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# Elimination of copper (II) ions from aqueous solutions by acidified and calcinated clays: kinetic and thermodynamic study

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**Abstract :** In this work, the purified natural clay is acidified and calcinated at different temperatures and then used to eliminate copper (II) ions in aqueous solution. Characterization tests such as X-ray diffraction, FTIR and SEM, were used to better understand the structure, morphology and behavior of the different adsorbents. The clay is activated by 0.1M hydrochloric acid and the calcination is carried out at different temperatures (500°C, 800°C and 1000°C). The experiments were carried out in batch mode by varying several parameters, namely the contact time, the dose of adsorbent, the pH of the solution, the initial concentration of copper (II) ions in the solution, stirring rate and the temperature of the reaction medium. The results obtained showed that equilibrium was reached after 10min for AC 500°C, 15min for AC800 °C and 20min for AC1000°C. In addition, the linearization of the adsorption isotherms showed that the Langmuir model better explains the adsorption mechanism for the three adsorbents (AC500 °C, AC800 °C and AC1000 °C). The adsorption would be a single layer phenomenon. As for the kinetic study, this work has shown that the pseudo second-order model better explains the adsorption kinetics. The thermodynamic study shows that the copper (II) adsorption process on the three samples is a spontaneous and exothermic phenomenon..

**Key-words :** Adsorption, Copper (II), Calcinated clays, Kinetics, Thermodynamics.

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## Introduction

The valorization of inorganic materials such as natural clays has experienced a significant boom in the field of environmental decontamination (Kofa et al., 2017, Hambate et al., 2017). This environment is increasingly undermined by natural (natural disasters) and anthropogenic (industrial and agricultural sectors) activities. Speaking of anthropogenic causes, the pollutants released by the agricultural and industrial sectors can affect all components of the environment (air, soil and water). Regarding to water, pollutants can be organic or inorganic in nature (Hambate et al, 2015, ofudje et al., 2017). Inorganic pollutants to name a few seem to be the most dangerous in the environment. Among other things, we can mention heavy metals including cadmium, chromium VI, lead, mercury, zinc, copper II etc. These metals, released into the environment can have harmful consequences (OUAKOUAK. AK et al., 2016). The WHO sets a maximum level of 2 mg /L of copper in drinking water (WHO, 2004). Copper II above 2 mg / L in drinking water can cause serious damage to organs such as the liver and kidneys of humans, and can be responsible for anemia or toxicity developed (Bhattacharyya and Gupta, 2011), can cause significant health problems like stomach cramps, skin irritation, vomiting, nausea and anemia. This is why the scientific community for several years has been working in the direction of limiting or seeing the disappearance of the polluting load of wastewater contaminated by this metal. Several depollution techniques exist for this purpose. Among others, the traditional biological methods based on the metabolic activity of microorganisms, electrocoagulation, chemical precipitation, ion exchange, reverse osmosis, (Achour et al., 2015), electroanalyses (Veglio et al., 2003) . These techniques are certainly promising but have limitations such as their implementation and cost (Chouchane et al., 2015). Faced with these obstacles, research has turned to a method that is easier to implement and less expensive: adsorption. Several adsorbent materials exist for this purpose, among others, activated carbon, alumina, clays, zeolites, lignocellulosic materials (Batana et al., 2019). The adsorption on activated carbon was for several years the most used because of its very large specific surface. However, the production of activated carbon is very tedious. To bypass the difficulties related to activated carbon, materials are available all over the planet and easily accessible such as clays (Bouhamed et al., 2012). Several studies (Achour et al., 2015) have shown that natural clays can eliminate Copper (II) in solution. In addition, acid activation of clay increases the adsorbing power of clay (Hambate et al., 2015 ). The retention of Copper (II) ions were carried out in our study by adsorption on acidified and calcinated clay from Makabaye (Far North Cameroon), kinetic and thermodynamic studies have made it possible to better elucidate the elimination processes.

## 1. Materials and methods

### 1.1 Sampling

The material used in this work is a clay taken from the MAKABAYE deposit in the Far-North region of Cameroon. The geographical coordinates of the clay sampling site are between 10 ° 34'32 "Latitude North and 14 ° 16'72" Longitude East.

### 1.2. Adsorption procedure

#### • Preparation of solutions

By diluting 1000 mg / L of copper sulphate solution, a series of solutions of well-determined concentrations was prepared.

The adsorption was carried out in batch mode. Throughout this work, a determined amount of adsorbent was brought into contact with a fixed volume of Cu (II) solution in a 100mL beaker with stirring at 300rpm. After a certain time, the suspension is filtered using filter paper (Bell, France No. 2) to separate the liquid phase from the solid phase. The filtrate was then assayed with a spectrophotometer at 800 nm and the amount retained was calculated using the following relationship:

$$Q_t = \frac{C_0 - C_r}{m} \times V \quad (1)$$

either:

$C_0$ : initial solute concentration;

$C_r$ : residual equilibrium solute concentration;

$m$ : mass of the adsorbent;

V: volume of the solution.

The effect of the mass of the adsorbent (0.01 to 0.09 g). The effect of pH on copper (II) adsorption was studied over a pH range of 1 to 9. The pH was adjusted using solutions of 0.1 M NaOH and 0.1 M HCl. The effect of the initial concentration of the adsorbate (150 to 750 mg.L<sup>-1</sup>) and that of the stirring speed (300 to 1100 tr/ min) were also studied. Pseudo first-order and pseudo second-order kinetic models were used to assess the adsorption kinetics. Langmuir and Freundlich equilibrium adsorption isotherms were investigated and the characteristic parameters for each isotherm were determined. In addition, the temperature varied from 30 to 60°C to assess the effect of this parameter on the adsorption phenomenon and to deduce the thermodynamic parameters.

## 1. Results and discussion

### 1.1. Structural and functional characterization of clay

#### • X-ray diffraction

Figure 1 shows the diffractogram of the different clays calcinated at different temperatures at a scanning angle of 5 to 60 ° C and at a scanning speed of 10 ° C / min. Previous work by (Hambate *et al.*, 2017) has shown that Makabaye clay consists mainly of Kaolinite, Feldspar, Quartz, and montmorillonite. The analysis of the different diffractograms shows that the intensity of the different peaks decreases when the temperature increases. This can be explained by the fact that the temperature has an influence on the minerals constituting the mother clay causing side reactions. This is the case with the dehydroxylation of kaolinite during calcination, thus giving metakaolinite.

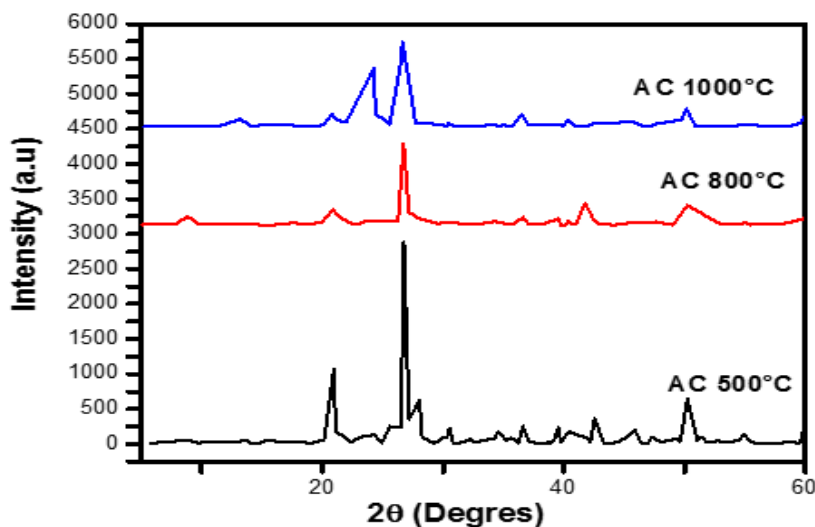
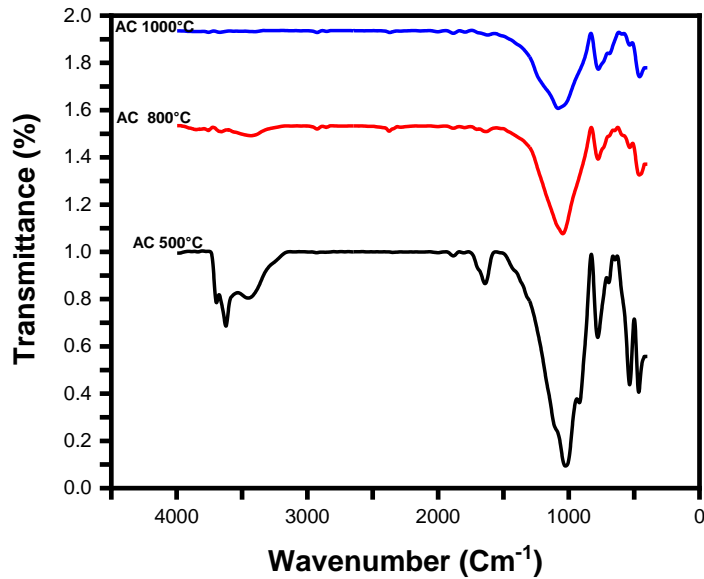


Figure 1: X-ray diffraction diffractograms of the three samples

#### • Fourier transform infrared (FTIR)

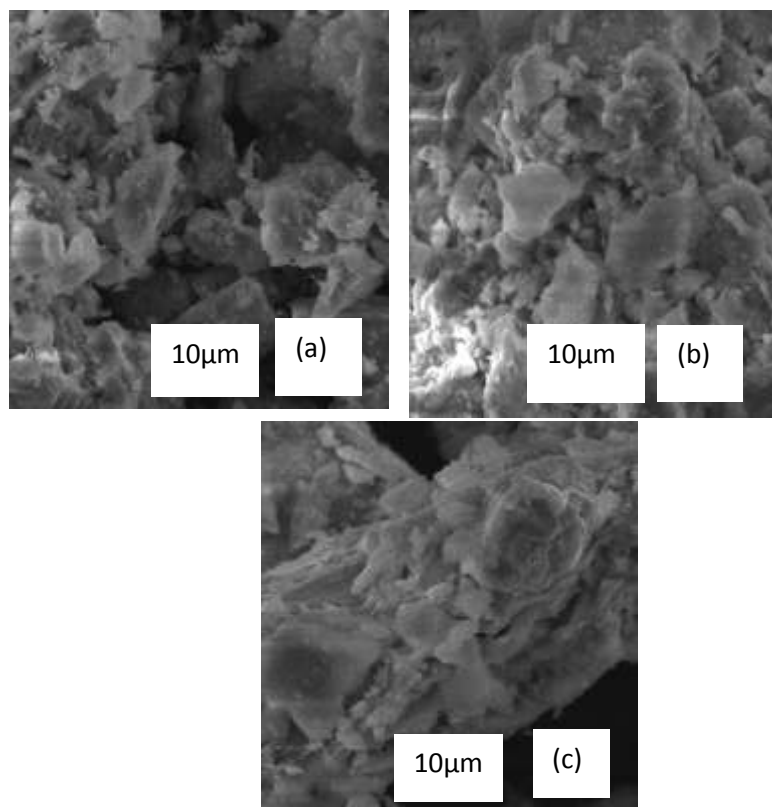
Figure 2 below shows the spectra of the FTIR analysis. The different absorption bands characteristic of acidified and calcinated clays at temperature (500°C, 800°C and 1000°C) recorded between 900 - 4000 cm<sup>-1</sup> show the decrease observed when the temperature increases. On the spectrum of clay acidified and calcinated at 500 ° C, the band located in the interval 3570-3650 cm<sup>-1</sup> with a less intense peak, which corresponds to the vibrations of elongation of the OH groups; however we notice that this band disappeared completely for clay acidified and calcinated at 800 ° C and for clay acidified at 1000 ° C. This could be explained by the increase in temperature. The band observed around 1640 cm<sup>-1</sup> is attributed to the deformation vibrations of the H<sub>2</sub>O molecules adsorbed between the sheets. This band disappears for clay acidified and calcinated at 800 ° C and for clay acidified at 1000 ° C. This is due to dehydration during the rise in temperature. The intense band in the 1000-1100 cm<sup>-1</sup> interval observed for the three adsorbents corresponds to the valence vibration of Si-O in the tetrahedral layer.



**Figure 2.** IR spectra of acidified and calcinated clay at (500 ° C; 800 ° C and 1000 ° C)

## 2. Morphological analysis

According to the images obtained by scanning electron microscopy (SEM), we notice that clays calcinated at different temperatures are made up of interfolial layers, however, the more the calcination temperature increases, the more the interfolial layers tighten.

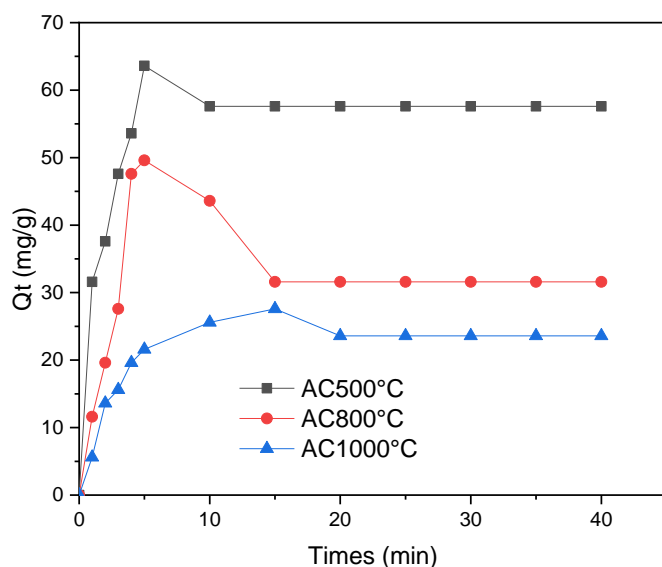


**Figure 3:** SEM images of clay ((a): AC 500 ° C, (b): AC 800 ° C, (c): AC 1000 ° C)

## 2. Optimization process

### 2.1. Contact time effect

The study was carried out by stirring at 300rpm with 0.05g of adsorbent in a volume of 20 mL of adsorbate for an initial copper ion concentration of 750 mg / L at room temperature. This stirring was done from 1 to 5 min in steps of 1 min and then from 5 to 45 min in steps of 5 min for all three samples. The results of the contact time effect for copper removal by AC 500 ° C, AC 800 ° C and AC1000 ° C are shown in Figure 4.

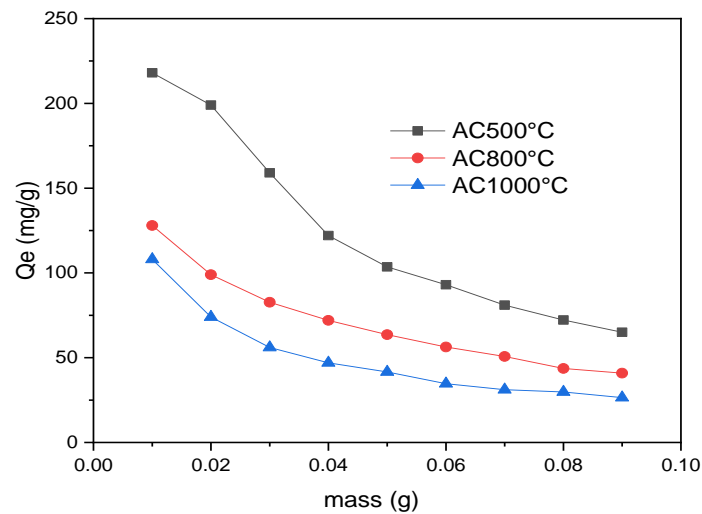


**Figure 4:** Influence of the contact time on the amount of copper adsorbed

It can be seen in Figure 4 that the adsorption of  $\text{Cu}^{2+}$  ions on the three samples is very rapid before the first five minutes. This can be explained by the fact that at the start of adsorption, the number of binding sites available on the surface of the adsorbent material is very large than the number of sites remaining after a certain time. The formation of a saturated state can be explained by an adsorption equilibrium where all sites on the adsorbent surface become occupied. Similar results were obtained by (Achour et al., 2003) during their study of copper adsorption by clays. It is noted that the maximum adsorptions of 57.6 mg / g (AC 500 ° C), 31.6 mg / g (AC 800 ° C) and 23.6 mg / g (AC1000 ° C) are reached respectively after 10 minutes, 15 minutes and 20 minutes. In general, three behaviors can be demonstrated depending on the calcination temperature between 500 ° C, 800 ° C and 1000 ° C; there is a very small decrease in the adsorbed amount, this could be explained by the fact that the AC500 ° C has more specific surfaces available than the AC800 ° C and AC1000 ° C. This is due to the fact that the higher calcination temperature, the more the vacant sites are reduced. These results show that the physicochemical properties of the materials could be controlled during the calcination temperature.

### 2.2. Mass effect

The influence of the mass of the calcinated clay applied on the adsorption capacity of  $\text{Cu}^{2+}$  ions allowed us to vary the amount of the adsorbent from 0.01 to 0.09g while setting the concentration of the pollutant in the solution at 750mg / L. The results of the influence of mass are shown in Figure 5.

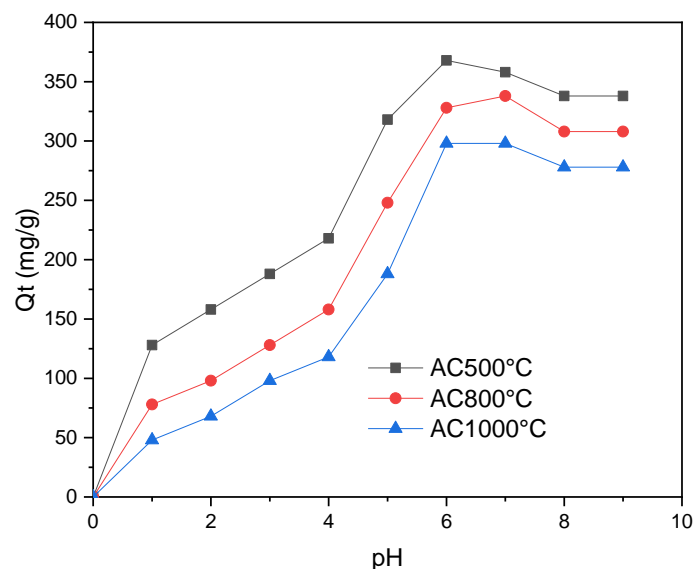


**Figure 5:** Influence of mass on the amount of copper adsorbed

Figure 5 shows that the amount used are higher for low masses of adsorbent and gradually decrease with increasing mass. This is probably due to the fact that a large amount of the adsorbent creates agglomeration of particles, resulting in a reduction in the total adsorption surface area and therefore a decrease in the amount adsorbed with increasing dose of adsorbent. When studying the influence of this same parameter, Fumba and *al* observed in 2014, the same trend when studying the adsorption of the pollutant.

### 2.3. Influence of pH

The adsorption of  $\text{Cu}^{2+}$  ions was carried out on acidified and calcinated clay. The pH is an important parameter to know if a large presence of hydroxide ions and hydronium ions can improve or decrease the adsorption of  $\text{Cu}^{2+}$  ions. The treatment pH was varied from 1, 2, 3, 4, 5, 6, 7, 8, and 9 by setting a contact time of 10 min, 15 min, and 20 min respectively, for the AC500, AC800 and AC1000. It was kept constant throughout the test by adding hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M). The results obtained in Figure 6 show a considerable influence of the pH value on the retention of copper at AC500 °C, AC800 °C and AC1000°C.

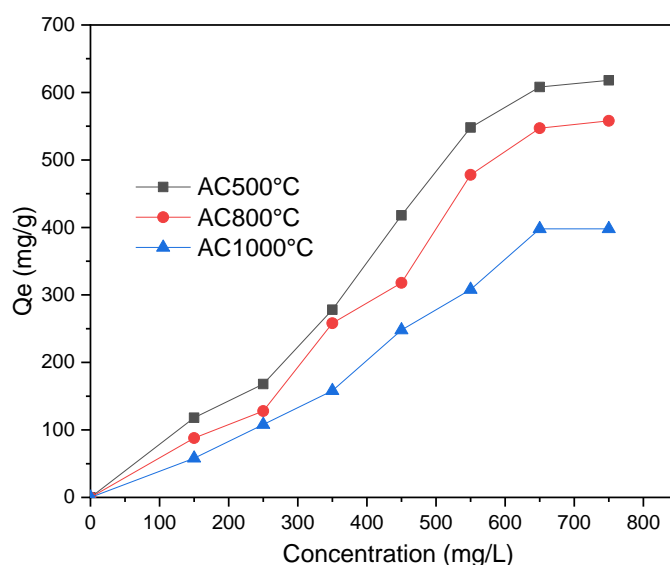


**Figure 6:** Influence of pH on the amount of copper adsorbed

Figure 6 shows that the amount of  $\text{Cu}^{2+}$  adsorbed on AC500, AC800, and AC1000 increases with pH. The elimination of  $\text{Cu}^{2+}$  is low at pH less than 4, because there would be competition between the cupric ions and the  $\text{H}^+$  protons coming from the acid, it is the  $\text{H}^+$  which are preferably fixed, and the Si-O- and Al groups -O- are more protonated and they are less available to form complexes with metal ions (OUAKOUAK. AK et al., 2016). At greater than 5, the amount of  $\text{Cu}^{2+}$  increases and reaches a maximum at pH = 7. This can be explained by the decrease in the concentration of  $\text{H}^+$  ions, which promotes the adsorption of  $\text{Cu}^{2+}$  on the surface of the adsorbents used. At that, we see a decrease which remains constant. These same observations were made by Siéwé et al, 2015; Larakeb et al., 2015.

#### 2.4. Influence of concentration

Copper ion concentrations are essential factors for effective adsorption. To demonstrate the effect of copper concentration on adsorption, experiments were performed at different concentrations of copper (II) ions; they were between 150 and 750 mg / L.



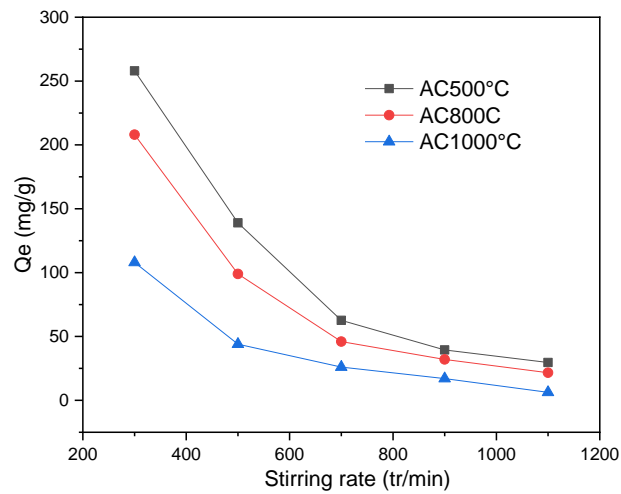
**Figure 7:** Influence of the concentration on the amount of copper adsorbed

According to Figure 7, the adsorption is low at smaller concentrations. As the concentration increases, the amount adsorbed on the three adsorbents increases until it reaches a saturation level for the amounts adsorbed. The low amount of adsorption at low concentration can be explained by the fact that the ratio of initial copper (II) moles and the available adsorption surface is low (Tumin et al., 2008). Consequently, the weak adsorption process becomes independent of the initial copper (II) concentration. On the other hand, at high concentration, the driving force, due to the concentration gradient, is stronger (Ghogomu et al., 2015).

Eventually, the saturation stage at higher concentrations means that adsorption sites become scarce. This result is in agreement with the work of (OUAKOUAK. AK et al., 2016).

#### 2.5. Influence of stirring rate

$\text{Cu}^{2+}$  adsorption tests (750mg / L) are carried out in distilled water with AC500, AC800, and AC1000, all of identical mass of 0.01g, and by setting the times respectively of 10 min, 15 min and 20 min. The pH was set at 7. The stirring rate was varied from 300 rpm to 1100 rpm in steps of 200. The results are shown in Figure 8.

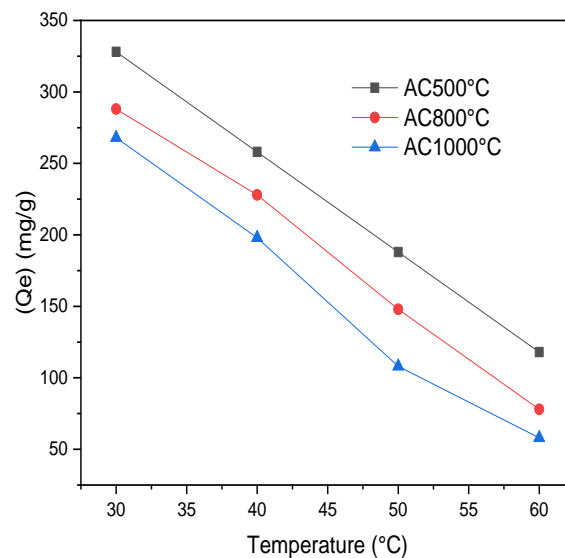


**Figure 8:** Influence of the stirring rate on the amount of copper adsorbed

The results obtained from figure 8 showed a considerable influence of the stirring rate value on copper adsorption by AC500, AC800, and AC1000. The rate of removal of copper from the solution by calcinated clay showed that the adsorption is most favorable at 300 rpm. As a result, the amount adsorbed gradually decreases, which allows us to say that this effect is probably due to the interface phenomenon. From the experimental results, we can conclude that the adsorption of the studied copper ions on calcinated clay is influenced by the stirring rate of the solution. Better adsorption is observed at 300 rpm, which suggests that the adsorption is controlled by the stirring rate.

## 2.5. Influence of temperature

The study of the influence of the applied temperature on the adsorption capacity of  $\text{Cu}^{2+}$  ions leads to varying the temperature from 30 to 60 °C while maintaining the initial concentration of the substrate in solution at 750 mg / L on AC500°C, AC800°C and AC1000°C of identical mass of 0.01 g, and setting the times respectively of 10 min, 15 min and 20 min. The pH was set at 7. The stirring rate is 300 rpm. The results of the influence of temperature are shown in Figure 9.



**Figure 9:** Influence of temperature on the amount of copper adsorbed



Figure 9 shows that the temperature curve begins at the top corresponding to the temperature of 30 ° C and gradually decreases with the increase in temperature up to the value 60°C. We can therefore say that the decrease in adsorption with the increase in temperature can be explained by the rapid increase in the desorption rate of the adsorbed species relative to the surface of the adsorbent. Similar were obtained by the previous work of Fayoud et al. (2015).

### 3. Mathematical simulation using some adsorption isotherm models

Several mathematical models can be used to describe the experimental data of the isotherm, the equilibrium relationship between the amount of adsorbate in the liquid phase ( $C_e$ ) and that adsorbed on the material ( $Q_e$ ). The adsorption equilibrium is analyzed by applying the Langmuir and Freundlich models which are commonly used by researchers for the study of adsorption isotherms of adsorbent / adsorbate systems (Bendaho et al 2014).

#### 3.1. Langmuir model

This model is widely used to explain the phenomenon of adsorption of a pollutant in the liquid phase. The copper (II) adsorption results on the three adsorbents is treated by the Langmuir model represented by the following equation:

$$Q_{ads} = q_{max} \cdot k_1 C_e / (1 + k_1 C_e) \quad (2)$$

With

$K_1$ : Equilibrium constant,

$q_{max}$ : Maximum adsorption capacity,

$Q_{ads}$ : Adsorbed quantity;

$C_e$ : Concentration at equilibrium.

The linearization of the equation is given in the form:

$$1/q_{ads} = (1/q_{max} k_1) 1/C_e + 1/q_{max} \quad (3)$$

#### 3.1. Freundlich model

The Freundlich model shows that the adsorption is multilayered. This isotherm equation is the most used to represent the experimental data, the concentrations adsorbed and in solution are related by the relationship:

$$q_{ads} = k_f C_e^{(1/n)} \quad (4)$$

The parameters  $K_f$  and  $n$  are determined experimentally from the linear form of the isotherm. The linearization of this equation involves passing the terms in logarithmic form.

$$\text{Log}(Q_{ads}) = \text{Log}(K_f) + 1/n \text{Log}(C_e) \quad (5)$$

With

$Q_{ads}$ : Adsorbed quantity,

$C_e$ : Concentration at equilibrium,

$K_f$ : Freundlich coefficient.

$n$ : affinity of the solute for the adsorbent

Figures 10 and 11 below summarize the linearized isotherms:

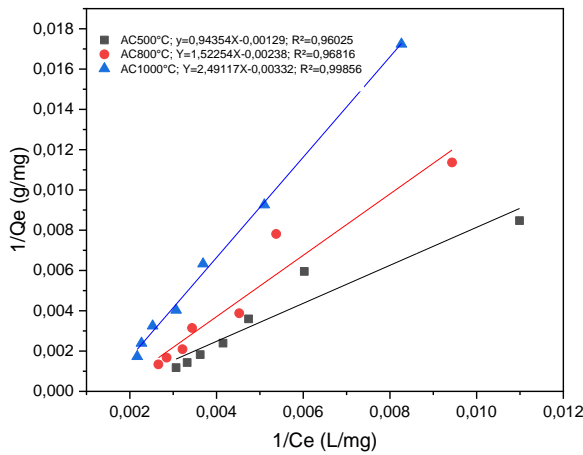


Figure 10 : Langmuir isotherm model,

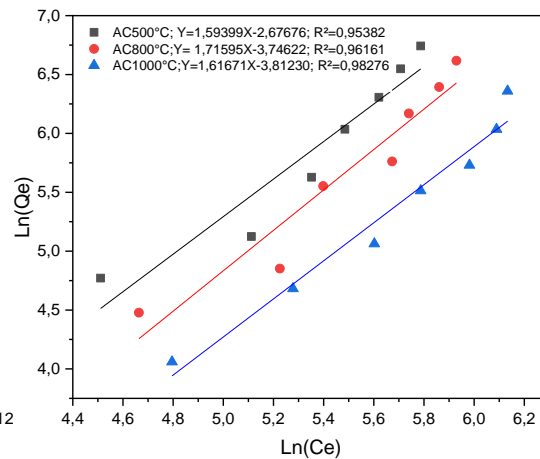


Figure 11 : Freundlich isotherm model

According to the results obtained from the two models of Langmuir and Freundlich, we notice in Figures 10 and 11, showing that the correlation coefficients obtained for the linear transformed of the adsorption isotherm of copper Cu (II) by acidified and calcinated clay are good correlation coefficients. The values obtained are summarized in Table 1.

Table 1: Constants of the adsorption models of Langmuir and Freundlich

Model	Parameters per adsorbent		
	AC500°C	AC800°C	AC1000°C
Langmuir	$K_L=0.001$	$K_L=0.002$	$K_L=0.001$
	$R_L=0.571$	$R_L=0.403$	$R_L=0.571$
	$Q_m=775.001$	$Q_m=420.167$	$Q_m=301.203$
	$R^2=0.960$	$R^2=0.968$	$R^2=0.998$
Freundlich	$K_F=0.068$	$K_F=0.023$	$K_F=0.024$
	$1/n=1.610$	$1/n=1.722$	$1/n=1.084$
	$R^2=0.953$	$R^2=0.961$	$R^2=0.982$

Langmuir's monolayer capacity,  $q_m$ , (table 1) for copper adsorption by AC500°C and AC800°C and AC1000°C shows a significant difference, 775 mg / g by AC500°C and 420.16 mg / g by AC800°C and 301.20 by AC1000°C: This indicates that the calcination temperature of the clay has a significant influence on the adsorption capacity of monolayer of clay and that Copper Cu (II) adsorption by AC500°C, AC800°C and AC1000°C does not occur by the same mechanism. It is noted in Table 1 above that the dimensionless  $R_L$  values are all less than 1, this indicates a favorable adsorption of Copper Cu (II) on the supports AC500°C, AC800°C and AC1000°C.

The value of  $1/n$  indicates the validity of the adsorption of the adsorbent-adsorbate system. A value of  $1/n$  between 0 and 1 indicates favorable adsorption (TSai *et al.*, 2005). The numerical values  $1/n = 1.51$  by

AC500C,  $1/n = 1.72$  by AC800°C and  $1/n = 1.08$  by AC1000°C indicate that adsorption  $n$  'is not favorable for AC500°C, AC800°C and AC1000 ° C.

#### 4. Kinetic Models

Kinetic modeling of the adsorption rate on activated and calcinated clays was carried out according to the following two models:

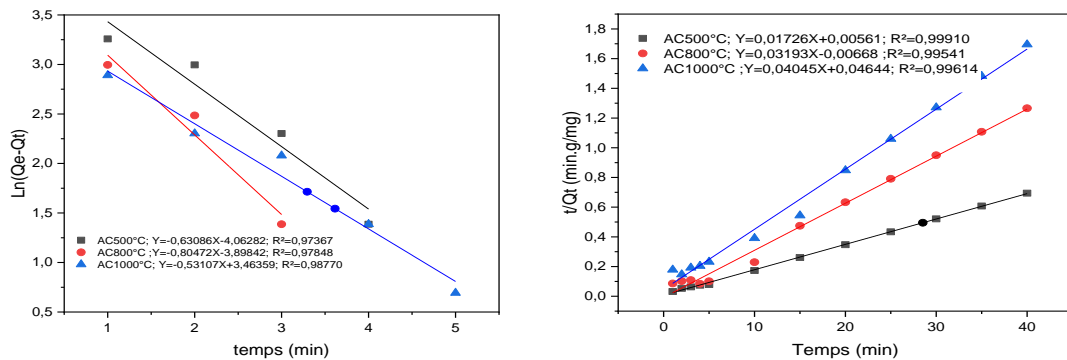
The linear form of the pseudo first-order kinetic model:

$$\ln(q_e - q) = \ln(q) - k_1 t \tag{6}$$

The linear form of the pseudo second-order kinetic model:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

Figure 12 summarizes the kinetic models:



**Figure 12:** pseudo first-order and pseudo second-order kinetic models

In view of the results presented in the figures, it appears that the values of the correlation coefficients  $R^2$  of the pseudo second-order model are very high and all order of 0.99 and exceed those obtained with the pseudo-model first order. Likewise, and according to Table 2 the value of  $q_e$  is found, we notice that this value calculated by the pseudo-second-order model is very close to that determined experimentally, which is justified by the adsorption kinetics of copper (II) by activated and calcinated clay of pseudo-second -order.

**Table 2:** Parameters of the kinetic copper adsorption models with AC500° C, AC800 ° C and AC1000° C

Kinetic parameters	AC500°C	AC800°C	AC1000°C
Pseudo first-order	$K_1 = 1.455 \text{ min}^{-1}$ $Q_e = 1155 \text{ mg/g}$ $R^2=0.973$	$K_1 = 1.854 \text{ min}^{-1}$ $Q_e \text{ (mg/g)}= 7914$ $R^2=0.978$	$K_1 = 1.221 \text{ min}^{-1}$ $Q_e \text{ (mg/g)}= 2907$ $R^2=0.987$
Pseudo second-order	$Q_{e_{exp}} = 56.61 \text{ mg/g}$ $Q_e \text{ calcul} = 57.906 \text{ mg/g}$ $K_2 = 0.052 \text{ g/min.mg}$ $R^2=0.999$	$Q_e \text{ exp (mg/g)}=31.612$ $Q_e \text{ calcul (mg/g)}=31.302$ $K_2 \text{ (g/min.mg)}=0.153$ $R^2=0.995$	$Q_e \text{ exp (mg/g)}=23.603$ $Q_e \text{ calcul (mg/g)}=24.701$ $K_2 \text{ (g/min.mg)}=0.030$ $R^2=0.998$

## 5. Thermodynamic Parameters

To determine the nature of the adsorption process, a thermodynamic study was performed. This study makes it possible to determine the amount of heat exchanged during the adsorption process and to specify the direction and the possibility of the spontaneous progress of the process. The thermodynamic parameters (free energy, enthalpy of adsorption and entropy) of copper (II) adsorption on activated and calcinated clays were obtained. The free energy variation of the adsorption reaction is given by:

$$\Delta G^\circ = -RT \ln K \quad (8)$$

$\Delta G^\circ$  is the variation of free energy ( $\text{kJ} \cdot \text{mol}^{-1}$ ),

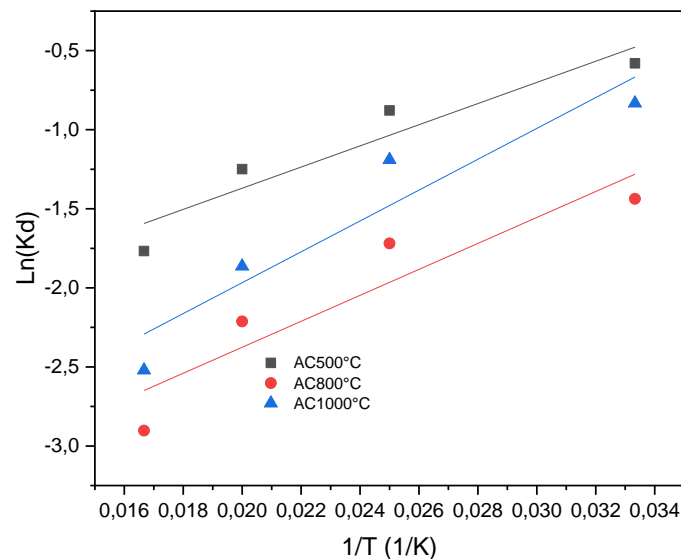
R is the universal gas constant ( $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ),

T is the temperature (K), and Kd is the constant balance.

$\Delta H^\circ$  and  $\Delta S^\circ$  are calculated from the Van'tHoff equation:

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

The plot of  $\ln(K_d)$  as a function of  $1/T$  (Figure 13) is a line with slope ( $\Delta H^\circ / R$ ) and ordinate at the origin ( $\Delta S^\circ / R$ ).



**Figure 13:** Representation of  $\ln(K_d)$  as a function of temperature ( $1/T$ )

According to the results of Table 3, it can be seen that the values of the standard adsorption enthalpy  $\Delta H^\circ < 0$ ; this can be explained that the adsorption of copper (II) in aqueous medium by calcinated clays is exothermic and as the standard enthalpy value of the adsorption is less than  $40 \text{ kJ} / \text{mol}$ , this shows that it is a physisorption (Fayoud *et al.*, 2015). The negative value of  $\Delta S^\circ$  indicates that there is a decrease in disorder in the solid / solute interface solution system during the adsorption process. The negative values of the standard free enthalpy  $\Delta G^\circ < 0$ , show that the process of adsorption of the adsorbate on the materials is a spontaneous process, and their decrease with increasing temperature indicates that the adsorption becomes less favorable. Similar results were obtained by Mahjoub *et al.*, (2008).

**Table 3:** Values of the thermodynamic parameters of copper (II) at different temperatures with:  $\Delta G^\circ$  (KJ/K.mol);  $\Delta H^\circ$  (KJ / K.mol) and  $\Delta S^\circ$  (KJ / K.mol)

Temperature (°C)	Parameters per adsorbent		
	AC 500°C	AC 800°C	AC 1000°C
<b>30</b>	$\Delta G^\circ = -12029.81$ $\Delta H^\circ = -32887.23$ $\Delta S^\circ = -112.80$	$\Delta G^\circ = -1256.63$ $\Delta H^\circ = -40830.01$ $\Delta S^\circ = -145.68$	$\Delta G^\circ = -12980.00$ $\Delta H^\circ = -47981.89$ $\Delta S^\circ = -164.31$
<b>40</b>	$\Delta G^\circ = -12426.64$ $\Delta H^\circ = -32887.23$ $\Delta S^\circ = -112.80$	$\Delta G^\circ = -12978.07$ $\Delta H^\circ = -40830.01$ $\Delta S^\circ = -145.68$	$\Delta G^\circ = -13408.17$ $\Delta H^\circ = -47981.80$ $\Delta S^\circ = -164.31$
<b>50</b>	$\Delta G^\circ = -12823.47$ $\Delta H^\circ = -32887.23$ $\Delta S^\circ = -112.80$	$\Delta G^\circ = -13392.50$ $\Delta H^\circ = -40830.01$ $\Delta S^\circ = -145.68$	$\Delta G^\circ = -13836.34$ $\Delta H^\circ = -47981.89$ $\Delta S^\circ = -164.31$
<b>60</b>	$\Delta G^\circ = -13220.29$ $\Delta H^\circ = -32887.23$ $\Delta S^\circ = -112.80$	$\Delta G^\circ = -13806.94$ $\Delta H^\circ = -40830.01$ $\Delta S^\circ = -145.68$	$\Delta G^\circ = -14264.51$ $\Delta H^\circ = -47981.89$ $\Delta S^\circ = -164.31$

## Conclusion

This work is a contribution to the recovery of clay acidified and calcinated at different temperatures (500 ° C, 800 ° C and 1000 ° C) for the depollution of wastewater containing heavy metals. The influence of parameters related to operating conditions such as contact time, mass, pH, initial copper (II) concentration, stirring rate, and temperature were examined. The kinetic study shows that the equilibrium is established after 10, 15 and 20 minutes, respectively, for the AC500 ° C, AC800 ° C and AC1000 ° C and the adsorption mechanism can be described by a kinetics of the pseudo- second order. The plot of the adsorption isotherms shows that the Langmuir model perfectly represents the adsorption of copper (II) on activated and calcinated clays. The thermodynamic parameters obtained indicate that the adsorption of copper (II) on activated and calcinated clays is a spontaneous and exothermic process. Activated and calcinated clays have been shown to be a carrier which has a generally high adsorption affinity towards copper (II).

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