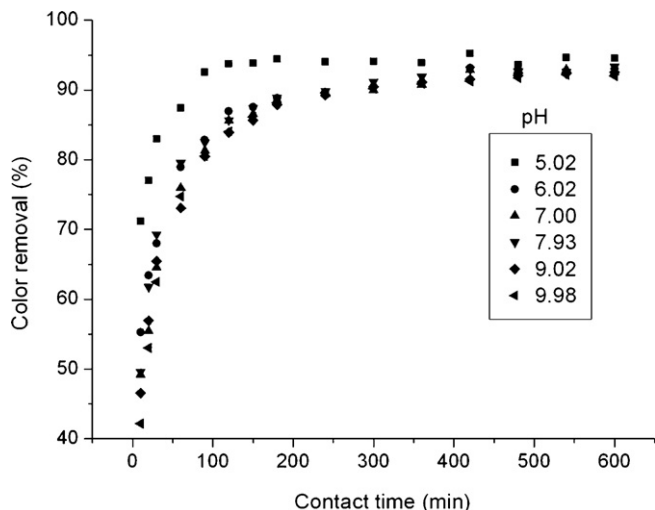


Fig. 3. Effect of pH on the percentage of color removal of Congo red.

has permanent negative charges that arise due to the isomorphous substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral layer and  $\text{Mg}^{2+}$  for  $\text{Al}^{3+}$  in the octahedral layer [2]. Therefore, Ca-bentonite can neutralize the acidic pH of the dye solution. On the other hand, Ca-bentonite has high calcium content, and thus,  $\text{Ca}^{2+}$  could neutralize the  $\text{OH}^-$  on the surface of Ca-bentonite, decreasing significantly the effect of pH on the adsorption. This means that this kind of bentonite may be suitable for the similar dyestuff wastewater treatment in different pHs.

### 3.3. Effect of initial dye concentration on adsorption

Four different concentrations, i.e., 50, 100, 150 and 200  $\text{mg L}^{-1}$ , respectively, were selected to investigate the effect of initial dye concentration ( $C_0$ ) on the adsorption of Congo red onto Ca-bentonite. The results obtained at 20 °C and nature pH (6.92) of Congo red solution are shown in Fig. 4. As shown in Fig. 4, with increasing initial dye concentration from 50 to 200  $\text{mg L}^{-1}$ , the amount of dye adsorbed by Ca-bentonite increases from 23.25 to 85.29  $\text{mg g}^{-1}$ . Fig. 4 also indicates that the adsorption of Congo red is fast at the initial stage, and then, it becomes slower near the equilibrium. It would be for that a large number of vacant surface sites are available for adsorption during the initial stage of the treatment time, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between Congo red dye adsorbed on the surface of Ca-bentonite and solution phase. It is clear that the adsorption process is highly dependent on initial concentration of solution.

### 3.4. Kinetics of adsorption

Pseudo-first-order, pseudo-second-order and the intraparticle diffusion model were used to test dynamical experimental data.

**Table 2**  
Comparison of the different kinetic model parameters at 20 °C

$C_0$ ( $\text{mg L}^{-1}$ )	Pseudo-first-order kinetic model		Pseudo-second-order kinetic model			Intraparticle diffusion model			
	$q_{1e}$ ( $\text{mg g}^{-1}$ )	$K_1$ ( $\text{min}^{-1}$ )	$R_1^2$	$q_{2e}$ ( $\text{mg g}^{-1}$ )	$K_2$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )	$R_2^2$	$C$	$k_p$	$r^2$
50	4.65	$4.07 \times 10^{-3}$	0.8269	23.88	$3.12 \times 10^{-3}$	0.9998	10.12	6.97	0.9163
100	13.60	$1.42 \times 10^{-3}$	0.9046	48.10	$1.52 \times 10^{-3}$	0.9999	22.27	18.82	0.9845
150	51.37	$2.79 \times 10^{-4}$	0.9820	88.26	$4.52 \times 10^{-4}$	0.9958	22.11	16.29	0.9492

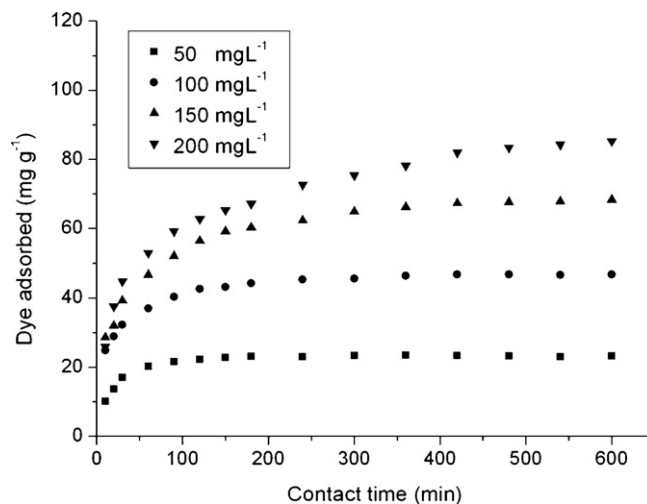


Fig. 4. Effect of initial dye concentration on the adsorption capacity of Ca-bentonite.

The pseudo-first-order kinetic model of Lagergren [28] is given by:

$$\log(q_{1e} - q_t) = \log q_{1e} - \frac{K_1}{2.303} t \quad (1)$$

where  $q_e$  and  $q_t$  are the amounts of dye adsorbed on adsorbent ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$ , respectively and  $K_1$  is the rate constant of pseudo-first-order adsorption ( $\text{min}^{-1}$ ). The slopes and intercepts of plots of  $\log(q_{1e} - q_t)$  versus  $t$  were used to determine the pseudo-first-order rate constant  $K_1$  and  $q_{1e}$ .

Pseudo-second-order rate equation can be expressed in the following form [29].

$$\frac{t}{q_t} = \frac{1}{K_2 q_{2e}^2} + \frac{t}{q_{2e}} \quad (2)$$

where  $K_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the rate constant of pseudo-second-order adsorption. The slopes and intercepts of plots of  $t/q_t$  versus  $t$  are used to calculate  $K_2$  and  $q_{2e}$ .

The sorption rate constant  $K_1$ ,  $K_2$  and  $q_e$  along with correlation coefficients for the pseudo-first-order and pseudo-second-order models are shown in Table 2. As can be seen from Table 2, with increasing concentration from 50 to 200  $\text{mg L}^{-1}$  at 20 °C, the rate constant of pseudo-first-order,  $K_1$ , decreases from  $4.07 \times 10^{-3}$  to  $2.79 \times 10^{-4} \text{ min}^{-1}$ , and the pseudo-second-order  $K_2$ , decreases from  $3.12 \times 10^{-3}$  to  $4.52 \times 10^{-4} \text{ g mg}^{-1} \text{ min}^{-1}$ . The values of  $q_{1e}$  and  $q_{2e}$  increased rapidly. The correlation coefficients ( $R_1^2$ ) for the Lagergren equation are not very high, between 0.8268 and 0.9820. The plots of the linearized form of the pseudo-second-order kinetic model for the adsorption of Congo red on Ca-bentonite are shown in Fig. 5. The correlation coefficients are much greater in this case, in the range of 0.9958–0.9999, confirming a very good agreement with experimental data. The value of the equilibrium adsorption capacity is found to be 48.10  $\text{mg g}^{-1}$ , which is close to the value of the experimental adsorption capacity (47.85  $\text{mg g}^{-1}$ ) for an initial dye concentration of 100  $\text{mg L}^{-1}$ . A similar phenomenon we have

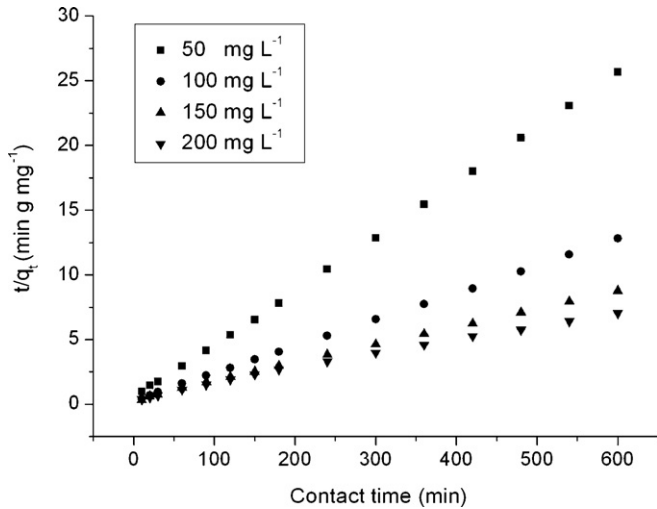


Fig. 5. Pseudo-second-order kinetic model for the adsorption of Congo red on Ca-bentonite.

also observed in the adsorption of tungsten species by biosorbent [30].

The intraparticle diffusion equation [31] is given by:

$$q_t = k_p t^{1/2} + C \quad (3)$$

where  $C$  is the intercept and  $k_p$  is the rate constant of intraparticle diffusion ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ) which is determined from the linear plot of  $q_t$  versus  $t^{1/2}$ , and it is usually used to compare mass transfer rates. According to this model, the plot of uptake,  $q_t$ , versus the square root of time,  $t^{1/2}$  should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin, then intraparticle diffusion is the rate controlling step [32,33].

The rate constant  $k_p$ ,  $C$  and  $r^2$  are shown in Table 2. The correlation coefficients ( $r^2$ ) for the intraparticle diffusion model are between 0.9163 and 0.9857 which are lower than the pseudo-second-order model, but it indicates that adsorption of Congo red onto Ca-bentonite may be followed by an intraparticle diffusion model. Fig. 6 shows the plots of fractional uptake for Congo red versus square root time on different concentration of Congo red. The plots do not pass through the origin, this is indicative of some degree of boundary layer control.

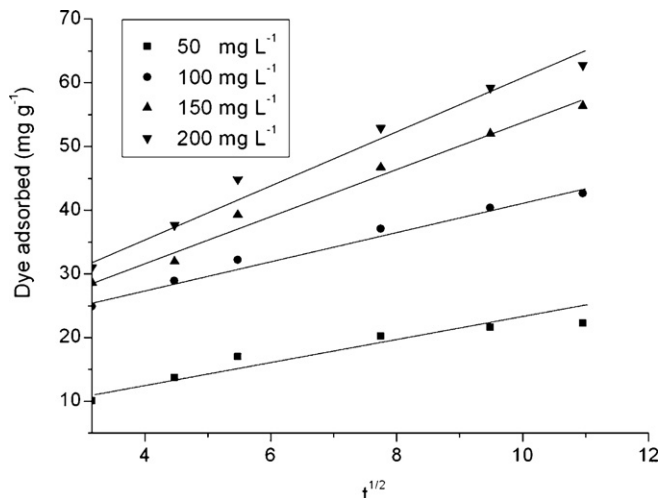


Fig. 6. Intraparticle diffusion for the adsorption of Congo red on Ca-bentonite.

Table 3

Adsorption isotherm constants for adsorption of Congo red on Ca-bentonite at 20 °C

Langmuir		Freundlich				
$q_{\max}$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	$r_L^2$	$R_L$	$K_f$	$n$	$r_F^2$
107.41	0.11	0.9775	0.093–0.570	26.91	3.23	0.9908

### 3.5. Adsorption isotherm

Adsorption isotherms are important for the description of how molecules of adsorbate interact with adsorbent surface. Hence, two important isotherms were selected in this study, which were, namely Langmuir, and Freundlich isotherms. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent [34]. Compared to the Langmuir isotherm, the Freundlich model is generally found to be better suited for characterizing multi-layer adsorption process [35].

The Langmuir isotherm is expressed:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{b q_{\max} C_e} \quad (4)$$

where  $C_e$  is the equilibrium concentration of the adsorbate ( $\text{mg L}^{-1}$ ),  $q_{\max}$  ( $\text{mg g}^{-1}$ ) and  $b$  ( $\text{mg}^{-1}$ ) are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively.  $q_{\max}$  and  $b$  are calculated from the slopes and intercepts of the straight lines of plot of  $1/q_e$  versus  $1/C_e$ .

The Freundlich adsorption isotherm can be expressed as:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (5)$$

where  $k_f$  and  $n$  are Freundlich adsorption isotherm constants, being indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively.  $k_f$  and  $(1/n)$  can be determined from the linear plot of  $\ln q_e$  versus  $\ln C_e$ .

The values of  $q_{\max}$ ,  $b$ ,  $k_f$ ,  $1/n$  and the correlation coefficients for Langmuir ( $r_L^2$ ) and for Freundlich ( $r_F^2$ ) are given in Table 3. It can be seen that the Freundlich model yields a much better fit than the Langmuir model. This, however, is indicative of the heterogeneity of the adsorption sites on the clay particles. From Table 3, it is noted that the values of  $n$  are bigger than 1, reflecting the beneficial adsorption. Furthermore, the value of  $k_f$  is 26.91 for Congo red. These results indicate that the Ca-bentonite has a high adsorption capacity for anionic Congo red dye in the solution.

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter  $R_L$  that is defined by the following equation:

$$R_L = \frac{1}{(1 + b C_0)} \quad (6)$$

where  $b$  and  $C_0$  are the same as defined before. The value of  $R_L$  calculated from the above expression. The nature of the adsorption process to be either unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ). Here,  $R_L$ -values obtained are listed in Table 3. The fact that all the  $R_L$ -values for the adsorption of Congo red onto Ca-bentonite are in the ranges of 0.093–0.570 shows that the adsorption process is favourable.

### 3.6. Adsorption thermodynamics

The thermodynamic parameters such as Gibbs free energy change  $\Delta G_0$ , standard enthalpy  $\Delta H_0$ , and standard entropy  $\Delta S_0$  were also studied to understand better the effect of temperature on the adsorption. Experiments were performed using 100  $\text{mg L}^{-1}$  dye solutions for 24 h at various temperatures.

**Table 4**  
Thermodynamic parameters for the adsorption of Congo red on Ca-bentonite

Temperature (°C)	$K_c$	$\Delta G_0$ (kJ mol <sup>-1</sup> )	$\Delta H_0$ (kJ mol <sup>-1</sup> )	$\Delta S_0$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )
20	14.3929	-6.4962	5.1376	0.0372
30	14.6160	-6.7567		
40	15.9019	-7.1991		
50	25.9375	-11.179		

The Gibbs free energy of adsorption  $\Delta G_0$  by using equilibrium constant ( $K_c$ ) is calculated from the following equation:

$$\Delta G_0 = -RT \ln K_c \quad (7)$$

Standard enthalpy,  $\Delta H_0$ , and standard entropy,  $\Delta S_0$ , of adsorption can be estimated from Van't Hoff equation:

$$\ln K_c = -\frac{\Delta H_0}{RT} + \frac{\Delta S_0}{R} \quad (8)$$

The  $K_c$  value is calculated from the equation [9]

$$K_c = \frac{C_{AE}}{C_{SE}} \quad (9)$$

where  $K_c$  is the adsorption equilibrium constant.  $C_{AE}$  is the amount of dye (mg) adsorbed on the adsorbent per  $L$  of the solution at equilibrium.  $C_{SE}$  is the equilibrium concentration (mg L<sup>-1</sup>) of the dye in the solution.

Thermodynamic parameters obtained are given in Table 4.  $K_c$  indicates the capability of the clay to retain a solute and also the extent of its movement in a solution phase [36]. As shown in Table 4,  $K_c$  is increasing with the increasing temperature from 20 to 50 °C. The negative values of  $\Delta G_0$  at different temperatures indicate the feasibility of the process and the spontaneous nature of the adsorption. Generally, the change in adsorption enthalpy for physisorption is in the range of -20 to 40 kJ mol<sup>-1</sup>, but chemisorption is between -400 and -80 kJ mol<sup>-1</sup>. The positive  $\Delta H_0$  (5.1376 kJ mol<sup>-1</sup>) reveals the adsorption is endothermic and physical in nature. Furthermore, slightly positive  $\Delta S_0$  of Congo red adsorption process indicates an irregular increase of the randomness at the Ca-bentonite-solution interface during adsorption.

#### 4. Conclusion

In this study, nature Ca-bentonite was selected as a local and cheaper adsorbent for the removal Congo red from the aqueous solutions. Adsorption of the Congo red was studied by batch technique and it was observed that >90% of dye removal was achieved by using 0.2 g of Ca-bentonite for an initial dye concentration of 100 mg L<sup>-1</sup>. The adsorption was highly dependent on concentration, but changed slightly with pH and temperature of the solution. Adsorption kinetics obeyed preferably the pseudo-second-order kinetics that provided the best correlation of the data in most cases. Furthermore, the results of the intraparticle diffusion model suggested that intraparticle diffusion was not the only rate-controlling step. Based on the Langmuir isotherm analysis, the monolayer adsorption capacity was determined to be 107.41 mg g<sup>-1</sup> at 20 °C. The  $R_L$  values showed that Ca-bentonite was favourable for the adsorption of Congo red. The data obtained from adsorption isotherms at different temperatures were fitted to Freundlich model. Thermodynamic parameters indicated that Congo red adsorption onto Ca-bentonite was spontaneous, exothermic and physical in nature.

The results of this study indicate that Ca-bentonite can be successfully used for the adsorption of Congo red from aqueous solutions. The only problem is that the mixture is difficult to separate after adsorption that limits the practical application of

Ca-bentonite. Therefore, the work is in progress to explore a new modified method that cannot only separate bentonite from water effectively but also improve the dye removal rate.

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