

PRELIMINARY STUDY ON COPPER IONS REMOVAL FROM SYNTHETIC AQUEOUS SOLUTIONS USING HARD ALMOND PEEL AS A LOW-COST MATERIAL

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ABSTRACT

In the present work, the usefulness of hard almond peels for the removal of copper ions from aqueous synthetic solutions has been investigated. Kinetic data and equilibrium sorption isotherm were measured in batch conditions. The influence of some parameters such as: contact time and initial copper ions concentration on copper ions sorption kinetics has been studied. Copper uptake was time contact and initial copper concentration dependent. Two simplified kinetic models including a first-order rate equation and a pseudo second-order rate equation were selected to describe the metal sorption kinetics. The process followed a pseudo second – order rate kinetics. The sorption process mechanism was found to be complex, consisting of external mass transfer and intraparticle mass transfer diffusion. Copper sorption process was particle-diffusion-controlled, with some predominance of some external mass transfer at the initial stages for the different experimental parameters studied. Langmuir and Freundlich models were used to describe sorption equilibrium data at natural pH of solution. Results indicated that the Langmuir model gave a better fit to the experimental data than the Freundlich model. Maximum copper uptake obtained was $q_m=78.25$ mg/g (1.231 mmol/g) under the investigated experimental conditions.

Keywords: Removal, sorption, copper ions, hard almond peel, kinetics, equilibrium, modeling

INTRODUCTION

The presence of heavy metals in the aquatic environment is a source of great environmental concern. 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 (Dönmez and Aksu, 1999; Özer et al., 2004). The potential sources of copper in industrial effluents include metal cleaning and plating baths, electrical industry, chemical catalysis, 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., 2004; Ulmanu et al., 2003) They become inefficient and expensive especially when the heavy metal concentration is less than 100 ppm. (Leusch et al., 1995; Rangsayatorn et al., 2004; Yan and Viraraghavan, 2001). This situation has in recent years led to the search of alternative low cost adsorbents including biosorbents, wastes from agriculture or industry and natural materials for the removal of pollutants such heavy metal ions from aqueous solutions.

In this work, the sorption of copper ions from synthetic aqueous solutions by hard almond peel, in single metal solutions, was investigated. Kinetic data and equilibrium sorption isotherm were measured in batch conditions. The influence of some parameters such as: contact time and initial metal concentration on copper ion sorption kinetics has been studied. Two simplified kinetic models including a pseudo first-order and pseudo second-order equations were selected to follow the sorption process. To identify the

main rate controlling steps in the overall uptake mechanism, a single intra-particle mass transfer diffusion model was tested. The sorption equilibrium data were obtained at natural pH of solutions. In order to describe the metal sorption isotherms mathematically and to obtain information about the maximum sorption capacity of this sorbent, the experimental sorption equilibrium data were analysed using Langmuir and Freundlich models.

MATERIALS AND METHODS

1- Sorbent material and metal ion

Hard almond peel waste used as sorbent is cheap and highly available lignocellulosic wastes in Algeria. It was collected from the region of Bensekrane (Tlemcen – Algeria), in summer 2006 in the form of large flakes. This waste was sun/air dried at ambient temperature during many days, crushed with a Moulinex Easy power R68 mill and sieved with an Automatic Sieve Shaker D403 device (Controlab) to keep only the size range 1.25-2 mm. This material obtained was used as sorbent material after the following treatment chosen arbitrary: 10 g of hard almond peel were contacted with 2 L of distilled water in a beaker agitated vigorously (at a speed of 400 rpm) by a magnetic stirrer at ambient temperature of $25 \pm 1^\circ\text{C}$ during 4 h, filtered, washed thoroughly with distilled water to remove all the adhering dirt particles until constant pH and no colour observed, then oven-dried at $85 \pm 5^\circ\text{C}$ for 24 h.

Copper solutions of desired concentration were prepared from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Prolabo, Lot 88 098, France) by dissolving the exact quantities of copper salts in distilled water. All chemicals were commercial products used without purification.

2- 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 copper concentration. For metal removal kinetics studies, 1 g of hard almond peel was contacted with 1 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 Varian Model AA-100 atomic

absorption spectrophotometer at $\lambda_{\text{max}} = 324.8$ nm. The metal uptake q_t (mg ion metal/g hard almond peel) was determined as follows:

$$q_t = (C_0 - C_t) \times V/m \quad (1)$$

where: C_0 and C_t are the initial and time metal ion concentration (mg/L), respectively, V is the volume of solution (mL), and m is the hard almond peel weight (g).

Blank 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 metal sorption experiments. Preliminary experiments had shown that copper sorption losses to the container walls were negligible.

3- Sorption Isotherm.

The sorption equilibrium isotherm was determined by contacting a constant mass 0.2 g of hard almond peel with a range of different concentrations of copper solutions: 50-500 mg/L. Mixtures sorbent-solution were agitated in a series of 250 ml conical flasks with equal volumes of solution 100 ml for a period of 24 h at room temperature $25 \pm 1^\circ\text{C}$. This contact time was beyond to that previously determined by kinetics tests using the same conditions to ensure that equilibrium was reached. The mixture pH was not controlled after the initiation of experiments. After shaking the flasks, the equilibrium pH was measured. The concentration of unbound copper ions at equilibrium was obtained using a Varian Model AA-100 atomic absorption spectrophotometer at $\lambda_{\text{max}} = 324.8$ nm, and the copper loading by hard almond peel was determined.

RESULTS AND DISCUSSION

1. Sorption kinetics

1.1. Effect of contact time: A preliminary experiment was performed to determine the equilibrium time. According to Fig. 1 obtained for an initial copper concentration 100 mg/L,

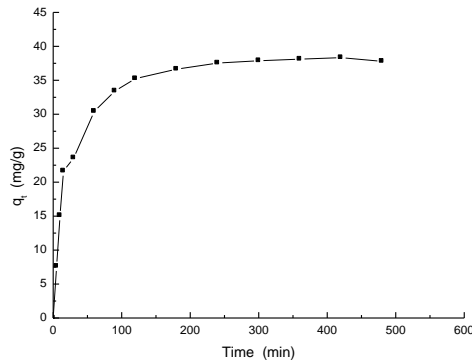


Fig.1. Kinetics of copper ions sorption by hard almond peels.
(Initial metal concentration: 100 mg/L, dose= 1g/L, dp= 1.25-2 mm, N= 400 tr/min, natural solution initial pH, T =25 °C

the kinetics of copper sorption by hard almond peels presents a shape characterized by a strong increase of the amount of copper ions sorbed during the first minutes of contact solution – sorbent, follow-up of a slow increase until to reach a state of equilibrium. The necessary time to reach this equilibrium is about 5 h and an increase of removal time to 24 h did not show notable effects. At equilibrium, about 36.73 % of initial copper solution was removed by hard almond peels ($q_e = 38.28$ mg/g) under these experimental conditions. During the course of copper sorption by hard almond peel, a decrease in the initial pH value ($\Delta pH = pH_0 - pH_e = 0.85$ unit) of the solution between the initial and equilibrium time was observed (Fig. not shown here).

1.2 Effect of initial copper ions concentration: Several experiments were also undertaken to study the effect of the initial copper concentration (50 – 200 mg/L), on the copper sorption kinetics from synthetic aqueous solution by hard almond peel. As shown in Fig. 2, for all initial copper ion concentrations studied, the obtained curves have the same shape. From the results obtained at equilibrium, the necessary time to reach equilibrium was about 5 h for 50, 100 and 150 mg/L, respectively, and 6 h for 200 mg/L. The amount of copper sorbed at the equilibrium increases with the increase in initial copper concentration: 24.02 mg/g ($C_0 = 50$ mg/L) and 59.27 mg/g ($C_0 = 200$ mg/L). Initial metal concentration provides an important driving force to overcome all mass transfer resistances of the metal ion between the aqueous and solid phases. Hence a higher initial concentration of copper will enhance the sorption process (Gulnaz et al., 2006).

During the phenomenon of copper ions sorption by hard almond peel, for all initial copper ions concentrations tested, a decrease in the initial pH value of solutions (Fig. not shown here) was also observed.

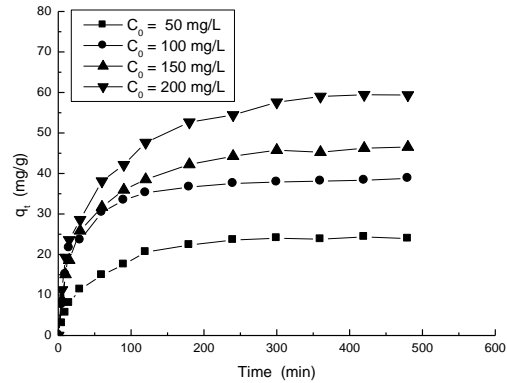


Fig.2. Effect of initial copper ions concentration on its sorption kinetics by hard almond peels. (Sorbent dose= 1g/L; dp= 1.25-2 mm ; N= 400 tr/min; solution initial pH : natural, T =25 °C)

1.3 Modelling

To analyze the kinetic data of copper sorption by hard almond peel under these experimental conditions tested, two common equations from the literature, namely, the first-order rate model of (Lagergren, 1898) and the pseudo second-order rate model (Ho and McKay, 2000) were chosen and shown below as Eqs. (2) and (3) in their linear forms:

$$\log (q_e - q_t) = \log q_e - k_L t / 2.3 \quad (2)$$

$$t/q_t = 1/k \cdot q_e^2 + t/q_e \quad (3)$$

where: k_L is the Lagergren rate constant of sorption (min^{-1}) and k the pseudo second-order rate constant of sorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$); q_e and q_t are the amounts of metal ions sorbed ($\text{mg} \cdot \text{g}^{-1}$) at equilibrium and at time t , respectively. For all initial copper ion concentrations tested, the different values of constants from the slope and intercept of linear plots of $\log (q_e - q_t)$ vs. t (see Fig. 3) and t/q_t vs. t (Fig. not show here) are summarized in the Table 1.

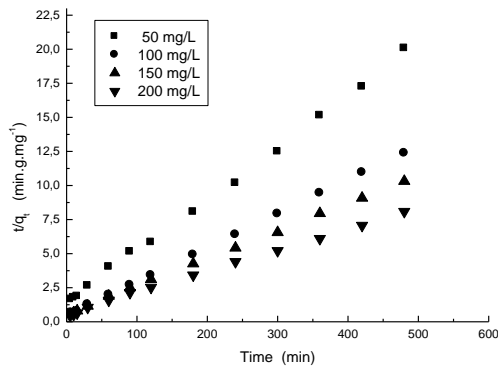


Fig.3. Pseudo-second order model for copper ions sorption kinetics by hard almond peels. (Sorbent dose = 1 g/L, particle size: 1.25-2 mm, agitation speed= 400 rpm, natural pH of solution, T= 25 °C)

Table 1. Models rate constants for copper ions sorption kinetics by hard almond peels: effect of initial copper ions concentration.

First-order kinetics model		Pseudo second-order kinetics model		
C_0 (mg/L)	$q_{e,exp.}$ (mg/g)	$q_{e,cal.}$ $k \cdot 10^3$ (mg/g)	$k_L \cdot 10^3$ R^2 (mg/g)	R^2 (min^{-1})
50	24.02	22.52	15.57	0.9907
100	38.28	23.85	14.24	0.9796
150	45.95	35.21	13.32	0.9259
200	59.27	51.40	12.49	0.9553
	1.02	0.9985		
	1.35	0.9999		
	0.74	0.9994		
	0.47	0.9981		

Compared to the first-order rate equation ($0.9259 < R^2 < 0.9907$), the pseudo second-order rate model adequately described the kinetics of copper ions sorption with acceptable correlation coefficient ($0.9981 < R^2 < 0.9999$). The calculated value of q_e is approximately closer to that obtained experimentally. These observations indicate that the sorption process follows a pseudo-second order kinetics. The equilibrium copper ions sorption capacity, q_e , increases with the increase in the initial copper ion concentration. In this model, all the steps of sorption such as: external diffusion, internal diffusion, and sorption are lumped together

and it is assumed that the difference between the average solid phase concentration and the equilibrium concentration is the driving force for sorption, and that the overall sorption rate is proportional to the square of the driving force (Wu et al., 2005).

3.1.4. Rate determining steps: From a mechanistic viewpoint, to interpret the experimental data, it is necessary to identify the steps involved during the sorption process. It is generally agreed that there are four consecutive steps which describe the overall sorption process of solute from a solution by a sorbent particle (Furusawa and Smith, 1973). These steps, as adapted to apply to the sorption of metal ions by a sorbent particle, are as follows:

- 1- External mass transfer of the metal ions from the solution bulk to the boundary film;
- 2- Metal ions transport from the boundary film to the surface of the sorbent particle;
- 3- Diffusion of the metal ions within the sorbent particle to the sorption sites: internal diffusion of metal ions;
- 4- Final uptake of metal ions at the sorption sites, via complexation, sorption, or precipitation, which is fast.

The first and the second step are external mass transfer resistance steps, depending on various parameters such as agitation and homogeneity of solution. In this study, the agitation given here to the solution (400 rpm) is considered as sufficient to avoid steps 1 and 2 being controlling steps. In the process of establishing the rate limiting step, the fourth step is assumed to be very rapid and is therefore not considered in any kinetic analysis (Findon et al., 1993): sorption is a quasi-instantaneous process, as well as complexation mechanism, precipitation seems to occur with a lower rate (Tsezos and Volesky, 1982). Consequently, the two rate limiting steps investigated are external film mass transfer and intraparticle diffusion, either singly or in combination. In a well – agitated batch system, the boundary layer surrounding the particle is much reduced, reducing the external mass transfer coefficient; hence, the third intraparticle diffusion resistance step is more likely to be the rate controlling step (Sag and Aktay, 2000). Weber and Morris (1962) demonstrated that in intraparticle diffusion studies, rate processes are usually expressed

in terms of square root of time. So q_t or fraction solute sorbed is plotted against $t^{0.5}$ as follow:

$$q_t = k_i \cdot t^{0.5} \quad (4)$$

where: q_t is the solute concentration in the solid and k_i the slope of the plot defined as an intraparticle diffusion rate parameter ($\text{mg metal g}^{-1}\text{sorbent time}^{-0.5}$). If particle diffusion is rate controlling, the plots q_t versus $t^{0.5}$ are linear (McKay and Blair, 1986). In theory, the plot between q_t and $t^{0.5}$ is given by four regions representing the external mass transfer followed by intraparticle diffusion in macro, meso and micropore (Ho and McKay, 1998).

Fig. 4 show plots of q_t vs. $t^{0.5}$ for the effect of initial copper ions concentration on its sorption kinetics by hard almond peel. Table 2 summarises the intraparticle diffusion rate parameters obtained.

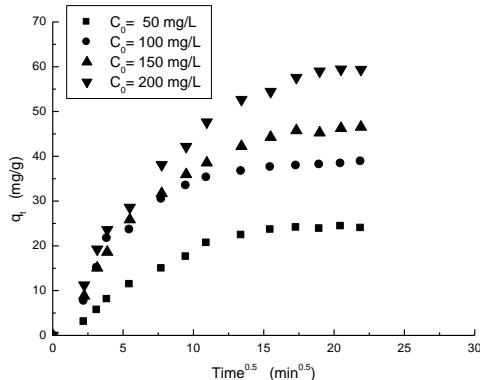


Fig. 4. Intraparticle diffusion plots for copper ions sorption kinetics by hard almond peels: effect of initial copper ions concentration.

Table 2. Parameters obtained from the intraparticle diffusion model for copper ions sorption by hard almond peels: effect of initial copper ions concentration.

C_0 (mg/L)	K_i ($\text{mg g}^{-1} \text{min}^{-0.5}$)	C (mg g^{-1})	R^2
50	0.66	13.42	0.9977
100	0.51	29.74	0.9939
150	1.27	24.80	0.9866
200	1.25	35.59	0.9641

As shown in Table 2, the values of intraparticle diffusion rate parameters obtained are different and dependent on initial copper ions concentration. As shown in Fig.4, three linear

portions were observed in the same experiment: a first linear portion followed by two other linear portions before equilibrium indicating multiple-stage diffusion of copper ions onto hard almond peel particles. Such a multiple nature of the curve confirms that intraparticle diffusion is not a fully operative mechanism for this system and reflects two stages: external mass transfer at initial time periods followed by intraparticle diffusion of copper ions onto the sorbent particles. The slope of the third linear portion characterizes the rate parameter corresponding to the intraparticle diffusion, whereas the intercept, C (mg/g), is proportional to the boundary layer thickness: the larger intercept the greater is the boundary layer effect (Kumar et al., 2005). For all experimental parameters studied, positive and significant ordinate intercepts, C (mg/g), is obtained indicating the influence of external rate control (Peniche-Covas et al., 1992). These observations indicate that copper ions sorption by hard almond peels is a complex process.

2- Sorption equilibrium

2.1- Metal sorption isotherm

Equilibrium data, commonly known as sorption isotherms, are basic requirements for the design of sorption systems. These data provide information on the capacity of the sorbent or the amount required to remove a unit mass of pollutant under the system conditions (özacar, 2003a,b). Fig. 5 shows the copper sorption ions isotherm (q_e vs. C_e) by hard almond peel at natural pH of solutions which is of L type according to the classification of Giles et al. (1960). for liquid-solid adsorption. From the plot of this isotherm, the maximum capacity of copper ion sorbed by hard almond peel is about 66 mg/g under these experimental conditions.

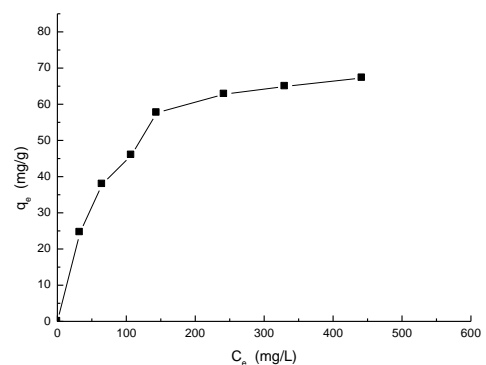


Fig. 5. Isotherm of copper ions sorption by hard almond peel at 25 °C

During the experiments of copper ions sorption equilibrium, it was also observed that the initial pH value of solutions decreased and the pH value at equilibrium increased with the increase in the initial copper ions concentration.

2.2. Modelling

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 (1918) and Freundlich (1906). This modelling permits us to determine the maximal capacity of sorption. 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.

a) The Langmuir model has the following form:

$$q_e = q_m \cdot K_L \cdot C_e / (1 + K_L C_e) \quad (5)$$

with: q_e : the amount of metal ion sorbed at equilibrium per g of sorbent (mg/g), q_m : the maximal metal sorption capacity of sorbent material (mg/g), C_e : the equilibrium metal ion concentration in the solution (mg/L) and K_L : the constant of equilibrium (L/mg) depending on temperature and the applied conditions. This equation can be linearized under the following shape:

$$C_e/q_e = 1/K_L \cdot q_m + C_e/q_m \quad (6)$$

If the equation of Langmuir is valid to describe the experimental results, it must verify the linearised shape of the basis equation, in system of coordinates $C_e/q_e = f(C_e)$, that will permit to obtain the constants q_m and K_L from the intercepts and slopes.

b) The Freundlich model has the form:

$$q_e = K_F \cdot C_e^n \quad (7)$$

where: q_e and C_e are as described before, K_F and n : positive constants depending on the nature of system solute- sorbent and temperature, $n < 1$. This equation can be linearized under the following form:

$$\ln q_e = \ln K_F + n \ln C_e \quad (8)$$

If this equation is verified with data of sorption equilibrium, we must obtain a straight line in the system of coordinates $\ln q_e = f(\ln C_e)$, the slope and the intercept to the origin give the values of constants n and K_F respectively.

Table 3. Parameters of Langmuir and Freundlich models for copper ions sorption isotherm by hard almond peel tested.

Langmuir model		Freundlich model			
q_{max} (mg/g)	$K_L \cdot 10^3$ (L/mg)	R^2	K_F	n	R^2
78.25	0.015	0.9969	7.34	0.38	0.9234

From results obtained (Figs. not shown here) and the model parameters determined by least squares fit of the experimental sorption data (see Table 3), it appears that the Langmuir model acceptably fits the experimental results over the experimental range with a good coefficient of regression. According to the low correlation coefficient obtained, the model of Freundlich is not adequate for modelling the isotherm of copper ions sorption by hard almond peel in all the metal ion concentrations domain studied. 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 these limitations, these models can provide information on metal-uptake capacities for any performance comparison between various sorbent materials (Kapoor and Viraraghavan, 1995). For comparison, this copper ions sorption capacity obtained by hard almond peel is also higher than those of some other sorbent materials reported in the literature although this direct comparison is difficult due to the varying experimental conditions used in these studies. Differences of metal uptake are due to the properties of each sorbent material such as structure, functional groups and surface area (Özer et al., 2004).

CONCLUSION

The results obtained confirm that hard almond peel can remove copper ions from synthetic aqueous solution under the experimental conditions tested here. The sorption kinetics performances are strongly affected by parameters such as: contact time and initial copper concentration. The amount of copper removed by hard almond peel increased with the increase of these parameters at a specific time. The kinetics of copper sorption followed a pseudo-second-order rate kinetics. Analysis of diffusion mechanisms of copper ions sorption by hard almond peels was problematic: diffusion mechanisms were predominant in rate controlling steps. Under these experimental conditions, the analysis of mechanistic steps involved in the copper ions sorption process confirms that the sorption process is particle-diffusion-controlled, with some predominance of some external mass transfer at the initial stages. An acceptable fitting of the equilibrium isotherm was obtained with Langmuir model in all the range of copper ion concentrations studied. This experimental study is quite useful in developing an appropriate technology for designing a waste water treatment plant. However, further work should be performed in order to better understand copper ions sorption binding mechanism by hard almond peel.

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