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ORIGINAL RESEARCH PAPER

STUDY OF REMOVAL OF CONGO RED BY LOCAL NATURAL CLAY

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Abstract: The adsorption behavior of anionic dye (Congo Red) from aqueous solutions onto natural clay originated from Agadir region (south Morocco) was examined in this work. Batch mode experiments were performed to describe the Influence of interacting parameters such as contact times (10 - 70 min), adsorbent dose (1 - 6 $g \cdot L^{-1}$), initial dye concentration (100 - 900 $mg \cdot L^{-1}$), temperature (22 - 50 °C) and *p*H values (2 - 12) on dye removal. According to the obtained results, the adsorption of CR onto clay natural was dependent on *p*H, initial dye concentration and temperature. Experimental data have been modeled according to both Langmuir and Freundlich models. Also, kinetic studies of CR onto clay were evaluated by pseudo-first order and pseudo-second order. It was found that the adsorption of the dye on the clay were well fitted by the Langmuir model with coefficient of correlation $R^2 = 0.98$ and maximum adsorption capacity 74.62 $mg \cdot g^{-1}$. Adsorption kinetics indicated that the adsorption of CR was found to follow a pseudo second-order model ($R^2 = 0.999$). The thermodynamic parameters were also calculated, which suggested that the adsorption of anionic dye onto clay is physiosorptive process, spontaneous, and endothermic in nature.

Keywords: *adsorption, anionic dye, isotherms, kinetics, thermodynamic study*

INTRODUCTION

Water pollution by certain industrial chemicals (dyes) has currently become a crucial problem, since it is a source of environmental degradation; particularly the use of dyes becomes more and more important in various domains, such as textiles, cosmetics, paper and pharmaceutical products [1]. These dyes can be classified in three categories: anionic, cationic and non-ionic [2]. The importance of protection the natural environment and removal of dyes from textile effluent are growing. Several processes of water decontamination often carried out by conventional chemical treatments such as: decantation, coagulation-flocculation and oxidation. The wastewater treated by this process still contains pollutants and are charged because of the number of reagents added. In the majority of cases, these methods are very expensive and onerous. It is necessary to reflect on severe technical efficiency and cheaper. Adsorption techniques have been successful in removing organic species from waters with the advantages of high treatment efficiency, simplicity of design, availability, ease of operation and also a cost effective [3 – 5]. Currently, activated carbon is the most adsorbent commonly used due to its adsorbent power that is very important facing dyes, despite its effectiveness, the active carbon is expensive because has high costs of manufacturing and regeneration [6, 7]. Research was then directed to treatment processes using natural materials such as clay. Clays have a nanometric size and layered structure which provides a large specific surface facing the adsorption and confers them a crucial role in the retention of a large number of natural or anthropogenic pollutants [8], also they are characterized by wide availability in nature, high chemical and mechanical stabilities and the presence of charge on their surface, therefore an adsorption faculty of the important dyes [9]. Many studies have already signed on the adsorption of cationic dyes onto natural clays because that anionic dye difficult to adsorb, for this reason we chose the anionic dye, Congo Red (CR) is a benzidine-based anionic diazo dye, chemical formula $C_{32}H_{22}N_6Na_2O_6S_2$, prepared by coupling tetrazotised benzidine with two molecules of napthionic acid [10] (Figure 1). It is used in testing for hydrochloric acid in gastric contents, in histologically to test for amyloidosis also as used especially as an indicator and as a biological stain. This anionic dye can be metabolised to benzidine, a known human carcinogen [11].

In this work, several experiments to remove this anionic dye using adsorption onto Moroccan Natural clay have been investigated.

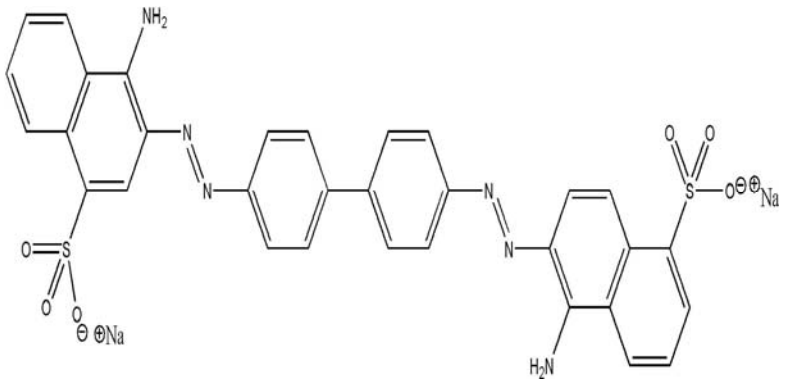

Figure 1. *Molecular structure of Congo red*

MATERIALS AND METHODS

Materials

The natural clay was collected from Agadir region and was crushed in two steps then sieved to 50 µm [12].

Characterization

Scanning electron microscope (SEM) was used to determine the surface morphology and the local composition of our adsorbent. SEM micrographs for samples were obtained with a SUPRA 40 VP COLONNE GEMINI ZEISS using a maximum voltage of 20 kV. X-ray emission from Energy Dispersive X-rays Spectroscopy (EDXS) allowed determining the local quantitative elemental composition clay.
We also characterized our support by XRD and BET already published in our work [12], in which we have found that the dominant peaks correspond to dolomite and the silica was also observed with less intense peaks, in addition the specific surface area was measured, it is equal to 76.971 $m^2 \cdot g^{-1}$.

Adsorption studies

Adsorption studies of Congo red dye were performed by adding in each experiment 0.2 g of adsorbent into a 100 mL flask containing 50 mL of dye solution of known concentration of desired time, temperature, and *p*H. The flasks were agitated and centrifuged at 4000 rpm for 5 min. The residual concentration of Congo Red was determined at maximum wavelengths of RC (498 nm) by UV-Vis spectrophotometer (Techcomp UV2300). The amount of dye adsorbed at equilibrium q_e ($mg \cdot g^{-1}$) was calculated from the following equation:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

where: V is the volume of dye solution used (mL), m is the weight of adsorbent (g), C_0 and C_e are, respectively, the initial and equilibrium concentrations of Congo Red ($mg \cdot L^{-1}$).
The effects of various parameters on CR adsorption by natural clay were investigated such as adsorbent dosage (1-6 $g \cdot L^{-1}$), contact time (10 - 70 min), initial dye concentration (100 - 900 $mg \cdot L^{-1}$), temperature (22 - 50 °C) and *p*H (2 - 12).

RESULTS AND DISCUSSION

Characterization of the samples

The SEM images reported in Figure 2a and 2b show that the morphology is uniform and consists of small and large grains (dimensions ranging between 2 and 5 µm). These grains are in the form dispersed and they are characterized by the presence of cavities and pores at the surface. These forms would be very interesting for adsorption because of the amount of cavities and pores observed. The EDXS (Figure 2c) local analysis is in

relatively good agreement with nominal composition of clay phase. This result confirms the clay phase obtained by the X-ray diffraction.

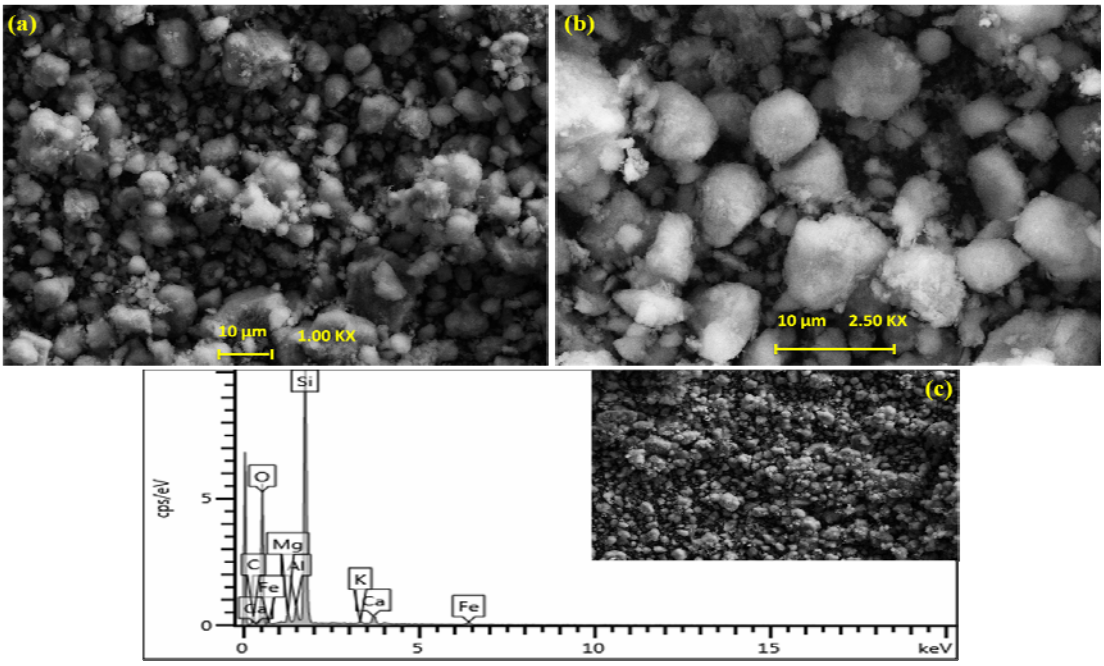

Figure 2. *SEM micrographs images (a:1.00 KX, b: 2.50 KX) and EDX (c) analysis of natural clay*

Effect of contact time

The effect of contact time on the adsorption capacity of CR was examined by varying the time from 10 to 70 minutes such as 4 $g \cdot L^{-1}$ of adsorbent dose with 50 mL of dye solution of concentration 100 $mg \cdot L^{-1}$ at room temperature was kept constant (Figure 3). It is evident that the amount of anionic dye CR adsorbed onto natural clay enhances rapidly by the increase of contact time between the adsorbate and the adsorbent in the first 20 minutes with 90.72 % of amount of dye retained and then slows down gradually until the equilibrium was reached at 60 minutes.

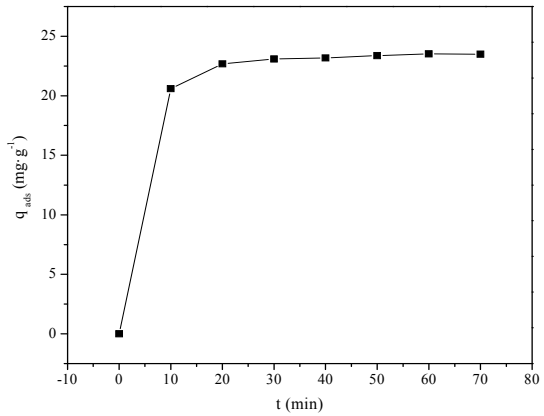

Figure 3. *The effect of contact time on CR removal*
Conditions: adsorbent dose = 4 $g \cdot L^{-1}$; C_0=100 $mg \cdot L^{-1}$; T=22 °C; initial pH

Effect of adsorbent dosage

The effect of adsorbent dosage on CR removal was carried by varying the dose of the natural clay from 1 to 6 $g \cdot L^{-1}$. Contact time, initial CR concentration, temperature and *p*H of 60 minutes, 100 $mg \cdot L^{-1}$ and 295.15 K respectively were kept constant. Figure 4 shows that the Congo Red removal percentage increased from 46.13 % to 95.63 % when the adsorbent dosage increases from 1 to 6 $g \cdot L^{-1}$. This adsorptive enhancement can be attributed to an increase in adsorption surface area of micropores and availability of more adsorption sites [11], the optimal adsorbent dosage to reach equilibrium is 4 $g \cdot L^{-1}$.

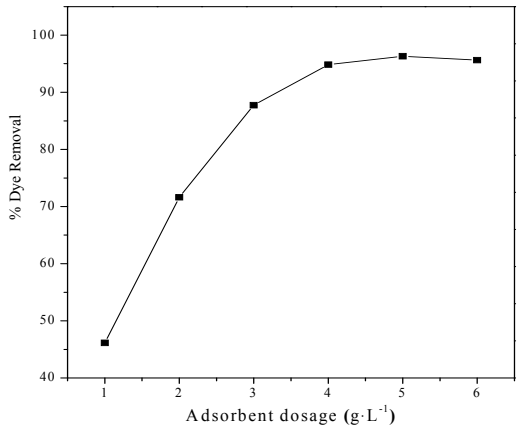

Figure 4. *The effect of adsorbent dosage on CR removal*
Conditions: C_0=100 $mg \cdot L^{-1}$; T=22 °C; initial pH; equilibrium time = 60 min

Effect of initial dye concentration and effect of temperature

The influence of initial CR concentration at different temperature on CR adsorption was investigated at 100 - 900 $mg \cdot L^{-1}$ with the initial dye solution *p*H and 4 $g \cdot L^{-1}$ of adsorbents at different temperature 22, 30, 40 and 50 °C for 60 minutes.
According to bibliographic searches, the adsorption process is highly dependent on the initial concentration of the dye [13 – 15]. As shown in Figure 5, for the concentration 22 °C with increasing initial CR concentration from 100 to 900 $mg \cdot L^{-1}$, the amount of dye adsorbed by natural clay increases sharply from 22.38 to 68.89 $mg \cdot g^{-1}$. It can be ascribed that an increase in adsorbate concentration leads to an increase in mass gradient between the aqueous and solid phases, which acts as a driving force for the transfer of dye molecules from bulk solution to the particle surface [16]. Regarding the effect of temperature, it is evident that the adsorption capacity increased with increase in the temperature from 22 to 50 °C. This could be attributed to the increasing temperature may lead to create a swelling effect inside the internal structure of adsorbent, penetrating the big Congo Red molecule further [17].

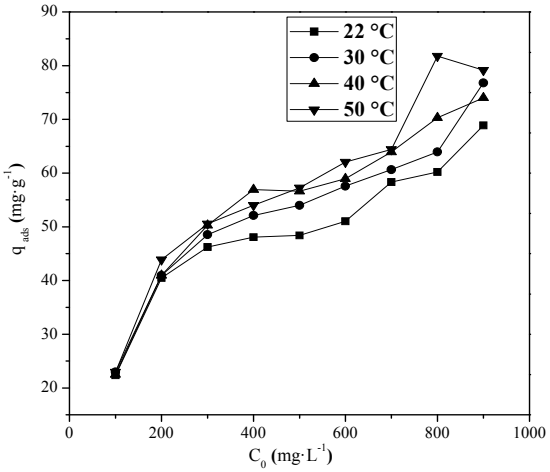

Figure 5. *The effect of temperature on CR removal. Conditions: adsorbent dose = 4 g·L^{-1}; initial pH; equilibrium time = 60 min*

Effect of solution *p*H

The initial *p*H values affect the molecular form of Congo red in the aqueous solution [10]. To study the influence of *p*H on the adsorption capacities of the natural clay were performed by adjusting the *p*H over a range of 2 - 12 (0.1 M) using HCl or NaOH solutions, with a constant initial dye concentration of 100 mg.L^{-1} and clay dose 4 g·L^{-1} at 22 °C. It was observed that color change is negligible in the *p*H range 6 - 10, the dye solution changed its color from dark blue at 2 - 4 to red at 10 - 12. In addition, and the red color is different from the original red in the *p*H range 10 - 12 [18, 19]. According to Figure 6, it can be said that the influence of the *p*H on the adsorption capacity of CR adsorbed is weak. With the increase of *p*H from 2 to 12, the adsorption amount decreased from 25.21 to 19.11 mg·g^{-1}. The decrease with increasing *p*H may be explained to the repulsion between acidic dye molecules and the abundance of hydroxyl ions at higher *p*H values [14, 20].

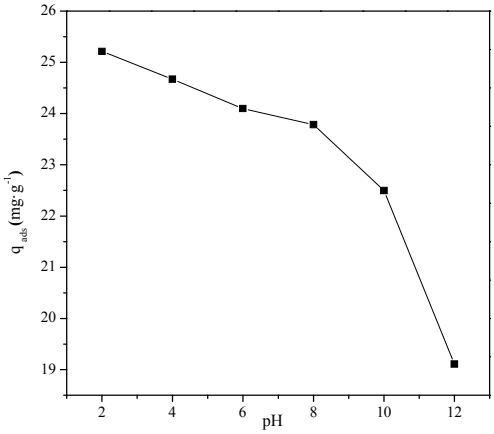

Figure 6. *The effect of pH values on CR removal Conditions: adsorbent dose = 4g·L^{-1} C_0 = 100 mg·L^{-1}; T = 22°C; equilibrium time = 60 min*

Adsorption kinetics

Many kinetic models have been employed to describe the diffusion mechanism of the adsorption process. We applied two kinetic models, pseudo first order [21], and pseudo second order [22].The linearized pseudo-first order and pseudo-second order kinetic equations were:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2{,}303} t \tag{2}$$

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \tag{3}$$

where: q_e and q_t (mg·g^{-1}) are the amounts of CR molecules adsorbed on the adsorbent at equilibrium and at any time t respectively, K_1 (min^{-1}) and K_2 (g·mg^{-1}·min^{-1}) are rate constants of pseudo-first order and pseudo-second order, respectively.

The Kinetics adsorption of CR dye on the natural clay was examined with 50 mL dye solution of concentrations 100 mg·L^{-1}, 4 g·L^{-1} of adsorbents at room temperature for a specific period of contact time (10, 20, 30, 40, 50, 60, 60 and 70 min). The result obtained is shown in Figures 7 and 8.

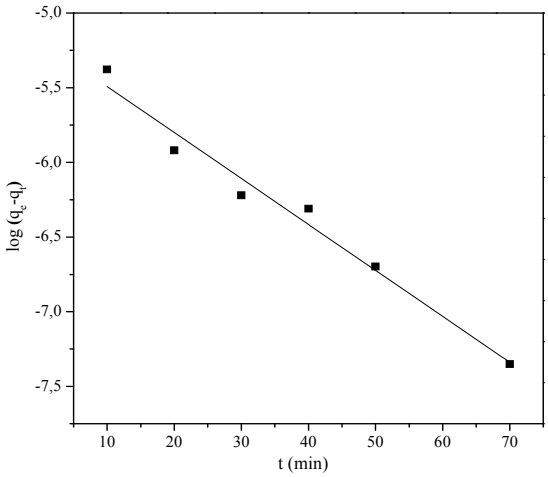

***Figure 7**. Pseudo-first-order model for adsorption of CR by natural clay*

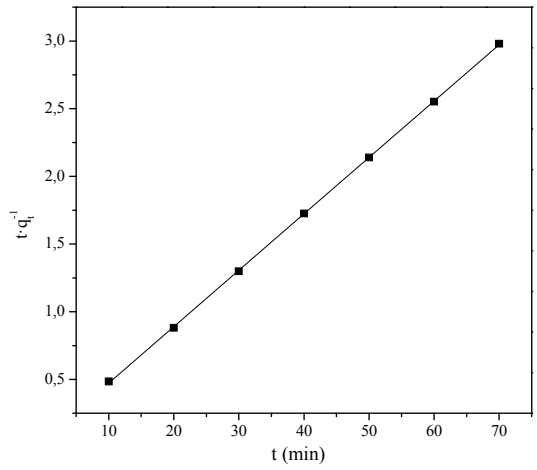

***Figure 8**. Pseudo-second-order model for adsorption of CR by natural*

Table 1 lists the results of kinetic parameters of both models. As can be seen, the values of R^2 (0.999) for the pseudo-second order kinetic model were higher than that of the pseudo-first order kinetic mode. In addition, the calculated value of adsorption capacity, q_e (23.98 mg·g^{-1}) is matched well with the experimental ones. These results implied that the adsorption was better described by the pseudo-second order kinetic, indicating that the adsorption mechanisms of CR dye depended on the adsorbate and adsorbent [23].

Table 1. *Kinetic parameters for the adsorption of Congo red onto natural clay*

Pseudo first-order kinetic model		
q_e cal [mg·g^{-1}]	**K_1 [min^{-1}]**	**R^2**
6,54787E-06	0,0308	0,97
Pseudo second-order kinetic model		
q_e cal [mg·g^{-1}]	**K_2 [g·mg^{-1}·min^{-1}]**	**R^2**
23,98081535	0,030506842	0,999

Adsorption isotherms

To study the interaction between adsorbate and adsorbent, two kinds of several isotherms equation were tested to fit the experimental data such as Freundlich [24] and Langmuir [25].

The Langmuir isotherm (Figure 9) is based on the assumption that the coverage of adsorbate molecules at the outer surface of the adsorbent occurs in a monolayer. In other words, once a dye molecule occupies a site no further adsorption occurs at that site. It is also assumed that the adsorbent surface is homogeneous [26] where all the adsorption sites are identical and energetically equivalent [27, 28]. It can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{4}$$

where: C_e (mg·L^{-1}) is the equilibrium concentration of the dye, q_e (mg·g^{-1}) is the amount of adsorbent at equilibrium, q_{max} (mg·g^{-1}) is the maximum adsorption capacity and K_L (L·mg^{-1}) is the Langmuir constant.

The essential characteristics of the Langmuir isotherm can be expressed in means of a dimensionless equilibrium parameter (R_L) [29], which is defined by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

where: C_0 (mg·L^{-1}) is the initial dye concentration and K_L (L·mg^{-1}) is the Langmuir constant. 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 Freundlich isotherm (Figure 10) is based on the assumption that the adsorption occurs on a heterogeneous surface and reversible adsorption [30], also its It is assumed that non-uniform distribution of the heat of adsorption over the surface of adsorbent takes up [31]. The Freundlich isotherm can be expressed in its linear form as follows:

$$Lnq_e = LnK_F + \frac{1}{n} LnC_e \tag{6}$$

where: q_e (mg·g^{-1}) denotes the amount of dye adsorbed, C_e (mg·L^{-1}) is the concentration of adsorbate, K_F ((mg·g^{-1}) (L·mg^{-1}) $^{1/n}$) and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively.
Adsorption isotherms was investigated for different concentrations and different temperatures ranging from 100 to 900 mg·L^{-1} and from 22 to 50 °C respectively, with 4 g·L^{-1} of adsorbents for 60 minutes and initial *p*H of the dye. The results obtained are shown in Figures 9 and 10.

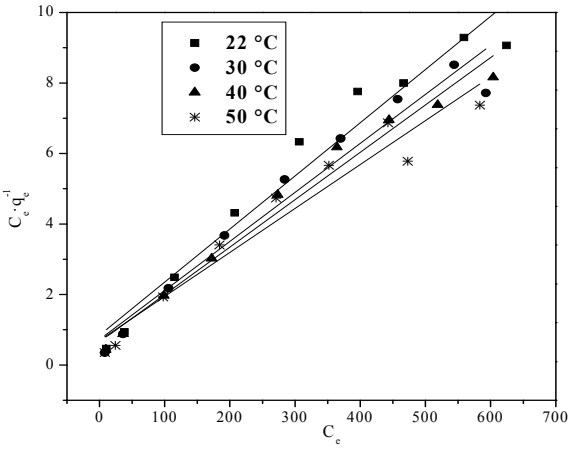

Figure 9. *Langmuir isotherm for adsorption of CR onto natural clay*

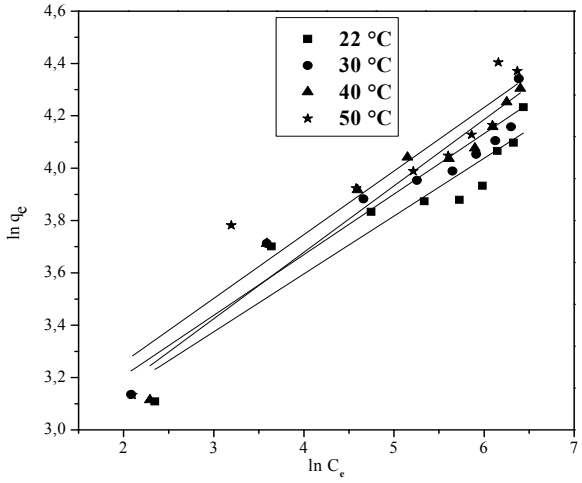

Figure 10. *Freundlich isotherm for adsorption of CR onto natural clay*

The calculated results of the Langmuir and Freundlich isotherm constants and correlation coefficients are shown in table 2.

Table 2. *Isotherm parameters obtained for adsorption of CR onto clay at different temperatures*

T [K]	Langmuir			
	K_L [L·mg^{-1}]	Q_m[mg·g^{-1}]	R_L	R^2
295.15	0 .017	66.225	0.058-0.358	0.961
303.15	0.019	71.942	0.055-0.344	0.961
313.15	0.02	74.626	0.051-0.329	0,98
323.15	0 .017	80	0.058-0.36	0.95
T [K]	**Freundlish**			
	K_F [[mg·g^{-1}] [L·mg^{-1}] $^{1/n}$]		n_F [L·g^{-1}]	R^2
295.15	15.066		4.526	0.899
303.15	15.544		4.321	0.939
313.15	14.365		4.944	0.941
323.15	16.009		4.111	0.894

In the present study, by basing on the correlation coefficients, it was possible to conclude that Langmuir isotherm ($R^2 = 0.98$) is the best fit of experimental data than the Freundlich model ($R^2 = 0.941$), which implies that the adsorption of CR on natural clay was monolayer. Thus the maximum adsorption capacities calculated from the Langmuir model was found to be 74.62 mg·g^{-1} and was consistent with the experimental data. The value of R_L of adsorption of CR onto clay fall between zero and one, and confirmed the favorable adsorption. The maximum adsorption capacities obtained in this study can be compared with other adsorption studies (Table 3).

Table 3. *Comparison of maximum adsorption of Congo Red onto various clay based adsorbents*

Adsorbent	Maximum adsorption capacities [mg·g^{-1}]	Reference
Kaolin	5.94	[32]
NaBentonite	35.84	[20]
Kaolin	5.44	[20]
Zeolite	3.77	[20]
Bentonite	40.4	[33]
Kaolin Q38	5.44	[34]
Kaolin K15GR	6.81	[34]
Kaolin Ceram	7.27	[34]
Kaolin	5.94	[35]
Natural clay	74.62	In this study

Adsorption thermodynamics

Thermodynamic studies were carried out to examine the mechanism of the adsorption process, where Thermodynamic parameter including change in Gibb's free energy (ΔG°), change in entropy (ΔS°) and change in enthalpy (ΔH°) can be calculated using following equations:

$$K_d = \frac{C_{ads}}{C_e} \tag{7}$$

$$\Delta G° = -RTLnK_d \quad (8)$$

$$\Delta G° = \Delta H° - T\Delta S° \quad (9)$$

where: K_d is the distribution coefficient for the adsorption, R is the ideal gas constant (8.314 J·mol^{-1}·K^{-1}), T is the absolute temperature in kelvin, C_{ads} and C_e (mg·L^{-1}) are the equilibrium concentrations of the Congo red on the adsorbent and in the solution phase respectively. The values of $\Delta H°$ and $\Delta S°$ were determined from a plot of lnK_d versus $1/T$ (not shown). The thermodynamic parameters are documented in Table 4.

Table 4. *Thermodynamic parameters of adsorption of Congo Red onto clay*

ΔH°	**ΔS°**	**ΔG° [kJ·mol^{-1}]**			
[kJ·mol^{-1})	**[J·mol^{-1}·K^{-1}]**	295.15 K	303.15 K	313.15 K	323.15 K
13.351936	56.702464	-3.3837962	-3.837416	-4.4044406	-4.9714652

The negative value of $\Delta G°$ (table 4) indicates the feasibility of Congo Red adsorption onto natural clay and its spontaneous nature. Generally, the value of change in Gibb's free energy fall in the range of -20 to 0 kJ·mol^{-1} for physical adsorption , while the value of $\Delta G°$ located in the range -400 to -80 kJ·mol^{-1} for chemical adsorption. The obtained value of $\Delta G°$ indicates that physiosorptive process [36]. The positive value obtained for $\Delta H°$ confirms the endothermic nature of adsorption of CR on clay. The positive values of $\Delta S°$ demonstrated the increased randomness at the solid/solution interface during adsorption process [37].

CONCLUSION

In the present study, natural clay from the Morocco investigated the adsorption of a toxic anionic dye, namely Congo Red, likely to be present in the industrial water. The obtained results showed that the adsorption tends to attain the equilibrium in nearly 60 min with 94 % of dye removal were achieved using 4 g·L^{-1} of adsorbent dose. In addition, initial dye concentration and temperature have a positive effect on the adsorption of RC onto clay, thus acid *p*H favored the adsorption process. It was concluded from the equilibrium and kinetic data that The Langmuir isotherm ($R^2 = 0.98$) provide the best correlation for the adsorption of CR onto clay with a maximum removal capacity of 74.62 mg·g^{-1} and pseudo-second-order model ($R^2 = 0.999$) described the adsorption kinetics. Moreover, thermodynamic results indicate that the CR adsorption onto natural clay was spontaneous, favorable, endothermic and physiosorptive. These results obtained in this study confirm that the natural clay originated from south Morocco can be used as alternative adsorbents for the removal of anionic dyes from wastewater.

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