



## Treatment of water loaded with cupric ions by adsorption on Acacia sawdust

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### Abstract

The objective of this paper is to study the ability of Acacia sawdust to eliminate copper ions by adsorption from water. Many experiments were conducted based on physical and chemical variables including: pH, temperature of the solution, initial concentration of copper ions, stirring speed, mass and particle size of Acacia sawdust. The results show that the maximum adsorption was observed for a pH value of 3.2. The adsorption capacity seems to be optimized when temperature, load and size of the Acacia sawdust and the initial concentration of the solution decrease. The modeling of adsorption isotherms has shown that Freundlich and Elovich models describe well this process of adsorption. Acacia sawdust shows great affinity for copper ions with a heterogeneity factor equal to 0.28 and a maximum capacity of adsorption of 2.  $\text{g}_{\text{Cu}^{2+}}/\text{g}_{\text{ads}}$ . The type of adsorption involved in this process is a nonspecific physical adsorption leading to the formation of multilayer.

**Keywords:** Copper, Wattle, sawdust Acacia, isotherms, adsorption.

### 1. Introduction

In faucet manufacturing, the faucet surface treatment is realized by the copper plating step in a bath that contains copper solution followed by rinsing. This latter generates an effluent loaded with copper ions that requires a treatment or a recovery before being discharged in streams. Copper is a trace element which is essential for living being. It may be a poison with high concentrations that could lead to liver saturation, followed by copper liberation in the blood and leading a hemolytic stage that may cause death [1]. Copper can also cause an undesirable bitter taste to water and when its concentration exceeds 1.0 mg / L, stains appear on laundry and plumbing fixtures. When copper exists in public water distribution network it promotes the corrosion of aluminum and zinc. Considered as a violent poison to microorganisms and not easily metabolized [2],  $\text{Cu}^{2+}$  ions are used as fungicides, pesticides and even as antibacterial [3]. For these reasons the concentration of copper must not exceed a certain limit in streams. Several processes of copper elimination have been developed such as precipitation and co-precipitation, electro deposition and electrocoagulation, cementation, separation by membrane, extraction by solvent, ion exchange, adsorption and bio sorption, etc. [4]. In this work, we studied the fixation of cupric ions of faucet fabrication industry effluents on Acacia sawdust. After that, the effect of physical and chemical factors on the adsorption capacity of Acacia sawdust such as the temperature, the pH of the solution, the initial concentration on cupric ions, the stirring rate and the mass and the particle size of the Acacia sawdust is reported. The modeling of Acacia sawdust adsorption isotherms is also realized to understand the nature of the involved reaction mechanisms.

### 2. Materials

The adsorbent used in this study is the Acacia sawdust of Fes-Boulmane region. It is dry, whitish and is applied at a raw untreated state. Acacia Sawdust was characterized by Scanning Electronic Microscopy and infrared spectroscopy. The granulometric separation is done by a Ro-Tap sieving column and a rotative Granulometer shaker. The method consists of introducing the sample in the higher sieve, where the opening of the sieves mesh is of increasing order from the bottom to the top of the column. Stirring the sieving column promotes grain moving downward until the sample is trapped within the sieve whose mesh size is smaller than the nominal size of particles. The range of available sieves in the laboratory covers a

spectrum of different shapes between 63  $\mu\text{m}$  and 500  $\mu\text{m}$ , in an interval corresponding to a quarter of  $\text{pHi}$ , which meets different ISO and ASTM standards.

The solutions treated in this work are:

- A synthetic solution with cupric ions load: prepared from copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ). The solution obtained is characterized by a pH of 8 and a conductivity of  $590\mu\text{s/cm}$ .
- An industrial effluent sampled from a surface treatment bath of copper faucet using the conditions normalized by Rodier [6].

### 3. Methods

The concentration of cupric ions was measured by:

- Molecular Absorption Spectrophotometry (MAS) when the concentration is less than  $0,15\text{ mol L}^{-1}$ .
- Volumetric Dosing for concentrations greater than  $0,8\text{ mol L}^{-1}$ .

The pH and conductivity were measured with a digital conductivity and pH meter laboratory (CONSORT C830)

The rate of copper binding on the adsorbent and the contact time necessary to obtain the maximum adsorption of copper on Acacia sawdust are evaluated by the study of the adsorption kinetics. Adsorption is controlled by the physicochemical parameters relative to the adsorbent (mass and particle size), the treated solution (concentration of the cupric ions solution) and the medium (pH, temperature and stirring speed).

The adsorption kinetics of copper is determined using a Jar-test, with a mixing speed of 120 rev/min, a constant mass of adsorbent equal to  $8\text{ g.L}^{-1}$ , with a solution containing cupric ions with a concentration  $[\text{Cu}]_0 = 2.54\text{ gL}^{-1}$ . After a contact time ranging from 10 minutes to 5 hours, the solutions were filtered and the amount of non-eliminated metal  $[\text{Cu}]$  is measured. The reduction rate of cupric ions is determined by the following relationship:

$$Cu^{2+} (\%) = \frac{[\text{Cu}_0] - [\text{Cu}_e]}{[\text{Cu}_0]} \times 100 \quad (1)$$

Where  $\text{Cu}_0$  is the initial concentration and  $\text{Cu}_e$  the concentration after the contact.

The operation is repeated until we have constant concentrations of cupric ions in the solution.

On a series of tests of optimizing the adsorption parameters, we followed the evolution of the rate of copper ions elimination, varying one parameter while others are kept constants. The corresponding conditions for these tests are:

- An adsorbent mass, ranging from 0,5 to 16 g per 1 L of cupric ions solution.
- A pH of the solution ranging from 3,2 to 12.
- An initial cupric ion concentration ranging from 2 to  $9\text{ g L}^{-1}$ .
- A stirring speed ranging from 50 to 250 rev/min.
- A granulometry ranging from 80 to 315  $\mu\text{m}$ .
- A temperature between 20 and  $90\text{ }^\circ\text{C}$ .

### 4. Results and discussion

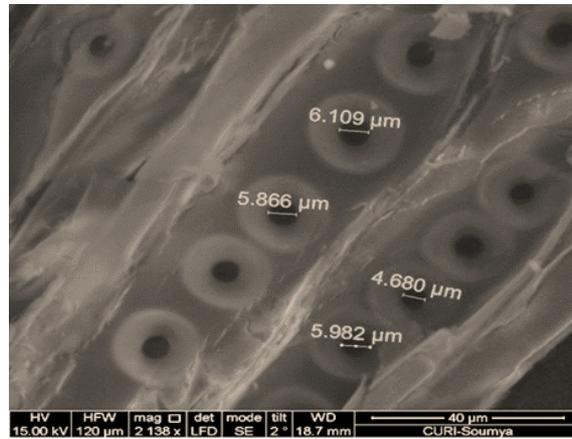
#### *Scanning Electron Microscopy and Infrared Spectroscopy analysis*

The analysis by Scanning Electron Microscopy (SEM) of the Acacia sawdust is performed using an Environmental SEM equipped by an EDAX probe, QUANTA 200 model, with a zooming of 2000x and 2138x. The results (Figure 1) show the presence of numerous pores with diameters between 4.8 and 6.11  $\mu\text{m}$  corresponding to cellulose microfibrils concentrated inside the fiber. The outer walls of the fiber are mainly composed of hemicellulose and the inter-fibers junction lamellae are composed of lignin [7].

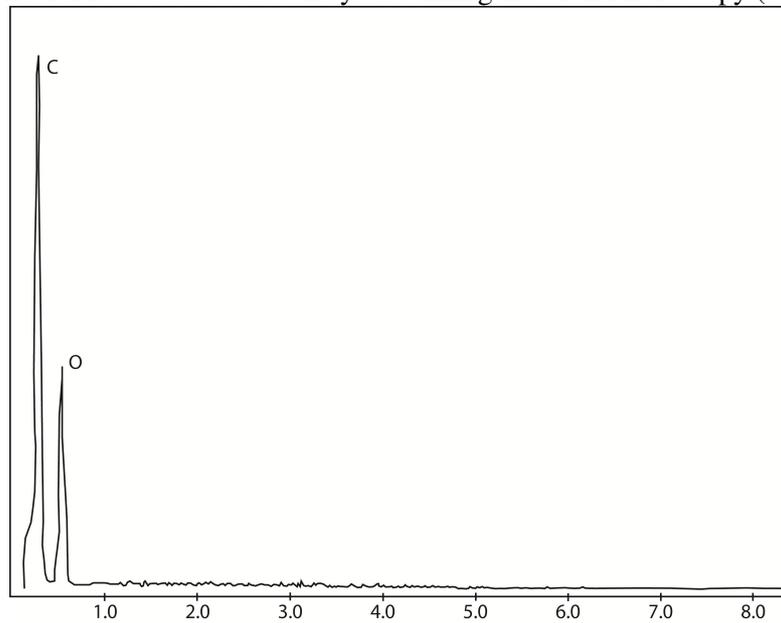
The results of the microanalyses of Acacia sawdust (Figure 2) reveal a high composition of carbon (C) and oxygen (O). There's also hydrogen (H) that is undetectable with this analysis. The weak peaks are probably due to the presence of other elements in trace amounts, such as nitrogen (N), calcium (Ca), potassium (K) and magnesium (Mg) [8].

The analysis by infrared spectroscopy (Figure 3) is performed using a spectrophotometer of Fourier type VERTEX 70. The uncertainty in frequency measurement is  $4\text{ cm}^{-1}$ . The results indicate the existence of a band at  $3329.9\text{ cm}^{-1}$  indicating the presence of OH groups in the cellulose and lignin which are the main components of wood. The  $1025.92\text{ cm}^{-1}$  band may correspond to R-O-R functions and the band of  $1643.92\text{ cm}^{-1}$  corresponds

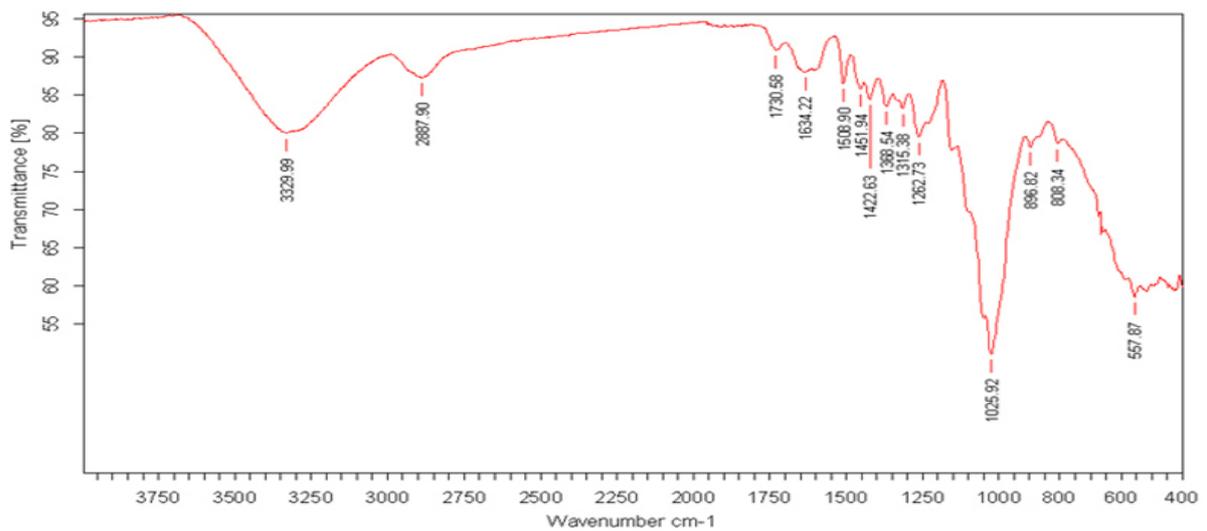
to C=O functions. The bands of  $1422.63\text{ cm}^{-1}$ ,  $1451.94\text{ cm}^{-1}$  and  $1508.90\text{ cm}^{-1}$  correspond probably to C=C functions.



**Figure 1.** Acacia sawdust seen by a Scanning Electron Microscopy (SEM).



**Figure 2.** Microanalysis Spectrum of Acacia sawdust.



**Figure 3.** Infrared Spectrums of the Acacia sawdust.

**Acacia sawdust particle size analysis**

The particle size analysis is determined according to AFNOR standards 2004, where the sawdust is poured into the sieving column. The results (Figure 4A) show that the slice holding the mass of the adsorbent corresponding to a particle size of Acacia sawdust of 200 µm. The following relation defines the uniformity coefficient U:

$$U = \frac{d_{60}}{d_{10}} \tag{2}$$

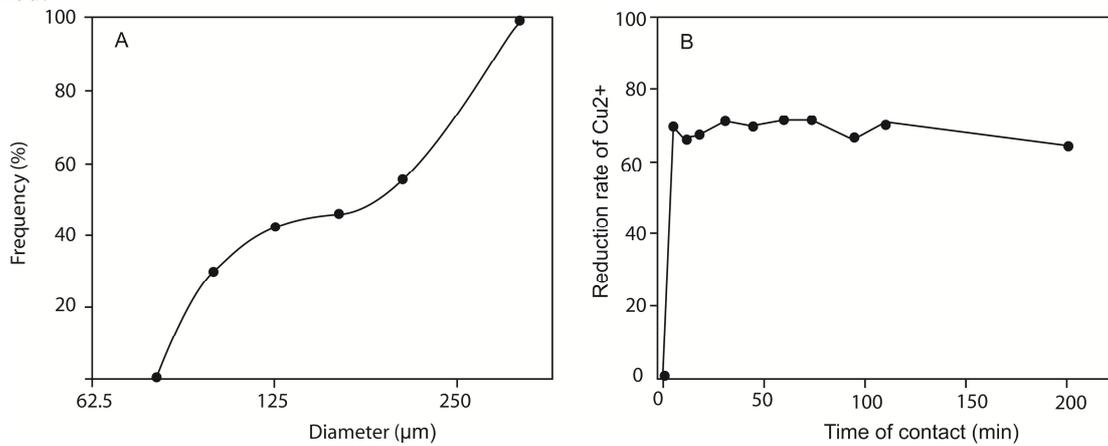
$d_{60}$  : grain size (µm) corresponding to 60 % of the cumulated weight.

$d_{10}$  : grain size (µm) corresponding to 10 % of the cumulated weight.

The obtained uniformity coefficient is 1,886, which is inferior to 2 for the whole sample. This indicates that the Acacia sawdust presents a uniform particle size.

Concerning the monitoring of the adsorption kinetics of cupric ions on Acacia sawdust, the result shows that the curve consists of two parts (Figure 4B):

- The first part is characterized by a rapid increase of cupric ions up to 70% during the first 15 minutes of the contact.
- The second part shows a stabilization of the curve indicating that the material is saturated and the equilibrium is reached.



**Figure 4.** (A) Particle size curve of the Acacia sawdust and (B) Reduction rate of cupric ions as a function of time.

The kinetics of copper fixation on the Acacia sawdust is very fast. This result corroborates with a similar study carried out by Youcef and Achour (2006) [9] who performed the adsorption of cupric ions on bentonite, and another study leads by B. Fatima (2000) [10], who tried the retention of metallic micropollutant (Pb, Cd, Cu, and Zn) on chitin. The rapid evolution of the fixation kinetics on Acacia sawdust shows the reversibility and the low energy of the involved exchanges. This indicates the presence of a physical adsorption mechanism with relatively weak Van der Waals or hydrogen sawdust-copper links.

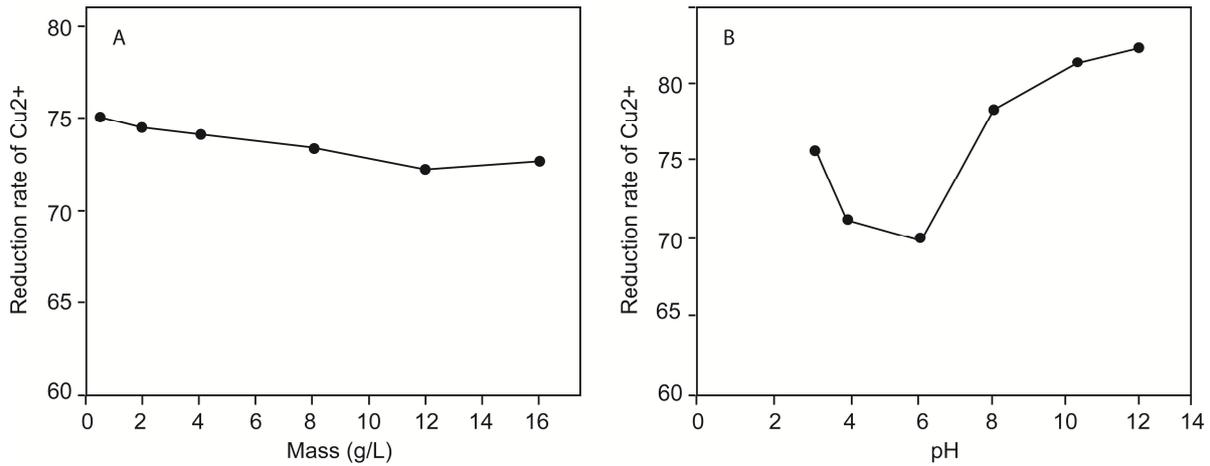
**Effect of adsorbent mass and pH medium**

The copper elimination performances don't seem to be affected by the increase of the Acacia sawdust mass (Figure 5A). However, we have seen a small decrease of cupric ions abatement rate for higher loads. This may be explained by the release of other materials of Acacia sawdust that inhibits the adsorption of cupric ions.

The variation of pH was assured by the addition of NaOH or H2SO4. The analysis of the represented curve on Figure 5B, shows a best adsorption for an acid environment with a pH of 3.2. This is probably due to electrostatic forces induces by the charges. The adsorption phenomena may be due to the filling of pores by physical adsorption. When the pH exceeds the value of 6, a precipitation of Cu<sup>2+</sup> ions by formation of Cu(OH)<sub>2</sub> precipitate occurs according to the reaction:



With  $K_s = 3.16 \times 10^{-19}$  at 25C [9].



**Figure 5.** Reduction rate of cupric ions as (A) function of mass of Acacia sawdust and (B) as function of pH.

The pH at the beginning of the precipitation increases when the concentration of the metal decreases. An approximate calculation allowed to theoretically determinate the precipitation domain of the copper hydroxide. The pH at the beginning of the precipitation is:

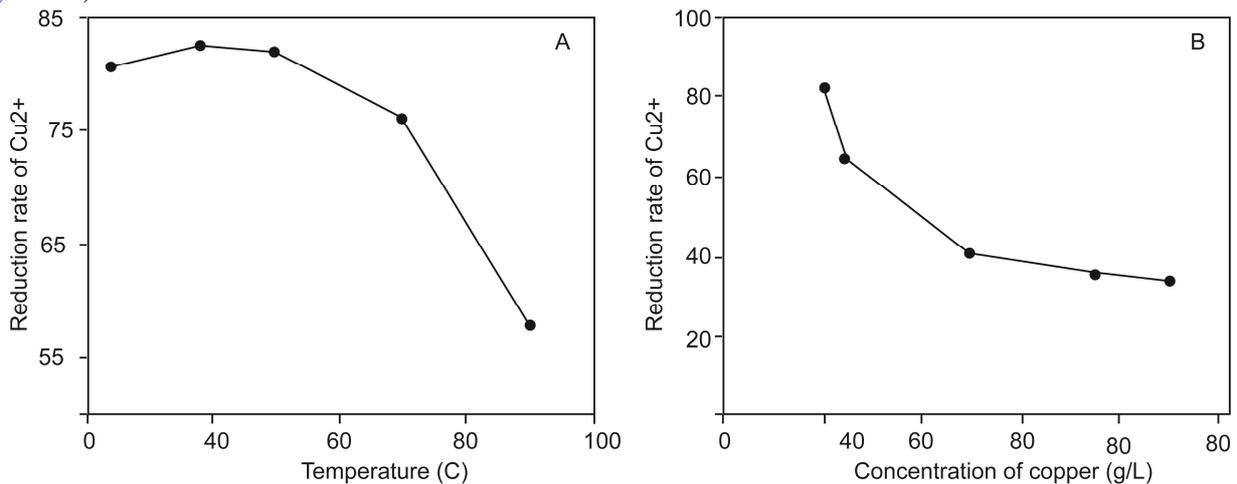
$$pH = 14 + \frac{1}{2} \log \left( \frac{K_s}{[Cu^{2+}]} \right) \quad (4)$$

The pH is equal to 6.4 for an initial concentration of the  $Cu^{2+}$  ions solution. This result is experimentally approved at some approximations.

**Effect of temperature and initial concentration of the cupric ions solution**

The monitoring of the evolution of copper elimination rate with the temperature variation (Figure 6A) indicates that the adsorption decreases when the temperature increases. This may be explained by the increase of interactions between Acacia sawdust particles and cupric ions. In addition, the type of adsorption is physical. The reaction releases an adsorption heat and low temperatures promote it.

The curve representing the evolution of cupric ions reduction rate as function of the initial concentration records a decrease of cupric ions fixation on Acacia sawdust when the solution becomes more charged by this ions (Figure 6B).



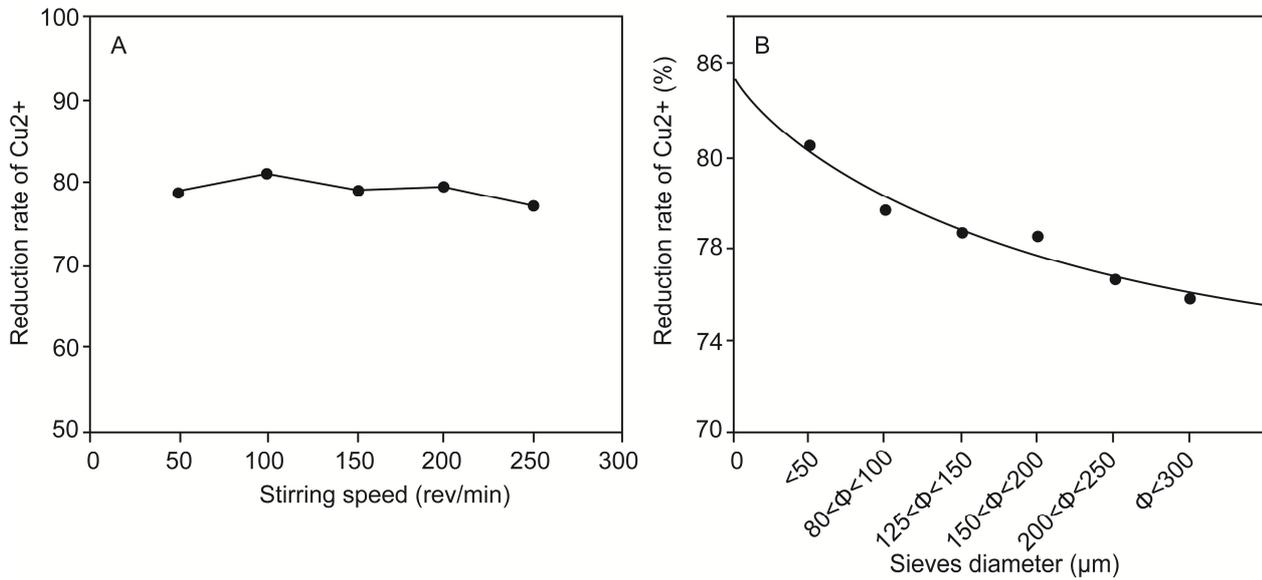
**Figure 6.** (A) Effect temperature on copper reduction rate and (B) cupric ions reduction rate as function of the initial concentration.

A combination of precipitation processes with lime followed by an adsorption on Acacia sawdust may significantly improve the cupric ions elimination rate and possibly reach the Moroccan standards [4].

**Effect of stirring speed and particle size**

The results of Figure 7A show that the stirring speed has almost no significant influence on adsorption process. However, a slight increase nearby 100 rev/mn of abatement rate of cupric ions was noticed.

The curve shape represented in the Figure 7B indicates that the particle size has a significant effect on adsorption. The lower is the size, the more is the retention of cupric ions on Acacia sawdust. Indeed, the smaller particles increase the specific surface and improve the adsorption capacity. The study performed by Ajmal et al. (1998) allowed verifying the same effect of small particle size on the cupric ions fixation capacity on Mangifera indica sawdust [11].



**Figure 7.** (A) Effect of stirring speed on cupric ions reduction rate and (B) effect of particle size on cupric ions reduction rate.

**Adsorption isotherms models**

The isotherms used are (1) the Langmuir equation based on the establishment of a monomolecular layer of the used solutions, (2) the Freundlich relationship that allows a practical representation of the adsorption equilibrium between a micro pollutant and a solid support surface and (3) the Elovich model that involves adsorption in several layers. Using isothermal equilibrium allows reaching the thermodynamic values induced by the phenomenon [8].

The Langmuir equation in its linear form can be expressed as:

$$\frac{m}{x} = \frac{1}{q_{max}} + \frac{1}{(b \times q_{max})} \times \frac{1}{C_e} \tag{5}$$

With  $x = (C_0 - C_e)/V$

Where  $C_e$  is the concentration of copper at equilibrium (g.L-1),  $x$  is a fixed amount of copper (g),  $m$  is the mass of Acacia sawdust (g),  $q_{max}$  is the ultimate or maximum capacity of adsorption (g<sub>sol</sub>/g<sub>ads</sub>) and  $b$  is a constant of adsorption equilibrium.

When  $m/x$  is plotted versus  $1/C_e$ , we get a straight line (Figure 8) with the following equation:

$$y = 0.085 x + 0.174 \tag{6}$$

The high correlation coefficient ( $R^2=0.86$ ) allows to determine the 2 characteristic parameters of the equilibrium:  $q_{max}$  et  $b$ .

The Freundlich's equation in its logarithmic form is expressed by the following equation:

$$\log\left(\frac{x}{m}\right) = \log(K) + \frac{1}{n} \log C_e \tag{7}$$

Where  $K$  is the Freundlich constant,  $n$  the heterogeneity factor

When  $\log(x/m)$  is plotted versus  $\log(C_e)$ , we get a straight (Figure 8) with the following equation:

$$y = 0.284 x + 0.548 \tag{8}$$

With the high correlation coefficient of 0.97, the Freundlich constant  $K$  and the heterogeneity factor  $n$  can be determined.

The Elovich equation in its logarithmic form is:

$$\ln\left(\frac{q}{C_e}\right) = \ln(K_e \times q_m) - q \times \left(\frac{1}{q_m}\right) \quad (9)$$

Where  $q$  is the amount of the adsorbed solute per unit of mass of adsorbent ( $\text{g}_{\text{Cu}^{2+}}/\text{g}_{\text{ads}}$ ) and  $K_e$  is Elovich's constant.

When  $\ln(q/C_e)$  is plotted versus  $q$ , we get a straight line (Figure 8) with the following equation:

$$y = -0.540x + 3.184 \quad (10)$$

With the high correlation coefficient of 0.9, the Elovich constant  $K_e$  and the maximum adsorption capacity  $q_{\text{max}}$  can be determined. The results obtained from the modelling of Langmuir, Freundlich and Elovich isotherms are summarized in Table 1.

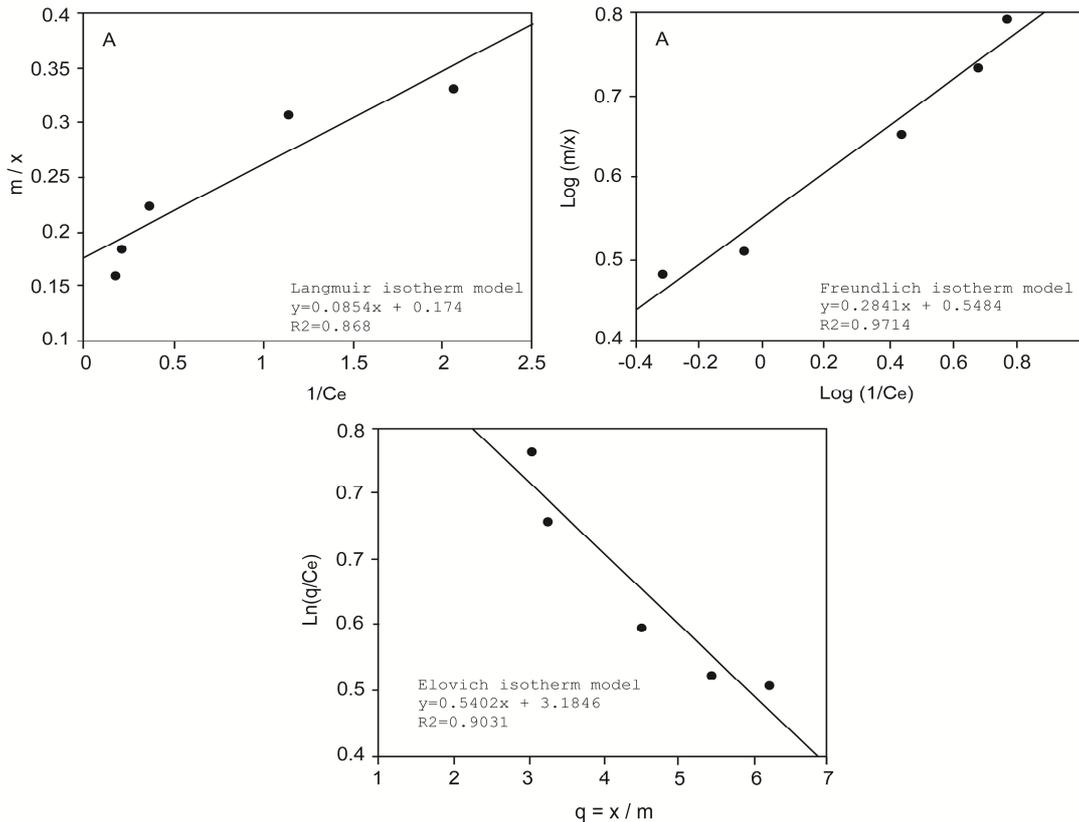


Figure 8. Langmuir, Freundlich and Elovich isotherm models.

Table 1. Parameters of Freundlich, Langmuir and Elovich isotherms.

Freundlich		Langmuir		Elovich	
b	k	$q_{\text{max}}$ (g.g-1)	B (L.g-1)	$q_{\text{max}}$ (g.g-1)	$K_e$
3.521	1.729	5.747	0.238	2.01	9.449

The application of the linearized forms of Freundlich, Langmuir and Elovich models confirms that the Freundlich's and Elovich's models are most suitable to describe the adsorption of copper ions on Acacia sawdust. Concerning the heterogeneity factor ( $n$ ), it is a measure of the affinity and capacity of each pair adsorbent / pollutant. Indeed, the effectiveness of an adsorbent is higher when the coefficient  $1/n$  is small [12]. The value of  $1/n$  is equal to 0,284, which indicates that the Acacia sawdust is significantly effective for the adsorption of copper ions. The maximum adsorption capacity  $q_{\text{max}}$  obtained in this study is 2.01  $\text{g}_{\text{Cu}^{2+}}/\text{g}_{\text{ads}}$  according to Elovich model.

**Removal of cupric ions from industrial effluents of faucets manufacturing**

Based on previous optimization test, we conducted an experiment to remove cupric ions from an industrial effluent of faucets manufacturing. The experiment was carried out on a sample of 100 mL of effluent diluted 10

times, with initial load of  $\text{Cu}^{2+}$  ions equal to  $60.32 \text{ g.L}^{-1}$ . We used 50 mg of Acacia sawdust with a particle size less than  $<80 \mu\text{m}$  which was stirred at a speed of 100 rev / min with 100 mL of effluent characterized by an acidic pH of 3.3. After 15 minutes of stirring, the solution was filtered. The amount of metal, which hasn't been eliminated, is determined by an indirect assay using the iodide ions and a calibrated sodium thiosulfate solution. The reduction of cupric ions in the effluent was 22% for the diluted solution. The low rate of  $\text{Cu}^{2+}$  ions reduction can be explained by the presence of other pollutants that compete and inhibit the adsorption of copper on the sawdust.

## Conclusion

In this work, the adsorption capacity of copper ions on sawdust Acacia was studied. The results indicate the following conclusions:

- The saturation of the adsorbent material was reached after 15 min of stirring.
- The adsorption was influenced by the physicochemical factors of the adsorbent, the effluent solution and the medium.
- The increase of cupric ions reduction rate was registered in an acidic medium with a decrease of load, particle size of Acacia sawdust, temperature and initial concentration of cupric ions in the solution.
- The stirring speed has almost no effect on the elimination of copper ions.
- The cupric ions adsorption follows Freundlich's and Elovich's isotherm models.
- The involved adsorption type is probably a non-specific physical adsorption leading to the formation of multilayers.

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