Copper removal in solution by sawdust: kinetic and thermodynamic study

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Abstract

This study presents the results obtained when okoumé sawdust is used for the removal of copper contained in wastewater. The tests show that one gram of sawdust can fix 29.56 mg of copper, according to the Langmuir model with kinetics of the pseudo first order where the time of the pseudo equilibrium is reached after 40 minutes of agitation. The elimination is envisaged in batch mode, at 20 ° C, a stirring speed of 200 rpm, at pH value of 4.4 and a particle size between $500 \leq \emptyset < 700\mu m$. Measured results also reveal that external diffusion controls the speed of the overall process of adsorption and diffusion into the pores is not the only mechanism limiting kinetics. The thermodynamic study shows that this sorption is spontaneous , exothermic and that no changes have been made in the structure of the sawdust

1. Introduction

The pollution of the water environment by toxic metals can generate risks for humans and their environment [1,2]. The management of the latter involves the implementation of special treatment processes such as solvent extraction [3], coagulation-flocculation [4], reverse osmosis [5] and adsorption on a solid [6]. It is in this spirit that we have set ourselves the goal of using sawdust as an adsorbent support. for the removal of toxic metals dissolved in water.

In this work, copper was chosen to represent the toxic metals contained in wastewater. Its removal from the aqueous medium by adsorption is considered in batch mode.in this study. The optimization of the influencing parameters (stirring speed, medium temperature, medium pH and solid particle size) can lead to improve the sorption capacity of the solid. The modeling, the kinetics, and the thermodynamic study make it possible to understand the phenomenon of copper absorption by sawdust. The sawdust used is of Gabonese origin and is taken from the plywood factories of the villa of Bejaia Algeria. Its composition consists essentially of cellulose, polysaccharides and lignin [7].

2. Materials and methods
2.1. Materials

The copper concentration was measured by atomic absorption spectroscopy method. using Perkin Elmer 3110 and the pH solution was adjusted with Ericsson pH metter. the reagents used in the different steps are: hydrochloric acid and copper nitrate produced Merck. the sawdust used is sourced from okoumé wood of Gabonese origin.

2.2. Methods
2.1.1. Preparation of sawdust
The sawdust used in this work was treated as follows:
- 50 g of sawdust are introduced into a beaker with a capacity of 2L. this drenier is filled with distilled water and is connected to a propeller agitator. The wash water is regenerated 06 times every 30 minutes,
- Sawdust washed and dried in the open air for 72 hours

- Dried sawdust is crushed and sieved to different particle sizes: Ø < 500μm, 500≤Ø < 700μm, 700≤Ø< 900μm,
- The sawdust portions are washed again until the pH of the water is neutral,
- The portions of the washed sawdust are dried at 100°C for 04 hours
- treated sawdust is stored in closed glass tubess.

2.1.2. Experimental protocol

The adsorption experiments are realized by adding of an amount of 1 gr of prepared sawdust to aqueous solution containing copper ions. The copper solutions were prepared from copper nitrate ($Cu(NO_3)_2$, $6H_2O$) dissolved in bi-distilled water. The continuous mixing was ensured during the experiment with a constant stirring speed using a mechanical agitator. The temperature was controlled with water bath shaker. The pH solution was fixed in desired value adding a few drops of concentrated ammonia. The adsorption kinetics was followed by sampling of 5 ml every 5 min.

2.1.3. Operating conditions

The operating conditions used in this process are represented as follows:
- Stirring speed (V): 50, 100, 150, 200, 250 rpm
- pH of solution (pH) : 2.,5 , 4.4 and 5.1
- Temperature of solution (T): 20, 40 and 60 °C
- Solid particle size (Ø) : Ø < 500μm, 500≤Ø < 700μm, 700≤Ø< 900μm
- Initial concentrations: $C_{initial.}$: 10, 20, 30, 40, 50, 60 , 70 mg/L;
- Mass of the sawdust (M): 1g

3. Results and discussion

3.1. Determination of equilibrium time.

The study of the kinetics of removal of copper by sawdust in aqueous solution showed that the pseudo equilibrium is reached after 40 minutes (Figure 1). indeed, we note that, after 40 munites, the residual copper concentration remains constant, this result allows us to conclude that the sawdust has arrived at the saturation phase. [8].
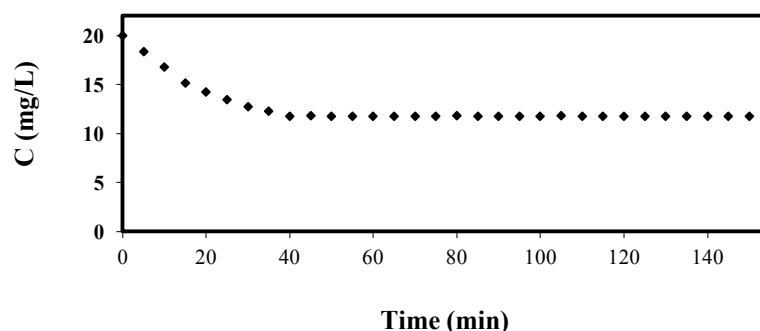

Figure 1. Residual concentration of copper as a function of time

C: 20 mg/L; V : 150 rpm; pH : 5.,2;T : 20°C; 100 ≤ Ø sciure < 150 μm; M : 1 g

3.2. Optimization of influencing parameters

The optimization of influencing parameters is an important step in the adsorption process [9]. It allows us to study the kinetics, set the values of influencing parameters and determine the maximum capacity adsorbed by the solid.

3.2.1 Effect of stirring speed

Stirring speed is an important parameter in the adsorption process. Indeed, it contributes in the distribution of the adsorbate in the adsorbent [10-12]. The speeds used are between 50 and 250 rpm (Figure 2).

The study of kinetics shows us that the adsorption of copper in solution by sawdust increases with the increase of the stirring speed and becomes random at 250rpm. The minimum residual concentration measured is 9.69 mg/L (Figure 2).

For stirring speeds ranging from 50 to 150 rpm, we note a correlation between stirring and adsorption of copper (Figure 2.3). The measured values of the residual concentrations and the calculated yields of these stirring are:

- 15.53mg/L, a yield of 22.3 % to 50 rpm
- 12.81mg/L a yield of 36 % to 100 rpm
- 10.88 mg/L a yield of 41.2 % to 150 rpm
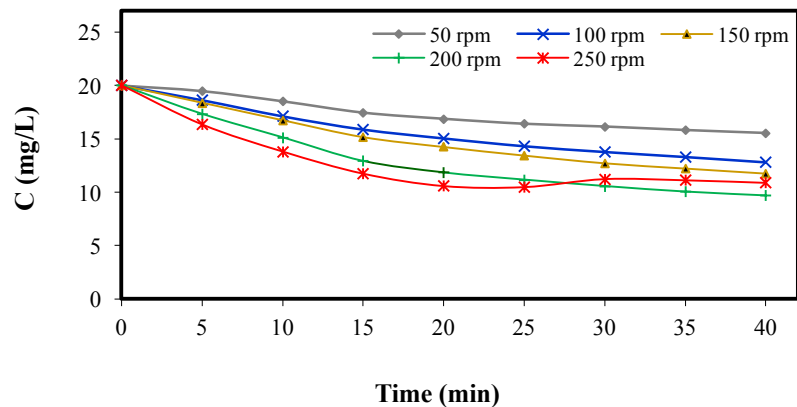- 9.69 mg/L a yield of 51.5 % to 200 rpm

Figure 2. . Residual concentration of copper as a function of time

C: 20 mg/L; V: 50, 100, 150, 200, 250 rpm; pH : 5.2;T : 20°C; $100 \leq \varnothing_{sciure} < 150 \, \mu m$; M: 1g
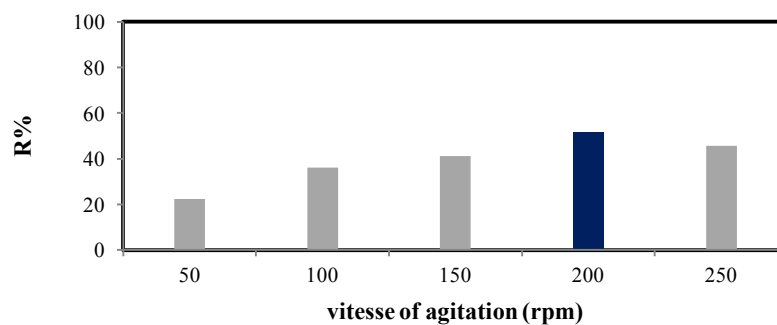

Figure 3. Copper removal efficiency as function of stirring speed

From 250 rpm, the adsorption of the copper by the sawdust becomes random is probably dregs for the effect of the strong agitation [13]. following the optimization of the stirring speed, we conclude that the latter participates in the transfer of copper from the solution to the adsorbent, which gives it an important role in external diffusion [14].

3.2.2 Effect of pH

The pH of the aqueous solution is an important variable, which can have an incidence on the extent of the adsorption, as it affects the metal in solution, as well as the surface properties of the adsorbent [15,16]. In this section, we varied the pH of the solution from 2.5 to 5.1.
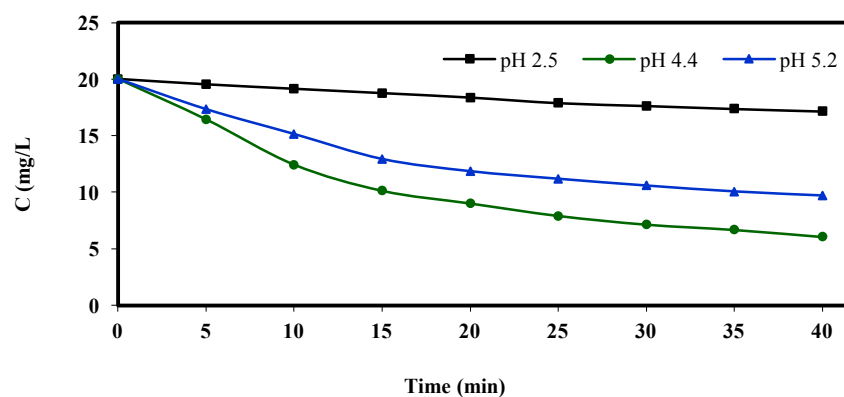

Figure 4. Residual concentration of copper as a function of time

C: 20 mg/L; V: 200 rpm; pH : 2.5, 4.4, 5.2;T : 20°C; $100 \leq \varnothing_{sciure} < 150 \, \mu m$; M: 1g

The kinetic study shows that the adsorption of copper by sawdust depends on the pH of the solution. and is most favorable at pH 4.4 [C $_{resid}$=7,36mg/L, R= 75,4%] (Figure 4,5). In addition, measurements made at strongly acidic pH (pH = 2.5) show that the adsorption of copper on sawdust is unfavorable. The residual concentration measured for medium after 40 minutes of stirring is 15.72 mg/L (Figure 4). This result can be explained by the massive presence of protons (H^+) which are obstacles for the diffusion of the copper ion within the aqueous solution [17,18].
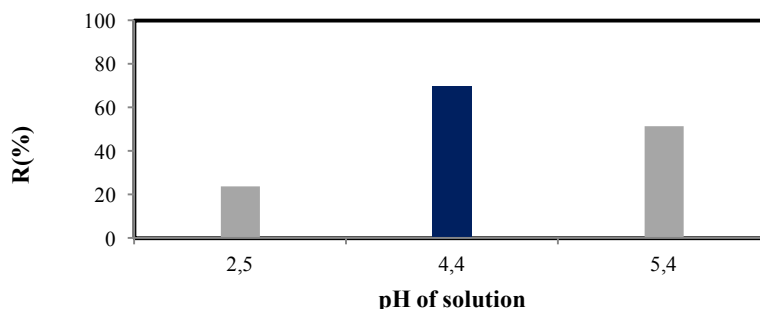

Figure 5. Copper removal efficiency as function of pH

The measured values of residual concentrations and calculated yields for the three solutions used are presented below:
- 17.15mg/L, a yield of 14.25 % to pH 2.5 (Figure 4, 5)
- 6.04mg/L, a yield of 69.86 % to pH 4.4 (Figure 4, 5)
- 9.69 mg/L, a yield of 51.1 % to pH 5.2 (Figure 4, 5)
-

3.2.3 Effect of temperature
The medium temperature is a very important parameter in the process of adsorptiont because it exerts considerable influence on the sorption rate [19,20]. The temperatures used in this experimental phase range from 20 to 60 ° C.
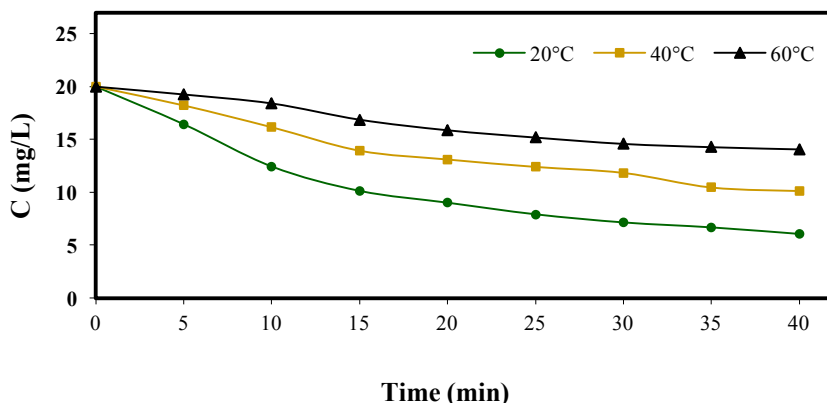

Figure 6. Residual concentration of copper as a function of time
C: 20 mg/L; V: 200 rpm; pH : 4.4, T : 20, 40, 60°C; $100 \leq Ø$ $_{sciure}$ < 150 µm; M: 1g

the kinetics of copper adsorption by sawdust reveal that fixation is maximal at 20 ° C and adsorption decreases with temperature rise (Figure 6.7). This results shows that removal of copper in aqueous medium by sawdust is exothermic [21].
The measured residual concentrations and corresponding yields for these different temperatures are given as follows:.
- 6.04mg/L, a yield of 69.8 % at 20°C (Figure 6, 7)
- 10.13mg/L, a yield of 49.35 % at 40°C (Figure 6, 7)
- 14.06 mg/L, a yield of 29.7 % at 60°C (Figure 6, 7)

3.2.4 Influence of particles size
The particle size of the adsorbent is strongly involved in the adsorption process because it affects the rate of diffusion of the cation from the solution to the adsorbent [22,23]. For this reason, we proceeded to the optimization of the grain size using grains of different diameters : $Φ$ < 500 µm; $500 \leq Φ$ <700 µm et $700 \leq Φ$ <900 µm.
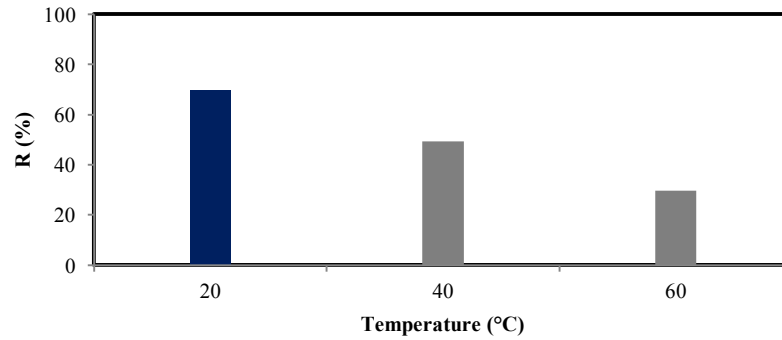
Figure 7. Copper removal efficiency as function of temperature

The experimental results show that the maximum adsorption is obtained for a particle size of between 500 and 700 μm with a yield of about 80.95% (Figure 8,9). On the other hand, for a particle size of diameter Φ <500 μm, the kinetics show that the adsorption of copper on sawdust is unfavorable. This consequence is probably due to the phenomenon of coalescence [24]. for grain diameters 700≥ Φ> 900 μm, the adsorption of copper ions on the surface of sawdust decreases. This consequence is probably due to the transfer phenomena involved during this sorption.
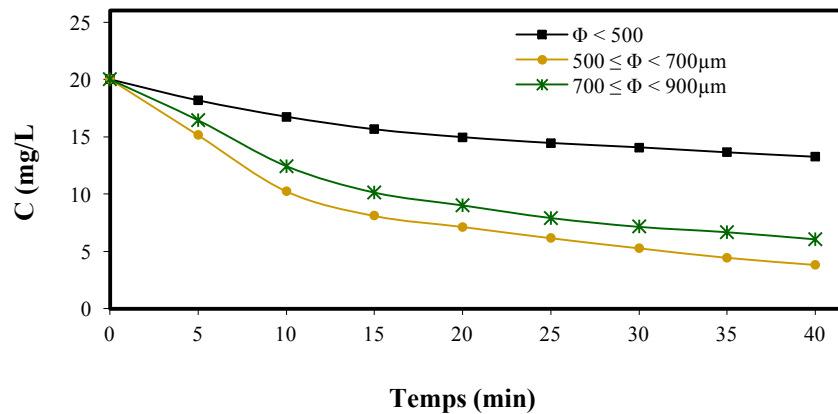

Temps (min)

Figure 8. Residual concentration of copper as a function of time

C: 20 mg/L; V: 200 rpm; pH : 4.4, T: 20°C; Φ <500 μm; 500≤ Φ <700 μm, 700≤ Φ <900 μm; M: 1g

The residual concentrations measured and the corresponding yields for these different particle sizes are given as follows:
- 13.22mg/L, a yield of 33,9 % for *Φ* < 500 μm (Figure 8, 9)
- 6.04mg/L, a yield of 80,95 % for 500 ≤ *Φ* <700 μm (Figure 8, 9)
- 3.81 mg/L, a yield of 69,8 % for 700 ≤ *Φ* <900 μm.(Figure 8, 9)

Following the results obtained, we can conclude that the particle size of the sawdust plays a preponderant role on the fixing and the transfer of the copper of the solution.

The influencing parameters optimization has given the following results
- Vitesse d'agitation V.= 200 rpm
- Le pH du milieu = 4,4
- La température du milieu (T°)= 20°C
- La granulométrie du solide = 500 ≤ *Φ* <700 μm

3.3 Effect of initial concentration.

The removal of copper on the sawdust by synthetic solutions [10, 20, 30, 40, 50, 60, 700 mg/L] was carried out under the abovementioned optimum conditions. The maximum amount adsorbed at equilibrium was determined using the residual method (eq. 1) [25,26].

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

Where: C_0 is Initial solute concentration (mg/L); C_e is residual solute concentration at equilibrium (mg/L); m is mass of the adsorbent and V is volume of solution.
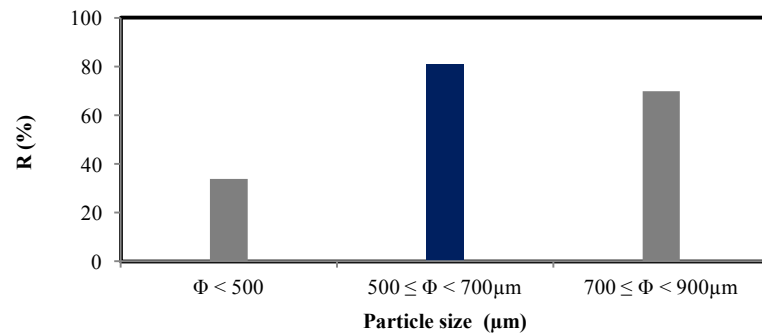

Figure 9. Copper removal efficiency as function of particle size of sawdust

Figures 10 to 12 show adsorption kinetics, yield values and the experimental adsorption isotherm, respectively.

Time (min)

Figure 10. Residual concentration of copper as a function of time

the kinetic study shows that The amount of cuivre adsorbed by sawdust grows with increase in initial concentration. this amount becomes stable from 50mg/L (Figure 10,12)

We find that the performance of the adsorption of copper by sawdust is more important for low initial concentrations solutions (Figure 11) .

Figure 11. Copper removal efficiency as function of initial concentration

The shape of the curve presented in Figure 12, increasing, linear and ends with a saturation plateau starting from 50 mg / l (initial solution). The maximum capacity of copper adsorbed on this point is 29.54 mg / g. This result allows us to conclude that this value represents the maximum amount of copper that can be fixed on one gram of sawdust.

Figure 12 : Adsorbed amount of zinc based on the initial concentration
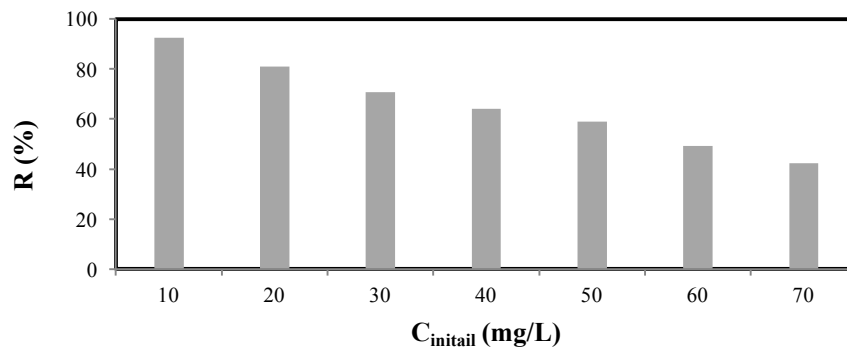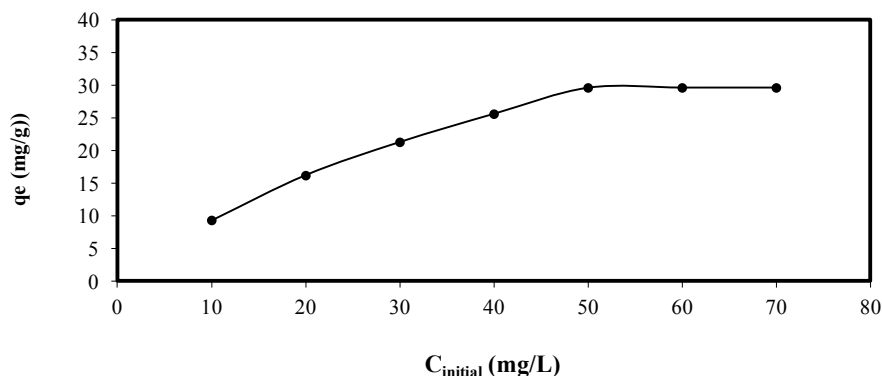
3.4. Adsorption isotherms

Equilibrium adsorption isotherms are among the most reliable data to understand the adsorption mechanism. it is presented by the relationship between mass of adsorbate per unit weight of adsorbent and liquid phase equilibrium concentration of adsorbate. Two equations of the adsorption iso therms are chosen in this study, in this case the Langmuir and Freundlich isotherms. The Freundlich model is well adapted to describe the equilibrium in aqueous phase and describe that the multilayer adsorption is processed on a heterogeneous surface [27]. Its empirical formula is:

$$q_e = \frac{x}{m} = k \cdot C_e^{1/n} \qquad (2)$$

Where q_e is the amount of adsorbent fixed at equilibrium by the adsorbent(mg g^{-1}), C_e is the residual concentration at equilibrium (mg L^{-1}) ; K_F and $1/n$ are the Freundlich constants related to adsorption and affinity. The linearized Freundlich relation is written as follows:

$$logq_e = logk + \frac{1}{n}logC_e \qquad (3)$$

The model of Langmuir [28], is most frequently employed to present the data on adsorption from solution. It is represented by the following equation:

$$q_e = \frac{b.q_m.C_e}{1+b.C_e} \qquad (4)$$

Where q_e is the amount of adsorbent fixed at equilibrium by the adsorbent (mg g^{-1}), C_e is the residual concentration at equilibrium (mg L^{-1}), q_{max} is the maximum saturation capacity of the adsorbent (mg g^{-1}) and b is the thermodynamic constant of the adsorption equilibrium (L.mg^{-1}). The linear form of the Langmuir equation is shown below (Eq.5):

$$\frac{C_e}{q_e} = \frac{1}{q_{max}}C_e + \frac{1}{q_{max}b} \qquad (5)$$

In this work, Langmuir and Freundlich isotherm models are used to fit the equilibrium adsorption data. The obtained plots are represented by Figure 13 and 14. The parameters of these equations are reported in Table 1.

According to the results obtained, the Langmuir model is more suited to this adsorption than that of Freundlich. This result is justified by the values of the regression coefficients and the adsorbed capacity [29,30](Table 1). Nevertheless, the constant of Freundlich n (n > 1), shows that the adsorption of copper by sawdust is favorable [31-33].
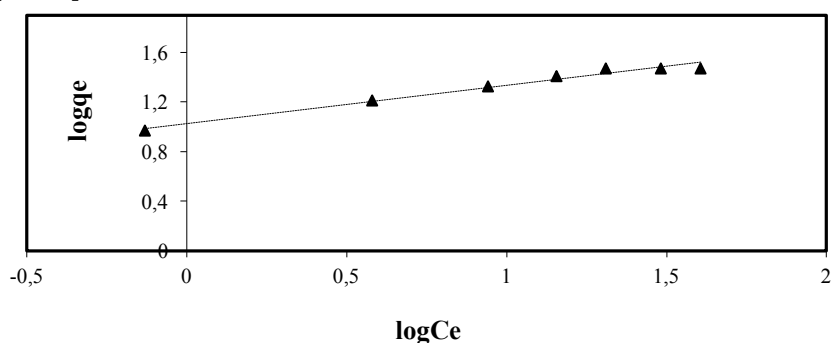

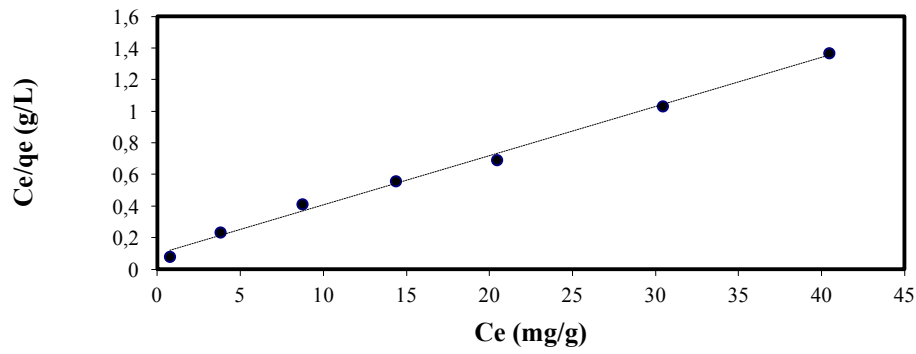**Figure. 13.** Presentation of Freundlich model

Fig. 14. Presentation of Langmuir model

Table 1. Isotherm parameters for adsorption of copper by sawdust

Freundlich model				Langmuir Model		
K_F $(mg.g^{-1})(ml.mg^{-1})^{1/n}$	n	q_{max} (mg/g)	R^2	q_{max} (mg/g)	b $(L.mg^{-1})$	R^2
10,61	3.25	26.81	0.94	30.58	0.32	0.99

Figure 15 shows the copper adsorption isotherm by sawdust in aqueous solution. The curves presented indicated that there is a high affinity among the copper and the adsorption sites of sawdust..The saturation of the adsorption sites takes place gradually until a plateau of saturation is reached. The maximum adsorbed amount is 29.96 mg/g.

The adsorption isotherm has a classical isotherm type I. The presence of a long plateau indicates a weak formation of the multilayers (Figure 15) [34,35]. which allows us again to conclude that the Langmuir equation gives a better representation of the experimental dat.

Figure. 15. Adsorption isotherm of zinc on sawdust

The parameters of the Langmuir model can evenly be used to establish the affinity between adsorbent and adsorbate, this Affinity is determined by the ratio R_L. [36,37]. R_L is a unitless quantity indicating whether the adsorption is more favorable as R_L tends to zero and more unfavorable as R_L tends towards 1 [38,39]. The ratio is calculated as follows (Eq.6):

$$R_L = \frac{1}{1+C_0 b} \tag{6}$$

Where R_L: the Ratio indicating the quality of the adsorption, b is the Langmuir isotherm constant $(L.mg^{-1})$ and C_0 is the initial concentration of solution (mg/L).

According to Figure 16, we find that the value of the R_L ratio decreases with the increase of the initial concentration. This result allows us to conclude that sawdust has good adsorption capacity.

This result confirme also that the Langmuir model is the most adopted for the adsorption of copper by sawdust in our experimental conditions

Figure 16. R_L as function of copper initial concentration

3.5 Kinetics of adsorption:

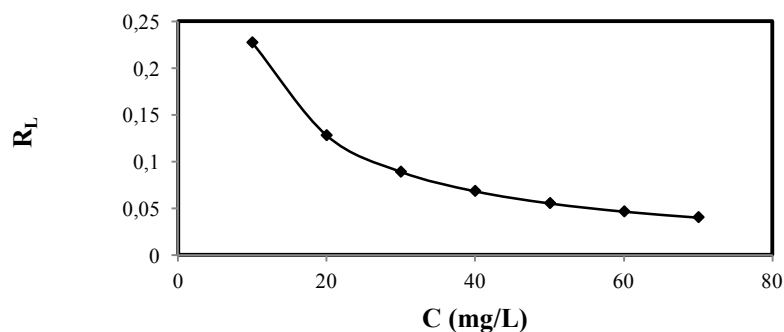The order of the reaction was carried out on three solutions of different concentrations (10, 20, et 30 mg/L), under the following operating conditions:. $V_{..}$: 200 rpm; pH: 4,4 ;T°: 20, C; particle size: $500 \leq Ø < 700 \mu m$

3.5.1 Pseudo first order.

The Lagergren relation [40] focused on the adsorbed amount is the first-rate equation established to describe the sorption kinetics in a liquid-solid system. This pseudo first order model is represented by the following relation:

$$\frac{dq}{dt} = k_L(q_{e-}q) \tag{7}$$

The integration of Equation 7 for boundary conditions: q= 0 à t= 0 et q= q à t= t :

$$ln\frac{q_{e-}q}{q_e} = -k_L \tag{8}$$

Where q_e is adsorbed quantity at equilibrium (mg/g), q is adsorbed quantity at time t (mg/g), t is Time of adsorption process in this study it is from 0 to 40 minutes, k_L is constant pseudo first order sorption speed(s^{-1}).

$$ln(q_e - q) = k_L t + lnq_e \tag{9}$$

Table 2 : Kinetic parameters of Lagergren model

C_0 (mg/L)	K min^{-1}	$q_{e \ théo.}$ (mg/g)	$q_{e \ exp.}$ (mg/g)	Δqe (mg/g)	R^2
10	0,091	8,38	9,26	0,87	98,6
20	0,087	17,32	16,19	1,13	97,1
30	0,093	23,73	21,25	2,48	98,5

If the relation of Lagergren is satisfied by carrying ln (qe-q) as a function of time t, we must obtain a straight line with a slope -k and an ordinate at the origin equal to ln (qe) [41]. In this case, the correlation coefficients must be $R_2 \geq 0.9$ and the values of the theoretically determined maximum sorption capacity at equilibrium are close to the experimental values [42,43]. From Tables 2, we find that the correlation coefficients are greater than 97% and the Calculated adsorbed capacity values are close to the experimental data.

from this result we conclude that the adsorption of copper by sawdust in solution follows a kinetic of the pseudo first order

3.5.2 Pseudo second order.

The application of the Blanchard model [44] allows us to define the pseudo-second order of the reaction in a sorption process. it is presented in the following form (éq.10):

$$\frac{dq}{dt} = k_B(q_e - q)^2 \tag{10}$$

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Where q_e is adsorbed quantity at equilibrium (mg/g), q is adsorbed quantity at time t (mg/g), t is time of adsorption process in this study it is from 0 to 40 minutes, k_B is constant pseudo second order sorption speed(min^{-1}).
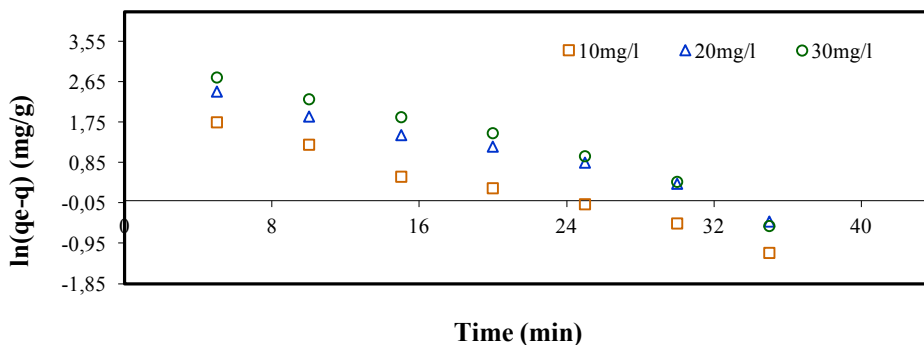

Figure 15. Pseudo first order kinetic

By integrating equation 10 and applying the boundary conditions we obtain the following :

$$\frac{t}{q} = \frac{1}{k_B q_e^2} + \frac{t}{q_e} \tag{11}$$

By taking t / q as function of time t, we will have to obtain a straight line of slope 1 / q_e and ordinate at the origin 1 / k_b. q_e^2 (Figure16). The Blanchard model is verified only if the correlation coefficients R ≥ 0.9% and the theoretical and experimental maximum capacities are close [45,46].

The application of the blanchard model to the experimental data gave the following results:
- The correlation coefficients are greater than 90% (Table 3), However the values of the theoretical adsorbed capacities found do not coincide with the experimental data (Table 3).

According from these results, we conclude that the pseudo-second order equation does not represent the kinetics of adsorption of copper by sawdust in solution.
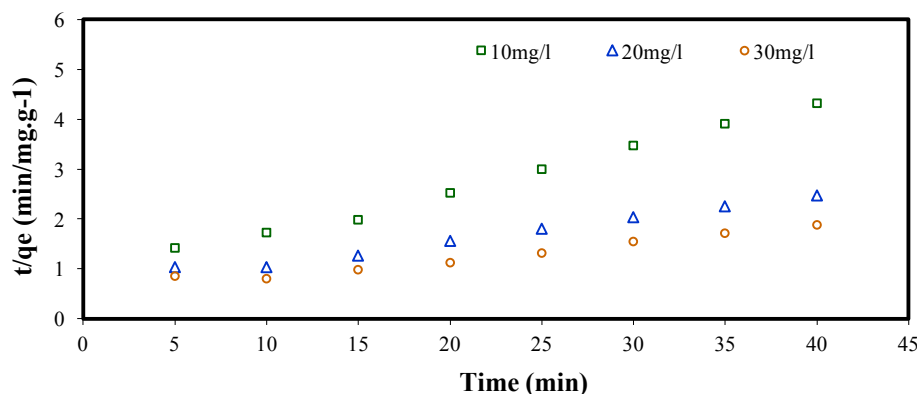

Figure 16: Pseudo second order kinetic

Table 3 : Parameters kinetic of Blanchard model

C_0 (mg/L)	K (mg/g.min)	$q_{e\ théo.}$ (mg/g)	$q_{e\ exp.}$ (mg/g)	Δq (mg/g)	R^2 (%)
10	8.68 x 10^{-3}	11.62	9.26	2.36	99.3
20	2.9 x 10^{-3}	22.72	16.19	6.53	98.3
30	1.88 x 10^{-3}	31.28	21.25	10.03	96.7

3.6 Adsorption mechanism
3.6.1 External transport
If the adsorption process is controlled by the external transport (resistance due to the boundary layer) the logarithm of residual concentration as function of time must be linear function [47]. The coefficients of correlations obtained are our references to illustrate this mechanism. The straight-line plot from the logarithm function lnC = f (t), has allowed us to conclude that external transport seems to be a step controlling the speed of the overall copper adsorption process in aqueous solution by sawdust (Fig. 17). This finding is justified by the values of the correlation coefficients (R> 90%). (Table 4).
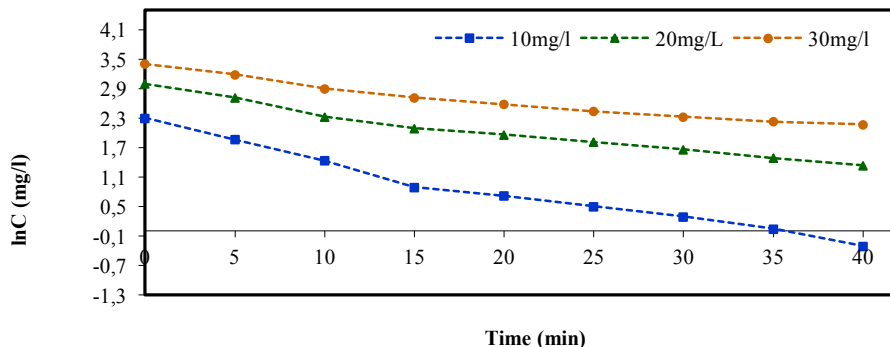
Figure 17 : Evolution of ln (C) versus time: study external transport

3.6.2 Internal transport.

Weber and Morris [48] reported that if intra-particular scattering is involved in the sorption process, by increasing the adsorbed amount as a function of the square root of time, we need to obtain a line. This step is limiting if the line passes through the origin [49].

The relation of Weber and Morris is presented as follows:

$$q = k_W \sqrt{t} + C \tag{12}$$

Where q is quantity adsorbed at time t, t is time measured in minute, k_w is the diffusion rate constant in the pores(mg/m. min $^{1/2}$), and C is a constant
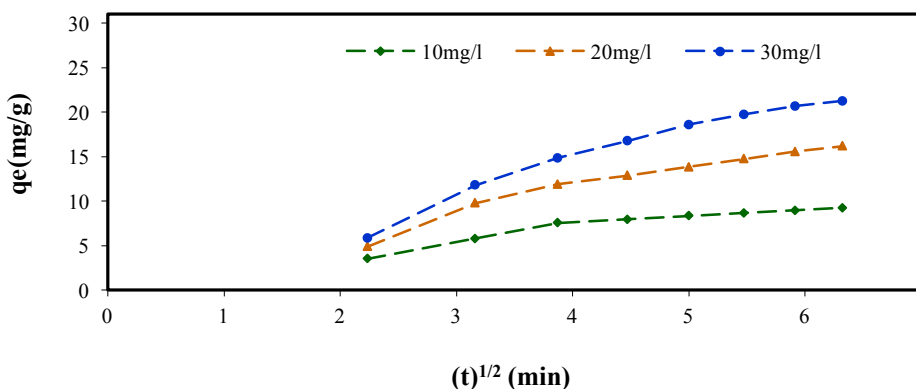

Figure 18 : Weber and Morris model Presentation

This step is limiting if the line passes through the origin. In the case where these lines do not pass through the origin, this indicates that the diffusion in the pores but is not the only limiting mechanism of the sorption kinetics. It appears that other mechanisms are involved [50-52].

According to figure 18, , we observe that the set of straight lines resulting from the function qe = f ($^{t1/2}$) is not pass through the origin, which shows that the diffusion of copper into the pores is not the only mechanism limiting sorption kinetics. From to R^2 and C values, we find that the copper adsorption by sawdust proceed on the surface instead in the pores.

Table 4: Values of internal and external transport parameters

C_0 (mg/L)	Weber and Morris parameters			External transport parameters
	C	R^2 (%)	k_w(mg/g.min)	R^2 (%)
10	1.564	90.1	1.303	96
20	0.863	93.3	2.547	96.5
30	-0.408	95.3	3.642	97.1

3.7 Thermodynamic study

The thermodynamic parameters of copper adsorption by sawdust can be related to the distribution coefficient (kd) by the following equation [53-55].

$$\Delta G^0 = -RT ln k_d \tag{13}$$

The distribution coefficient is defined by the equation below [56-58]:

$$k_d = \frac{q_e}{C_e} \qquad (14)$$

The variation of the free enthalpy is given by the following relation::

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (15)$$

of these three equations, we deducting the following équationship (éq. 16) :

$$ln k_d = -\frac{\Delta H^0}{R} \times \frac{1}{T} + \frac{\Delta S^0}{R} \qquad (16)$$

By plotting the logarithm of the distribution coefficient versus the inverse of the temperature, we obtain a line (Figure 19) and by extrapolation of the latter we determine enthalpy and entropy. The variation of free energy is calculated by equation 13.

Values of the distribution coefficient k_d are reported in Table 5 and the thermodynamic parameters are presented in Table 6.

The results from the thermodynamic study (Table 6) show the following phenomena:
- the negative values of ΔG^0 indicates that the adsorption process is spontaneous [59-61].
- the negative values of ΔG^0 decreased with an rise in temperature, which shows that copper adsorption is less efficient at high temperatures [62-65]
- the negative value of ΔH^0 shows that the adsorption copper by sawdust is exothermic [66-68].
- the negative value of ΔS^0 reveals that the randomness of copper adsorption by sawdust has decreased at the solid/solution interface [69-71].

Table 5: Values of the distribution coefficient at different temperatures

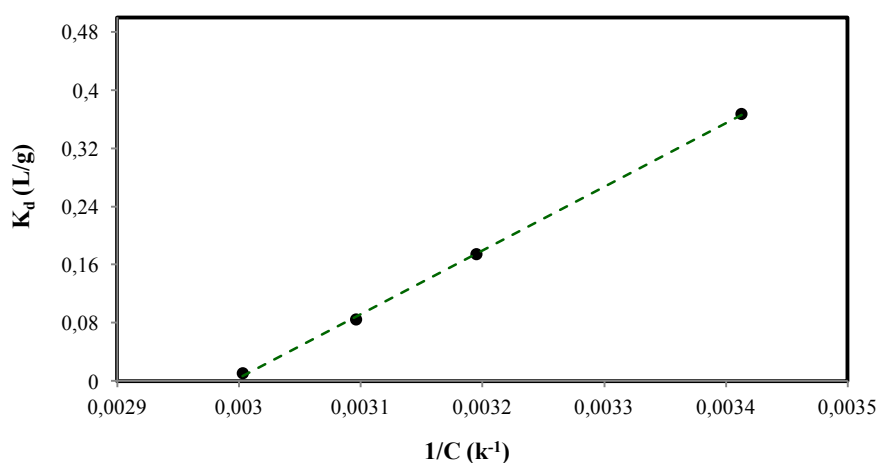| Température (k)	293	303	313	323
K_d $(L.g^{-1})$	1.226	1.074	0.907	0.800

Figure 19: Evolution of the distribution coefficient as a function of the inverse of the temperature

Table 6: Thermodynamic parameters

Température (k)	ΔG $(kj/mole)$	ΔH $(kj/mole)$	ΔS $(j/mole\ k)$
293	-0.895		
303	-0.455	-7.284	-21,815
313	-0.228		
293	-0.028		

Conclusion

The kinetic study of the copper adsorption on sawdust as an adsorbent, allowed us to conclude that the fixation of copper in aqueous medium by this material is feasible, where the yield is maximum for low concentrations. The maximum capacity of adsorbed copper per gram of sawdust is 29.58 mg.

The equilibrium is reached after 40 minutes of agitation and the adsorption of copper is favorable for pH 4.4, at 20° C, for stirring speed 200 rpm and a particle size between 500-700 μm. Adsorption is more appropriate to the Langmuir model and follows a pseudo-first order kinetics.

The affinity ratio R_L shows that the sawdust has a high adsorption capacity and the Freundlich constant n indicates that the adsorption is favorable.

The study of adsorption mechanism shows that external transport seems to be a step controlling the speed of the overall process of copper adsorption in solution. However the diffusion into pores is not the only mechanism limiting the sorption kinetics.

The thermodynamic parameters show that adsorption of Zn by sawdust is spontaneous, exothermic and that randomness decreases at the interface during adsorption

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