

## **REMOVAL OF COPPER IONS FROM AQUEOUS SOLUTIONS BY DRIED ACTIVATED SLUDGE**

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### **ABSTRACT**

In the present work, the usefulness of dried activated sludge has been investigated for the removal of copper ions from aqueous solutions. Kinetic data and equilibrium sorption isotherms were measured in batch conditions. The influence of initial pH, metal concentration and copper salt nature on the metal removal kinetics has been studied. Copper uptake was time contact, initial copper concentration, initial pH solution and copper salt type dependent. Maximum copper sorption was found to occur at around pH 5.5-6.0. Three simplified kinetic models including a pseudo first-order equation, pseudo second-order and second-order equations were selected to follow the sorption process. The process follows a pseudo second – order kinetics. Langmuir and Freundlich models were used to describe sorption equilibrium data at natural initial pH of solution. Results indicated that the Langmuir model gave a better fit to the experimental data than the Freundlich equation. Maximum copper uptake obtained was  $q_m = 62.50$  mg/g (0.556 mmol/g) at natural pH of solution.

**KEY WORDS:** removal, biosorption, copper, activated sludge.

### **INTRODUCTION**

The presence of heavy metals in the aquatic environment is a source of great environmental concern. Conventional techniques, such as chemical precipitation, ion exchange, activated carbon adsorption, etc., membrane separation processes have limitations for the removal of heavy metals from wastewater. They become inefficient and expensive especially when the heavy metal concentration is less than 100 ppm. (Leusch et al. [1], Yan and Viraraghavan [2], Rangsayatorn et al. [3]). Copper is known to be one of the heavy metals most toxic to living organisms and it is one of the more widespread heavy metal contaminants of the environment (Özer et al. [4], Dönmez and Aksu [5]). The potential sources of copper in industrial effluents include metal cleaning and plating baths, pulp, paper board mills, wood pulp production, the fertilizer industry, etc. The conventional methods of copper (II) removal from wastewaters are precipitation, ion exchange, electrolysis, adsorption on activated carbon, etc (Özer et al. [4]). This situation has in recent years led to a growing interest in the application of biomaterials technology for removal of trace amounts of toxic metals from dilute aqueous wastes.

Biomaterials including algae, bacteria, fungi, higher plants, and products derived from these organisms, have been demonstrated to remove certain chemical species (Singh et al. [6], Yin and Blanch [7], Sadowski et al. [8]). The general term "Biosorption" has been used to describe a property of microorganisms to retain toxic heavy metals from aqueous solutions (Corder and Reeves [9]). Very little information (Gourdon et al. [10], Atkinson et al., [11], Tsezos and Volesky [12], Gourdon et al. [13,14], Tien and Huang [15]) are available for heavy metals biosorption from aqueous solutions by activated sludges in the literature.

The objective of this work is to obtain the basic information to the design of sorption equipment, i.e. kinetic data and equilibrium in batch system. In this work, biosorption of copper from aqueous solutions, by dried activated sludge in single metal solutions was investigated in a well-stirred batch reactor. Kinetic experiments were performed at various contact time, initial metal concentration, initial pH and copper salt nature. The sorption equilibrium data were described by typical Langmuir and Freundlich sorption equations. Three simplified kinetic models including a pseudo first-order equation, pseudo second-order and second-order equations were selected to follow the sorption process

## **MATERIALS AND METHODS**

### **1. Sorbent Material and Metal Ion**

Dried Activated sludge (a mixed microbial community) from a conventional biological wastewater treatment plant in our region (Maghnia - Algeria), in the form of large flakes having a 0.2-5.0 mm particle size, was used throughout this work without any preliminary purification.

Copper solutions of desired concentration were prepared from  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Windor Laboratories Limited), by dissolving the exact quantities of copper salts in distilled water. All chemicals were commercial products used without purification.

### **Sorption Kinetics**

The initial solution metal concentration was 100 mg/L for all experiments except for that carried out to examine the effect of the initial concentration of copper. For metal removal kinetics studies, 0.6 g of dried activated sludge was contacted with 0.3 L of metal solutions in a beaker agitated vigorously by a magnetic stirrer using a water bath maintained at a constant temperature of 25°C. In all cases, the working pH was that of the solution and was not controlled. The residual copper concentration in the aqueous solution at appropriate time intervals, was obtained by using a  $\text{Cu}^{2+}$ - ion selective electrode technique. Based on the ready availability of this electrode in our laboratory, this method was chosen. The electrode used for measurement of copper was Orion Model 9448 and was used in conjunction with Orion Model reference electrode and an Orion Model 710A meter, which provided readings accurate to  $\pm 0.1$  mV. For the measurement of pH, an Orion Model 9107 combination electrode, with the

aforementioned meter, was used. pH readings were monitored to + 0.01 unit. The Cu<sup>2+</sup> - ISE calibration curve was Nernstian in the entire working range of this study, and periodically, electrode was recalibrated. For certain experiments, this copper concentration was also done using a Perkin Elmer Model 2280 atomic absorption spectrophotometer. No differences in the results obtained by these two methods of analysis were. The metal uptake  $q$  (mg ion metal/g dried activated sludge) was determined as follows:

$$q = (C_0 - C_t) \times V/m$$

where  $C_0$  and  $C_t$  are the initial and final metal ion concentration (mg/L), respectively,  $V$  is the volume of solution (mL), and  $m$  is dried activated sludge weight (g) in dry form.

To study the influence of pH of copper solution, the initial pH value was varied within the range 3-6 to avoid metal solid hydroxide precipitation. Initial pH was adjusted to the required value by adding 0.1 M HCl or 0.1 M NaOH.

Blanc runs, with only the sorbent in 100 mL of distilled water, were conducted simultaneously at similar conditions to understand the pH change of solution during sorption experiments. Blanks were also run simultaneously, without any sorbent to determine the impact of pH change on the metal solution.

Preliminary experiments had shown that cadmium adsorption losses to the container walls were negligible

## **2- Sorption Isotherm**

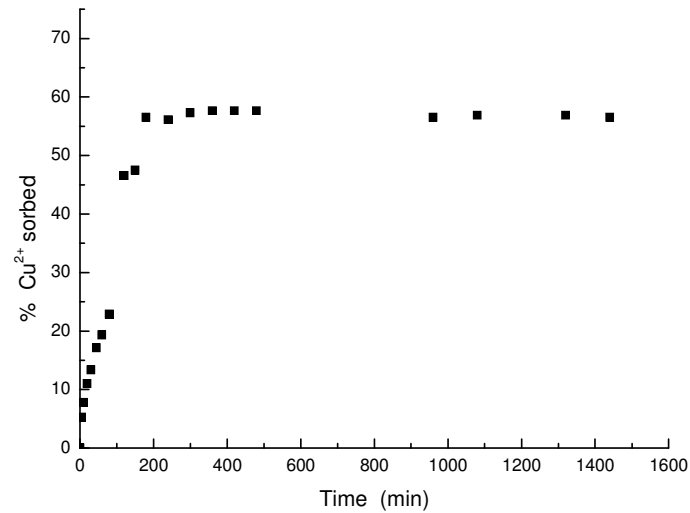
The equilibrium isotherm was determined by contacting a constant mass (0.2 g) of activated sludge with a range of different concentrations of copper solutions. Activated sludge and copper solution were agitated in a series of 250 ml conical flasks with equal volumes of solution (100 ml) for a period of 24 hours at room temperature. The contact time was previously determined by kinetics tests using the same conditions. The reaction mixture pH was not controlled after the initiation of experiments. After shaking the flasks for 24h, the final pH was measured. The final concentration of unbound copper was obtained by using a Cu<sup>2+</sup>- ion-selective electrode (Cu-ISE) technique and the copper loading by activated sludge calculated.

## **RESULTS AND DISCUSSION**

### **1 - Uptake Kinetics of Metal**

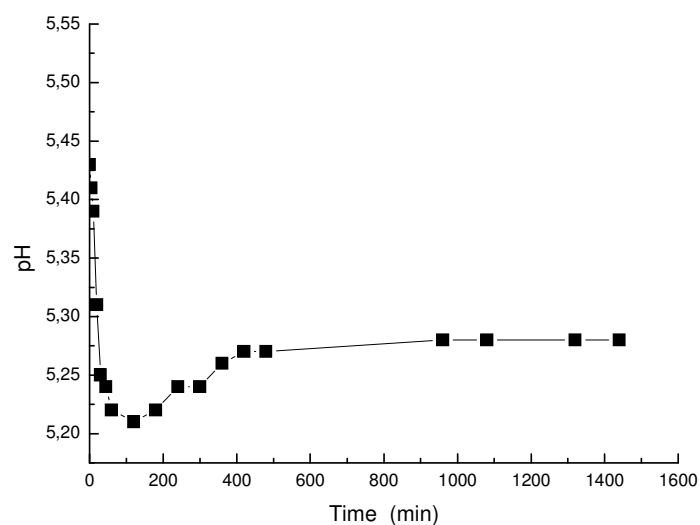
A preliminary experiment was performed to determine the steady-state equilibrium time. According to the Figure1 obtained for an initial copper initial 100 mg/L, the kinetics of copper removal by a dried activated sludge presents a shape characterized by a strong increase of the amount of cadmium sorbed during the first minutes of contact solution – activated sludge, follow-up of a slow increase until to reach a state

of equilibrium. As an approximation, the removal of copper ions can be said to take place in two distinct steps: a relatively fast one followed by a slower one. The necessary time to reach this equilibrium is about 3 hours and an increase of removal time to 24 hours doesn't show notable effects. At equilibrium, about 60% of initial copper solution was removed by dried activated sludge.



**Figure 1: Kinetics of copper biosorption by a dried activated sludge at  $C_0=100$  ppm.**

During the course of copper removal by dried activated sludge, we noticed an evolution in the value of the initial pH of the solution presented in Figure 2. This can be interpreted by a competition between copper ions and  $H_3O^+$  for binding sites.



**Figure 2: pH profile of copper biosorption by a dried activated sludge**

The kinetics of copper sorption by dried activated sludge can be modelled using by the first-order rate equation of Lagergren [16], the pseudo-order rate equation (Ho [17]) and the second order rate equation shown below as Eqs.(1)-(3), respectively:

$$\log(q_e - q_t)/q_e = -K_L t / 2.3 \quad (1)$$

$$t/q_t = 1/2K'q_e^2 + t/q_e \quad (2)$$

$$1/(q_e - q_t) = 1/q_e + kt \quad (3)$$

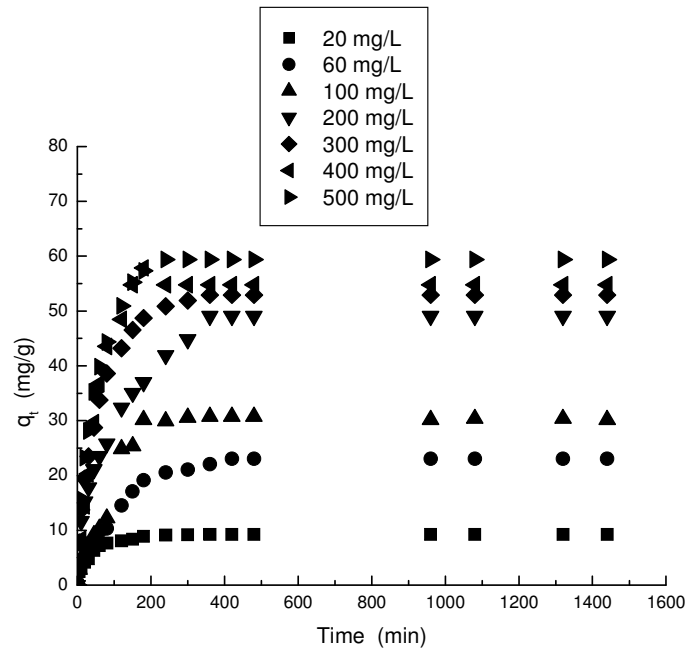
where  $K_L$  is the Lagergren rate constant of sorption ( $\text{min}^{-1}$ );  $K'$  the pseudo second-order rate constant of sorption ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ) and  $k$  the rate constant ( $\text{g.mg}^{-1}.\text{min}^{-1}$ );  $q_e$  and  $q_t$  are the amounts of dye sorbed ( $\text{mg.g}^{-1}$ ) at equilibrium and at time  $t$ , respectively. For an initial copper concentration of 100 mg/L, the different values of constants from the slopes and intercepts of linear plots of  $\log(q_e - q_t)/q_e$  vs.  $t$ ,  $t/q_t$  vs.  $t$  and  $1/(q_e - q_t)$  vs.  $t$  (Figures non shown presented here) are summarized in the Table 1. Only, the pseudo second –order reaction rate model adequately described the kinetics of copper sorption with high correlation coefficient ( $R^2 > 0.986$ ): consequently, it was used to describe all the kinetics of copper sorption by dried activated sludge.

**Table 1: Models rate constants for copper biosorption kinetics by dried activated sludge at  $C_0=100$  mg/g**

$K_L \cdot 10^3$ ( $\text{min}^{-1}$ )	$R^2$	$K' \cdot 10^4$ ( $\text{g.mg}^{-1}.\text{min}^{-1}$ )	$R^2$	$k \cdot 10^3$ ( $\text{g.mg}^{-1}.\text{min}^{-1}$ )	$R^2$
17.18	0.934	2.53	0.986	11.89	0.670

## 2. Effect of Initial Copper Concentration

Several experiments were also undertaken to study the effect of varying the initial copper concentration on the copper removal kinetics from solution. The results obtained are shown in Figure 3, and indicate that the obtained curves have the same shape. From the results obtained at equilibrium and presented in Table 2, the necessary time to reach equilibrium is variable and initial copper concentration dependent: it was in the range of 3-7 h. We also notice that the capacity of copper removal at the equilibrium increases with the initial copper concentration.



**Figure 3: Effect of initial copper concentration on the kinetics of copper biosorption by a dried activated sludge**

**Table 2: Experimental results obtained at equilibrium from the kinetics of copper biosorption by dried activated sludge at different initial cadmium concentrations**

$C_0$ (mg/L)	20	60	100	200	300	400	500
pH <sub>e</sub>	6.26	5.51	5.28	5.17	5.12	5.04	4.98
t <sub>c</sub> (min)	300	420	180	360	360	150	240
q <sub>e</sub> (mg/g)	9.21	23.02	30.16	49.08	52.92	54.79	59.41

During the phenomenon of copper removal, we also noticed an increase of the initial pH of the solution for all studied concentrations (figures not shown here), without just reaching the pH value of copper precipitation.

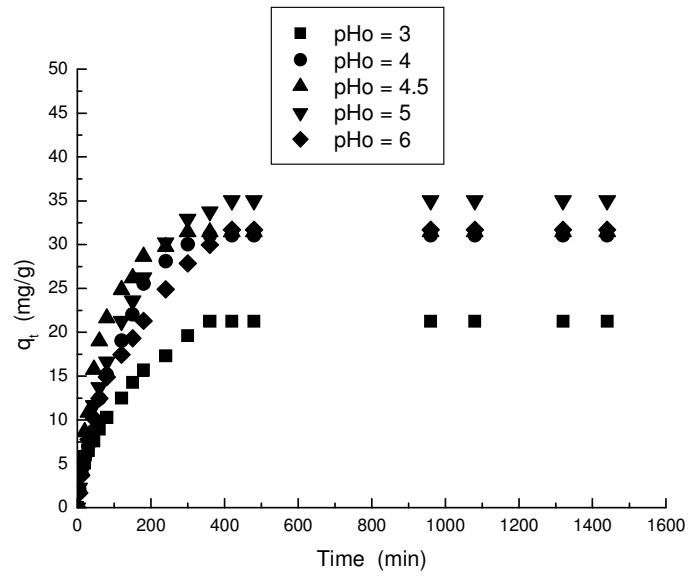
When the previous data were only fitted to the pseudo second-order rate equation, straight lines (Fig. not shown here) were obtained with high correlation coefficients ( $R^2 > 0.99$ ) indicating that the process follows a pseudo second-order kinetics. The equilibrium biosorption capacity,  $q_e$ , increases with an increase in the initial copper concentration (see Table 3). The values of  $q_e$  obtained from the fitting to the pseudo second-order reaction rate model are very similar to the experimental values obtained from the sorption kinetics at equilibrium.

**Table 3: Pseudo second-order rate constants for copper sorption kinetics by dried activated sludge: Effect of initial copper concentration.**

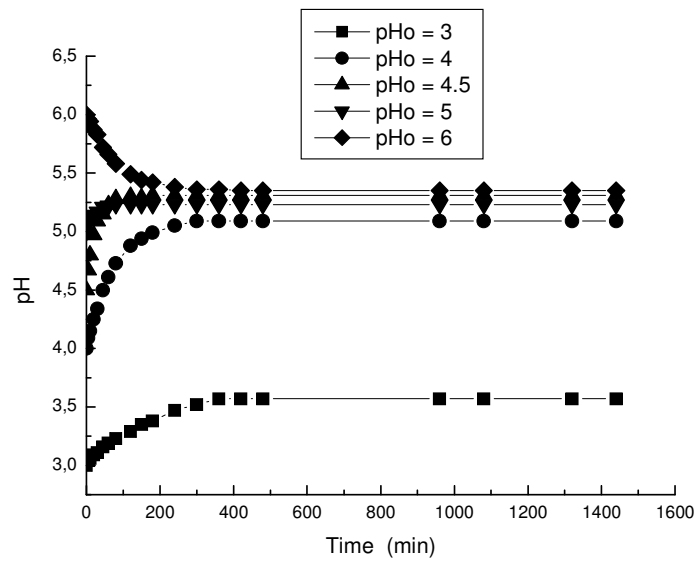
$C_0$ (mg/L)	$q_e$ (mg/g)	$K'.10^4$ ( $\text{min}^{-1} \cdot \text{g} / \text{mg}$ )	$R^2$
20	9.35	34.19	1
60	24.37	3.25	0.997
100	32.18	2.53	0.993
200	51.84	1.52	0.986
300	54.29	3.45	1
400	56.43	3.08	0.998
500	60.72	3.76	0.999

### 3. Effect of Initial pH

As shown in Fig. 4, initial pH of copper solution has an influence on the kinetics of copper biosorption by dried activated sludge. From the Table 4, the necessary time to reach equilibrium is initial pH dependent: it was in the range of 6-7 h. We also notice that the capacity of copper removal at the equilibrium increases with the initial pH. Fig. 5 shows the amount of copper sorbed  $q_e$  at equilibrium for an initial copper concentration of 100 mg/L, against initial pH of solution. As can be seen, the copper uptake is dependent on pH. Other authors found the same trend for copper adsorption ([Vallaescusa et al., [18]), metal removal increases when pH increases. The fact can be explained by competition between the proton and metal cation for surface sites at low pH. In addition, as the pH is increased there is a decrease of positive surface charge which results in a lower coulombic repulsion of the sorbing metal ions. The pH can also influence the speciation of metal ions and distribution diagrams of copper species as a function of pH show that only cationic species ( $\text{Cu}^{2+}$ ,  $\text{Cu}(\text{OH})^+$ ) are present in solution over the range studied. (Vallaescusa et al. [18]).



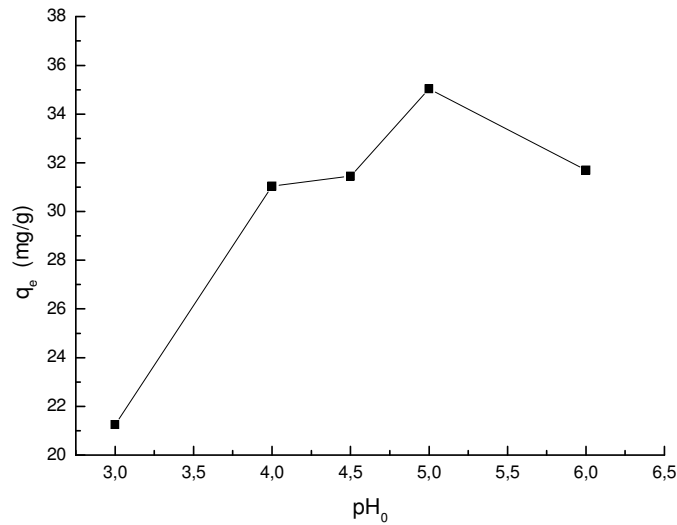
(a)



(b)

Figure 4: Effect of initial pH on the kinetic of copper biosorption by dried activated sludge at  $C_0 = 100$  mg L. (a)  $q_t = f(t)$ ; (b)  $pH = f(t)$





**Figure 5: Copper uptake by dried activated sludge as a function of initial pH.  
Co = 100 mg/L**

**Table 4: Experimental results obtained at equilibrium from the kinetics of copper biosorption by dried activated sludge: Effect of initial pH.**

<b>pH<sub>0</sub></b>	3	4	4.5	5	6
<b>pH<sub>e</sub></b>	3.57	5.09	5.31	5.23	5.35
<b>t<sub>e</sub> (min)</b>	360	360	300	420	420
<b>q<sub>e</sub> (mg/g)</b>	21.25	31.04	31.45	35.03	31.70

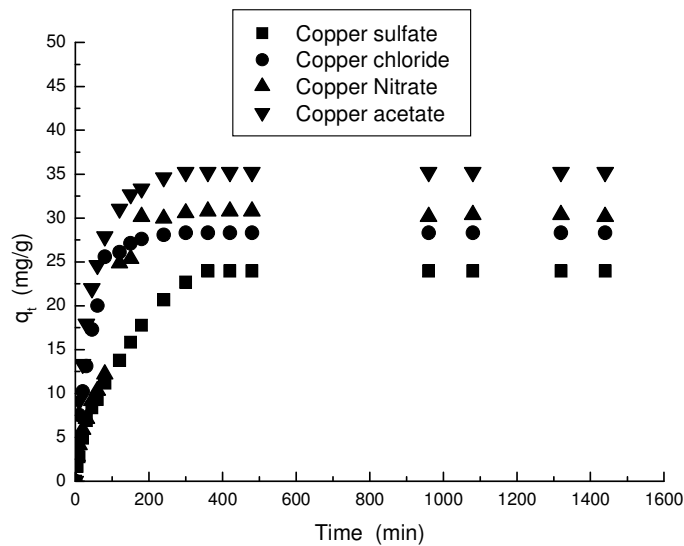
As shown in Table 5, the kinetic data of copper biosorption are good described by the pseudo second-order rate equation with high regression coefficient ( $R^2 > 0.996$ ).

**Table 5: Pseudo second-order rate constants for copper biosorption kinetics by dried activated sludge: Effect of initial pH.**

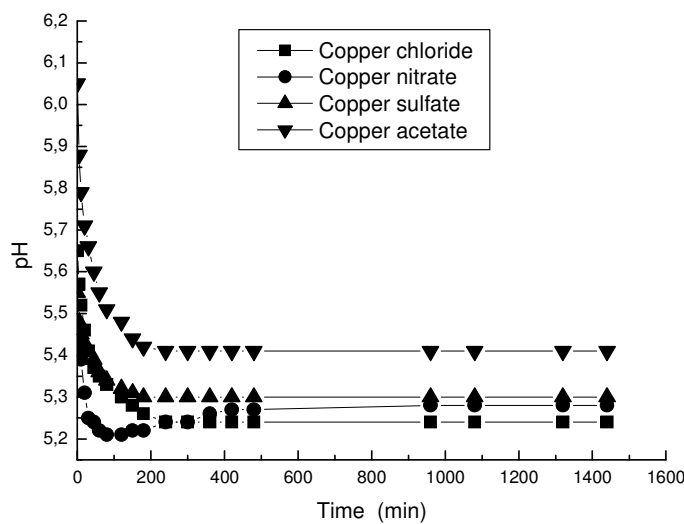
pH <sub>0</sub>	q <sub>e</sub> (mg/g)	K'.10 <sup>4</sup> (min <sup>-1</sup> .g / mg)	R <sup>2</sup>
3	22.55	3.34	0.997
4	33.27	2.03	0.996
4.5	32.70	3.81	0.999
5	37.69	1.65	0.997
6	34.34	1.60	0.997

### 4. Effect of Copper Salt

Fig.6a and Table 6, shows that the nature of copper salt used influences the capacity of copper biosorbed at equilibrium and the time required to reach equilibrium. As mentioned above, the same phenomenon in the initial pH variation during the sorption experiment was observed (see Fig. 6b)



(a)



(b)

**Figure 6: Effect of the nature of copper salt on the kinetics of copper biosorption by dried activated sludge at  $C_0 = 100 \text{ mg L}$ . (a)  $q_t = f(t)$ ; (b)  $\text{pH} = f(t)$**

**Table 6. Experimental results obtained at equilibrium from the kinetics of copper biosorption by dried activated sludge: Effect of copper salt nature**

<b>Copper salt</b>	<b>Copper nitrate</b>	<b>Copper acetate</b>	<b>Copper chloride</b>	<b>Copper sulfate</b>
pH <sub>e</sub>	5.28	5.41	5.24	5.30
t <sub>e</sub> (min)	300	300	240	360
q <sub>e</sub> (mg/g)	30.77	35.22	28.31	23.94

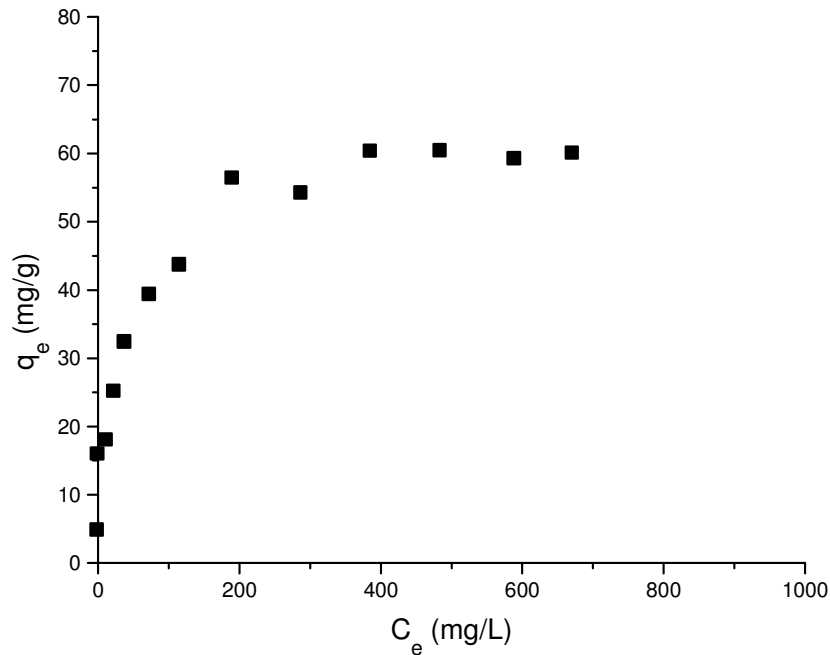
When these data were only fitted to the pseudo second-order rate equation (Fig. not shown here), straight lines were obtained indicating that the process follows a pseudo second-order kinetics. The constants obtained are summarized in the Table 7. The correlation coefficients are greater than  $R^2 = 0.99$ . The calculated q<sub>e</sub> values also agree very well with the experimental data. These confirm that the kinetic data obtained follows the pseudo-second kinetic model. A variation in the rate constants value was observed according to the nature of copper salt used.

**Table 7: Pseudo second-order rate constants for copper biosorption kinetics by dried activated sludge: Effect of copper salt nature**

<b>Copper salt</b>	<b>q<sub>e</sub> (mg/g)</b>	<b>K'.10<sup>4</sup> (min<sup>-1</sup>.g / mg)</b>	<b>R<sup>2</sup></b>
Copper nitrate	32.18	2.53	0.993
Copper acetate	35.95	6.77	1
Copper chloride	28.86	9.05	0.999
Copper sulfate	25.63	2.61	0.997

## EQUILIBRIUM OF SORPTION

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. These data provide information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions (Özacar [19, 20]). Figure 7 shows the sorption isotherm (q<sub>e</sub> versus C<sub>e</sub>) of copper by dried activated sludge at natural pH of solutions. Sorption is of Langmuir's type according to the classification of Brunauer et al. [21] and of L type according to the classification of Giles [22]. From the graph of this isotherm, the maximum capacity of copper removal by activated sludge is about 60 mg/g.



**Figure 7: Isotherm of copper biosorption by a dried activated sludge**

During experiments of sorption equilibrium, it was observed that the initial pH of the solution increased slightly and equilibrium pH varied with the initial concentration. This can be interpreted by a competition between cadmium ions and  $H_3O^+$ . As a result of the competition among cadmium ions and  $H_3O^+$  ions, only some of superficial groups of activated sludge become available to cadmium ions for sorption.

In order to optimise the design of a sorption system to remove pollutant from effluents, it is important to establish the most appropriate correlation for the equilibrium curve. Two isotherm equations have been tested in the present study, namely, Langmuir [23] and Freundlich [24]. This modelling permits us to determine the maximal capacity of removal. The quality of the isotherm fit to the experimental data is typically assessed based on the magnitude of the correlation coefficient for the regression; i.e. the isotherm giving an  $R^2$  value closest to unity is deemed to provide the best fit. The Langmuir model has the form:

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

and the Freundlich model has the form:

$$q_e = K C_e^n \quad (5)$$

where:  $q_e$  is the amount of metal ion sorbed at equilibrium per g of sorbent (mg/g);  $C_e$  the equilibrium concentration of metal ion in the solution (mg/L);  $q_m$  and  $b$  are the Langmuir model constants;  $K$  and  $n$  the Freundlich model constants. If the equation of Langmuir is valid to describe our experimental results, it must verify the linearized

shape of the basis equation, in system of coordinates  $C_e/q$  vs.  $C_e$ , that will permit us to obtain the constants  $q_m$  and  $b$  from the intercept and slope. If the equation of Freundlich is also verified, we must obtain a right in the system of coordinates  $\ln q_e$  vs.  $\ln C_e$ , the slope and the intercepts to the origin give  $n$  and  $k$  respectively. From results obtained (Fig. no shown here), it appears that the Langmuir model best fits the experimental results over the experimental range with good coefficients of correlation. The model parameters determined by least squares fit of the experimental sorption data are :  $q_m = 62.50$  mg/g (0.556 mmol/g),  $b = 0.037$  L/mg ( $R^2 = 0.996$ ) . According to coefficients of correlation  $R^2 = 0.900$  obtained with  $K = 12.62$  and  $n = 0.253$ , we deduct that the model of Freundlich is not adequate for modelling the isotherm of removal of cadmium by chitin in all the studied concentration domain.

The applicability of these models should be considered as a mathematical representation of the sorption equilibrium over a given metal-ion concentration range. The mechanistic conclusions from the good fit of the models alone should be avoided. In spite of the above limitations, these models can provide information on metal-uptake capacities and differences in metal uptake between various species (Kapoor and Viraraghavan [25]).

Copper uptake by alternative sorbents has been widely studied. Among these materials, are *Rhizopus arrhizus* (Sag et al., [26]), sunflower stalks (Sun et al., [27.], pine bark (Al-Asheh and Duvnjak [28], apple waste (Lee and Yang [29], grape stalks wastes (Villaescusa and Fiol [30]). In these studies carried out at pH 4.0 except that grape stalks at pH 6 uptakes of 0.53, 0.46, 0.15 and 0.17 mol Cu kg<sup>-1</sup> dry material, respectively, were reported and  $1.59 \times 10^{-4}$  mol/g at pH=6.

## CONCLUSION

The results obtained confirm that activated sludge can remove copper ions from aqueous solution. The sorption performances are strongly affected by parameters such as : initial pH of solution, initial concentration of copper ion, initial pH. The amount of copper removed by activated sludge increased with the increase of these parameters at a specific time. The biosorption process followed a pseudo second - order rate kinetics. Theoretical Langmuir and Freundlich isotherms were compared with experimental data and a good fitting was obtained with Langmuir model in all the range of concentrations studied. However, further work should include performing experiments for making different analysis in order to better understand metal binding mechanism.

## Acknowledgements

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