

Removal of copper (II) ions from aqueous solution by adsorption on activated carbon prepared from Shell walnuts

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Abstract— Shell walnuts (SWN) are a local natural abundant agricultural waste in Morocco. The Shell walnuts were investigated as an adsorbent for the removal of copper ions from aqueous solutions. Effects of various parameters such as contact time, particle size and mass of adsorbent, initial pH, and initial concentration of Cu (II) were studied for a batch experiments. The optimal equilibrium time of removal of metal ions is established after 60 minutes. The adsorption isotherms were analyzed using the Langmuir model and Freundlich. The kinetics of copper (II) ion was discussed using two kinetic models, the pseudo-first-order, and pseudo-second-order. It was shown that the adsorption of copper ions could be described by the pseudo-second order kinetic model.

Keywords: Copper (II) ions, Kinetics, Activated carbon, Adsorption isotherm and Shell walnuts.

1 INTRODUCTION

Nowadays *heavy metal pollution* is a principle source of environmental contamination. These heavy metals have accumulating characteristics in nature and cannot be biodegraded, and this environmental issue is threatening the health of human beings seriously. Copper (II) is known to be one of the heavy metals and is widely used in many industries. The effluents from these industries usually contain considerable quantity of copper, which spreads into the environment through soils and water streams and finally accumulates along the food chain which causes human health hazards. The higher concentration of copper will cause severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage, and central nervous system irritation followed by depression [1]. These heavy metals are toxic to human beings and other living species if their concentrations exceed certain limits. These limits suggest a stricter requirement for the elimination of the copper in industrial effluents before rejecting it into surface water and ground water, for the protection of human health and the environment. The adsorption is the method the most widely used because it is one economically practicable, simple, effective, multi-purpose and environment-friendly method in the practice [2, 3]. Although the commercially activated carbon has the high surface area, the microporous character and the high capacity of adsorption, it proved its potential as an adsorbent for the removal of heavy metals from industrial wastewater, it is expensive with relatively high operating costs and it needs the regeneration after every cycle of adsorption there [4].

Hence, there is a growing demand to find low-cost and efficient, locally available adsorbents for the sorption of copper such as the sugar beet pulp [5], peanut hull [6], Cinnamomum camphora leaves powder [2], Rice shell [7], Herbaceous peat [8], Base treated rubber leaves [9], Pine cone powder [10], Tree fern [11], Groundnut shells [12], Cedar sawdust [13], sawdust [14], Banana Peels [15] etc. Because of the low cost and of the big availability of these materials, it is not essential to have a complicated process of regeneration. This method of low-cost adsorption attracted many scientists and engineers.

The objective of this research is to develop little expensive and effective adsorbents from the sources of natural wastes, such as shell walnuts (SWN), to replace the existing commercial materials. The effect of various experimental parameters such as, contact time, initial copper (II) concentration and has been investigated. Equilibrium modelling was carried out using Langmuir and Freundlich adsorption isotherms.

The nature of the sorption process has been evaluated with respect to its kinetic aspects.

2 MATERIALS AND METHODS

2.1 Adsorbent

The SWN used in this work were collected from Imlil-marrakech region in Morocco, SWN were extensively washed in running tap water to remove dirt and dust, and then rinsed with distilled water. Dried in an oven at 105 °C for 12 hours. The above dried natural waste was ground to a fine powder. 13 g of SWN was immersed in 100 mL of ZnCl₂ solution (0.5 M) for 5 h with agitation, and then dried in an oven for 24 h at 110 °C. The zinc treated SWN was placed in a crucible and pyrolysed at 600°C for 1 h. The resulting activated carbon was washed with 0.1 M HCl solution to remove excess zinc chloride and rinsed with warm water. The final product of ACSWN was dried at 110 °C for 24 hours. The ACSWN were

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screened to three different particle sizes ($D < 63 \mu\text{m}$, $63 \mu\text{m} < D < 80 \mu\text{m}$, $80 \mu\text{m} < D < 100 \mu\text{m}$) and kept in desiccators for further study.

2.2 Metal solutions

The heavy metal used in this study is the hydrate of copper sulfate. This is g/mol . Solutions of Cu (II) was prepared by dissolving predefined amounts of $(\text{CuSO}_4 \cdot 5\text{H}_2\text{O})$ in distilled water, so as to achieve a metal cation of the formula $(\text{CuSO}_4 \cdot 5\text{H}_2\text{O})$, with molecular weight 249.68 concentrations of 1000 mg/L^{-1} in each flask. Different initial concentrations of metal ions were prepared by diluting the stock solution. The pH of the solutions was adjusted using 0.1 N HCl and 0.1 N NaOH to achieve the desired values.

2.3 Adsorption experiments

Activated carbon from sell wulnuts ACSWN was tested for the adsorption of Cu (II) from an aqueous solutions using batch technique. 100 ml of aqueous solutions of Cu (II) at different initial concentrations ($200, 300, 400, 500 \text{ mg/L}$) were transferred into 250 ml Erlenmeyer. ACSWN was added with different doses and different adsorbent size, with continuous shaking at 120 rpm . The solution pH was varied (from 2 to 8). After the adsorption time ($10\text{-}120 \text{ min}$), solutions were decanted and Cu (II) concentrations were determined using complexometric dosage. The data obtained in batch studies were used to calculate the equilibrium metal adsorptive quantity by using the following equation:

$$q_e = (C_0 - C_e)V/M \quad (1)$$

Where q_e is the amount of heavy metal ion adsorbed onto per unit weight of the adsorbent in mg/g , V is the volume of solution treated in liter, C_0 is the initial concentration of metal ion in mg/L , C_e is the equilibrium metal ion concentration in mg/L and M is the mass of the adsorbent in grams.

% Removal of metal ion was calculated using the following equation:

$$\% \text{ Removal} = (C_0 - C_e).100/ C_0 \quad (2)$$

2.4 Adsorption kinetics

Adsorption kinetics modules were carried out in order to determine the contact time required to reach the equilibrium. 100 ml samples of $300\text{-}500 \text{ mg.L}^{-1}$ metal ion solutions were mixed with 0.15 g of ACSWN of particle size $< 80 \mu\text{m}$ at constant temperature $25 \text{ }^\circ\text{C}$. Pseudo-first-order model, and pseudo-second-order model, was studied.

2.5 Adsorption isotherms

Adsorption isotherms were studied for different initial Cu (II) concentrations (300 and 400 mg.L^{-1}), and different adsorbent mass was added to 100 ml Cu(II) solution, constant shaking (120 rpm), contact time of 60 min was used to study Freundlich and Langmuir isotherms.

3 RESULTS AND DISCUSSION

3.1 Effect of the pH

The pH is one of the determined parameters of controlling the adsorption behavior of cationic molecule onto suspended ad-

sorbent. In this study, the effect of this parameter was studied for adsorption of heavy metals Cu^{2+} on 0.15 g of adsorbent at ambient temperature, with 300 mg/l as initial concentration of copper Cu^{2+} , the stirring speed of 120 rpm and with a contact time of 60 min . The range of solution pH was adjusted between 2 and 8, with NaOH or HCl solution (0.1M).

As shown in Fig. 1, the adsorption capacity increases from 88.89 mg/g to 124.445 mg/g when the solution pH values increase from 2 to 6. The variation in the removal of heavy metals Cu^{2+} with respect to pH can be explained by considering the surface charge of adsorbent.

A strongly acidic pH (pH = 2): the copper ions are not retained. This can be explained in that the concentration of cations H^+ is high in solution which induces a competition for the cations H^+ , with Cu^{2+} cations for sites negatively charged.

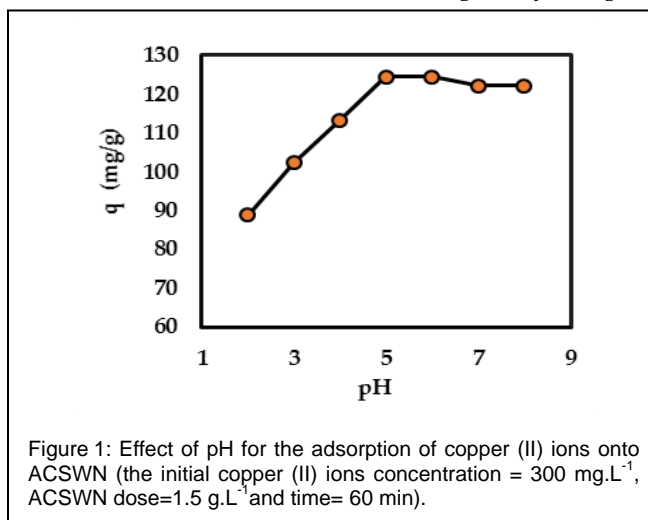
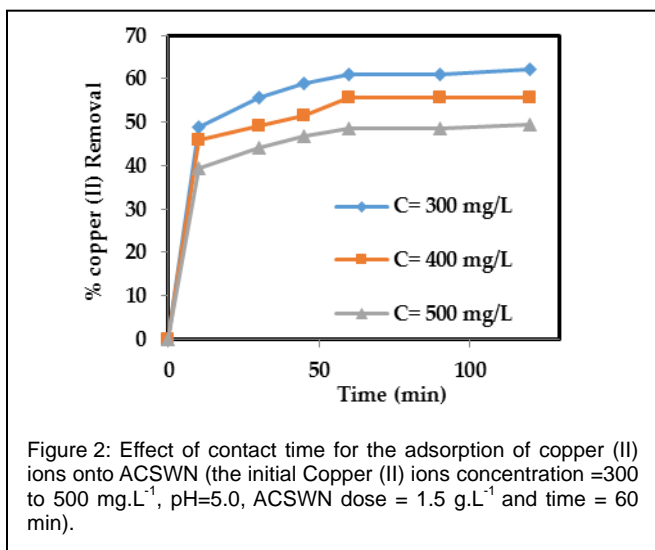


Figure 1: Effect of pH for the adsorption of copper (II) ions onto ACSWN (the initial copper (II) ions concentration = 300 mg.L^{-1} , ACSWN dose= 1.5 g.L^{-1} and time= 60 min).

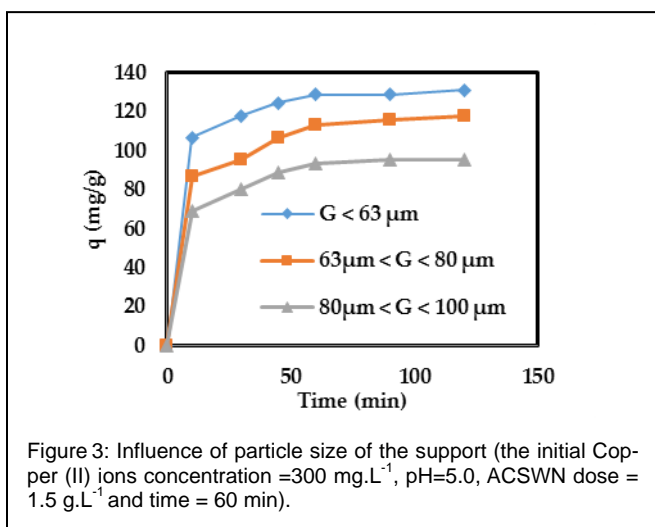
3.2 Effect of contact time

The effect of contact time on copper (II) adsorption on ACSWN was studied and the results were shown in Fig.2. The data obtained from the adsorption of copper (II) ions onto the ACSWN showed that the adsorption increases with increase in contact time. The adsorption of copper (II) ions onto ACSWN was rapid during the first minutes, and equilibrium was nearly reached after 60 min for different initial copper (II) ion concentrations. Hence, in the present work, 60 min was chosen as the equilibrium time. Generally the removal rate of adsorbate is rapid initially, but it gradually decreases with time until it reaches equilibrium. The rate in percent of copper (II) ions removal is higher in the beginning due to the larger surface area of the adsorbent being available for the adsorption of the metals. As the surface adsorption sites become exhausted, the rate of adsorption is controlled by the rate of transport from the exterior to the interior sites of the adsorbent particles [15]. It is also important to note that, since active sorption sites in a system have a fixed number and each active sites can adsorb only one ion in a monolayer, the metal adsorption by the adsorbent surface will be rapid initially, slowing down as the competition for the decreasing availability of active sites intensifies by the metal ions remaining in the solution [16, 17].



3.3 Effect of the size

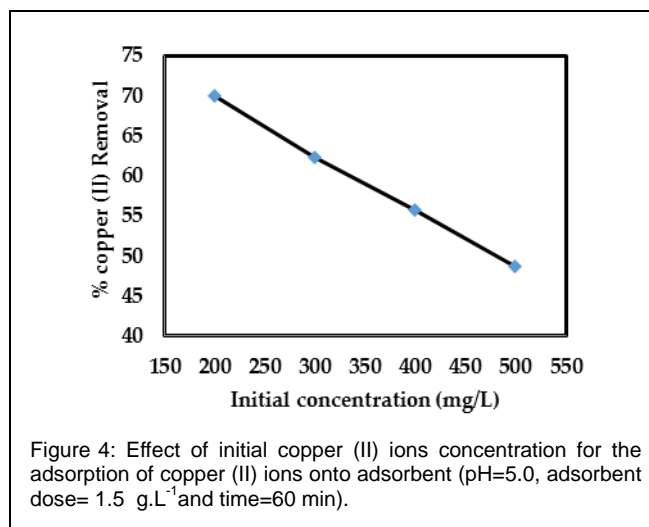
In this study, we used the various fractions of size. The kinetics of adsorption of copper (II) ions is represented on the figure 4. The capacity of adsorption is preferable for a range of lower size (63 < μm), because the adsorption depends on the external surface of the adsorbing material increased with the fineness of its particles.



3.4 Effect of initial copper (II) ion concentration

The copper (II) uptake is particularly dependent on initial copper (II) ion concentration. The different concentrations of copper (II) ions solutions of 200, 300, 400 and 500 mg.L⁻¹ were used and the experiments were performed at room temperature with contact time of 60 min. Fig.4. Shows the effect of metal concentration on the percent removal of copper (II) ions. From figure, it was shown that the percentage copper (II) ion adsorption decreased from 70 % to 48.66 % with the increment of the initial copper (II) ions concentration. At the lower copper (II) ion concentrations, the copper (II) removal percentage

was higher due to a larger surface area of the CNS being available for the adsorption of copper (II) ions. When the concentration of the copper (II) ion solution became higher, the copper (II) removal percentage was lower because the available sites of the adsorption became less.



3.5 Effect of the mass of the nut shells

To examine the effect of the adsorbent mass, we varied the amount of adsorbent from 50 mg to 150 g using a fixed solution volume.

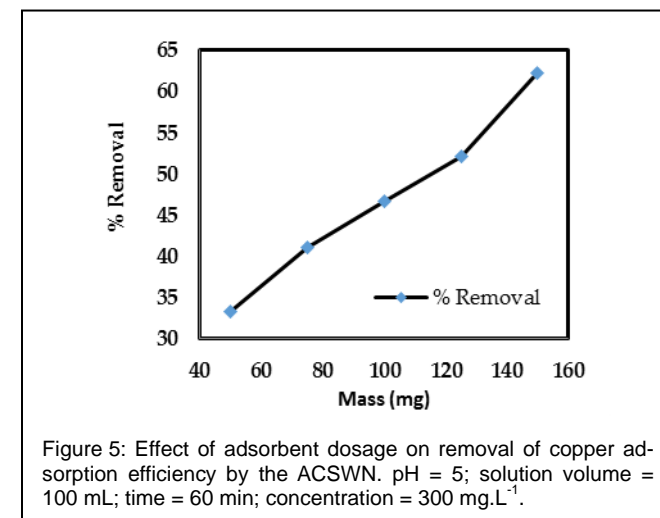
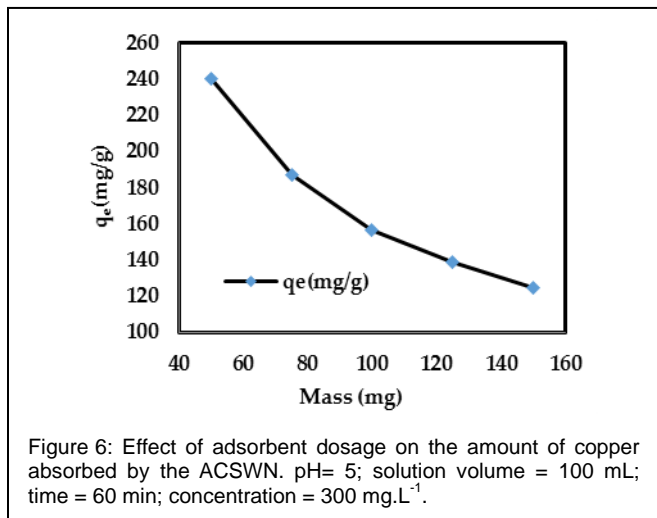


Figure 5 shows that the copper removal efficiency increases strongly with the increasing amount of the adsorbent till 150 mg. In contrast, Figure 6 shows that the amount of copper absorbed (q_e) in mg decreases rapidly. The decrease in biosorption efficacy with increasing doses of biomass can be explained as follows:

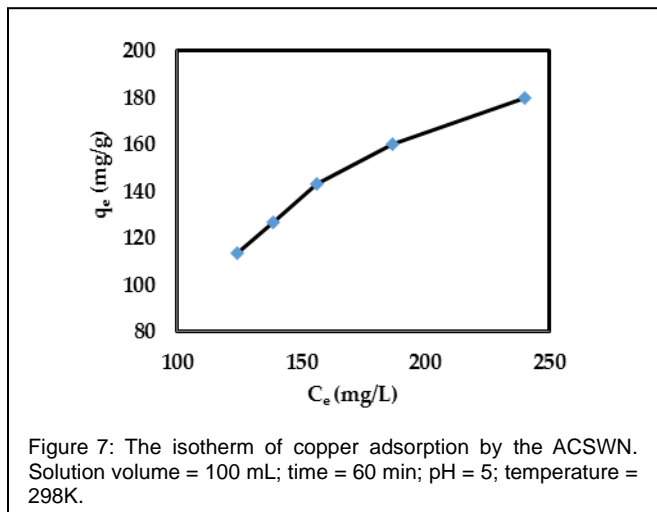
-As the amount of adsorbent added to the copper solution is low, Copper ions can easily access the adsorption sites. The addition of adsorbent can increase the number of adsorption sites but copper ions have greater difficulty in approaching these sites because of congestion.

-A large amount of adsorbent creates aggregates of particles, resulting in a reduction of the total surface area for adsorption, and therefore, a decrease in the amount of adsorbate per unit mass of adsorbent. [18, 19].



3.6 Adsorption isotherm

The adsorption isotherms provide evaluation of copper adsorption capacity on the support. These curves link the amount of copper adsorbed per unit mass of the support (q_e) to the concentration of copper remaining in solution (C_e). Figure 7 shows the isotherm of copper adsorption by the ACSWN.



To determine the amount of copper adsorbed per unit mass of the adsorbent (q_e), several authors have proposed theoretical or empirical models to describe the relationship between the amount adsorbed and the residual concentration both at equilibrium. The main models described in literature are [20, 21].

3.6.1 Langmuir model

$$q_e = q_m K_L C_e / (1 + K_L C_e) \quad (3)$$

$$C_e / q_e = 1 / K_L q_m + C_e / q_m \quad (4)$$

Where q_e: adsorption capacity at equilibrium (mg.g⁻¹);

q_m: adsorption capacity of saturation (mg.g⁻¹);

K_L: Langmuir constant.

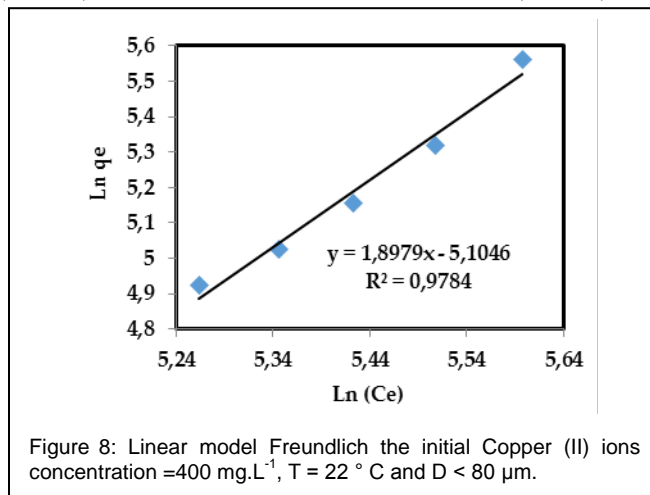
The plot of C_e/q_e in function of C_e, allows to determine q_m and K_L.

Another parameter; R_L can explain the adsorption according to Langmuir as following:

$$R_L = 1 / (1 + K_L \cdot C_0) \quad (5)$$

Based on the R_L value, we can say that the adsorption is favorable when R_L tends to zero

(R_L → 0) or unfavorable when R_L tends to one (R_L → 1)



3.6.2 Freundlich model

The simple and empirical model of Freundlich is the most commonly used [21],

$$q_e = K_F \cdot C_e^{(n)} \quad (6)$$

The linear form is the following:

$$\ln q_e = \ln K_F + n \ln C_e \quad (7)$$

The application of equations Langmuir and Freundlich on test results obtained are shown in Figures 8 and 9.

The parameters of these two equations are reported in Tables 1. According to the results, the Freundlich equation is the most suitable for this sorption than Langmuir.

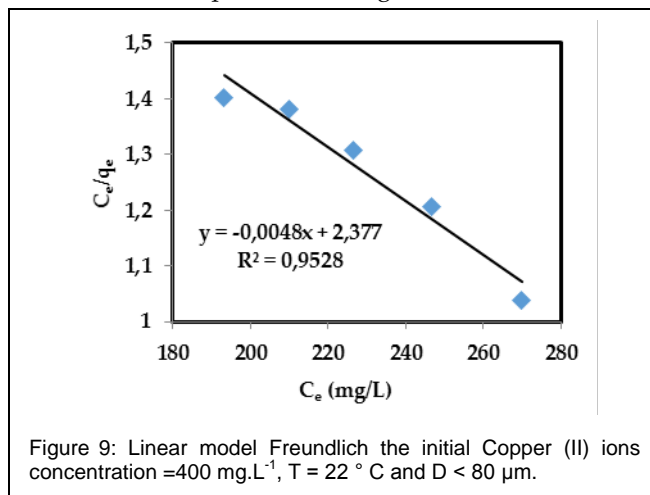


TABLE 1: PARAMETERS OF ISOTHERMS MODELS OF COPPER AD-

SORPTION BY SUPPORT.

Initial concentration (mg.L ⁻¹)	Parameters Freundlich model			
	400	K _F (mg.g ⁻¹)	n	q _m
0.006		1.8979	520.72	0.9784
Parameters Langmuir model				
q _m (mg.g ⁻¹)		K _L (L.mg ⁻¹)	R _L	R ²
208.33		0.0020	0.1101	0.9528

3.7 Adsorption isotherm

Various kinetic models, namely pseudo-first-order, pseudo-second order, have been used for their validity with the experimental adsorption data for copper (II) onto ACSWN. The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface including the diffusion process. The mechanism of adsorption depends on the physical, and chemical characteristics of the adsorbent as well as on the mass transfer process. The results obtained from the experiments were used to study the kinetics of metal ion adsorption. The rate kinetics of copper (II) ion adsorption was analysed using pseudo-first-order, and pseudo second-order. The application of two kinetics models on test results obtained are shown in Figures 10 and 11. The parameters of these kinetic models are reported in Tables 2.

3.7.1 Model of pseudo-first order

The first model of pseudo-first order is expressed as follows:

$$dq_t/dt = k_1 \cdot (q_e - q_t) \tag{8}$$

q_e and q_t (mg.g⁻¹) is the quantities adsorbed in the balance and in time t

k₁ (min⁻¹) is the constant of speed of adsorption of the so-called model - first order.

The integration of the equation (8) becomes:

$$\ln (q_e - q_t) = \ln q_e - k_1 \cdot t \tag{9}$$

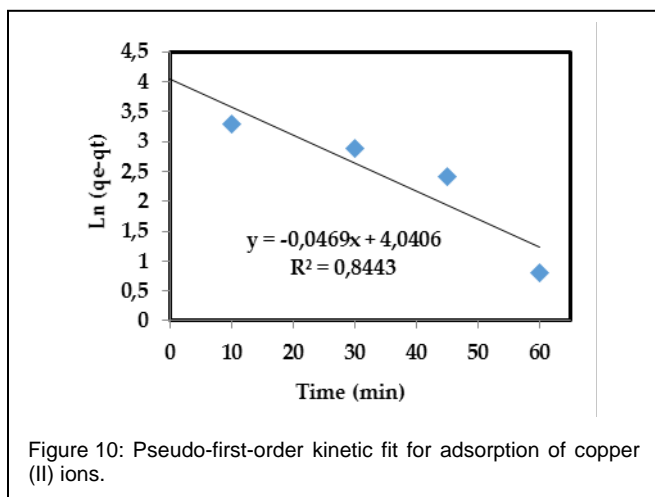


Figure 10: Pseudo-first-order kinetic fit for adsorption of copper (II) ions.

3.7.2 Model the pseudo-second order

The model of the pseudo-second order is expressed by the following equation:

$$dq_t/dt = k_2 \cdot (q_e - q_t)^2 \tag{10}$$

Where:

K₂ is the constant of speed of adsorption of the model the so called second order (g.mg⁻¹.min⁻¹).

q_t : the capacity of adsorption at the moment t.

q_e: the capacity of adsorption in the balance.

The integration of the equation (10) gives:

$$1/q_t = 1/q_e + 1/k_2 q_e^2 t \tag{11}$$

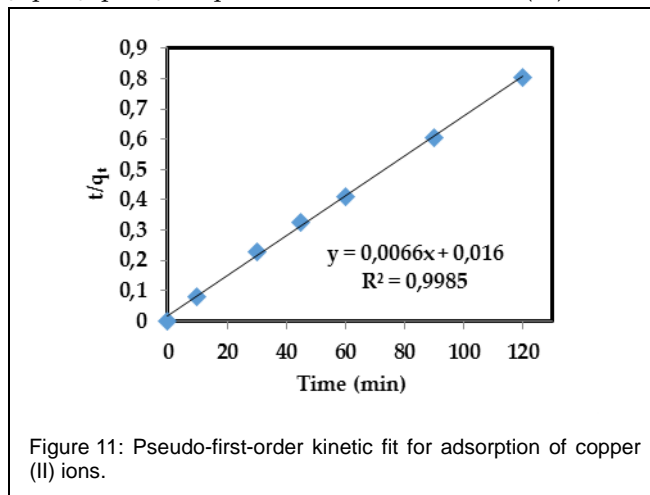


Figure 11: Pseudo-first-order kinetic fit for adsorption of copper (II) ions.

TABLE 2: PARAMETERS OF ISOTHERMS MODELS OF COPPER ADSORPTION BY SUPPORT.

Initial concentration (mg/L)	Pseudo-first order		
	400	q _{th} (mg.g ⁻¹)	K ₁ (min ⁻¹)
56.86		0.0469	0.8443
Pseudo-second order			
q _{th} (mg.g ⁻¹)		K ₂ (g.mg ⁻¹ .h ⁻¹)	R ²
151.515		0.00272	0.9985

4 CONCLUSION

The study of the process of adsorption of copper (II) ions on activated carbon wul nutshells (ACSWN) was the object of this work. The results showed that the capacity of adsorption of a mass of ACSWN increases with the increase of the initial concentration of the copper (II) ions in the solution.

The modeling of the results of adsorption demonstrated that the model of the pseudo second order offers a better correlation of the kinetic data and that the model of Freundlich describes better the isotherm of adsorption.

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