



Removal of Cu (II) Ions from Aqueous Solution by Adsorption Using Natural Clays: Kinetic and Thermodynamic Studies

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Received 10 June 2017

Revised 05 Jan 2018

Accepted 01 Feb 2018

Keywords

- ✓ Removal,
- ✓ Clays,
- ✓ Copper (II),
- ✓ Langmuir,
- ✓ Freundlich,
- ✓ Dubinin–Radushkevich.

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Abstract

This study deals with adsorption kinetic, equilibrium and thermodynamic of Cu(II) ions from aqueous solution onto two natural local clays. The adsorbents were crushed, screened and characterized using different chemical and physical techniques like X-ray fluorescence, X-ray diffraction, Fourier transform infrared, etc. The effects of Cu (II) ion concentration, temperature, mass of adsorbents and pH of adsorption have been investigated. The maximum yield of adsorption was found in 90% and 30% of clay I and clay II respectively, at the conditions of initial concentration 500 mg. L⁻¹, adsorbent mass 3 g.L⁻¹, pH 6 and 298 K. They were explained by pseudo-second order in kinetic models. The experimental data of adsorption in equilibrium condition are tested by the isotherm equations like Freundlich, Langmuir and Dubinin-Radushkevich at different concentrations. Calculated thermodynamic quantities such as free energy (ΔG), the enthalpy (ΔH) and the entropy of adsorption (ΔS) indicate that the adsorption reaction was spontaneous, endothermic and controlled by physical mechanisms.

1. Introduction

Water pollution by toxic heavy metals from landfills and industrial waste is a universal environmental concern. In actuality, the presence of heavy metals in the water is responsible for many health problems for all kinds of lives [1]. Heavy metal contamination is found in aqueous waste stream from a lot of industries like metal plating, tanneries, car radiator manufacturing, mining, painting, heavy metal contamination is found in aqueous waste stream from a lot of industries like metal plating, tanneries, car radiator manufacturing, mining, painting, also agricultural sources where fertilizers and fungicidal sprays are widely used [2,3]. Chemical precipitation has been suggested to remove heavy metals from aqueous solutions. However, to meet strict regulatory requirements, the precipitation-coagulation system to remove metal is mostly insufficient. The adsorption process has been shown to be an economical alternative method to eliminate the trace of heavy metals in the water. A lot of scientific researchers have used many adsorbents to eliminate heavy metal ions from aqueous solutions. Recently some authors imply adsorbents such as native and activated bentonite [4], palygorskite and sepiolite [5], Kolubara lignite [6], clay and magnetite composite [7], montmorillonite and calcareous clays [8], iron oxide modified sepiolite [9], red mud [10], natural kaolinite clay [11], zeolites, clay and diatomite [12], Unye clay [13], expanded perlite [14], pottery materials [15], Fithian illite [16], to remove the copper ions from aqueous solutions. The heavy metal adsorption on clays has been elaborate largely because the knowledge of this process could help in the environmental remediation of pollution by heavy metals. In fact, clay minerals generally have a negative surface charge and high surface area [17], which is an advantage for the adsorption of heavy metals from the solution. The removal of heavy metals, such as Cu, from aqueous solution has been investigated using a wide variety of clay minerals, like montmorillonite [18,19], kaolinite [20,21], sepiolite [22], and illite [23], etc.

As a continuation of the investigations of our research group in the use of clays in the treatments of waste waters from tanneries in Fes [24,25], we deal in the present study the comparative adsorption characteristics for removal of Cu(II) ions from aqueous solution by two natural clays, a brownish clay 'I' and a white clay 'II'. The

impact of factors, like as contact time, pH, adsorbent dosage, initial concentration of Cu (II) and temperature, were investigated by batch experiments. The kinetic, the thermodynamic and the mechanism of Cu(II) ion adsorption onto the two adsorbents were also studied.

2. Materials and methods

2.1. Adsorbents

The adsorbents used for the Cu(II) uptake was local clay materials: a brownish Clay 'I' from Northeast of Morocco and white Clay 'II' from Chaouia Ouardigha region of Morocco. These materials were crushed and sieved until the particle diameter was less than 63 μm and characterized by various physicochemical techniques, such as spectrometry of X-ray fluorescence [OXFORDMDX1000], diffraction of X-rays [Diffractometer X' PERT PRO on powder, of Panalytical equipped with a detector with scintillation X' Celerator High-speed, equipped with a copper anticathode ($\lambda = 1.5418 \text{ \AA}$)], IR with a furrier transform [VERTEX 70] and scanning electron microscope equipped with an EDX probe model QUANTA 200. The concentration of Cu (II) is determined by spectrophotometry UV-screw [VR-2000].

2.2. Adsorbate

A concentration of 500 mg.L⁻¹ of Cu (II) was prepared from a solution stock of [Cu(NO₃)₂.3H₂O]. A succession of experiments was realized to examine the adsorption behaviour of adsorbents for Cu(II) ions.

2.3. Kinetic and equilibrium study

The kinetic and equilibrium adsorption was studied using the batch experiment method. 1 g of the adsorbent was placed within 200 mL of copper (II) solution (500 mg. L⁻¹), at room temperature, on a magnetic stirrer at 250 rpm. During the experiment study, the reaction time was varied between 5 min and 6h. then, the suspension was filtered and the supernatant was analysed by spectrophotometer UV-vis VR-2000 at equilibrium time.

The adsorption yield of metal ions was calculated as follows:

$$R(\%) = \frac{([C]_0 - [C]_t)}{[C]_0} \times 100 \quad (1)$$

Where C₀ and C_t are the concentrations of copper in initial condition and at any time, respectively.

In this study, the effects of various factors such as pH from 2 to 6 (The pH of the solution was adjusted with dilute HCl or NaOH solution), concentration of the solution from 250 mg. L⁻¹ to 1750 mg. L⁻¹, the amount of adsorbent from 1 g. L⁻¹ to 10 g. L⁻¹, and contact time on copper (II) removal efficiency was examined.

The adsorption equilibrium amount of metal ions from aqueous solution was calculated from:

$$q_e = \frac{([C]_0 - [C]_e) \times V}{m} \quad (2)$$

Where q_e (mg. g⁻¹) is the adsorption amount of equilibrium, C₀ (mg. L⁻¹) is the initial concentration of the Cu(II) ions, C_e (mg. L⁻¹) is the concentrations of copper (II) at equilibrium, V (L) is the volume of the solution, and m (g) is the adsorbent mass.

Two kinetic models have been applied to study the adsorption reaction rate of Cu (II) ions onto clays 'I' and 'II', pseudo-first order and pseudo-second order. The experimental equilibrium data of adsorption are tested by three isotherm models at different concentrations, the Freundlich model, Langmuir model and Dubinin–Radushkevich (D–R) model. The fit goodness of the experimental data was examined by the comparison of the correlation coefficient R². The thermodynamic study was realized at the temperature between 298 and 333K.

3. Results and Discussion

3.1. Characterization of the adsorbents

3.1.1. Spectrometry of X-ray fluorescence

The analyses carried out on the investigated adsorbents (Table 1) show that clay 'I' contain significant amounts of calcium oxide (32.57%) and quartz (31.13%). The clay 'II' has a mass ratio SiO₂/Al₂O₃ ≈ 1, which indicates a strong content of kaolinite. Moreover, the value of loss on the ignition (12.25%) is not very distant from that of kaolinite 13.9% [25].

3.1.2. X-ray diffraction (XRD)

Clays diffractograms are presented in Fig. 1 and 2. The diffractogram obtained for Clay 'I' indicate the presence of CaCO₃ calcite and SiO₂ silica quartz [26]. Diffractogram of Clay 'II' shows the characteristic peaks of kaolinite at 2θ = 12.35° and 24.86°, the main peak of the illite at 2θ = 8.84° and the characteristic peaks of quartz (SiO₂) at 2θ = 26.71° [25].

Table 1: Chemical composition of the Clay 'I' and 'II'(%).

		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	LOI*
Clay	'I'	31.13	3.10	0.68	32.57	0.88	0.11	0.95	0.00	29.45
	'II'	47.74	36.21	1.31	0.24	0.61	0.03	1.96	0.00	12.25

*loss of Ignition at 1000 °C

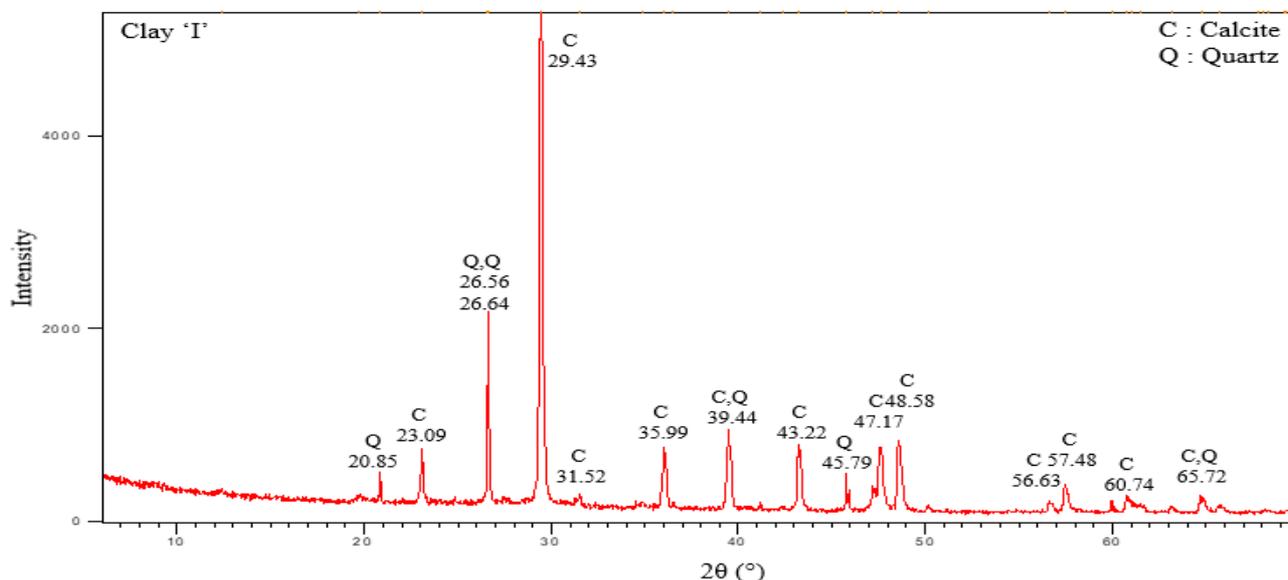


Figure1: Diffractogram of Clay 'I' (C= calcite, Q= quartz).

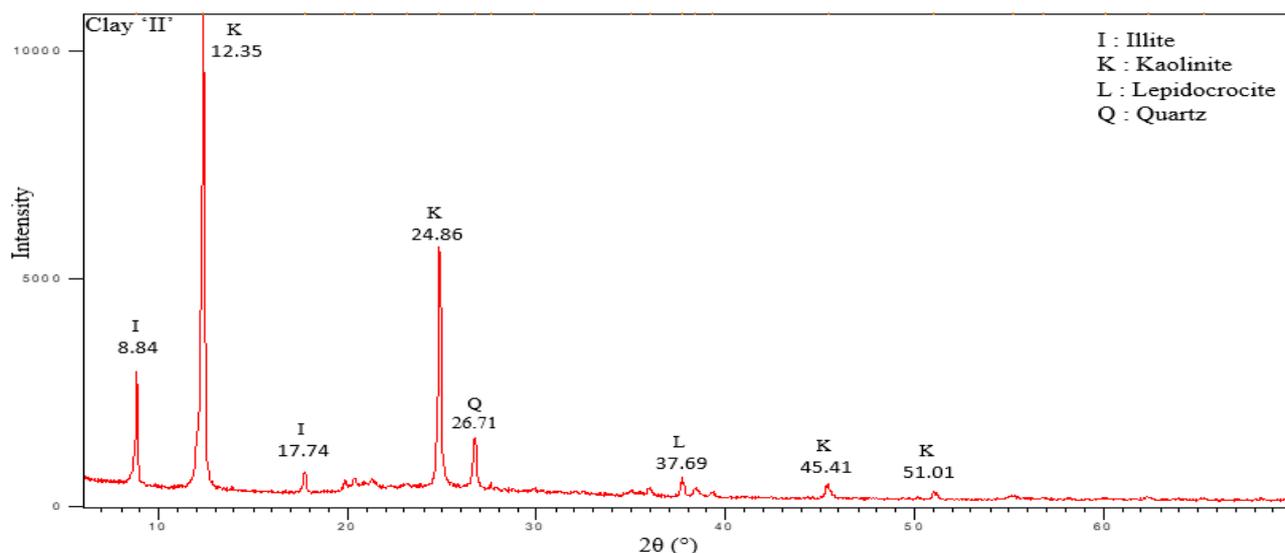


Figure2: Diffractogram of Clay 'II' (I= Illite, K= Kaolinite, Q= Quartz).

3.1.3. Fourier transforms infrared spectroscopy

Figs. 3 and 4 depict the infrared spectrum (IR) of the adsorbents 'I' and 'I'. The spectrum IR of Clay 'I' showed two vibrations intense bands at (1405 cm⁻¹, 871 cm⁻¹) which are elongation bands of C-O and a less intense band at 712 cm⁻¹, these are characteristics of the calcite. The shoulder in 1010 cm⁻¹ (vibrations band of elongation Si-O) and the band at 469 cm⁻¹ are assigned to quartz as already observed in XRD [26].

The Clay 'II' presents the bands at 3685 and 3619 cm⁻¹ which are attributed to the silanol groups O-H, a band about 1114 cm⁻¹ corresponds to the vibration of Si-O, the bands at 997 and 1024 cm⁻¹ are respectively attributed to symmetric and asymmetric of Si-O-Si, that at 909 cm⁻¹ is attributed to the deformation of groups Al-OH, and the bands at 523 and 455 cm⁻¹ are assigned respectively to the deformations of the connections Si-O-Al and Si-O-Si [25].

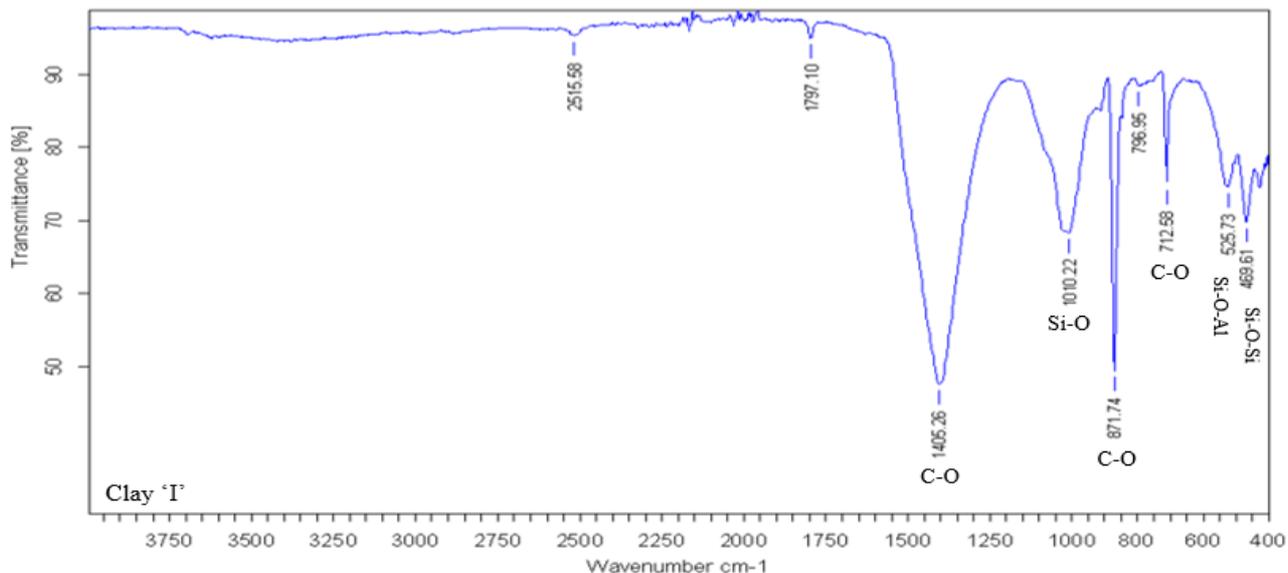


Figure 3: FTIR spectra of Clay 'I'.

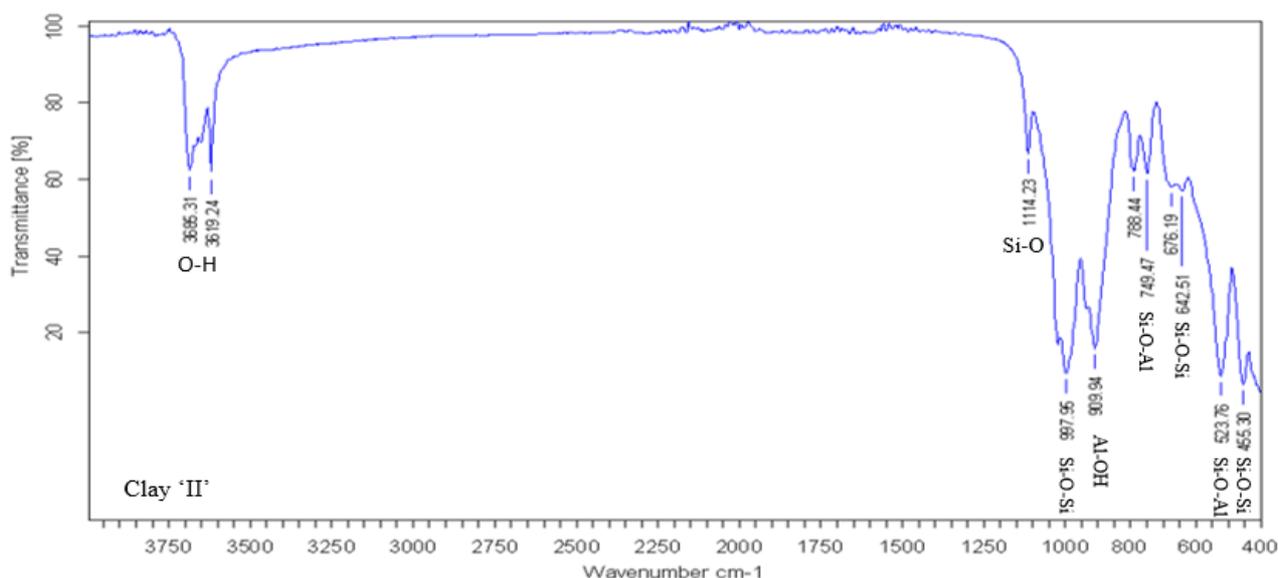


Figure 4: FTIR spectra of Clay 'II'.

3.1.4. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

Scanning electron microscope (SEM) was used to check the solid morphology and average crystal size of clay materials as shown in Fig. 5. Fig. 5a shows the Clay 'I' particles are mostly irregular in shape and the clay has a porous surface. The Clay 'II' (Fig. 5b) is formed by sheets clinged closely to each other.

3.2. Effect of contact time and initial concentration

The method of adsorption is influenced by various conditions, such as contact time, initial concentration of adsorbate, pH, amount of adsorbent and temperature. Fig. 6 summarizes the Cu(II) ions adsorption onto the Clay 'I' and 'II' at different concentrations. The maximum adsorbed amount for Cu(II) was achieved at 180 min and 60 min, respectively for Clay 'I' and 'II'. It is also observed that the quantity adsorbed increased with the increase of solution concentration and almost a constant value was obtained at higher concentration of the solution. This may be demonstrated by the clay sites become saturated with adsorbed cations and after addition of sorbent ions would not be expected to increase the quantity adsorbed considerably [27].

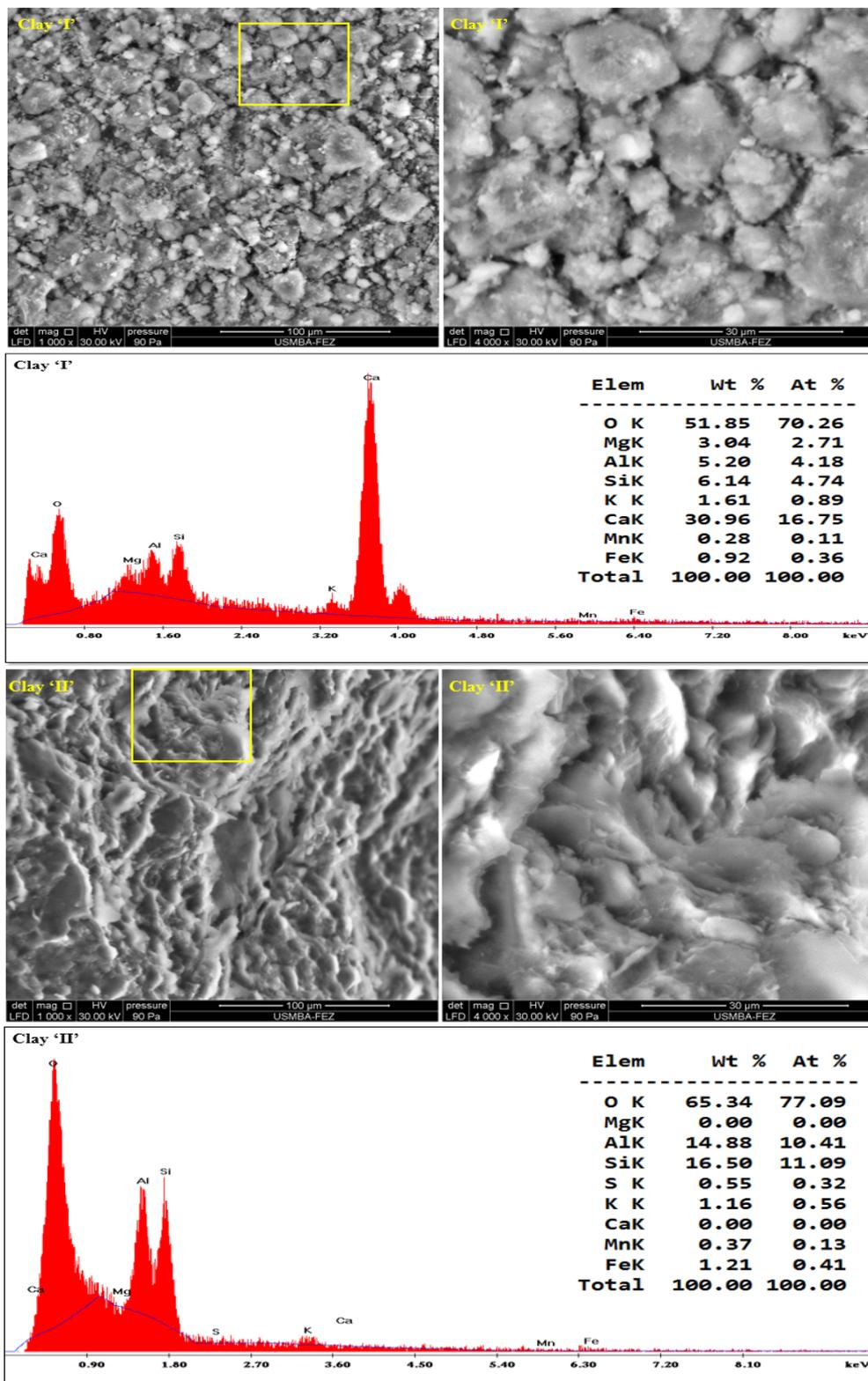


Figure 5: SEM images and EDX microanalysis spectrum of Clay 'I' and 'II'.

3.3. Effect of adsorbent dosage

The mass effect of adsorbents has been studied on Cu(II) removal and the results have been shown in Fig 7. this figure was shown that the adsorption amount q_e of Cu(II) removal decreases with the adsorbent mass increase of 1 g.L^{-1} to 10 g.L^{-1} . However, the percent metal removal (%) increased rapidly with the adsorbent's amount added. The decrease in adsorption amount (q_e) and the increase in the metal removal (%) with increasing adsorbent mass is principally due to adsorption sites of clay remaining unsaturated all periods of the adsorption reaction. Similar results have been reported by Vengris for adsorption of nickel, copper and zinc on a modified clay sorbent [28].

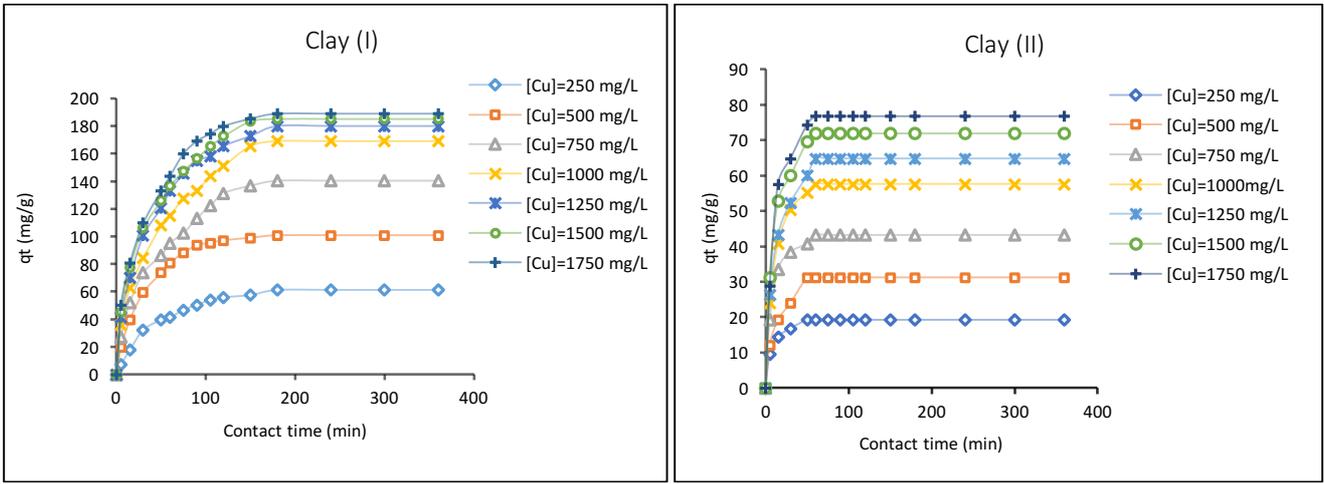


Figure 6: The adsorption amount of Cu(II) onto Clay 'I' and 'II' according to adsorption contact time for various initial concentrations. ($pH_0=5.08$, adsorbent dosage $m_{ads} = 3g \cdot L^{-1}$, $T= 25\pm 2 \text{ }^\circ C$).

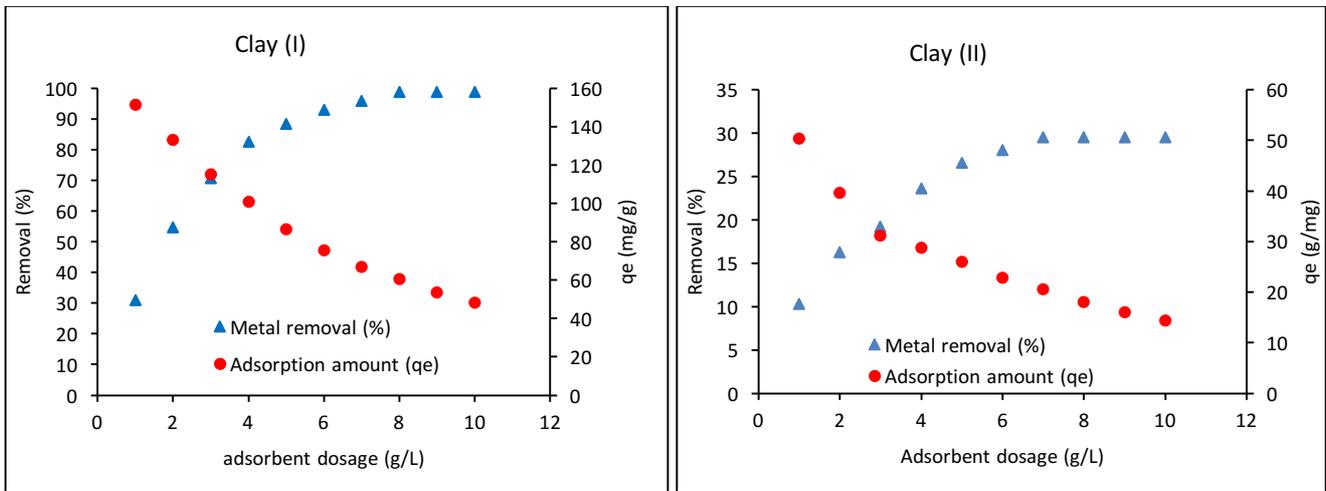


Figure 7: Effect of adsorbent dosage forms Clay 'I' and 'II' ($[Cu]_0 = 500mg \cdot L^{-1}$, $pH_0 = 5.08$, $T = 25\pm 2 \text{ }^\circ C$).

3.4. pH effect

Cu(II) ion adsorption onto Clay 'I' and 'II' was studied in the range of pH between 2.0 and 6.0 for the constant conditions of concentration and adsorbent mass at room temperature. Fig.8 indicates that the pH has an appreciable effect on the adsorption behaviour of metal ions. The adsorption capacity for two clays is found maximum at $pH=6.0$. This probably attributed to the clay surface that containing a lot of active sites.

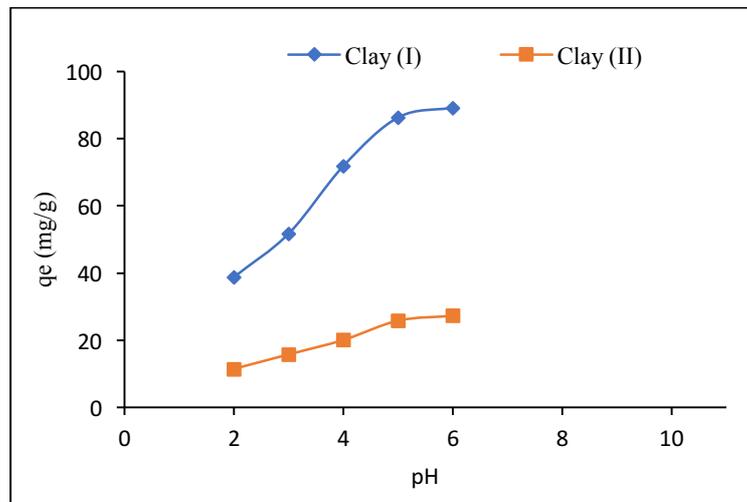


Figure 8: pH effect of adsorption ($[Cu]_0 = 500 mg \cdot L^{-1}$, $m_{ads} = 3g \cdot L^{-1}$, Contact time = 180 min for Clay 'I' and 60 min for Clay 'II', $T = 25\pm 2 \text{ }^\circ C$).

Thus, it becomes charged positively at low pH, leading to increase the concurrence between H⁺ and the Cu²⁺ ions for vacant adsorption sites. However, this concurrence decreases when the pH increases, as the active sites become more negatively charged with the surface of clay, which improves the adsorption of the positively charged metal ions by attraction force electrostatic [29].

3.5. Kinetic study

Two kinetic models, pseudo-first order and pseudo-second order have been applied to study the step which controls the reaction rate in the adsorption process.

3.5.1. Pseudo-first order

Lagergren demonstrated that, the adsorption rate of aqueous solutions on the adsorbent is based on the adsorption capacity and following a first order equation [30]. The non-linear form of the first order equation is given by the next equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

Where q_t (mg.g⁻¹) is the adsorption amount of instant t , q_e (mg.g⁻¹) is the equilibrium adsorption amount, and k_1 (min⁻¹) is the pseudo-first order constant. After integration we have applied the initial condition of $q = 0$ to $t = 0$, the equation becomes in the following form:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

The parameters k_1 and q_e could be calculated from the slope and intercept of the plots of the log ($q_e - q_t$) versus t and are given in Table 2. The regression coefficients R^2 (0.896–0.952) found are not satisfactory. Finally, we can say that the adsorption kinetics do not respond to the Lagergren model (pseudo first order kinetics).

3.5.2. Pseudo-Second Order

As the kinetic model of first order gives only k_1 , the expression of the second order was used to describe the kinetics of the adsorption processes. The pseudo-second order kinetic model equation [31] is expressed as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

The integration of this equation to $T = 0$ and $q_t = 0$ takes the linear form (6).

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q} \quad (6)$$

Where k_2 (g.mg⁻¹ min⁻¹) is the rate constantly of the pseudo-secondorder.

The kinetic parameters are given in Table 2. It is seen that the pseudo-second order model well represented the experimental data ($R^2 \geq 0.997$). This suggests that adsorption Cu(II) onto Clay 'I' and 'II' predominantly follow the pseudo-second order kinetic model. Besides, the calculated data (q_e , cal) agree well with the experimental data (q_e , exp). Similar results were found in the adsorption of Cu(II) ions on various adsorbents by several authors [32,33].

Table 2: The parameters data of pseudo-firstorder and pseudo-secondorder for the adsorption of Cu(II) onto Cay 'I' and 'II' at various temperatures.

Adsorbent	T (K)	q_e , experimental (mg.g ⁻¹)	Pseudo-first order			Pseudo-second order		
			k_1 (min ⁻¹)	q_e , calculated (mg.g ⁻¹)	R^2	k_2 (g.mg ⁻¹ min ⁻¹)	q_e calculated (mg.g ⁻¹)	R^2
Clay 'I'	298	163.06	$1.34.10^{-2}$	9.80	0.952	$2.911.10^{-4}$	175.43	0.997
	313	208.63	$1.09.10^{-2}$	8.943	0.933	$2.014.10^{-4}$	227.27	0.998
	323	220.62	$1.06.10^{-2}$	8.95	0.912	$2.204.10^{-4}$	238.09	0.998
	333	223.02	$1.08.10^{-2}$	8.86	0.923	$2.202.10^{-4}$	238.09	0.998
Clay 'II'	298	43.16	$2.13.10^{-2}$	4.009	0.954	$8.193.10^{-3}$	43.66	0.999
	303	67.14	$3.38.10^{-2}$	5.8287	0.896	$5.362.10^{-3}$	68.02	0.999
	313	88.72	$3.14.10^{-2}$	7.2181	0.924	$2.524.10^{-3}$	90.09	0.998
	323	115.10	$1.76.10^{-2}$	5.5962	0.913	$4.155.10^{-3}$	116.27	0.999

3.6. Adsorption isotherms

The isotherms study was carried out to understand the adsorption phenomenon of Cu(II) on clay materials at various concentrations. Three isotherm models such as Freundlich, Langmuir and Dubinin–Radushkevich (D–R) model were examined in this work.

3.6.1. Freundlich Isotherm

The Freundlich model can be applied to non-ideal sorption on heterogeneous surfaces and multiplayer sorption [34]. This model can be written as follows:

$$q_e = K_F \cdot C_e^{1/n} \quad (7)$$

Where K_F and $1/n$ are the constants of Freundlich connected to the adsorption capacity and the intensity of adsorption of the adsorbent respectively. The linear form of the equation of Freundlich can be written in logarithmic form according to the following relation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (8)$$

3.6.2. Langmuir Isotherm

The Langmuir model suppose that adsorption takes place at specific homogeneous sites onto the adsorbent and is successfully practiced in many monolayer adsorption processes [35]. This isotherm model written as follows:

$$q_e = \frac{q_m \cdot K_L C_e}{(1 + b \cdot C_e)} \quad (9)$$

Where K_L is the constant of Langmuir ($L \cdot mg^{-1}$). The linear form equation of the Langmuir is:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L \cdot q_m} \quad (10)$$

3.6.3. Dubinin–Radushkevich (D–R) Isotherm

The parameters data of equilibrium were also used to the D–R isotherm model to describe if adsorption occurred by chemical or physical processes [36].

$$\frac{q_e}{q_{mDR}} = \exp(-K_{DR} \varepsilon^2) \quad (11)$$

Where $\varepsilon = RT \ln(C_S/C_e)$ and q_{mDR} is the maximum adsorption capacity of the adsorbent ($mg \cdot g^{-1}$), R gas constant ($8.314 J \cdot mol^{-1} K^{-1}$), T temperature (K), K_{DR} Dubinin–Radushkevich constant ($mol^2 \cdot kj^{-2}$), and ε Polanyi potential ($J \cdot mol^{-1}$).

The linear form of the Dubinin–Radushkevich equation is:

$$\ln q_e = \ln q_{mDR} - K_{DR} \varepsilon^2 \quad (12)$$

If a linear relationship is obtained between $\ln q_e$ vs. ε^2 , the value of K_{DR} and q_m can be determined. Then, the mean free energy of adsorption, E ($mol \cdot kj^{-1}$), can be calculated from K_{DR} with the following equation:

$$E = \frac{1}{\sqrt{2K_{DR}}} \quad (13)$$

The free energy of adsorption (E) studied from the D-R isotherm model provides important indication about the adsorption properties as chemical or physical adsorption. Therefore, if $8 < E < 16 \text{ kJ} \cdot mol^{-1}$, the adsorption procedure follows by a chemical process of adsorption and if $E < 8 \text{ kJ} \cdot mol^{-1}$, the adsorption procedure is of a physical kind [37]. The curves of the linear transforms of Freundlich, Langmuir and Dubinin–Radushkevich obtained are presented in Fig.9, and the values of parameters calculated from the slope and intercept of Fig. 9 are tabulated in Table 3. These data suggest that the correlation coefficient (R^2) were found to be 0.997 for the clay ‘I’ and 0.995 for the ‘II’, indicating that the equilibrium data fitted well with the Langmuir model. The magnitude of n gives an indication of the favourability of adsorption, especially for values larger than 1. The value of n (Table 3) suggests that copper is favourably adsorbed by the Clay ‘I’ and ‘II’.

The mean adsorption energy (E) was calculated as $0.020 \text{ kJ} \cdot mol^{-1}$ for the adsorption of Cu(II) onto Clay ‘I’ and $0.006 \text{ kJ} \cdot mol^{-1}$ for ‘II’ (Table.3). These results indicate that the adsorption process of the metal ions onto these clays may be carried out via physical adsorption.

3.7. Thermodynamic Study

The thermodynamic parameters of adsorption isotherms are the free energy (ΔG°), the enthalpy (ΔH°) and the entropy (ΔS°), which is given according to equations 16 and 17, and whose values are presented in Table 3. These parameters explain the mechanism of the process of adsorption of Cu (II) onto clay ‘I’ and ‘II’.

$$Kc = \frac{q_e}{C_e} (14) \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (16)$$

$$\Delta G^\circ = -RT \ln K_c \quad (15) \quad \ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (17)$$

K_c is the equilibrium constant, q_e ($\text{mg} \cdot \text{g}^{-1}$) the equilibrium adsorption capacity and C_e ($\text{mg} \cdot \text{L}^{-1}$) is the equilibrium concentration of the adsorbate.

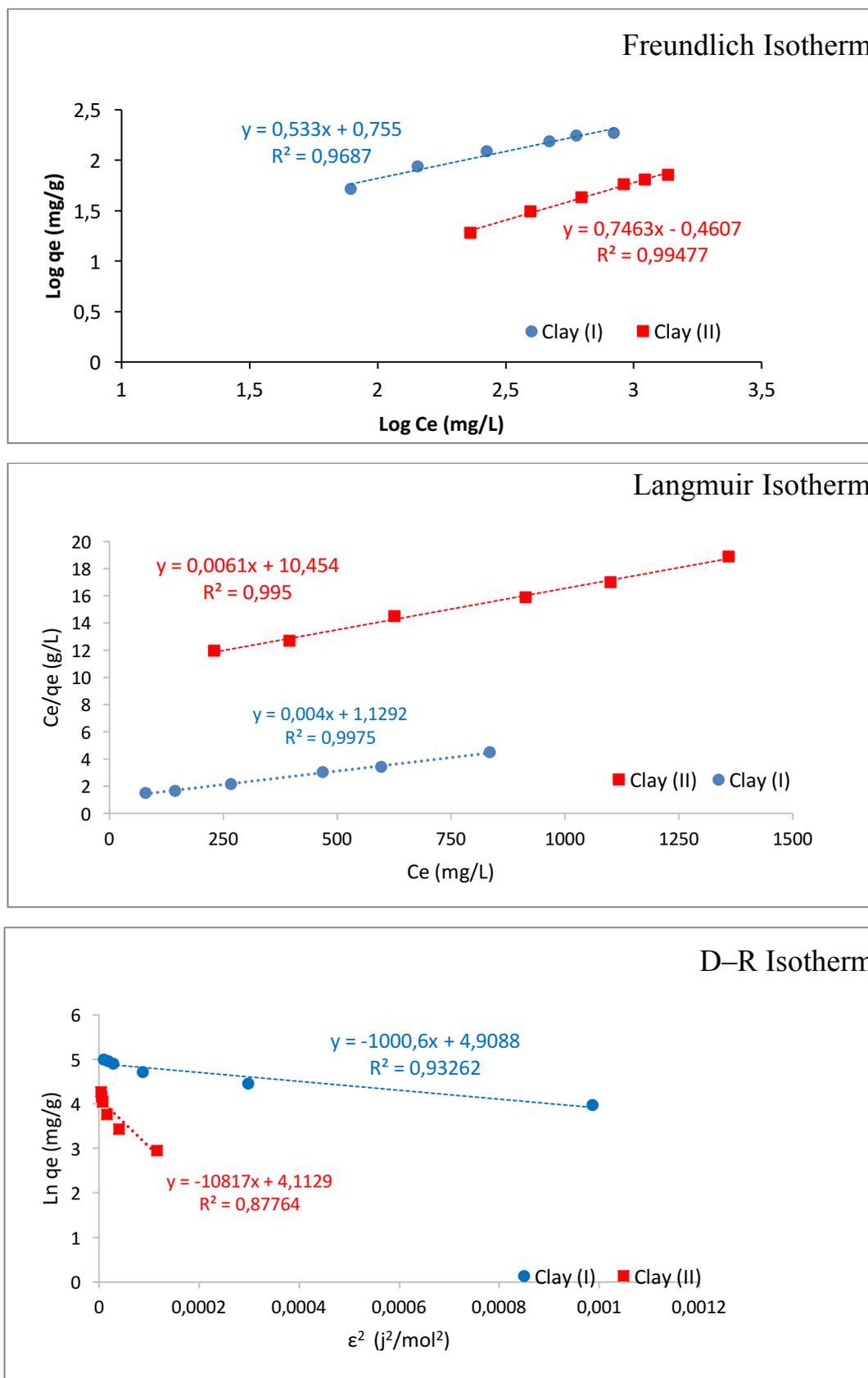


Figure 9: The Freundlich, Langmuir and D-R action on the adsorption of the Cu(II) onto Clay ‘I’ and ‘II’.

Table 3: Parameters of isotherm models for Cu (II) adsorption onto Clay 'I' and 'II'.

Adsorbent	Freundlich			Langmuir			Dubinin–Radushkevich			
	n	K _F	R ²	q _m	K _L	R ²	q _m	K _{DR}	E	R ²
Clay 'I'	1.876	7.585	0.968	250	4.516.10 ⁻³	0.997	210.12	1205.5	0.020	0.888
Clay 'II'	1.339	2.88	0.994	163.93	0.583.10 ⁻³	0.995	61.12	10817	0.006	0.877

As stated by Eq. (17), the standard enthalpy (ΔH°) and the standard entropy (ΔS°) values were obtained from the slope and the ordinate at the origin of $\ln K_c$ as a function of $1/T$, respectively. Where $\Delta H^\circ/R$ is the slope and $\Delta S^\circ/R$ is the ordinate of origin. The negative values of ΔG° indicated that the reaction of the adsorption process is thermodynamically feasible and spontaneous (Table 4), and it became more negative with the increase of temperature. Therefore, higher temperature supported the Cu(II) ion adsorption onto Clay 'I' and 'II' due to a greater force behavior of adsorption. The positive value of ΔH° for the various clays indicates the endothermic nature of the adsorption. In our case, the positive values of ΔS° for the different adsorbents, reflects the affinity of Cu(II), and indicates the increase in randomness at the solid / liquid interface during the adsorption procedure.

Table 4: Thermodynamic parameters for the Cu(II) adsorption onto Clay 'I' and 'II'.

Adsorbent	ΔG° (kJ.mol ⁻¹)				ΔH° (kJ.mol ⁻¹)	ΔS° (j.mol ⁻¹ .K ⁻¹)	R ²
	T=298 K	T=303 K	T=313 K	T=323 K			
Clay 'I'	-53.138	-55.815	-57.599	-59.384	39.152	178.448	0.977
Clay 'II'	-10.414	-12.593	-14.045	-15.498	32.863	145.23	0.995

Conclusion

The main aim of this study was to evaluate two clays from two different areas of Morocco as possible adsorbents for removal of Cu(II) from synthetic wastewater. The limit adsorption yield was found as 90% of clay 'I' and 30% of clay 'II', from the initial concentration 500 mg.L⁻¹, adsorbent dosage 3 g.L⁻¹, pH 6.0 and 298 K. The adsorption kinetics followed pseudo-second order kinetic model at different temperatures. The adsorption isotherms for initial solution pH at 298 K are well interpreted by Freundlich and Langmuir model and the standard values free energy propose that the adsorption process between adsorbent and metal ions was largely due to physisorption. The thermodynamic study suggested the feasibility, endothermic and spontaneous kind of Cu(II) ions adsorption onto two clays in temperature area of 298 to 333K. The results showed that the brown Clay 'I' of the oriental region of Morocco has been found very effective and environmentally friendly adsorbent which can be used in wastewater treatment without any chemical treatment.

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