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Adsorptive removal of anionic dye from aqueous solutions by Algerian kaolin: Characteristics, isotherm, kinetic and thermodynamic studies

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Abstract

Experimental investigations were carried out using available Algerian kaolin as alternative adsorbent for removal of toxic anionic dye namely Congo red from aqueous solutions. The effect of contact time, initial dye concentration, pH and temperature were experimentally studied in batch mode to evaluate the adsorption capacity, kinetic and equilibrium. Experimental results revealed that optimal adsorption took place at basic pH and high dye concentration. The dye uptake process obeyed the pseudo second order kinetic expression and was best described by the Langmuir isotherm. Thermodynamic studies showed congo red adsorption on Algerian kaolin was exothermic and spontaneous in nature. The results indicate that this local kaolin could be employed as low-cost alternative for removal of anionic dyes from industrial wastewater.

Key words: Kaolin, Adsorption, Congo red, Kinetic, Thermodynamic.

1. Introduction

The introduction of waste products in the environment is a worldwide problem that has been highlighted by various environmentalist groups. Colored organic effluent is produced in industries such as textiles, rubber, paper, plastic, cosmetics, etc. Discharging of dyes into water resources even in a small amount can affect the aquatic life and food web. Dyes can also cause allergic dermatitis and skin irritation. Some of them have been reported to be carcinogenic and mutagenic for aquatic organisms.

The treatment of dyes in industrial wastewater possesses several problems since dyes are generally difficult to biodegradate and photodegradate. Many different techniques including cloud point extraction, oxidation processes, nanofiltration, ozonation and coagulation have been used for the removal of colored dyes from wastewater [1-4]. However, adsorption is the most popular physicochemical treatment for the removal of dissolved organics from waters. A number of non-conventional, low cost adsorbents have been tested for dye removal. These include peat [5], red mud [6], coir pith [7], Neem leaf [8], activated sludge [9], waste organic peel [10], tree fern [11] and minerals [12]. Moreover, the removal of dye by activated carbon produced from non-conventional sources such as coir pith [13], sawdust and rice-husk [14], pinewood [15] and others have also been investigated. However, the adsorption capacity of the above adsorbents is not large.

Kaolin has received considerable recognition as an adsorbent because of its high adsorption capacity. It is generally referred to as clay that is mainly composed of kaolinite and a lower amount of minerals such as quartz and mica etc. It is the most abundant mineral in soils and sediments and interacts with other soil elements to contribute to the mechanical stability of the soil column [16].

The adsorption properties of kaolinite are likely determined by its surface structure and the edges [17,18] . The edges possess a variable charge that can be correlated to the reaction between ionisable surface groups along the edges and the clay mineral surface and the ions present in aqueous solution.

Congo red (CR) or 1-naphthalenesulfonic acid, 3,3′-(4,4′-biphenylenebis (azo)) bis (4-amino-) disodium salt is a benzidine-based anionic diazo dye prepared by coupling tetrazotised benzidine with two molecules of napthionic acid [19] (Fig. 1). This anionic dye can be metabolised to benzidine, a known human carcinogen [20]. Effluent containing congo red is largely produced from textiles, printing, dyeing, paper, and plastic industries etc. [19, 21]. The treatment of contaminated congo red in wastewater is not straightforward, since the dye is generally present in sodium salt form giving it a very goodwater solubility. Also, the high stability of its structure makes it difficult to biodegrade and photodegrade.

In the present study, detailed experiments are carried out to remove this dye by adsorption technique using Algerian kaolin as an adsorbent.

2. Materials and methods

2.1. Materials

2.1.1. Kaolin and characterization

The kaolin light gray sample used in this investigation was collected from a natural deposit, located in Tabelbala in province Bechar (Algeria). The surface area and CEC of kaolin were measured using methylene blue technique [22]. The sample of kaolin powder was characterized by using infrared (FT-IR), X-ray diffraction (XRD) and scanning electron microscopic (SEM) techniques.

The FT-IR absorption spectra was recorded on KBr pressed pellets of the powdered sample in the range 4000-400 cm^{-1}, using a Perkine-Elmer FTIR 1000 spectrophotometer. The X-ray diffraction pattern of powder was recorded on a Phillips-1730 (PAN analytical) X-ray diffractometer using Cu Kα radiation (λ=1.54Å).

2.1.2. Congo red

Congo red (CR), a diazo dye was used as a surrogate indicator to simulate industrial wastewater in order to evaluate the adsorption capacity of kaolinite in the study. The Congo red obtained from Fluka, was used as received without any purification. The chemical formula of CR is $C_{32}H_{22}N_6Na_2O_6S_2$ with Color Index 22120 and molecular weight of 696.663g.mol^{-1} (see fig. 1.). The CR sodium salt is responsible for dying cotton full red and is the first synthetic dye capable of directly dying cotton [19]. The color of CR changes from red to blue in the presence of inorganic acids. The change of color is due to the resonance between charged canonical structures [23].

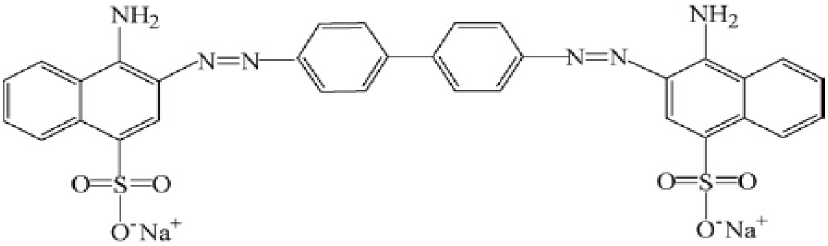

Figure 1: Structure of CR.

2.2. Adsorption experiments

A stock solution of 1g/L was prepared by dissolving the appropriate amount (1g) of CR in a liter of deionized water .The working solutions were prepared by diluting the stock solution with deionised water to give the appropriate concentration of the working solutions. The pH of the solutions was adjusted by addition of either HCl or NaOH solutions.

The UV-Vis Spectrophotometer (UV.1700 Pharmrspac) was used to determine the concentrations of Congo red dye in solution. pH measurements were done using Orien pH meter. The concentration of the residual dye was measured using UV-visible spectrometer at a λ_{max} corresponding to the maximum adsorption for the dye solution (λ_{max}= 497 nm) by withdrawing samples at fixed time intervals, centrifuged and the supernatant was analyzed for residual Congo red (CR). Calibration curve was plotted between absorbance and concentration of the dye solution to obtain absorbance-concentration profile.

The amount of adsorbed CR (mg g^{-1}) was calculated based on a mass balance equation as given by Eq. (1) [24]:

$$qe = \frac{(Co - Ce)V}{W} \quad (1)$$

where qe is the equilibrium adsorption capacity per gram dry weight of the adsorbent, mg g^{-1}; C_0 is the initial concentration of CR in the solution (mg L^{-1}); C_e is the final or equilibrium concentration of CR in the solution (mg L^{-1}); V is the volume of the solution (L); and W is the dry weight of kaolin (g).

The sorption capacity at time t, q_t (mg/g) was obtained as Eq. (2) [24]:

$$q_t = \frac{(Co - Ct)V}{W} \tag{2}$$

Where C_0 and C_t (mg/L) were the liquid phase concentrations of solute at initial and a given time t, V was the solution volume and W the mass kaolin (g).

3. Results and discussion

3.1. Characterisation of adsorbent

SEM micrograph of the untreated clay sample suggests a very cohesive material (Fig. 2). The micrograph confirms that the material is forming micron-size agglomerates. A higher magnification micrograph of the same structure shows that the micro-size particles are composed of individual platelets, which onglomerate into larger size particles.

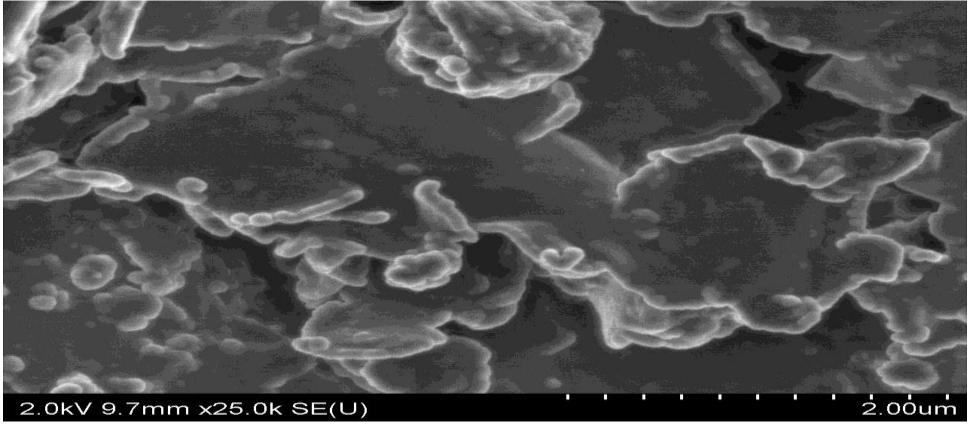

Figure 2: SEM of kaolin clay.

Fig. 3 represents the XRD diffractogram of kaolin. Kaolin showed two intense diffraction peaks at 2θ value of 12.4° and 26.7°, less intense peaks at 2θ of 45.7°, 48.0°, 50.1° and 60.1° and humps at 2θ = 19.8–21.9°, 35.0–36.0° and 37.8–39.2°, which are all associated with kaolinite (K). Diffraction peaks of quartz (Q) could be found at 2θ values of 20.9°, 30.1°, 50.9° and 62.3°.

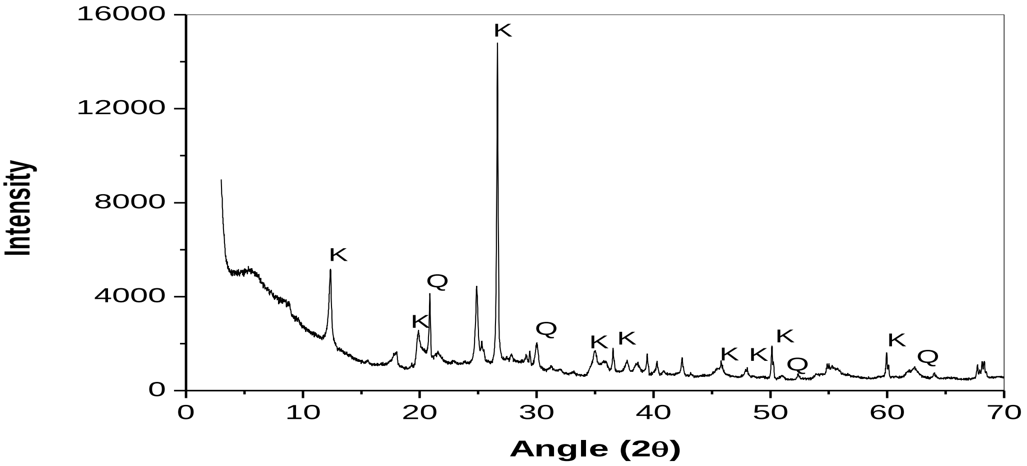

Fig. 3. XRD pattern of kaolin (K = kaolinite; Q = quartz).

Fig. 4 shows the IR spectra of kaolin. Kaolin showed characteristic peaks at 3698 cm^{-1} and 3620 cm^{-1}, corresponding to the OH^- stretching vibration. H_2O stretching was also found at 1636 cm^{-1}. Bands at 1033 cm^{-1} and 984 cm^{-1} were assigned to Si-O bonds in the SiO_4 molecules [25]. The other band at 913 cm^{-1} was attributed to Al^{IV}-OH vibrations [26]. The bands at 798 cm^{-1}, 750 cm^{-1} and 694 cm^{-1} were Si-O symmetric stretching [27]. Absorption at 535 cm^{-1} was assigned as Si-O-Al^{VI}, where the Al is in octahedral coordination [26, 28].

The average surface area and CEC of kaolin which were measured using methylene blue technique [23] were 10.60 m^2/g and 8.01meq/100g, respectively.

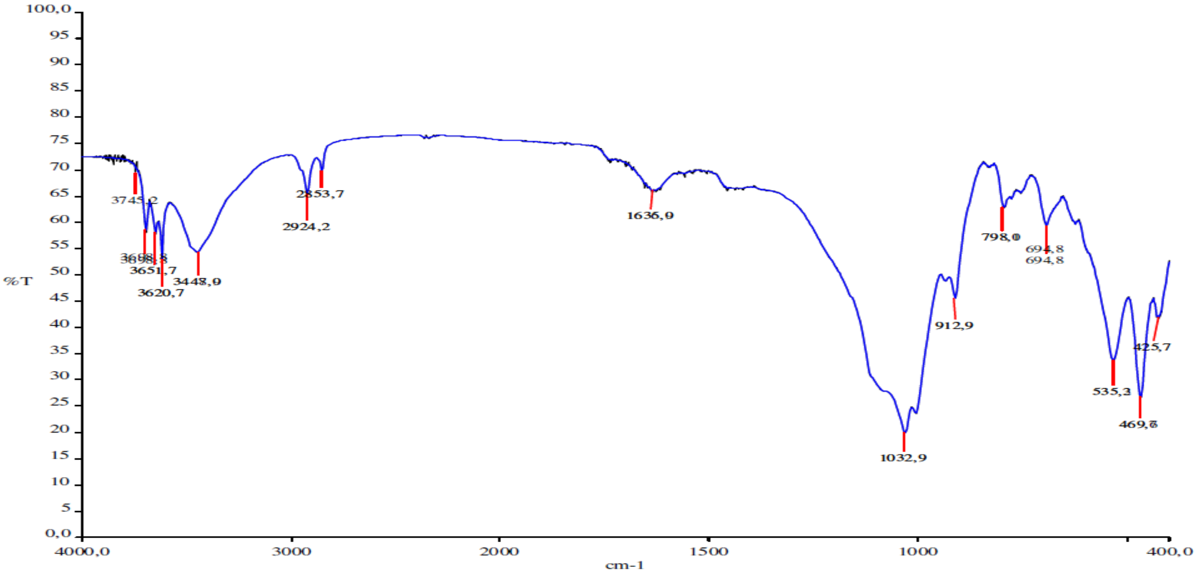

Figure 4: IR spectra of kaolin

3.2. Effect of contact time

The effect of contact time on the amount of anionic dye, CR, adsorbed onto kaolin at room temperature (27°C) was examined at the 100 mg/L concentration of dye with 0.1g kaolin dose. As can be seen from the Fig. 5, when the equilibrium time was increased, the amount of adsorption was not drastically increased. The adsorption of CR occurred very quickly from the beginning of the experiments during the first 15 min, then a slight increase until 40min where the maximum adsorption of CR onto clay was observed; it can be said that beyond this there is almost no further increase in the adsorption and it is thus fixed as the equilibrium time.

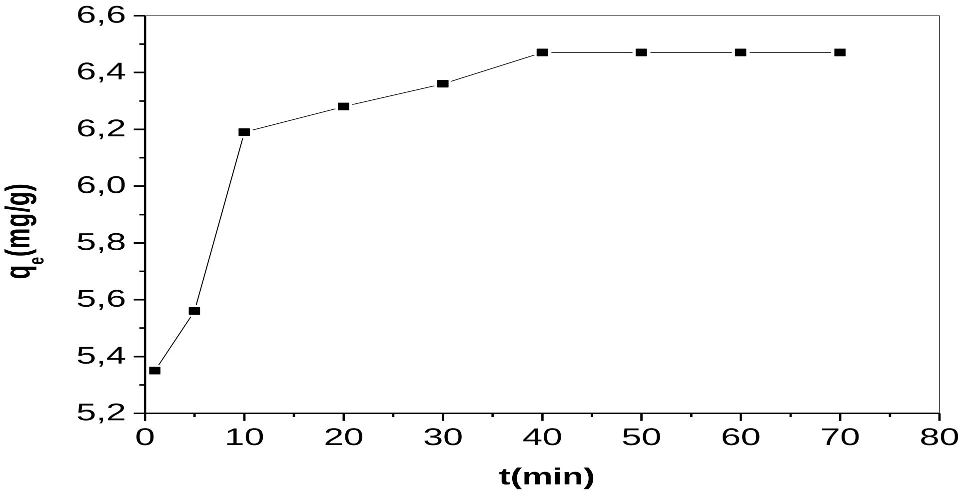

Figure 5: Effect of contact time (C_0 = 100 mg/L, m_{Kaolin} = 0,1g, pH=6,9).

3.3. Effect of initial dye concentration

The effect of initial dye concentration was investigated under equilibrium conditions. By considering the amount of dye adsorbed per unit of kaolin (mg g^{-1}), adsorption capacity of kaolin increased as the initial dye concentration increased.The maximum adsorption capacity attained for kaolin 5.76 mg g^{-1} (Fig. 6). The adsorption was preceding the saturation of kaolin at 150 mg L^{-1} of dye. It can be proposed that an increase in the initial dye concentration leads to an increase in mass gradient between the solution and adsorbent, and thus acts as a driving force for the transfer of dye molecules from bulk solution to the particle surface. The increase in the proportional dye adsorption is attributed to the equilibrium shift during the clay adsorption process.

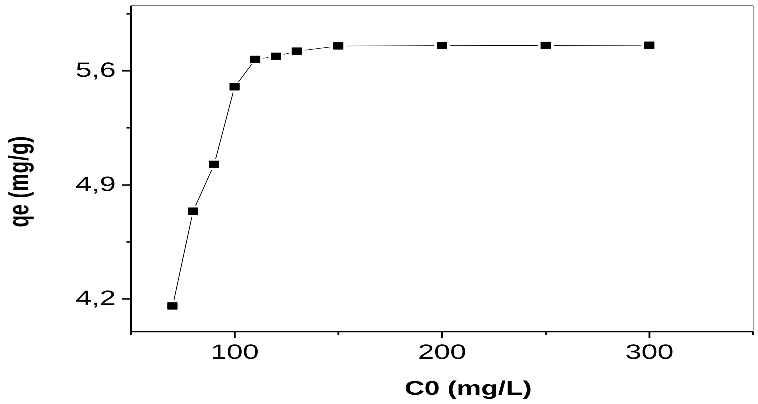

Figure 6: Effect of initial dye concentration.

3.4. Effect of pH

The pH of solution has been identified as the most important parameter affecting dye adsorption onto the clay. But the study of the influence of this parameter is not easy mainly under strongly acidic pH, because of the formation of protonated species (bluish color), which possibly leads to a change in the structure of the dye. The negatively charged adsorbent surface sites can be protonated, too. The red color is stable in the pH range of 5–13.

The adsorption of CR on kaolin was studied in this pH range. Fig.7 shows, the increase in CR removal by kaolin with increasing pH and reached maximum (q_e(max) = 9,98 mg/g) at pH10 and then decreased at higher pH, the high negatively charged adsorbent surface sites did not favour the adsorption of deprotonated CR due to electrostatic repulsion. Also, an abundance of OH^- ions in basic solution creates a competitive environment with anionic ions of CR for the adsorption sites causing a decrease of adsorption [13, 29].

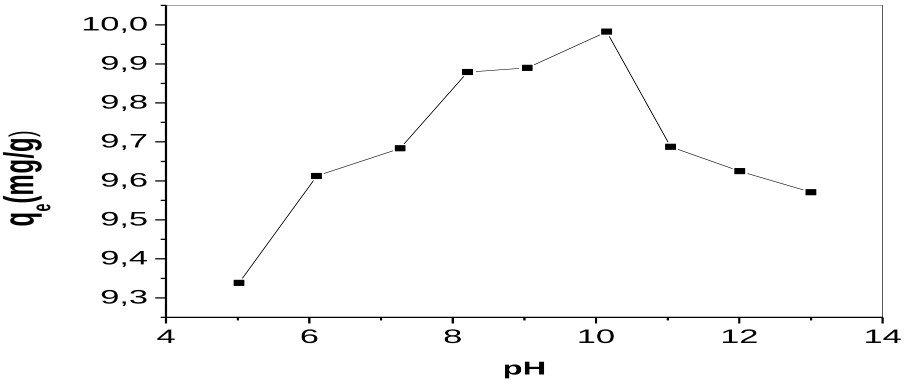

Figure 7: Effect the pH on the q_e.

3.5. Adsorption isotherms

To investigate an interaction of adsorbate molecules and adsorbent surface, two well-known models, the Freundlich [30] and Langmuir [31] isotherms, were selected to explicate dye–clay interaction in this study.

3.5.1. Langmuir isotherm model

The basic assumption of Langmuir model is that the formation of monolayer takes place on the surface of the adsorbent, indicating that only one dye molecule could be adsorbed on one adsorption site and the intermolecular forces decrease with the distance. It is also assumed that the adsorbent surface is homogeneous in character and possesses identical and energetically equivalent adsorption sites [32-34]. It was presented as Eq.(3):

$$q_e = q_m K_L C_e / 1+K_L C_e \tag{3}$$

A linear Langmuir adsorption isotherm is presented in Fig. 8. The values of q_m and K_L of linear expression of Langmuir adsorption isotherm were calculated from the slopes and intercept of the linear plot of C_e/q_e versus C_e in Fig. 8 and table 1 according to Eq. (4).

$$1/q_e = 1/q_m + (1/K_L q_m)*(1/C_e) \tag{4}$$

The isotherm was found to be linear over the entire concentration range studies with a good linear correlation coefficient ($R^2 = 0.9979$) (see table 1), showing that Langmuir equation represents the best fit of experimental data than the other isotherm equation.

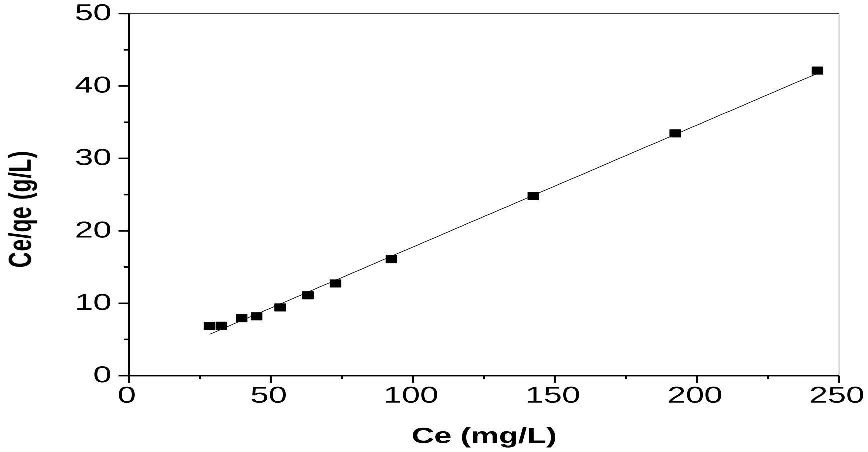

Figure 8: Linear Langmuir adsorption isotherm.

The fact that Langmuir isotherm fits the experimental data very well confirms the monolayer coverage of dye onto kaolin particles (q_m= 5.94 mg/g) 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 (5) [35-37].

$$R_L = 1 / 1+K_LCo \quad (5)$$

Where C_0 (mg/L) is the initial dye concentration and K_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 unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The influence of isotherm shape on whether adsorption is favourable or unfavourable has been considered. For a Langmuir type adsorption process, the isotherm shape can be classified by a dimension less constant separation factor (R_L), given by Eq. (7). The calculated R_L values as different initial CR concentrations are shown in Fig. 9. It was observed that the value of R_L in the range 0–1 confirms the favourable uptake of the CR process. Also lower R_L values at higher initial CR concentrations showed that adsorption was more favourable at higher concentration. The degree of favourability is generally related to the irreversibility of the system, giving a qualitative assessment of the kaolin–CR interactions. The degrees tended toward zero (the completely ideal irreversible case) rather than unity (which represents a completely reversible case).

3.5.2. Freundlich isotherm model

While Langmuir isotherm assumes that enthalpy of adsorption is independent of the amount adsorbed, the empirical Freundlich equation, based on sorption on heterogeneous surface, can be derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites. The Freundlich equation is purely empirical based on sorption on heterogeneous surface and is given by Eq. (6):

$$q_e= k_f C_e^{1/n} \quad (6)$$

Eq.(7) can be rearranged to obtain a linear form by taking logarithms Eq.(7):

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (7)$$

The slope and the intercept correspond to (1/n) and k_f, respectively. It was revealed that the plot of ln q_e and ln C_e yields a straight line (Fig. 10). The results are indicated in table 1. The favourable adsorption of this model can be characterised such that if a value for n is above unity, adsorption is favourable and a physical process [38]. In the present study the value of n (n= 1.295) is greater than 1, indicating that the adsorption process is favourable. But the value of correlation coefficient ($R^2 = 0.90878$) is lower than the Langmuir isotherm value.

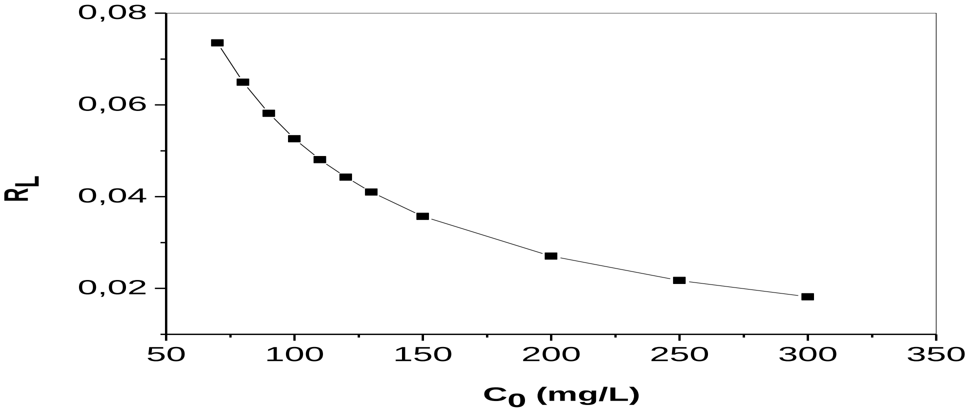

Figure 9: Plot of separation factor versus initial Congo red concentration.

Table 1: Langmuir and Freundlich adsorption isotherm constants

Langmuir			Freundlich		
q_m (mg/g)	K_L (L/mg)	R^2	n	k_f	R^2
5.94	0.18	0.9979	1.295	0.1072	0.90878

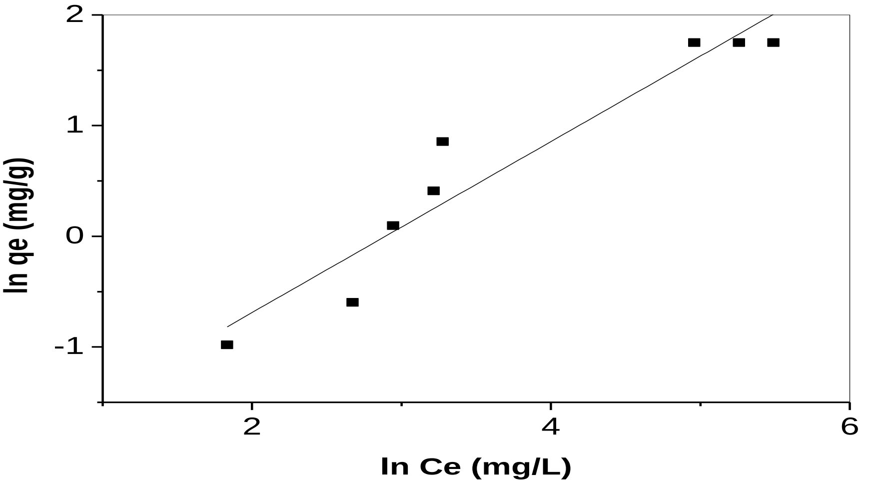

Figure 10: Linear Freundlich adsorption isotherm

3.6. Effect of temperature on thermodynamic parameters

The effect of temperature on the CR adsorption on the kaolin was investigated from 25 °C to 60 °C (Fig. 8). The Gibbs energy, ΔG^0 (kJ mol^{-1}), can be calculated from Eqs. (8) and (9).

$$\Delta G° = \Delta H° - T\Delta S° \quad (8)$$

$$\Delta G° = - RT \ln Kc \quad (9)$$

Kc, the equilibrium constant, represents the ability of the adsorbent to retain the adsorbate and extent of movement of the adsorbate within the solution [39]. The Kc is the ratio of the equilibrium concentration of the dye (qe) attached to adsorbent compared to the van't Hoff equation as equilibrium CR concentration in solution (C_e), and can be deduced from Eq. (10) [40] or Eq. (11).

$$Kc = q_e / C_e \quad (10)$$

$$\ln Kc = \Delta S°/R - \Delta H°/RT \quad (11)$$

The values of ΔH° (kJ mol^{-1}) and ΔS° (J mol^{-1} K^{-1}) can be obtained from the slope and intercept of a linear plot between ln Kc and 1/T (fig. 11).

Thermodynamic parameters obtained are given in Table 2. Kc indicates the capability of the clay to retain a solute and also the extent of its movement in a solution phase [41].As shown in Table 2, ΔG° is slightly increasing with the increasing temperature from 25 to 60° C. The negative values of ΔG°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^{-1}, but chemisorption is between -400 and -80 kJ mol^{-1}. The negative ΔH° (-3.34 kJ mol^{-1}) reveals the adsorption is exothermic and physical in nature. Furthermore, slightly positive ΔS° of Congo red adsorption process indicates an irregular increase of the randomness at the kaolin-solution interface during adsorption.

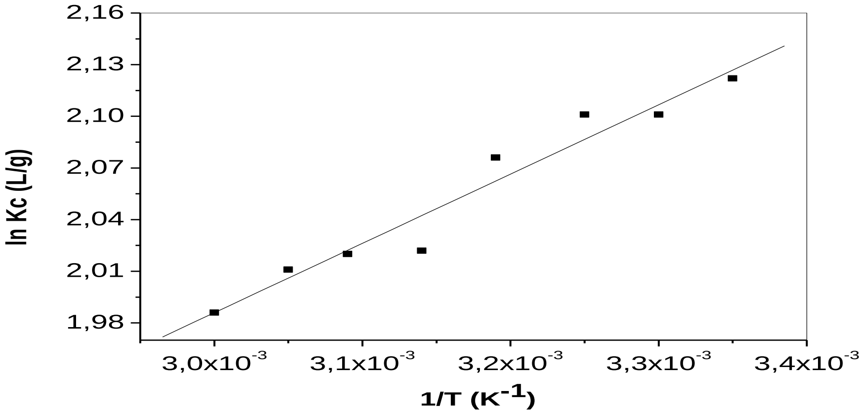

Figure 11: Effect of temperature on CR adsorption.

Table 2: Thermodynamic parameters

-ΔG° (KJ.mol^{-1})								ΔH° (KJ.mol^{-1})	ΔS°(J.mol^{-1}.K^{-1})
60° C	55° C	50° C	45°C	40°C	35°C	30° C	25° C	-3.34	6.46
5.50	5.48	5.42	5.40	5.34	5.29	5.29	5.26		

3.7. Kinetic of sorption

Kinetic models have been used to investigate the mechanism of sorption and potential rate controlling steps, which is helpful for selecting optimum operating conditions for the full-scale batch process [42]. Pseudo-first-order and pseudo-second-order kinetic models were used.

3.7.1. Pseudo-first-order model

The pseudo-first-order rate expression based on solid capacity is generally expressed as follows Eq (12) [43]**:**
$dq_t/dt = k_1(q_e - q_t)$ (12)
Where, q_e is the amount of CR adsorbed at equilibrium (mg/g), q_t is the amount adsorbed at time t (mg/g), k_1 is the rate constant of first order adsorption (min^{-1}). After integration and applying boundary conditions, $t = 0$ to t and $q_t = 0$ to q_e; the integrated form of equation (13) becomes:
$\log (q_e - q_t) = \log q_e - k_1 t / 2.303$ (13)

Value of adsorption rate constant k_1 for the CR adsorption onto kaolin was determined from the straight line plot of $\log (q_e - q_t)$ against t (see fig. 12). The data were fitted with a poor correlation coefficient (Table. 3), indicating that the rate of removal of CR onto kaolin does not follow the pseudo-first-order equation.

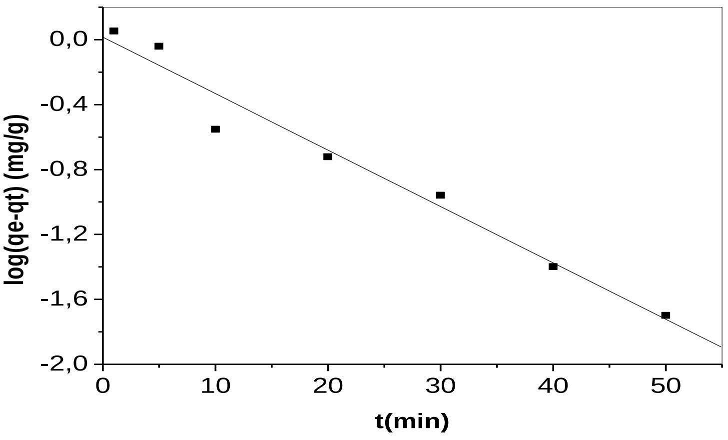

Figure 12: Pseudo-first order plot of CR sorption onto kaolin.

Table 3: Pseudo first order model rate constants for kaolin

R^2	k_1	q_e (mg/g)	Concentration of CR (mg/L)	Dose of Kaolin (g/L)
0.98333	0.080	1.035	100	10

3.7.2. Pseudo-second-order model

Ho and Mc [44] presented the pseudo-second order kinetic as Eq (14):

$$dq_t/dt = k_2(q_e - q_t)^2 \qquad (14)$$

Where, k_2 is the rate constant of second order-adsorption (g/mg.min). For the same boundary conditions the integrated form of equation (15) becomes:

$$t/q_t = 1/k_2q_e^2 + t/q_e \qquad (15)$$

The initial sorption rate, *h* (mg/ g. min), at *t* = 0 is defined as Eq (16)

$$h = k_2q_e^2 \qquad (16)$$

Where, k_2 and h values were determined from the slope and intercept of the plots of t/q against t (Fig. 13).

The values of the parameters and correlation coefficient are also presented in Table 4. The correlation coefficient of examined data was found very high ($R^2 > 0.9999$). This shows that the sorption of CR onto Algerian kaolin followed the pseudo-second-order kinetic model. A good agreement with this adsorption model was confirmed by the similar value of calculated q_e and the experimental one; and calculated Langmuir monolayer adsorption, q_m. The best fit to the pseudo-second order kinetic indicated that the adsorption mechanism depended on the adsorbate and adsorbent [21].

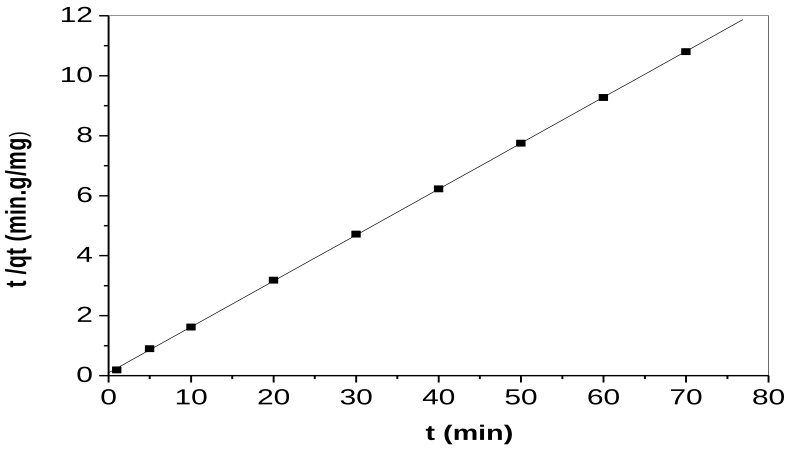

Figure 13: Pseudo-second order plot of CR sorption onto kaolin.

Table 4: Pseudo second order model rate constants for kaolin

R^2	h	k_2	q_e (mg/g)	Concentration of CR (mg/L)	Dose of Kaolin (g/L)
0.99997	10.44	0.245	6.53	100	10

Conclusion

The Algerian Kaolin is an effective adsorbent for removal of the toxic anionic dye, congo red, from aqueous solution. The adsorption was highly dependent on various operating parameters, like: contact time, pH, initial concentration and temperature. The results gained from this study were well described by the Freundlich theoretical but Langmuir equation represented the best fit of experimental data. The kinetic data indicated that the adsorption process was controlled by pseudo-second-order equation. Thermodynamics studies indicated that adsorption of congo red on kaolinite was stable over an extensive range of temperature; it was also exothermic and took place spontaneously in nature. These results show how and why Algerian kaolinite can be effectively used as a liner in water treatment plants for the removal of dye. Reuse of spent kaolin and recovery of adsorbed dye may be of further scope of research.

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