

## Research Article

# Kinetic and Thermodynamic Study of the Adsorption of Cu<sup>2+</sup> In an Aqueous Medium by Activated Carbons from Plant Biomasses

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## Abstract

The study of the adsorption performance of Cu<sup>2+</sup> ions by activated carbons from plant biomasses such as Cocoa pod Shells (CPS) and Cassava Peelings (CaP) has made it possible to highlight certain parameters influencing adsorption. Adsorption tests have shown that the equilibrium time is a function of the initial concentration of Cu<sup>2+</sup> ions. Equilibrium was established after 40 min and 80 min upon adsorption of Cu<sup>2+</sup> ions on CPS and CaP respectively with a mass of 0.1 g at pH=4. Thus, the adsorption mechanism is described by pseudo-second-order kinetics which showed good correlation for the two carbons. The maximum adsorption capacity determined by Langmuir's mathematical model is 526.315 mg/g for CaP and 909.091 mg/g for CPS. The thermodynamic parameters relating to the adsorbent/adsorbate system studied indicate that the adsorption process of Cu<sup>2+</sup> ions in solution on the CaP and on the CPS is spontaneous ( $\Delta G < 0$ ). The reaction is favorable at low temperature and exothermic ( $\Delta H < 0$ ) for CaP while in the case of CPS the reaction is favorable at high temperature and endothermic in nature.

**Keywords:** Activated carbon, Langmuir isotherm, Adsorption kinetics, Thermodynamic parameters

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## Introduction

Various physical, chemical and biological techniques have been developed and tested for the treatment of effluents contaminated by pollutants [1-3]. One of the techniques that is commonly used is adsorption. It uses porous solids such as plant biomass (waste) as adsorbents to remove organic pollutants and heavy metal. The principle of adsorption consists of fixing on these biomasses the heavy metal likely to be present in industrial wastewater and which present a great danger to the environment due to their toxicity. However, this removal technique is subject to the influence of several parameters: temperature, the characteristics of the adsorbate, the adsorbent and the medium. In addition, modeling isotherms and adsorption kinetics can determine the adsorption power of activated carbon. It is therefore in this context of study that the research work which consists in the recovery of plant waste and in the kinetic and thermodynamic study of the adsorption of Cu<sup>2+</sup> in an aqueous medium by activated carbon derived from biomasses falls. vegetable: cocoa pod shells and cassava peelings. The aim of the study is to determine the parameters of the adsorbing power and the performance of the prepared activated carbon.

## Material and Methods

### Adsorbent

The adsorbent consists of Cocoa Pod Shells (CPS) and Cassava Peelings (CaP). These different plant biomasses were washed until all impurities were removed. They were then dried, then crushed and sieved in order to have particles of sizes between 0.2 mm and 0.5mm (**Figures 1** and **2**). The ground material from the different biomasses was rinsed and then dried in an oven for 24 hours. Activation was done using a mass of 30 g of dried ground material from each plant biomass in 100 mL of orthophosphoric acid. The mixture (acid + dried ground material) is stirred (500 rpm) for 24 h at room temperature. After acid impregnation, the mixture was filtered and then the biomass was dried in an oven at 110 °C for 24 h. Thus, the calcination of the acid-impregnated biomasses was carried out in a muffle furnace at 450 °C for 3 hours. The coals obtained were then cooled for 30 min in a desiccator and then washed several times with distilled water until the mixture reached a pH of around 7 and dried in an oven for 24 h. This makes it possible to obtain an activated carbon (AC) from the various plant biomasses concerned (CPS and CaP).



**Figure 1** Cocoa pod shells (a: fresh; b: dried and c: crushed)



**Figure 2** Cassava peelings (d: fresh; e: dried and f: crushed)

### Adsorbat

The metallic pollutant considered in this study is copper (Cu). The different solutions of  $\text{Cu}^{2+}$  ions were prepared from hydrated penta copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) of purity 99% dissolved in distilled water in order to obtain ranges of concentration solutions from 50 mg/L to 500 mg/L for establishing the calibration curve.

### Operating procedure

*Preparation of the EDTA solution and the buffer solution at  $\text{pH} = 10$*

Ethylenediaminetetraacetic acid (EDTA) is an aminopolycarboxylic acid with the formula  $[\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2]_2$ . This white water soluble solid is widely used to bind to metal ions. Thus, 0.34 g of EDTA is introduced into a 1 L flask. A little distilled water is added until the compound is completely dissolved. Then we complete it all up to the gauge line. The buffer solution was prepared from a 0.1 N solution of ammoniac ( $\text{NH}_4$ ) and 0.1 N hydrogen chloride (HCl), the pH is maintained at 10.

### Complexation reaction of EDTA with $\text{Cu}^{2+}$ ions

Complexation is a widely used method in the assay of heavy metal and is based on the use of ligands. It lies in the formation of easily detectable complexes in UV-Visible [4]. According to Sperling and Welz [5], EDTA forms very stable cyclic complexes with cations. At  $\text{pH} = 10$ , these exist in the following form  $\text{MY}^{2-}$  and are analyzed by UV-visible spectrophotometry. It is with this in mind that we have chosen UV-visible spectrophotometry to measure  $\text{Cu}^{2+}$  metal cations after their complexation with EDTA. The reaction of the determination  $\text{M}^{2+}$  cation is:  $\text{M}^{2+} + \text{H}_2\text{Y} \rightleftharpoons \text{MY}^{2-} + 2\text{H}^+$ ;  $\text{MY}^{2-} : \text{Cu}^{2+} - \text{EDTA}$  Complex.

### Determination of $\text{Cu}^{2+}$ ions

For the determination of the cations  $\text{Cu}^{2+}$ , a UV-Visible scan of the complex  $\{\text{Cu}^{2+} - \text{EDTA}\}$  at  $\text{pH} = 10$  made it possible to determine the wavelength  $\lambda$  where the absorbance is maximum ( $\lambda = 660 \text{ nm}$ ). The method consists of using two different mixtures. The first which is introduced into the reference cell contains, distilled water, the solution of the EDTA complexing agent ( $1.80 \cdot 10^{-3} \text{ M}$ ) and the buffer solution at  $\text{pH} = 10$  as for the second mixture, the latter is identical to the first only the distilled water is replaced by the metallic solution  $[\text{Cu}^{2+}] = 4.70 \cdot 10^{-4} \text{ M}$ . Once the maximum wavelength is determined, the absorbance is measured at different concentrations of the metal cations at  $\text{pH} = 10$  and in the presence of the same concentration of the complexing agent in order to establish calibration curves.

*Determination of the quantity of Cu<sup>2+</sup> ions adsorbed and the rate of elimination*

The Cu<sup>2+</sup> ions concentration was determined using the calibration curve performed with a range of known concentrations of copper in solution. Thus, the quantity of Cu<sup>2+</sup> ions adsorbed during the time of the experiments is given by the following relation:

$$q_t = \frac{(C_i - C_r)}{m} \times V ; T(\%) = \frac{C_i - C_r}{C_i} \times 100$$

With  $q_t$  : Amount of metal adsorbed a time  $t$  (mg/g) ;  $C_i$  : Initial concentration of Cu<sup>2+</sup> (mg/L) ;  $C_r$  : Residual Cu<sup>2+</sup> concentration at time  $t$  (mg/L) ;  $V$  : Volume of the metallic solution (L) ;  $m$  : Mass of activated carbon Masse de charbon actif (g)

*Determination of the influence of the contact time*

0.1 g of the activated carbon obtained from each plant biomass was introduced into 100 mL of the Cu<sup>2+</sup> solution of concentration 100 mg/L at pH = 4. Each mixture is stirred using a magnetic stirrer. For each solution, the samples were taken at different times: 5 ; 10 ; 15 ; 20 ; 25 ; 30 ; 40 ; 60 ; 80 ; 90 ; 100 ; 120 ; 140 ; 160 min.

*Determination of the influence of the mass of the adsorbent*

In order to determine the mass at which the adsorption will be maximum, the tests were carried out beforehand by stirring 100 mL of a metallic solution of Cu<sup>2+</sup> ions with a concentration of 100 mg/L with a mass variation of 0.06 to 0.5 g in 250 mL Erlenmeyer flasks, with constant stirring at 500 rpm at the contact time, at room temperature and at pH = 4. Volumes of 5 mL of each solution were taken, then centrifuged and the residual concentration was determined after complexation with EDTA.

*Determination of the influence of the initial concentration of the metal solution*

The initial concentration of the Cu<sup>2+</sup> solution has an influence on the adsorbent capacity of the adsorbents. In order to study its influence, different initial concentrations of Cu<sup>2+</sup> ions from 50 mg/L to 500 mg/L were considered.

*Determination of the influence of temperature on adsorption*

Tests were carried out to assess the effect of temperature. At variable temperature of 30°C, 40°C, 50°C and 60°C, to a mass of 0.1 g of the activated carbon was added a volume of 100 mL of concentration of 100 mg/L of the metal solution in 250 mL Erlenmeyer flasks, stirred at 500 rpm at the corresponding equilibrium time.

*Determination of adsorption kinetics*

In order to determine the adsorption kinetics, 0.2 g of activated carbon was contacted with 200 mL of Cu<sup>2+</sup> solution at different initial concentrations (100 mg/L ; 200 mg/L ; 300 mg/L ; 400 mg/L), and the whole is stirred at 30°C. Then the solution is filtered by centrifugation at 4000 rpm for 10 minutes and finally assayed by UV-visible spectrophotometry after complexation with EDTA. The kinetics make it possible to estimate the quantity of pollutants adsorbed as a function of time. The literature reports several models of adsorption equilibrium. For the study we chose the pseudo second order model [6]. The pseudo-second order is expressed by the equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \rightarrow \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \times t.$$

The constants  $q_e$  and  $k_2$  are determined by plotting the line  $\frac{t}{q_t}$  against  $t$ .

$k_2$ (mg/g.t) : Rate constant for pseudo second order kinetics ;  $q_t$ (mg/g) : Adsorption capacity at time  $t$  ;  $q_e$ (mg/g) : Adsorption capacity at equilibrium.

*Determination of the Langmuir adsorption isotherm*

The adsorption isotherm was carried out at four different temperatures (T=30°C; T=40°C; T=50°C and T=60°C). To do this, to 0.1 g of activated carbon is added 100 mL of the metal solution at varying concentrations (100 mg/L ; 150

mg/L ; 200 mg/L ; 300 mg/L ; 400 g/L and 500 mg/L). The mixture is stirred at 500 rpm for the respective contact times using a magnetic stirrer making it possible to adjust to the desired temperature. Each solution is centrifuged at the end of the adsorption process and then assayed by UV-visible spectrophotometer after complexation with EDTA. The Langmuir model is a classical model of adsorption, relatively chemisorption. The Langmuir isotherm equation is [7]:

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

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant called the separation factor  $R_L$  defined as follows:  $R_L = \frac{1}{1 + K_L C_0}$

**Table 1** Adsorption quality according to Langmuir

Separation factor	$R_L > 1$	$R_L = 0$	$R_L = 1$	$0 < R_L < 1$
Adsorption	Adverse	Linear	Irreversible	Favorable

$q_{max}$ (mg/g): Maximum adsorption capacity ;  $q_e$ (mg/g): Adsorption capacity at equilibrium ;  $C_e$ (mol/L) : Concentration at equilibrium ;  $K_L$ (L/mg) : Langmuir constant.

#### Determination of thermodynamic adsorption parameters

Tests on the thermodynamics of the adsorption of  $\text{Cu}^{2+}$  ions were carried out. To conduct this study, 0.1 g of charcoal is added to 100 mL of the  $\text{Cu}^{2+}$  solution with an initial concentration  $C_0=500$  mL/g and the whole is stirred using a stirrer at different temperatures. The residual concentration and the amount adsorbed at equilibrium allow the spontaneity of the reaction to be evaluated thermodynamically. The measurement of the heat of adsorption is the main criterion that differentiates chemisorption from physisorption. The heat of adsorption ( $\Delta H$ ) is given by the Gibbs-Helmholtz relationship [8].

$$\Delta G^\circ = -RT \ln K_d \text{ et } \Delta G^\circ = \Delta H - T \cdot \Delta S \rightarrow \ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

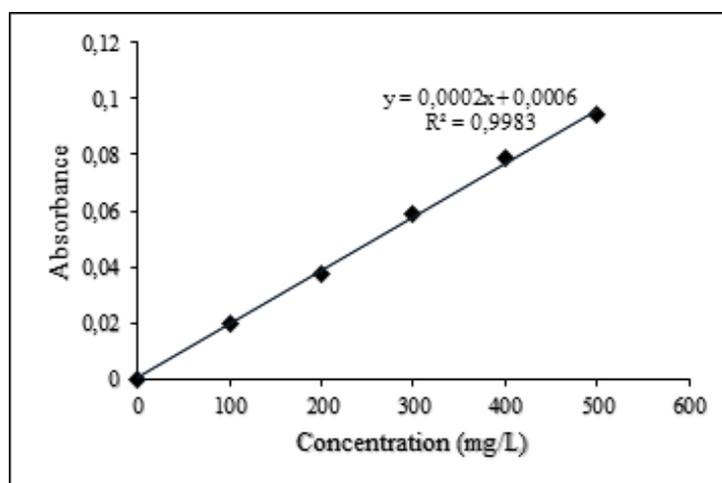
The parameters  $\Delta H$  and  $\Delta S$  can be calculated respectively from the slope and the y-intercept from the above equation.

## Results and Discussion

### Results

#### Calibration curve

**Figure 3** shows the calibration curve which was obtained with a UV-visible spectrophotometer after complexation with EDTA from standard  $\text{Cu}^{2+}$  solutions ranging from 100 to 500 mg/L.

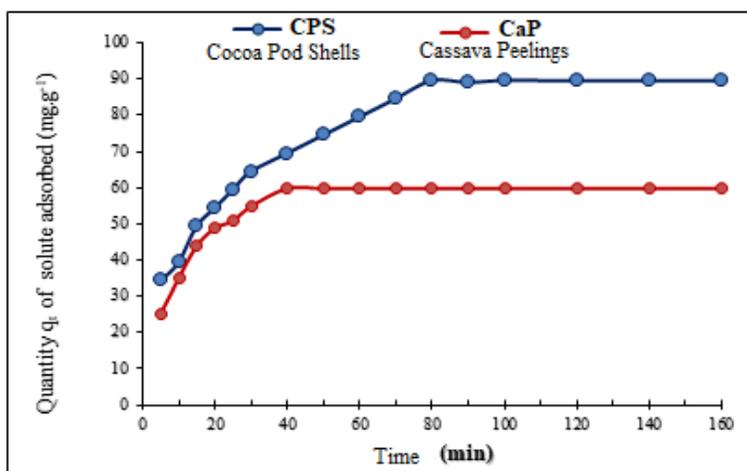


**Figure 3**  $\text{Cu}^{2+}$  calibration curve

The calibration curve shows good linearity with a high correlation coefficient ( $R^2 = 0.9983$ ).

*Parameters of the adsorption of  $\text{Cu}^{2+}$  ions on activated carbon*

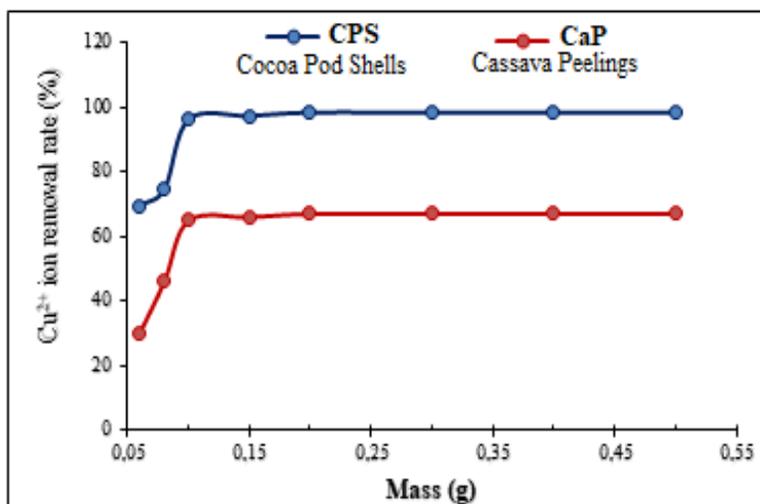
*Influence of contact time:* **Figure 4** shows the adsorption curves of the quantity  $q_t$  of solute  $\text{Cu}^{2+}$  adsorbed as a function of the contact time of the different activated carbons from the CPS and the CaP with the  $\text{Cu}^{2+}$  solution.



**Figure 4**  $\text{Cu}^{2+}$  adsorption kinetics by activated carbon

The amount of solute adsorbed in relation to the adsorption time shows that the  $\text{Cu}^{2+}$  amount adsorbed increases proportionally with the contact time until reaching the optimum value after 40 and 80 min respectively for CaP and CPS. Beyond its values, a plateau forms where the adsorption saturation of the  $\text{Cu}^{2+}$  ions occurs. We also note that the amount adsorbed by CPS is greater than that of CaP for respective values of 89.5 mg/L and 60 mg/L.

*Influence of the mass of the adsorbent:* **Figure 5** shows the evolution of the elimination rate of  $\text{Cu}^{2+}$  ions in solution as a function of the mass of the different activated carbons of the CPS and the CaP.



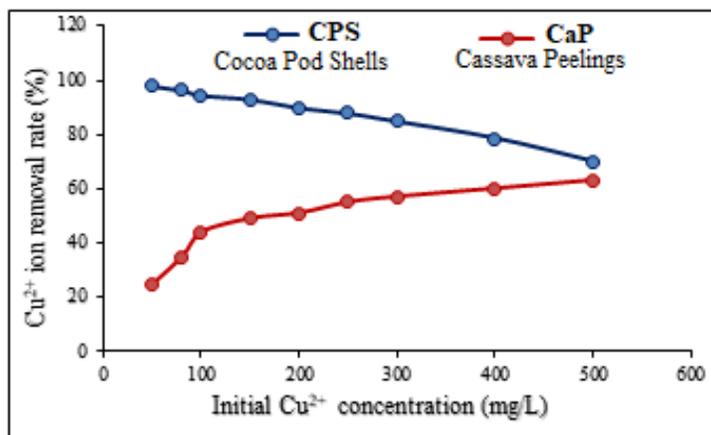
**Figure 5** Influence of the mass of the adsorbents

The results of Figure 5 show that the rate of  $\text{Cu}^{2+}$  ions removed increases from 30 to 67% and from 69.5 to 96% respectively for CaP and CPS for mass variations of 0.06 to 0.1 g for both activated carbon. For masses greater than 0.1 g, the rate remains constant at 67% for CaP and at 96.5% for CPS. We also note that the removal rate of  $\text{Cu}^{2+}$  ions is higher for CPS than for CaP.

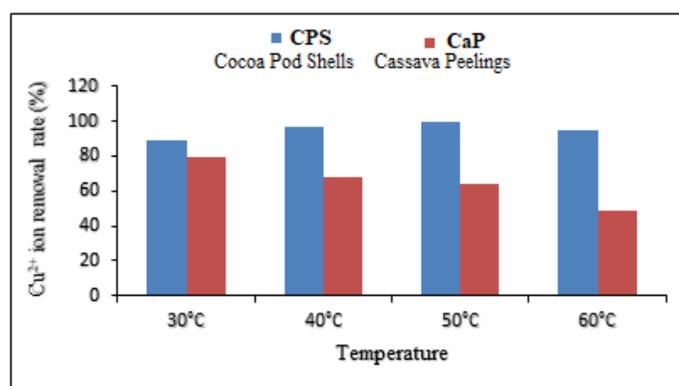
*Influence of the initial concentration:* **Figure 6** shows the variation in the rate of elimination of  $\text{Cu}^{2+}$  by the different activated carbon as a function of its initial concentration in the solution.

We notice that the rate of elimination of  $\text{Cu}^{2+}$  ions decreases when the initial  $\text{Cu}^{2+}$  concentration increases for the CPS while the opposite effect is observed in the case of the CaP, that is to say that the rate of elimination with increasing initial concentration. And always note that the high  $\text{Cu}^{2+}$  removal rate is produced for CPS.

*Influence of temperature:* **Figure 7** shows the histograms of the rate of  $\text{Cu}^{2+}$  removal by CPS and CaP as a function of temperature.



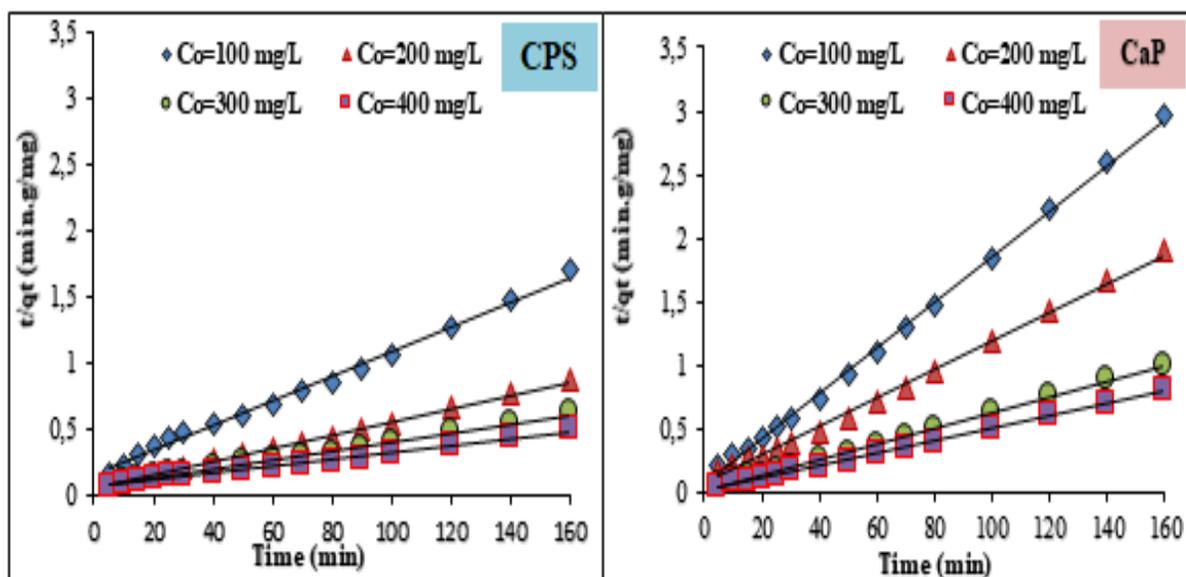
**Figure 6** Elimination rate of adsorbed solutes as a function of the initial concentration of Cu<sup>2+</sup>



**Figure 7** Cu<sup>2+</sup> ion removal rate as a function of temperature

Figure 7 shows that an increase in the copper removal rate from 89.5% to 99.5% is observed when the temperature goes from 30 to 50 °C then decreases to 94% for a temperature of 60°C for CPS. As for CaP, there is a decrease in the copper removal rate from 79% to 49% for temperatures between 30 and 60°C. This figure also shows that CPS has a higher elimination rate compared to CaP.

*Modeling of the adsorption kinetics of Cu<sup>2+</sup> ions on activated carbon:* The pseudo-second order kinetic model is applied in order to better understand the process of adsorption of Cu<sup>2+</sup> ions on the different activated carbons studied. Thus, this model of the kinetics is illustrated by **Figure 8**. It represents the graphs  $\frac{t}{qt} = f(t)$ . The values of the model parameters are given in Table 2.



**Figure 8** Pseudo-second order kinetics of Cu<sup>2+</sup> cations at different initial concentrations.

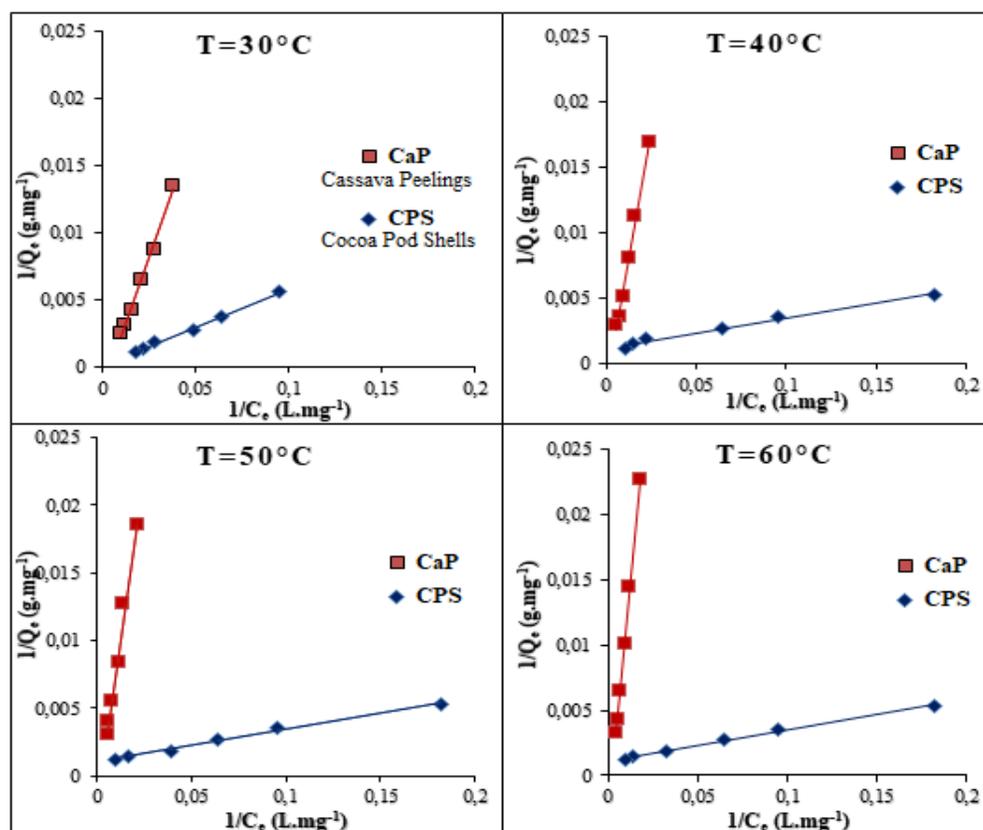
**Table 2I:** Parameters of the pseudo-second order kinetics model

Activated carbon	Concentration (mg/L)	$q_{e,th}$ (mg.g <sup>-1</sup> )	$q_{e,exp}$ (mg.g <sup>-1</sup> )	$k_2$	$R^2$
CaP	100	55.866	54	$4.51 \cdot 10^{-3}$	0.999
	200	88.495	84	$5.78 \cdot 10^{-3}$	0.997
	300	163.934	159	$1.68 \cdot 10^{-3}$	0.999
	400	208.333	199	$1.16 \cdot 10^{-3}$	0.999
CPS	100	106.383	94.5	$6.15 \cdot 10^{-4}$	0.995
	200	204.082	184.5	$4.20 \cdot 10^{-4}$	0.998
	300	294.118	254.5	$1.95 \cdot 10^{-4}$	0.996
	400	384.615	324.5	$1.24 \cdot 10^{-4}$	0.993

It is generally observed that the representation of the pseudo-second order model gives good linearity of the regression lines with very good correlation coefficient (close to 1) for the two activated carbons.

#### Modeling of the absorption isotherm of Cu<sup>2+</sup> ions on activated carbons

In order to determine the maximum adsorption capacities at different temperatures, we applied the Langmuir model in its linear form. The regression curves obtained are shown in the following **Figure 9**:

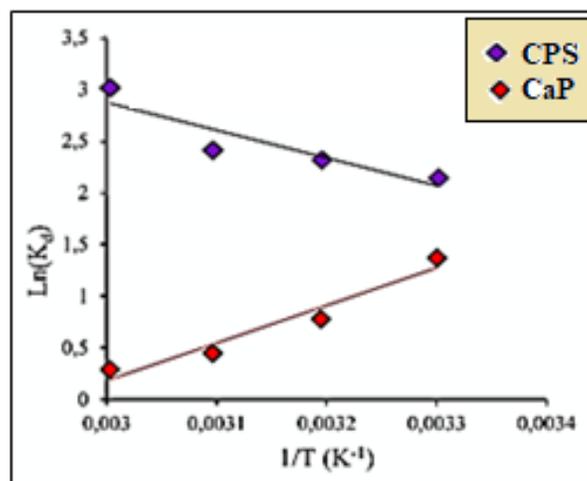
**Figure 9** Langmuir isotherms at 30°C, 40°C, 50°C, 60°C**Table 3** Langmuir parameters derived from adsorption isotherms

Activated carbon	Temperature (°C)	$q_{max}$ (mg/g)	$k_L$ (L/mg)	$R^2$	$R_L$
CaP	30	526.315	0.0048	0.995	0.722
	40	454.545	0.0028	0.995	0.816
	50	416.667	0.0025	0.994	0.833
	60	232.558	0.0028	0.997	0.816
CPS	30	500.000	0.0035	0.997	0.852
	40	833.333	0.0522	0.986	0.277
	50	909.091	0.0458	0.990	0.299
	60	909.091	0.0470	0.993	0.299

From the results of the Table 3 above, it can be seen that for the two activated carbons the correlation coefficients according to the Langmuir model are very close to 1 for all temperatures. Since the  $R_L$  parameter is between 0 and 1, therefore, we can say the Langmuir isotherm is favorable for the adsorption of  $\text{Cu}^{2+}$  ions in solution on activated carbon (CaP and CPS).

### Thermodynamic study

For the determination of thermodynamic quantities such as enthalpy  $\Delta H$ , enthalpy  $\Delta S$  and free energy  $\Delta G$  we applied the Vant'Hoff relationship at different temperatures for a range of concentration studied. **Figure 10** below shows the variation of  $\text{Ln } k_d = f\left(\frac{1}{T}\right)$ .



**Figure 10** Variation of  $\text{Ln } k_d = f\left(\frac{1}{T}\right)$

Examination of the results shows that the value of free energy  $\Delta G^\circ$  increases proportionally with temperature for CaP. In addition, it is observed that all the thermodynamic parameters are negative. But in the case of CPS, we observe that the value of the free energy  $\Delta G^\circ$  decreases when the temperature increases and all its values are negative with positive values of enthalpy  $\Delta H^\circ$  and entropy  $\Delta S^\circ$ .

**Table 4** Parameters of thermodynamic quantities

C (mg/L)	Activated carbon	$\Delta H^\circ(\text{KJ/mol})$	$\Delta S^\circ(\text{J/mol.K})$	$\Delta G^\circ(\text{KJ/mol})$			
				303 K	313 K	323 K	333 K
500	EM	-30.125	-88.852	-3.203	-2.314	-1.426	-0.537
	CC	22.468	91.354	-5.213	-6.126	-7.040	-7.953

### Discussion

The results of the kinetic study reveal that the rate of  $\text{Cu}^{2+}$  removal increases rapidly to values of 60% for CaP and 89.5% for CPS. After 40 and 80 min respectively and onwards, of these the rate remains constant. This rapid increase can be explained by the availability of adsorption sites and the relatively large concentration gradient onset of adsorption and the decrease in the rate of elimination until a plateau is formed is explained by the decrease and to the saturation of the adsorption sites on the surface of the adsorbent. This result is supported by Wang [9]. In view of these results we can say that adsorption is important with CPS than with CaP. The influence of mass has shown that the number of sites participating in the adsorption phenomenon increases with increasing mass in both cases. Therefore, the increase in removal efficiency is due to the increasing availability of vacant sites for  $\text{Cu}^{2+}$  ion binding. A plateau in the removal rate for masses greater than 0.1 g for the two coals is due to the saturation of the adsorption sites. A similar result is observed in the kinetic and thermodynamic study of the adsorption of Cd and Zn ions on activated carbon [10]. CPS has better adsorption capacity compared to CaP. Regarding the influence of the concentration, the decrease in the removal rate with increasing the initial concentration in the case of CPS is possibly due to the saturation of the adsorption sites on the surface of the adsorbent. The same results have been reported by Yeddou and Bensmaili [11]. The opposite behavior has been observed in the case of CaP. According to Azouaou [12] this result can be explained by the availability of vacant sites on the surface of the adsorbent. We also notice that CPS has a higher adsorption capacity than CaP. The study of the influence of temperature reveals that in the case of CPS the rate of removal of  $\text{Cu}^{2+}$

ions increases from 89.5% to 99.5% for temperatures ranging from 30 to 50°C. This result means that the rise in temperature facilitates the diffusion of  $\text{Cu}^{2+}$  ions into the sites of the adsorbent where the endothermic process occurs. For a temperature above 50°C, a drop in the rate of elimination is observed, which is due to the opposite phenomenon (desorption) [13]. In the case of CaP, the opposite trend is observed for temperatures between 30°C and 60°C. This behavior may be the result of increased desorption at the adsorbate / adsorbent interface [14]. This assertion is supported by Sedira [1] in the case of metal adsorption on an activated carbon from date stones. Under the same study conditions, we can conclude that CPS has a higher adsorption capacity compared to CaP. The parametric analysis of the pseudo-second order modeling shows that the carbons used for the adsorption of  $\text{Cu}^{2+}$  ions exhibit very good correlation (close to unity). The adequacy of the theoretical results to those found experimentally suggests that the process of adsorption of  $\text{Cu}^{2+}$  ions from activated carbons is governed by chemisorption. According to several research works, the adsorption kinetics of metal ions are best represented by the pseudo-second order model [1, 2, 15]. The study of the straight lines of regressions obtained from the linear formulation of the Langmuir model showed that the correlation coefficients of the two carbons (CPS and CaP) obtained between 0.994 and 0.997 are close to 1, thus showing that the model of Langmuir represents at best the adsorption of  $\text{Cu}^{2+}$  ions so it is applicable. According to the results of the Langmuir isotherm, we can say that these high values are due to the adsorption of  $\text{Cu}^{2+}$  ions on monolayers. And furthermore, there are no interactions between ions in solution, so one ion is not influenced by another during adsorption. The study of the thermodynamic parameters of the adsorption of the  $\text{Cu}^{2+}$  ion by our different carbons allowed us to obtain the following results : all the thermodynamic parameters are negative for the CaP, similar results were obtained for the adsorption cadmium and zinc by activated carbon [11]. Negative values of  $\Delta G^\circ$  indicate that the adsorption of  $\text{Cu}^{2+}$  ions on CaP and CPS is spontaneous [16, 17]. For CaP we observe an increase in free energy  $\Delta G^\circ$  with temperature, indicating the adsorption of  $\text{Cu}^{2+}$  ions is favored at low temperature. The negative value of  $\Delta H^\circ$  indicates the phenomenon of adsorption is exothermic which is in agreement with the results of Vinod *et al.* [18]. The negative value of  $\Delta S^\circ$  indicates that no crucial change has occurred in the internal structure of the activated carbon come from CaP during the adsorption of these metal ions, it is the decrease in randomness at the solid interface / solution during the adsorption process [19]. As for CPS, the decrease in free energy with increasing temperature means that the adsorption of  $\text{Cu}^{2+}$  ions to this adsorbent is favored at high temperature. The positive value of  $\Delta H^\circ$  indicates that the adsorption is endothermic in nature, the positive value of  $\Delta S^\circ$  implies an increase in the disorder at the solids/solution interface during the adsorption of metal ions. Similar behavior is reported by Agrawal and Sahu [20] in the removal of cadmium from manganese nodule residues. The results allow to conclude that the coals produced from the two biomasses can be used for the removal of  $\text{Cu}^{2+}$  ions in solution with high capacities (909.091 mg/g for CPS and 526.315 mg/g for CaP). And finally to say that the adsorption reactions of  $\text{Cu}^{2+}$  ions on the two adsorbents in solution are thermodynamically possible.

## Conclusion

This study has demonstrated the adsorption performance of metal ions in media by activated carbon from plant biomasses. The influence of parameters related to operating conditions such as contact time, mass of adsorbent, initial concentration of  $\text{Cu}^{2+}$  ions and temperature was examined. The kinetics study showed that equilibrium was established 40 and 80 min upon adsorption of  $\text{Cu}^{2+}$  ions in solution on CaP and CPS respectively with a mass of 0.1 g at pH=4. Thus, the adsorption mechanism can be described by pseudo-second-order kinetics which have shown good correlation. The plot of the adsorption isotherms shows that the Langmuir model perfectly represents the adsorption of  $\text{Cu}^{2+}$  ions on the activated carbons studied with a maximum adsorption capacity of 526.315 mg/g for CaP and of 909.091 mg/g for CPS. The study of thermodynamic adsorption parameters has shown that the adsorption process of  $\text{Cu}^{2+}$  ions in solution on CaP and CPS is spontaneous ( $\Delta G < 0$ ). The reaction is favorable at low temperature and exothermic ( $\Delta H < 0$ ) for CaP while in the case of CPS the reaction is favorable at high temperature and endothermic in nature. Although both carbons (CPS and CaP) have good metal ion removal performance, comparison of all results shows that  $\text{Cu}^{2+}$  ion adsorption on CPS is more efficient than that performed on CaP. Cocoa pod shells and cassava peels have been shown to be carriers which have a generally high adsorption affinity to  $\text{Cu}^{2+}$  ions. They can be used as adsorbents in the field of wastewater treatment of metal pollutants.

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