

## VALORIZATION OF LUFFA CYLINDRICA FOR WATER TREATMENTS COPPER CHARGERS. STUDY OF THE POSSIBILITY OF REGENERATION BY CHEMICAL DESORPTION

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### ABSTRACT

It is well known now that the various industries food generally produce large amounts of wastewater should be treated imperative for preserving the environment, thereby avoiding a real danger to the ecosystem.

These waters carry pollutants are usually organic in nature. This study was motivated by the fact that no quantitative study on the physico-chemical fibers of the luffa *Cylindrica*, hence the idea of using the retention by adsorption of contaminants.

Faced with the need for new material more efficient, economical biodegradable and produces no by-products more troublesome than the starting materials, using plant material for the disposal of these chemicals in aqueous effluents has received a significant credibility in recent years.

In the first step, we studied the kinetics of adsorption (static adsorption of the copper / fiber of *Luffa cylindrica*) using copper pollution model and method of analysis as UV spectrophotometry, the estimated surface specific (0.082 m<sup>2</sup>/g) proved too porous biomaterial, although its maximum adsorption capacity (0.101 mg/g) in optimal conditions is low. In the second step two comparative models (Langmuir and Freundlich) were tested for the adsorption isotherm obtained.

We completed this work by studying the possibility of regeneration (30.2 %) and reuse this material. For that several parameters have been optimized: the nature of the desorbent, its pH<sub>i</sub> (1.5), and the contents of *Luffa cylindrica* desorbed, hence the method and very promising for the treatment of water loaded with heavy metals.

It allows them to concentrate and get into a smaller volume. What makes the process more economical.

**Key words:** fiber of *Luffa Cylindrica*, biosorption, desorption, waste water treatment.

### 1 INTRODUCTION

The use of heavy metals in industry leads to increased release of toxic residues in the environment, the result is a significant danger to living organisms because of the accumulation of heavy metals into the food chain [1].

The recovery of these metals in water is inefficient or costly technique with conventional physico-chemical (precipitation, neutralization ...etc.

Faced with the need for new material more efficient, economical, biodegradable, use of plant material (*Luffa cylindrica*) for the

disposal of toxic products in aqueous effluents has received a significant credibility in recent years.

There are numerous in the literature study on plant fiber but very few are devoted to the study of fibers of the *Luffa Cylindrica*. Indeed, the *Luffa* is a plant of the gourd family, a fruit *cylindrica* slightly curved and angled right and very variable in size. The sponge-like structure, consisting of consolidated fibrous cord between them [2].

In this work, we consider in the first stage of adsorption kinetics of a copper / fiber to determine the equilibrium constant of

adsorption, in a second step two comparative models (Langmuir model and Freundlich) were tested for the adsorption isotherms obtained.

We later studied the possibility of regeneration of this material. For that several parameters were optimized: the nature of desorbent, pH ...etc.

This study is completed by the determination of the new biosorption capacity after regeneration of the material.

## 2 MATERIALS AND METHODS

Adsorption is influenced by the adsorbent and the adsorbate related parameters which are, pore size distribution and specific surface area, molecular structure, polarity of solution and size of ions or molecules.

Many theories have attempted to develop the existing relationship between the quantity adsorbed and the amount adsorbed at equilibrium.

### 2. 1. Langmuir Model

In this model one consider that the solid surface is homogenous and that the adsorbed molecules do not interact between them and they can form at most a single layer of molecules on the surface of the solid (adsorbed phase forms a monolayer Molecular) [3].

If one consider  $\theta$  fraction of the surface covered by adsorbed molecules and  $(1-\theta)$  the uncovered portion. The net amount accumulated during the adsorption and desorption is written:

$$\frac{dq}{dt} = k_a(1-\theta)C_e - k_d\theta \quad (1)$$

At equilibrium  $\frac{dq}{dt} = 0$ , the above equation becomes

$$\theta = \frac{k_L C_e}{1 + k_L C_e} \quad (2)$$

With  $(k_L = \frac{k_a}{k_d})$  is the equilibrium constant of

adsorption was  $\theta = \frac{q}{q_m}$

$$\frac{q}{q_m} = \frac{K^L C_e}{1 + K^L C_e} \quad (3)$$

q: Amount of solute adsorbed per unit mass of adsorbent (mg/g).

$q_m$ : Maximum capacity of adsorption (mg/g).

$C_e$ : The concentration of solute in the liquid phase at equilibrium (mg/l).

$K_L$ : The equilibrium constant of Langmuir [4].

The linearization of the Langmuir equation can deduct the ultimate capacity ( $q_m$ ) and constant  $k_d=1/K^L$ , this linearization is given by the following equation:

$$\frac{1}{q} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (3. a)$$

### 2. 2. Freundlich Equation

The Freundlich equation is strictly empirical or theoretical basis and without the adsorbed amount is a power law for pressure and gas concentration for liquids [5, 6].

$$q = k_F C_e^{\frac{1}{n}} \quad (4)$$

The linearization of equation (4) is written as

$$\log(q) = \log k_F + \frac{1}{n} \log C_e \quad (4. a)$$

$K_F$  and  $n$  are constants related to the couple adsorbate / adsorbent at a given temperature kept constant during the experiment; generally  $n$  takes the values going from 0.8 to 2.

### 2. 3. Analysis of Samples

Introduced 1g of material being cut into small pieces in solutions of different initial concentration of  $CuSO_4$  for a period of three hours. During all the experiments and precise time, 10ml of samples are filtered using paper Wathman N°6 then analyzed using a UV spectrophotometry.

## 3. REULTATS AND DISCUSSION

### 3. 1. Estimation of Specific Surface

The specific surface of our biosorbent was estimated by the technique of adsorption of methylene blue at concentrations below 7 micromolar as shown in figure 1.a and 1.b.

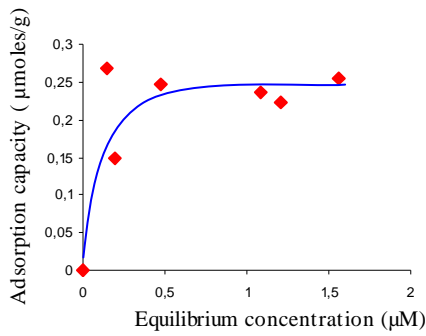


Figure 1a. Adsorption Isotherm of Methylene blue On Luffa Cylindrica

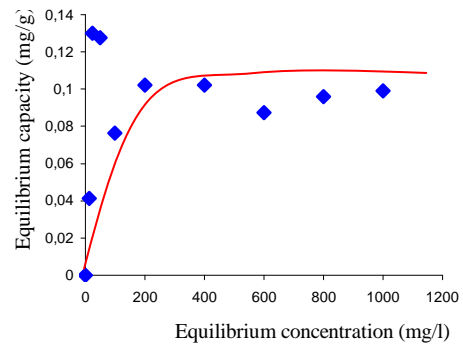


Figure 2a. Isothermal Adsorption of Copper on the Luffa Cylindrica

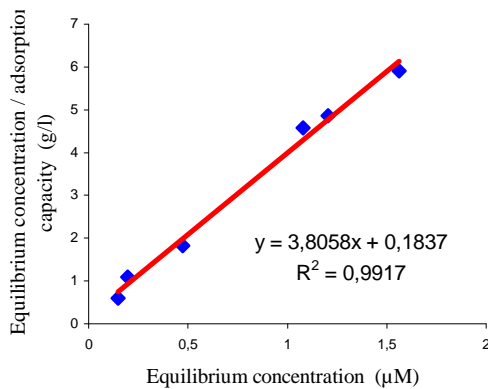


Figure 1.b. Transform for Linear Langmuir Biosorption of Blue on Mythylène Luffa Cylindrica

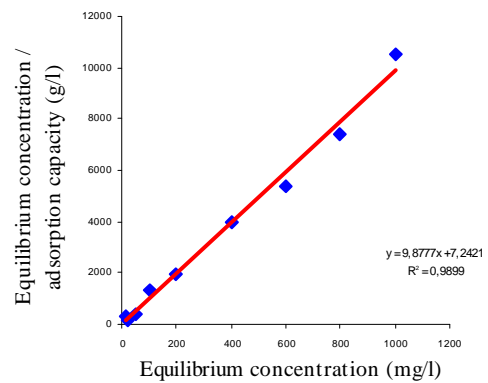


Figure 2b. Linear Transform for the Langmuir Biosorption of Copper on Luffa Cylindrica

### 3. 2. Biosorption of Copper

The isotherm corresponding to the adsorption of copper on the Luffa Cylindrica, is represented by varying the amount of metal adsorbed per gram of biosorption ( $q$ ) versus the equilibrium concentration ( $C_e$ ) for different initial concentrations, figure 2.a.

The isotherm is of type (I) expressing a monolayer adsorption to saturation of sites. The Langmuir model is more representative to describe the biosorption of  $\text{Cu}^{2+}$  on Luffa Cylindrica since its correlation coefficient  $R^2$  is 0.9899 while that of Freundlich model is 0.9385 as shown in figure 2.b and 3.

This is explained by the fact that the specific surface of our biosorbent ( $0.0827 \text{ m}^2/\text{g}$ ) is smaller, it is enough simply to apply an optimum pH maintained equal to 5.

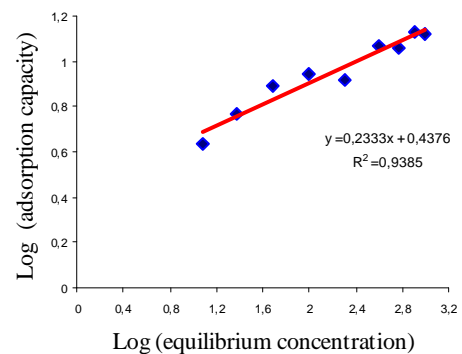


Figure 3. Transform for Linear Freundlich Biosorption of Copper on Luffa Cylindrica

### 3. 3. Desorption of Copper

*The nature of the desorbing:* the results obtained are shown in figure 4.

The desorption of copper seems to be instantaneous. We also note that the hydrochloric acid concentration reaches a higher desorption ( $0.63 \text{ mg/l}$ ) compared to nitric acid ( $0.23 \text{ mg/l}$ ) and sulfuric acid ( $0.30 \text{ mg/l}$ ).

The hydrochloric acid provides a maximum refresh rate of 11.31% compared to other acids. For this, we can say that hydrochloric acid is the optimum desorbent.

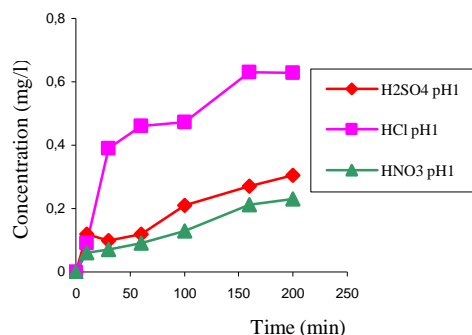


Figure 4. Influence of The Nature of the Desorbent

**The initial pH of the desorbing:** the desorbent used is hydrochloric acid at different initial pH, we observe that the pH1 give better desorption with an average regeneration rate 11.31%, figure 5.

At low pH the major linkage groups (carboxyl nature) resumed their protons, the electrostatic bonding, anionic site  $\text{Cu}^{2+}$  is broken and freeing the metal cations in the middle (which explains the increase in pH during the desorption, figure 6).

By comparing the appearance of materials to pH1, pH1,5 and pH3 we noticed that the structure of the latter degrades with decreasing pH. To minimize losses, we have excluded the pH1. A pH1,5 is chosen as the optimum, it is a compromise between the quality of desorption (obtained with a pH1) and the quality of the material (obtained with pH3). In addition, the pH can easily increase and reached the pK (COOH) at pH3; desorption yield will be reduced [7, 8].

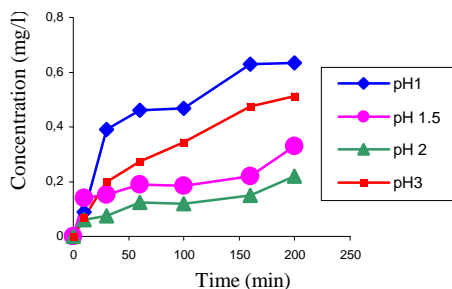


Figure 5. Optimization of pH of Desorbing

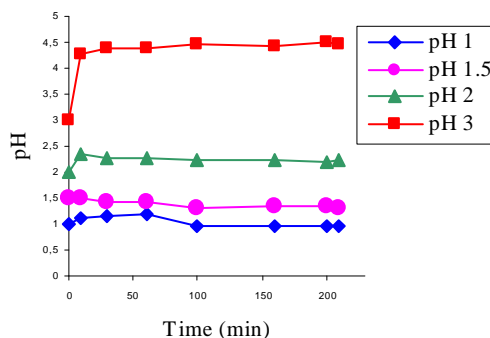


Figure 6. Evaluation of pH During the Desorption at Different Initial pH

**Content loaded material:** it must be remembered that the purpose of this part is to minimize waste by taking the maximum desorbing possible Luffa Cylindrica charged. The experiments were carried out taking into account previously set (HCl, pH1.5).

However, the cost of desorption in this case is very important. In addition, we generate volumes of acid greater than the volume of treated waste water desorbed by the material.

For contents material 18 g/l and 22 g/l, the regeneration rates are 28.32% and 30.2% respectively. Taking into account these economic and environmental imperative, we opted for the largest possible content of material that does not create problems of agitation (18 g/l and 22 g/l), figure7

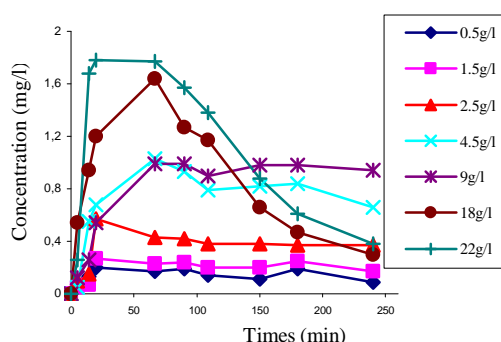


Figure 7. Optimization of Content Material to be Desorbed at pH = 1.5

### 3. 4. Study of the Adsorption Isotherm after a Cycle of Adsorption - Desorption

To judge the usefulness of desorption to the following conditions (HCl, pH1.5), construction (Material=22 g/l), we have made

an adsorption isotherm after a cycle of adsorption-désorption. The results are shown in figures 8, 9 and 10.

The isotherm is always of type (I) expressing a point of saturation monolayer adsorption sites, figure 8 [9].

Using the linear transformation of Langmuir and Freundlich, we obtained the following results:

The Langmuir model is still more representative in describing the biosorption of  $\text{Cu}^{2+}$  on *Luffa Cylindrica* regenerated, because its correlation coefficient  $R^2$  is 0.9075 while that of Freundlich model is 0.7872, figure 10.

The regenerated material has a maximum capacity of adsorption smaller than that recorded by the native material. A cycle of adsorption-desorption of the material lost 30% of its adsorption capacity. These results confirm once again the futility of treating the material [9].

We note also a decrease in the dissociation constant resulting in an increase in affinity. The desorption at acidic pH could make the material more hydrophilic which increases  $\text{Cu}^{2+}$ -material.

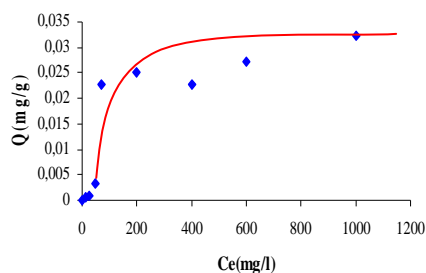


Figure 8. Adsorption Isotherm of Copper on *Luffa Cylindrica* after Regeneration

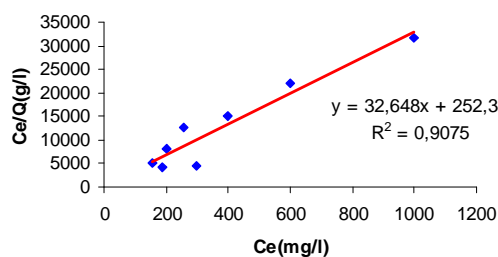


Figure 9. Transformed Linear for Langmuir Biosorption of Copper on *Luffa Cylindrica* Regenerated

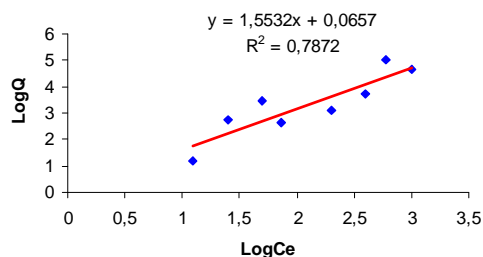


Figure 10. Transform for Linear Freundlich Biosorption of Copper on *Luffa Cylindrica* Regenerated

#### 4. CONCLUSION

The aim of our study is to develop a material that is *Luffa Cylindrica* and performance of removing heavy metals (copper) in industrial wastewater by adsorption.

The estimation of specific surface area proved too porous biomaterial, although its maximum adsorption capacity under optimal conditions is low.

The desorption is possible in the following conditions:

- Hydrochloric acid is the optimum desorbent

The optimization of the content material to desorb took into account economic and environmental imperative. The rate of regeneration remains unsatisfactory (30.2% for the content of 22g/l).

However, they can be improved by coupling the chemical desorption method with a recovery of copper

The regenerated material for a grade of 22g/l, has a maximum capacity of adsorption smaller but still significant 0.03mg/g, a cycle of adsorption desorption lose the biomaterial 30% of its adsorption capacity.

The method and very promising for treatment of water loaded with heavy metals. It allows them to concentrate and get into a smaller volume which makes the process more economical.

Finally, the prospects we believe that further study may be undertaken on the effect of *Luffa Cylindrica* for industrial wastewater treatment.

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