

Kinetic and Thermodynamic Study of Adsorption of Copper (II) Ion on Moroccan Clay

Hanane Essebaai, Ilham Ismi, Ahmed Lebkiri, Said Marzak and El Housseine Rifi

Laboratory of Organic Synthesis and Extraction Processes, Department of Chemistry, Faculty of Sciences, University Ibn Tofail, BP 133 Kénitra 14000. Morocco

Abstract: Highly efficient low-cost adsorbent was applied for copper (II) ions uptake from aqueous solution. Characteristics of natural adsorbent were established using scanning X-ray diffraction (XRD), X-ray fluorescence, electron microscope (SEM) and Fourier Transform Infra-Red (FTIR). Various physicochemical parameters such as contact time, initial copper(II) ions concentration, adsorbent dosage, pH of copper (II) ions solution and temperature were investigated. The result showed that the adsorption of copper (II) ions by natural clay was favorable at pH=5,5. The adsorption was found to increase with increase in initial copper (II) ions concentration, and contact time. Equilibrium adsorption data were fitted using three isotherms and kinetic data tested with four kinetic models. Freundlich isotherm best described the adsorption of copper (II) ions onto utilised clay, the maximum monolayer adsorption capacity (q_{max}) was 8 mg/g. Pseudo-second-order model best described the kinetics of the adsorption process. Thermodynamic parameters such as Gibbs free energy, enthalpy and entropy were determined. It was found that copper (II) ions adsorption was spontaneous ($\Delta G^{\circ} < 0$) and endothermic ($\Delta H^{\circ} > 0$).

Keywords: Adsorption, Thermodynamic, Clay, Copper, Characterization, isotherms, kinetic data.

1. Introduction

The contamination of various water resources by heavy metals is a significant concern today because of their potential influences on living organisms^{1,2,3}. Heavy traffic, industrial development and urbanization lead to pollution of waters by heavy metals^{4,5}.

Various methods of metal ions treatments such as precipitation, ion exchange, a process linked to the membrane, solvent extraction and adsorption⁶⁻¹², as well as adsorption with natural adsorbent among others¹¹; are presently in use for the treatment of metal ions.

Adsorption with natural adsorbent of low cost has been found to be effective because of the simplicity in its design and operation, ability to adsorb a broad range of pollutants; fast adsorption.

Kinetics. Investigations into the use of low cost and non-toxicity adsorbent aid environmental protection¹³⁻¹⁵.

The objective of this work is to study the capacity of adsorption of copper ions (II) by natural clay. The effects of contact time, initial Copper ions

concentration, the mass of adsorbent, temperature, and pH on the adsorption of the copper(II) ions onto the natural clay were examined. The experimental data have been tested for different isotherm models. The pseudo-first order and pseudo-second order models are used to correlate the adsorption kinetics data of copper (II) ions onto natural clay. The kinetics, as well as the diffusion parameters, are also evaluated. Thermodynamic parameters like change in free energy, enthalpy and entropy for the process of removal copper (II) ions have been determined and reported.

2. Material and Methods

2.1. Adsorbent material

The material used in this work is a clay that is taken from the Berrechid region (Morocco).

The study area is located 16 km northwest of the city of Benhmed, as shown in Fig. 1.

The clay utilised was washed several times with distilled water to remove adhered dust particles. The cleaned material was kept in an oven for 24 h at 110°C. The dried mass was then crushed and sieved. The mean size of 0.112 mm was selected and used in the adsorption experiments.



Figure 1. Geological setting of the sampling area.

2.2. Preparation of metallic solutions

Metal solutions are prepared to dissolve from the 1000 mg / l solution of the hydrated copper sulfate salt ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (purity 98.5%) in distilled water. The pH of the solution was adjusted by adding 0.1 M H_2SO_4 or 0.1M NaOH. (Hanna: instrument 211).

2.3. Technique of adsorption

The extraction of metal cations Cu^{2+} by the natural clay was conducted by contacting 100 ml of the metal solution, with a known mass of clay into beakers of 250 ml at a temperature of 20°C . Then the system is stirred until equilibrium. Samples were carried out in the aqueous solution. Each sample was diluted adequately with distilled water and analyzed using

flame atomic absorption spectrometry. The used spectrometer was Varian AA Spectrometer 220 types (CUAE2TI centers, University, Kenitra).

3. Results and discussion

3.1. Clay characterization

3.1.1. X-ray fluorescence spectroscopic analysis

The chemical composition of the clay was determined by X-ray fluorescence type "Axios", with wavelength dispersion 1kW, method of preparation Pastille (PROT-ELE03-v01). This type of chemical analysis was carried out at the laboratories of the UATRS, CNRST, Rabat.

Table 1. Chemical composition of the raw clay(%).

Composition	Content (%)	Composition	Content (%)
SiO_2	50,5	SO_3	0.053
Al_2O_3	23,6	MnO_2	0.0471
Fe_2O_3	5,57	Cl	0.0426
CaO	3,4	BaO	0.0361
MgO	2.35	I	0.0171
K_2O	2.22	ZrO_2	0.0168
Na_2O	1.3	SrO	0.0162
TiO_2	0,654	Rb	0.0124
P_2O_3	0.186	Y_2O_3	0.0063
SO_3	0.053	P.A.F	9.93

The chemical analysis showed that the main constituents of the raw clay are silica, alumina and

iron oxides (Table 1). The excess of SiO_2 is due to the presence of quartz, as shown by XRD.

3.1.2. X-Ray Diffraction

Mineral analysis of the clay was performed by X-ray diffraction (XRD) powder using a Philips Analytical Diffractometer type functioning at wavelength $K\alpha$ of copper ($\lambda = 1,5405\text{\AA}$) as shown in Fig. 2. The identification of various crystalline phases was carried out by referring to the database and using a data processing software PANalytical X'Pert Pro Highscore Plus (CUAE2TI centers, University, Kenitra).

The diffractogram of clay studied shows that the clay is composed of kaolinite with a 38.7%, Muscovite with a 22.2%, Illite with a 14.8%, Halloysite with a 12% and Quartz with a 12.3%.

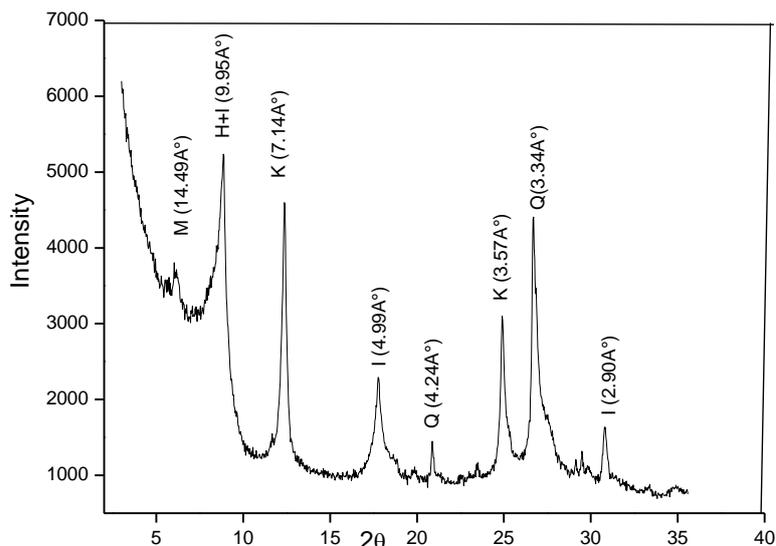


Figure 2. XRD spectra of the examined clay

Quantification of argillaceous phases was carried out by the method of Reitveld (filtering), the quality of the refinement has been confirmed by reliability factors R_p 15%, R_{wp} 20% and $\chi = 1.76$.

3.1.3. Infrared spectroscopy

Infrared transmission spectra (IR) were recorded on an FFT / IR-4600 type A spectrometer, spectra were recorded between $4000-400\text{ cm}^{-1}$.

The groups may be incorporated into the clay structure studied were revealed using the Fourier transform spectrometry model FT/IR-4600 type A. The spectrum obtained is shown in Fig. 3.

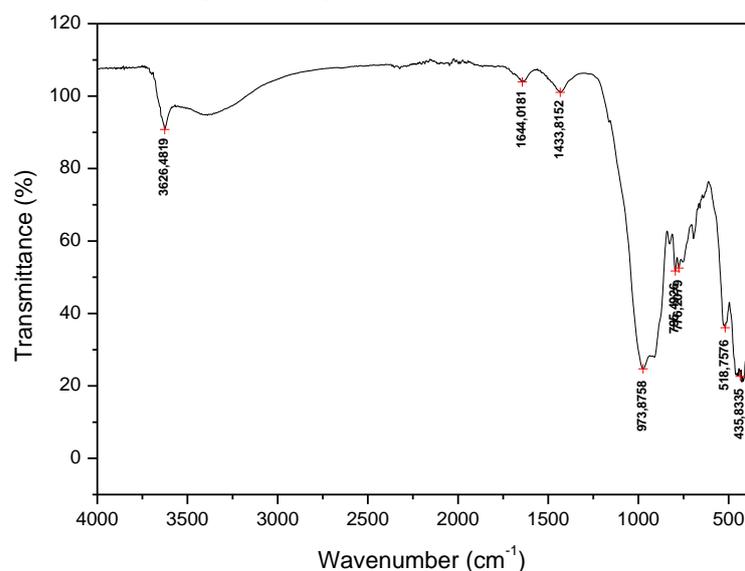


Figure 3. Infrared spectrum of the examined clay

The infrared spectrum of the clay Moroccan shows absorption bands associated with the following bonds (Table 2):

- The band that lies between $3200-3700\text{ cm}^{-1}$ show a peak at 3626 cm^{-1} is the stretching vibration of the hydroxyl group -OH linked to the constitution water.
- The band between $1300-1700\text{ cm}^{-1}$ has the peaks at 1644, and 1433 cm^{-1} corresponds to deformation vibrations of the OH bond due to water molecules adsorbed between the layers.

- The presence of the Si-O: Are characterized by an absorption band between $900-1200\text{ cm}^{-1}$. The infrared spectra confirmed the presence of silica compounds.
- We also note a wideband located towards the 795 cm^{-1} and 776 cm^{-1} attributed probably to the Si-O stretching of quartz and silica deformation vibrations. That to 518 cm^{-1} 435 cm^{-1} are assigned respectively to the deformation vibration of Si-O-Al and Si-O-Si.

Based on the bibliographic data ¹⁶⁻¹⁹ we can only confirm the results previously obtained by XRD

Table 2. absorption bands of natural clay.

Bands (cm ⁻¹)	Assignment
3626	OH stretching of structural hydroxyl groups
1644	OH deformation of water
1433	OH deformation of water
973	Si–O stretching
795	Si–O stretching of quartz and silica
776	Si–O stretching of quartz
518	Al–O–Si deformation
435	Si–O–Si deformation

3.1.4. Scanning electron microscope

A scanning electron microscope (SEM) equipped with an X-ray energy dispersion spectrometer (EDS) was used to characterize the morphology of clay particles and to perform point elemental analysis. This type of

chemical analysis was carried out at the CAC centers at Cadi Ayyad University, Marrakech.

SEM images recorded before and after adsorption of copper ions on raw clay are presented in Fig.4.

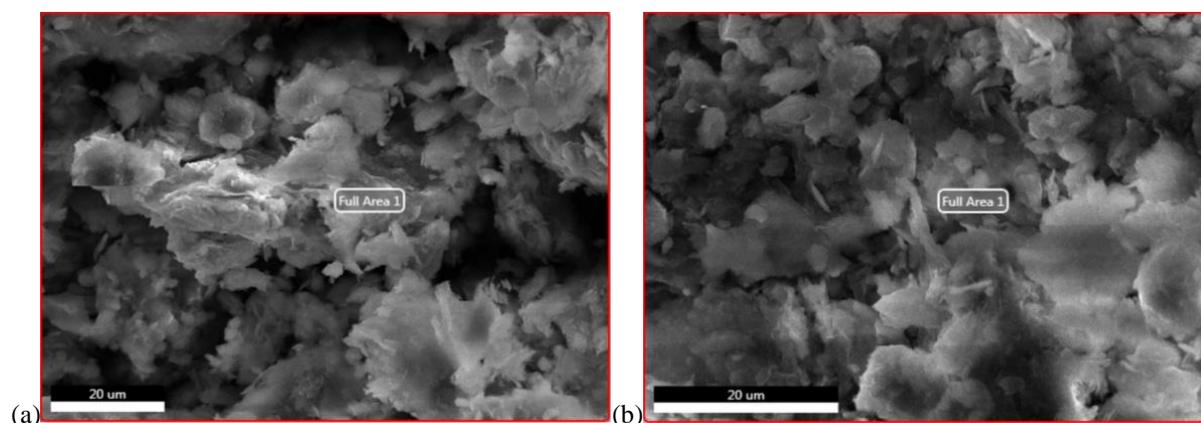
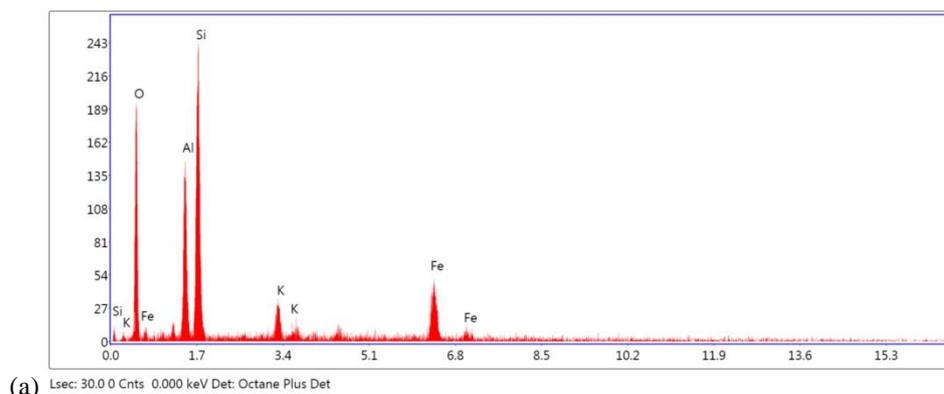


Figure 4. SEM images recorded before (a) and after (b) adsorption process of copper ions on raw clay.

The enlarged images produced by SEM at 2000 times magnification show that the studied material micrograph of the samples (Fig. 4 a and b), generally present a granular structure illustrate some tiny particles as well as particles of a somewhat larger size indicating crystallinity. When comparing the micrograph of the raw sample and after adsorption,

there is a little difference. Raw sample (a) is more heterogeneous with more open porosity.

EDX (Fig. 5) elemental analysis over several selected crystals showed that they are composed of Si, Al, O, Ca, Mg and Fe the most significant constituent composition it is oxygen average of 47.2% by weight and 23.3% Si is a component of the clay.



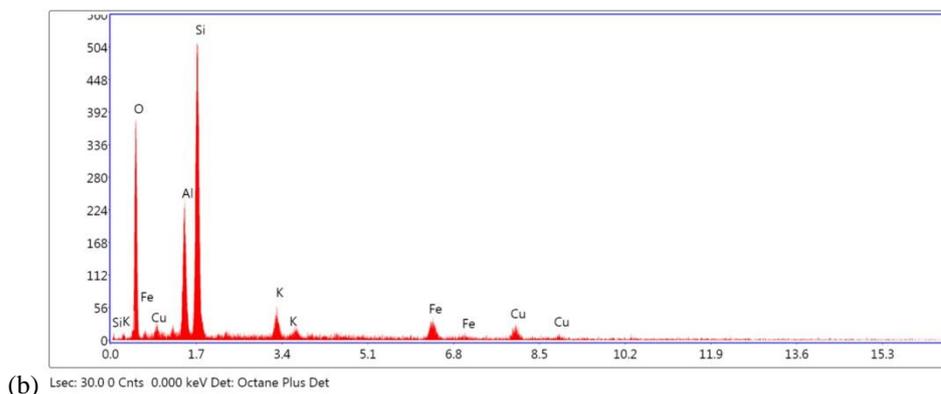


Figure 5. EDX elemental analysis recorded raw clay

The spectrum of the natural clay sample EDX (Fig. 5a) shows the absence of the characteristic peak of copper. On the other hand, on the clay spectrum after adsorption, there are two peaks of copper. This means that the copper has been inserted into the clay matrix, which explains the compacted clay surface morphology observed after adsorption of the copper ions (Fig.5b). This result indicates that the copper ions were adsorbed on the clay surface.

3.2. Adsorption study

3.2.1. Effect of contact time

To study the effect of contact time on the adsorption of copper by crude Moroccan clay, a mass of 0.5 g of clay was put into contact with 100 ml of a copper solution.

The mixture is stirred for 140 minutes. Then we followed the variation of the amount of copper

adsorbed (mg/g) versus contact time for various initial concentrations of copper up of 10, 25, 50 to 100 mg/L and at a constant temperature and pH ($T=20\text{ }^{\circ}\text{C}$ and $\text{pH}=5.5$).

The amount of the solute adsorbed per mass unit of the adsorbent is given by the following equation:

$$q_t = (C_o - C_t) \cdot \frac{V}{m}$$

With:

q_t : Adsorption capacity ($\text{mg}\cdot\text{g}^{-1}$).

C_o : Initial concentration of the solute ($\text{mg}\cdot\text{L}^{-1}$).

C_t : Instantaneous concentration of the solute ($\text{mg}\cdot\text{L}^{-1}$).

m : Mass of adsorbent (g).

V : Volume of the solution (L).

The curves representing the variation of the adsorption capacity of the copper by the crude clay in function of time are shown in Fig. 5.

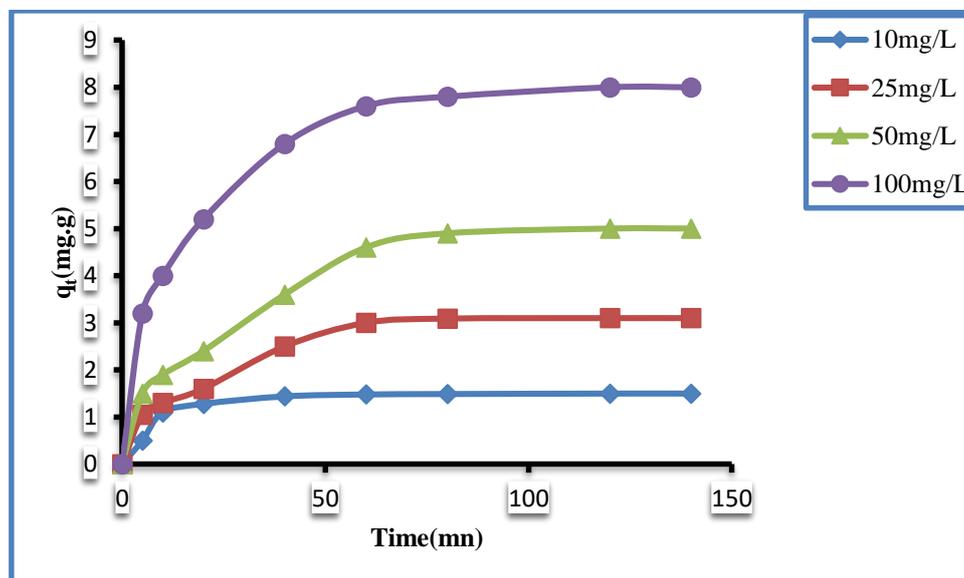


Figure 6. Variation of the amount of copper absorbed by the clay as a function of time ($m_{\text{clay}}=0.5\text{g}$, $T=20^{\circ}\text{C}$, $\text{pH}=5.5$, $V_{\text{aq}} = 100\text{ml}$)

From the curves shown in Fig. 6, it is found that the amount of adsorption q_t (mg of adsorbate per gram of adsorbent) increases with contact time in proportion as the copper concentration of the metal solution increases. The extraction equilibrium is reached after 40 min for a low concentration of copper ($10\text{ mg}\cdot\text{L}^{-1}$)

while it reached after 80 minutes for a high concentration of copper (25 and $100\text{ mg}\cdot\text{L}^{-1}$).

3.2.2. Effect of pH

The effect of pH imposed on the solution of copper (II) known by an initial concentration of $10\text{ mg}\cdot\text{L}^{-1}$ of

the clay adsorption capacity was studied. The pH range varies from 3 to 7, and the amount of clay used

is 0.5 g, the system is stirred for 120 minutes. The results obtained are illustrated in Fig. 6.

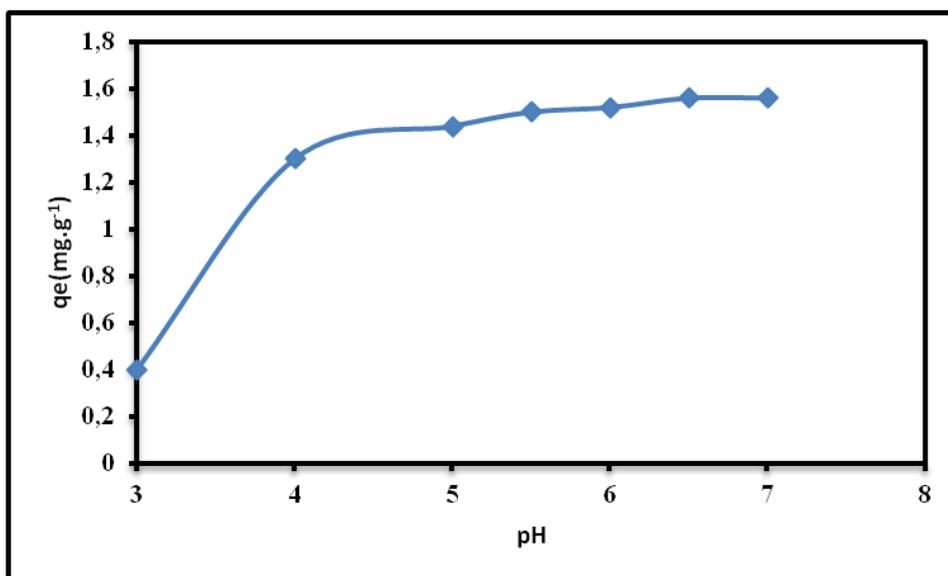


Figure 7. Evolution of the adsorption capacity of clay in Cu (II) as a function of pH. ($V_{aq} = 100\text{ml}$, $[\text{Cu}^{2+}]_i = 10\text{mg.L}^{-1}$, $m_{\text{clay}}=0.5\text{g}$, $T=20^\circ\text{C}$).

From the data of Fig. 7, it is noted that the quantity of copper (II) fixed by the clay at equilibrium is all the more important as the pH imposed on the metal solution is high. Indeed, from pH = 3 to 5.5 the retention capacity of Cu (II) increases from 0.4 to 1.5 mg.g⁻¹. This result can be explained by the fact that, at low values of pH, the surface of the adsorbent would also be surrounded by H⁺ ions, which would decrease the interaction of copper with the adsorbent. After that, the retention capacity increasing from 1.5 to 1.6 mg.g⁻¹ for pH values from 5.5 to 7 respectively. This study agrees with some reported works using The of natural clay (Cankiri bentonite) by Sevil Veli et al. ²⁰.

3.2.3. Effect of temperature

The influence of temperature on the adsorption capacity of copper by the clay was studied in the range 20-60°C. The trials were performed on mixtures of 100 ml of the copper solution at the concentration of 10 mg/L, with a mass of 0.5g of clay Moroccan in a beaker of 250 ml and at pH=5.5. These mixtures are kept at constant agitation for a duration of 120 minutes. The residual copper concentration was determined by atomic absorption spectrometry in flame. The results obtained are shown in Fig. 8.

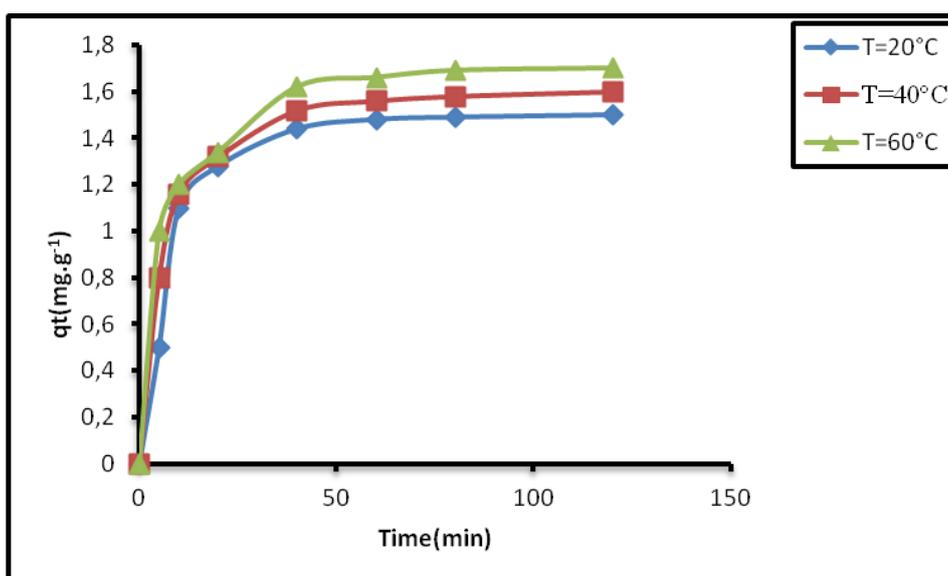


Figure 8. Effect of temperature on the adsorption of copper onto clay Moroccan versus time (20°C, 40°C and 60°C)

From the results in Fig. 8, we can see that the heating slightly favors increasing the ion capacity of Cu^{2+} on clay. This result may be due to the increased mobility of copper ions which promotes their penetration into support. The same results were found by Francisco Arias and al.²¹ adsorbing Zn^{2+} ion by a Kaolin clay.

3.3. Kinetic study

To describe the phenomenon of copper adsorption on Moroccan clay, we applied four kinetic models: The first pseudo model, the pseudo-second-order model, the model of Elovich and intraparticle diffusion model.

3.3.1. First-order Lagergren model

Lagergren showed that the adsorption rate of the solute onto the adsorbent is based on the adsorption capacity and followed by a first order equation²². The linear form of the first-order equation is given by the following equation:

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

q_e and q_t are the amounts of Cu (II) adsorbed (mg/g) at the time of equilibrium and at any instant of time, t , respectively. k_1 (L/min) is the rate constant of the first order of the adsorption reaction.

For each starting concentration, the curve $\log(q_t - q_e)$ as a function of time t (Fig. 9) is a straight line indicating that the adsorption kinetics is first-order, from which the constant k_1 is estimated. The first order constants are summarized in Table 3.

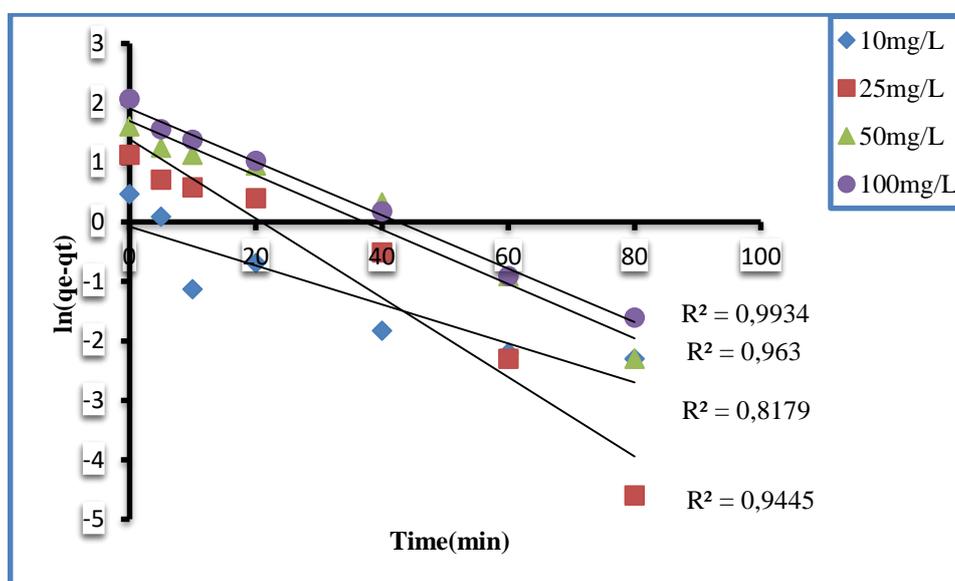


Figure 9. The first order kinetic model of adsorption of copper on the clay at various concentrations

3.3.2. Second-order kinetic model

The term of the second-order kinetic model was used to describe the kinetics of the adsorption process, the linear form of the equation is given by the following relationship:

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

with, k_2 (g/mg.min) is the rate constant of the second-order reaction²³.

In such circumstances, the curves of t/q_t versus t should give a linear relationship, which allows the calculation of q_e and k_2 from the slope. This model has the advantage of determining the adsorption capacity

theoretically in order to compare the theoretical results with experimental.

The application of the kinetic model to experimental results is shown in Fig. 10 and constants were summarized in Table 3.

These results showed that the adsorption reaction is best described by the equation of the pseudo-second-order for four concentrations of copper 10,25, 50 and 100 mg.L^{-1} . Indeed, the correlation coefficients are closer to the unit; they exceed 0.9967, and the value of the theoretical adsorption capacity ($q_{e,theo}=8.78$) is almost equal to that experimental ($q_{e,exp}=8$). This study agrees with some reported works using²⁴.

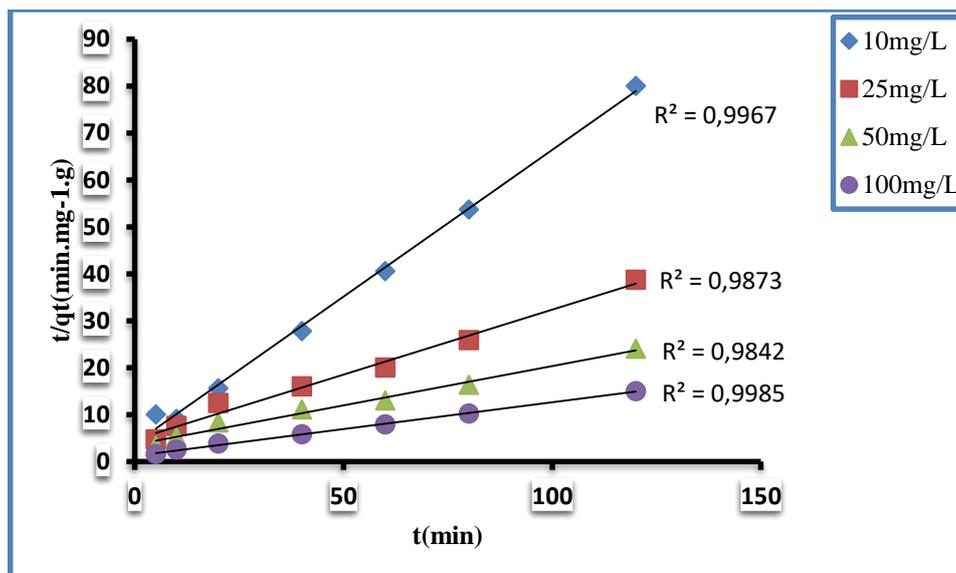


Figure 10. Second-order kinetic model of adsorption of copper on the clay at various concentrations

3.3.3. Elovich kinetic model

The model Elovich is one of the most used models to verify and describe the chemisorption during an adsorption²⁵. This model is expressed in the following linear form:

$$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln(t)$$

With α ($\text{mg.g}^{-1} \cdot \text{min}^{-1}$) is the initial adsorption rate and β (g.mg^{-1}) is the constant of desorption related to the

extent of surface coverage and energy activation for the chemisorption.

The equation of Elovich was used to correlate our experimental data by plotting the curves $q_t = f(\ln t)$ as shown in Fig. 11. The values of the constants α , β and R^2 are summarized in Table 3.

According to the data of Table 3 reveals that the correlation coefficients of the three lines obtained are higher than 0.81, which is in agreement with a chemisorptions process type of adsorption of copper onto the clay Moroccan.

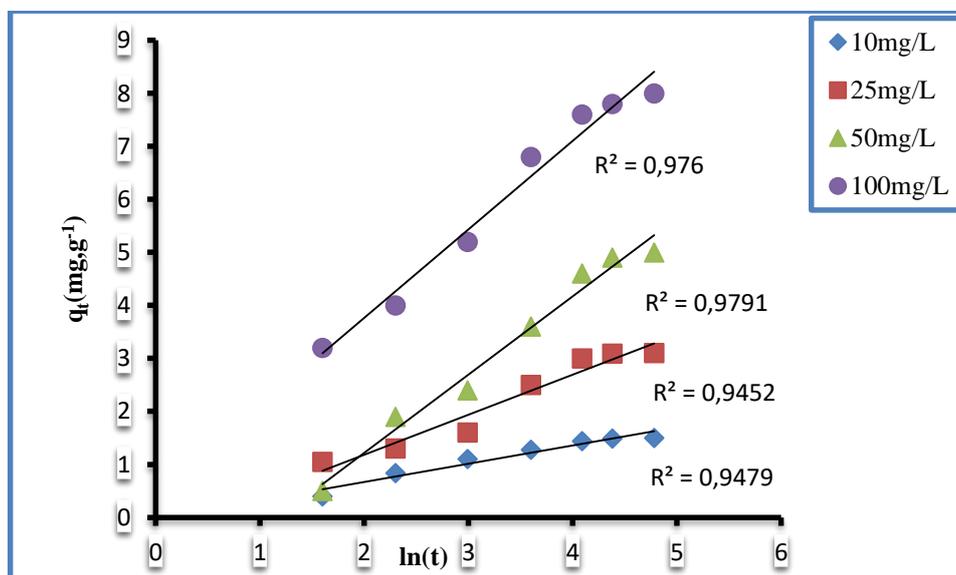


Figure 11. Elovich kinetic models for the adsorption of copper on the clay at different concentrations.

3.3.4. Intraparticle Diffusion model

The diffusion mechanism was further analyzed by the equation of the intraparticle diffusion rate, expressed in equation²⁶.

$$q_t = k_d \cdot t^{1/2} + C$$

Where K_d is the intraparticle diffusion rate constant (mg/g.min), and C is the intercept at the origin. The constant K_d was obtained from the slope of the q_t curve for $t^{1/2}$. The intraparticle diffusion is the only rate-determining step if the plot is linear and passes through the origin. The application of this model to

the experimental results is shown in Fig. 12 and the values of the parameters are given in Table 3. As indicated by the presence of the intercept $C \neq 0$ shows that the traces do not pass through the origin. The

presence of the boundary layer effect (C) showed that there is sorption of cuprous cations on the clay surface, indicating that the internal diffusion is not the only rate-limiting step of adsorption.

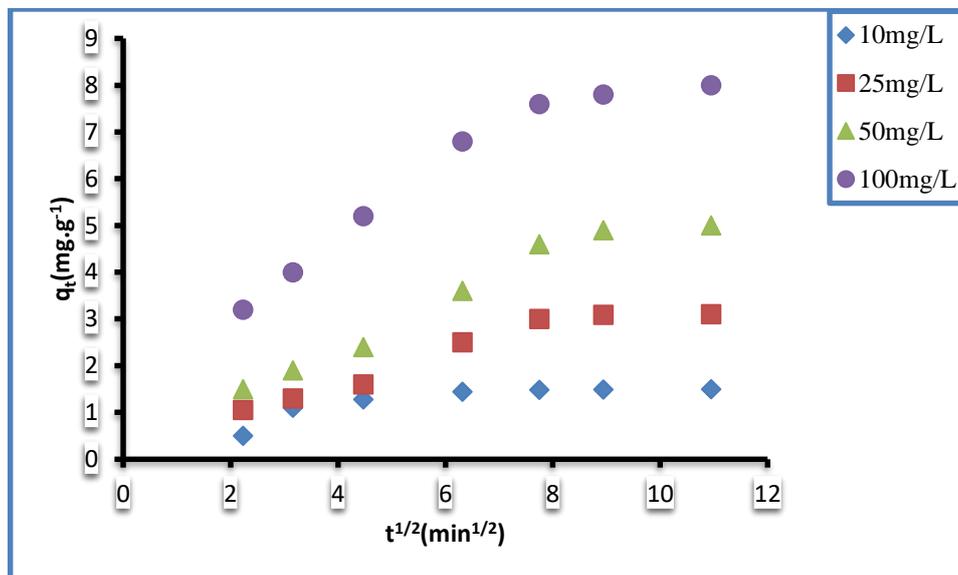


Figure 12. Curves illustrating the model Intraparticle diffusion for the adsorption of copper on clay at different concentrations of copper.

Table 3. Parameters of kinetic models.

[Cu ²⁺] (mg/L)	Pseudo-first ordre			pseudo-second ordre			Elovich			Intra-particle Diffusion		
	k ₁	q _e	R ²	k ₂	q _e	R ²	β	α	R ²	K _d	C	R ²
10	0.026	0.61	0.8179	0.1	1.59	0.9967	0.59	0.78	0.817	0.092	0.675	0.653
25	0.035	2.01	0.9445	0.016	3.61	0.9873	0.79	0.64	0.951	0.269	0.544	0.914
50	0.035	3.6	0.963	0.007	5.98	0.9842	1.32	0.5	0.956	0.4536	0.575	0.945
100	0.9934	0.0448	0.9934	0.013	8.78	0.9985	3.5	2.17	0.976	0.588	2.404	0.914

3.4. Isotherms Adsorption

Adsorption isotherms are based on the equilibrium distribution of a solute between the two phases involved in the process, namely the solid and the

solution. The result obtained from the adsorption isotherm of cuprous cations on Moroccan clay is shown in Fig. 13.

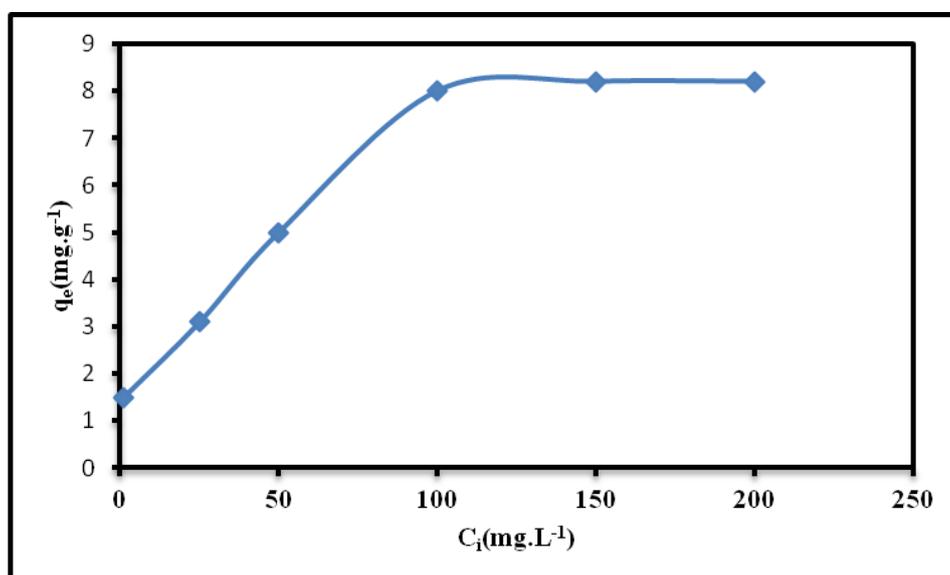


Figure 13. Adsorption isotherms of copper on clay

To describe the behavior of copper during the adsorption process, the isotherm obtained in the present study was adjusted by the following models: Langmuir, Freundlich and Dubinin-Radushkevich.

3.4.1. Freundlich Isotherm

The Freundlich model ²⁷, which indicates the heterogeneity at the surface of the adsorbent, has been applied to measure the adsorption capacity. The linear form of the Freundlich equation can be written in logarithmic form according to the following relation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

K_F and n are Freundlich constants related to the adsorption capacity and the adsorption intensity.

The experimental results obtained for the different concentrations of copper studied were modeled by the Langmuir equation and represented in Fig. 14. The values of the parameters of this isotherm are given in Table 4.

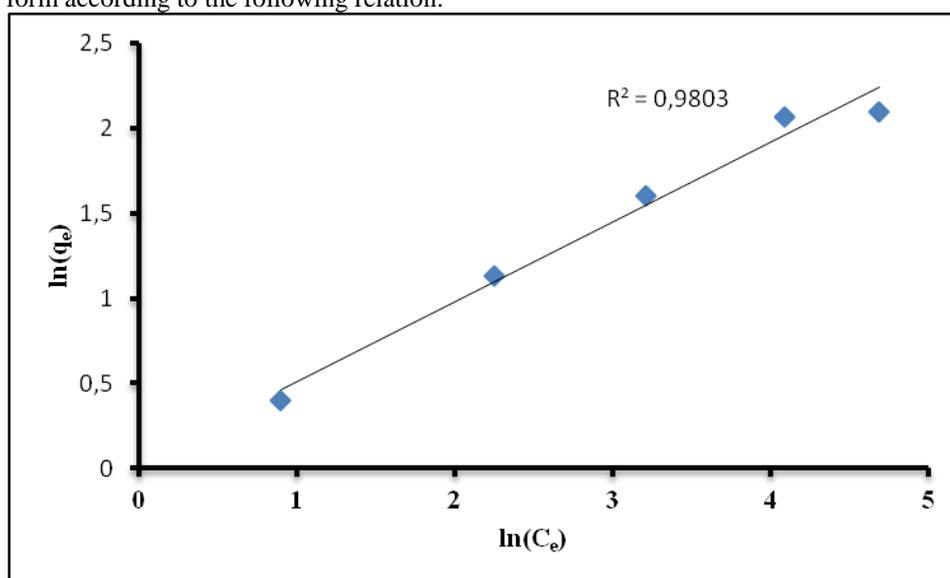


Figure 14. Adsorption isotherms of copper on the clay according to the Freundlich model

From the data in Table 4, the value of the Freundlich constant $1/n$ is less than 1, which indicates that the adsorption of the Cu^{2+} cations on the Moroccan clay is favorable according to this model. The value of the correlation coefficient is very close to unity ($R^2=0.98$), showing that the experimental results are better correlated by the Freundlich equation.

3.4.2. Isotherm of Langmuir

The Langmuir model makes it possible to determine if a monolayer is adsorbed and if there is no interaction between the adsorbed molecules. The Langmuir equation is valid for only one monolayer adsorbed with a well-defined number of uniform and identically energetic adsorption sites. The linear form of the Langmuir isothermal equation can be expressed as follows ²⁸.

$$\frac{1}{q_e} = \left(\frac{1}{K_L \cdot q_{max}} \right) \frac{1}{C_e} + \frac{1}{q_{max}}$$

With:

q_e : quantity of substance adsorbed on 1 g of clay,
 q_m : amount required to cover the entire surface with a monolayer of the adsorbed substance ($\text{mg}\cdot\text{g}^{-1}$)

C_e : concentration of copper in solution at equilibrium ($\text{mg}\cdot\text{L}^{-1}$),

K_L : adsorption energy constant.

The constants q_m and K_L can be determined from the slope of the line obtained from the representation of $1/q_e$ in function $1/C_e$.

Fig. 15 shows the application of the Langmuir equation to the experimental results. The values of the parameters of this model are given in Table 4.

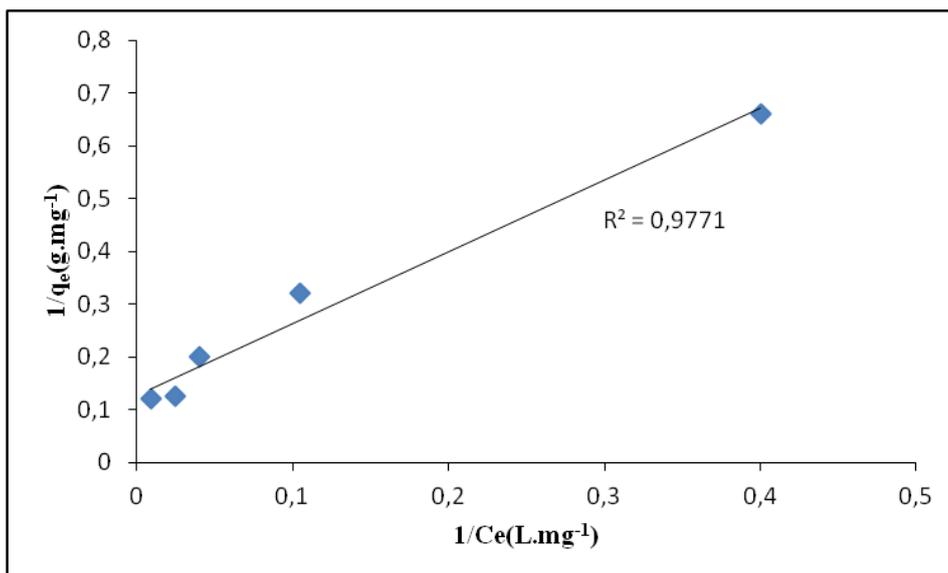


Figure 15. Adsorption isotherms of copper on the clay according to the Langmuir model

An essential characteristic of the Langmuir isotherm can be expressed in terms of an adimensional separation factor (R_L)²⁹, defined as follows:

$$R_L = \frac{1}{1 + K_L C_i}$$

With:

C_i : initial concentration of copper (mg.L⁻¹).

The adsorption is said to be favorable if $0 < R_L < 1$ and unfavorable if $R_L > 1$.

Fig.16 illustrates the evolution of the separation parameter R_L as a function of the initial concentration of copper. The estimated values of R_L are less than unity ($R_L < 0.3$), showing favorable adsorption of copper on the Moroccan clay according to the Langmuir model, which confirms the results obtained from the Freundlich model.

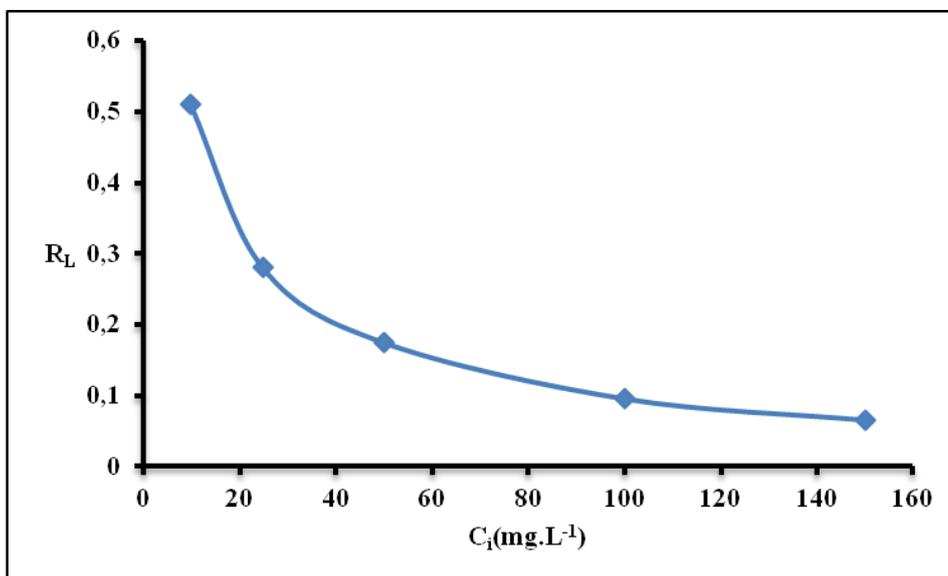


Figure 16. Evolution of the separation factor R_L as a function of the initial concentration of copper.

3.4.3. Isotherm of Dubinin-Redushkevich

The Dubinin-Redushkevich isotherm (D-R)³⁰ is applied to determine the nature of the adsorption mechanism based on potential theory assuming that the surface of the adsorbent is heterogeneous. The linear form of the Dubinin Redushkevich equation (D-R) is expressed as:

$$\ln q_e = \ln(q_s) - (B\varepsilon^2)$$

With q_s (mol.g⁻¹) is the theoretical monolayer saturation capacity of the adsorbent and ε is the Polanyi potential since R is the gas constant (8.314 J.mol⁻¹.K⁻¹) and T is the absolute temperature (K).

The isothermal constants of q_s and B are obtained from the ordinate and the slope of the curve of $\ln q_e = f(\varepsilon^2)$ respectively.

Fig. 17 shows the application of the Dubinin-Redushkevich model to the experimental results. The parameters of this model are grouped in Table 4.

Based on the correlation coefficient value ($R^2 = 0.684$), it is found that the D-R isotherm did not

provide a good fit. Consequently, the adsorption of Cu^{2+} ions by Moroccan clay is well described by the Freundlich model, which indicates that the adsorption is carried out in a multilayer.

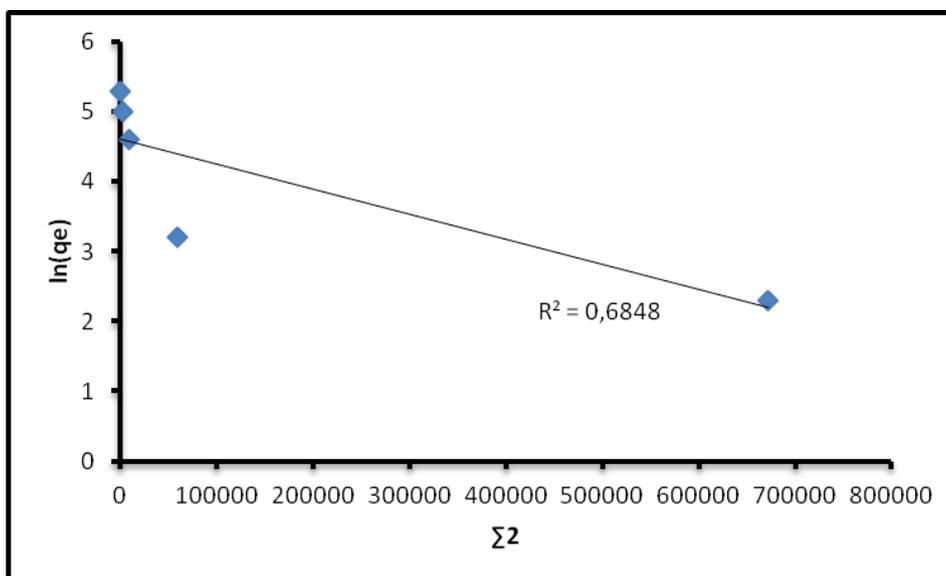


Figure 17. Adsorption isotherms of copper on the clay according to model of Dubinin-Redushkevich

Table 4. Constant adsorption isotherms of copper on clay.

Langmuir parameters	q_m (mg. g ⁻¹)	7.83
	K_L (L. mg ⁻¹)	0.009
	R^2	0.977
Freundlich parameters	K_F	0.47
	n	1.93
	R^2	0.999
D-R parameters	q_s (mol. g ⁻¹)	12.55
	$B \cdot 10^{-6}$ (mol ² . kJ ⁻²)	4
	R^2	0.684

3.5. Thermodynamic study of copper adsorption

Thermodynamic parameters such as Gibbs free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) were calculated using the following equations^{31,32}:

$$k_c = \frac{C_a}{C_e}$$

$$\Delta G^\circ = RT \ln K_c$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

K_c is the equilibrium constant, C_a is the concentration at equilibrium in phase adsorbent (mg/L), and C_e is

the equilibrium concentration in solution (mg/L). ΔH° and ΔS° were obtained from the slope and the ordinate at the origin of ΔG° as a function of T .

From the straight line obtained in Fig. 18, it was possible to deduce the various parameters grouped in Table 5. The enthalpy values of free ΔG° are negative, indicating the feasibility and spontaneity of adsorption of copper on Moroccan clay, whereas the negative value of ΔS° shows that there is a decrease of Disorder in the solid/solute interface solution system during the adsorption process. The obtained value of ΔH° is positive, indicating that the adsorption of copper on the Moroccan clay is endothermic³³.

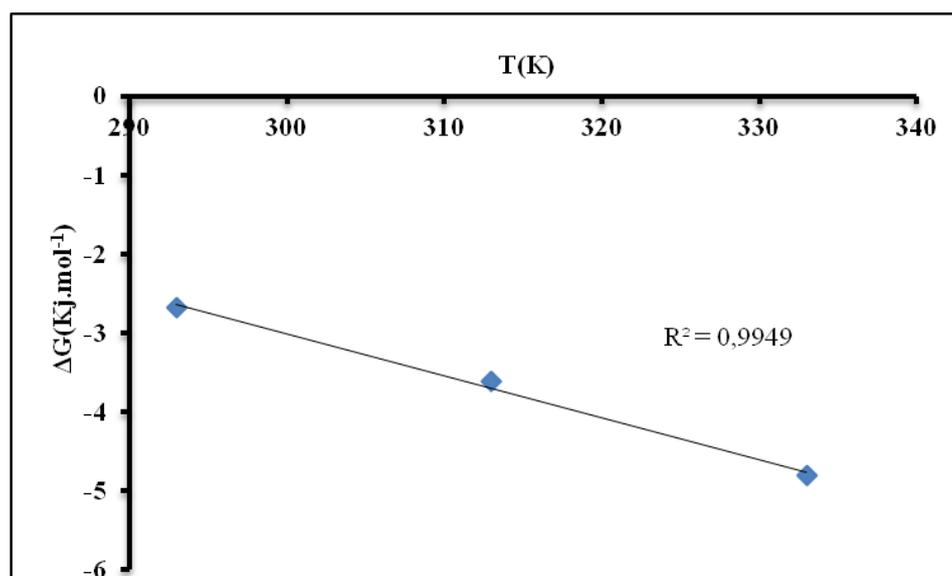


Figure 18. Determination of thermodynamic parameters

Table 5. Thermodynamic parameters of Cu (II) adsorption on clay.

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mole)	ΔS° (KJ/mol.K)
293	-2.676		
313	-3.607	12.941	0.0531
333	-4.802		

4. Conclusions

In this study, natural clay shows promising adsorption capacity for copper (II) ions removal. The operating parameters for the sorption were copper solution concentration (10mg/L), sorbent dosage (0.5 g/100 ml), contact time (60 min) and temperature (293 K). Removal of copper(II) ions is pH-dependent and the optimum adsorption was obtained at pH=5.5. Kinetics adsorption models of copper (II) ions on the natural clay were studied and modeled using four kinetic models. The classification of the kinetic models according to the simulation of the adsorption study is: Pseudo-second-order > pseudo-first-order > elovich > Intra-particle-diffuse. The rate of sorption was found to obey pseudo-second-order kinetics with a good correlation coefficient. Also, adsorption isotherms of these copper (II) ions on the natural clay were studied and modeled using three isotherm models. The classification of the models according to the simulation of the adsorption isotherms is Freundlich > Langmuir > D-R. An excellent prediction in the studied concentration can be obtained by the Freundlich isotherm. The negative ΔG° values indicated that the sorption of copper (II) ions onto clay were feasible and spontaneous. The positive ΔH° value depicted the endothermic nature of the sorption.

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