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On the Adsorption Mechanisms of Copper Ions over Modified Biomass

S. Montes,[1] G. Montes-Atenas,[2] F. Salomo,[1] E. Valero,[1] O. Diaz[3]

[1] Laboratory of Surface Physics and Chemistry, Materials Chemistry Department, Faculty of Chemistry and Biology, University of Santiago of Chile, Av. Lib. Bernardo O'Higgins 3363, Santiago, Chile
[2] Institute of Science, Faculty of Engineering, University of Diego Portales, Av. Ejercito #441, Casilla 298-V, Santiago, Chile
[3] Biology Department, Faculty of Chemistry and Biology, University of Santiago of Chile, Av. Lib. Bernardo O'Higgins 3363, Santiago, Chile

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The contamination of aqueous solution due to the presence of soluble heavy metals has been a subject of great interest for a great number of researchers throughout the last two decades (Gaballah and Kilbertus 1998). Soluble hydrolyzed heavy metal affects the environment – depending on their concentrations- instantaneously as well as at a long term (Smith et al. 1998; Suhendrayatna et al. 1999). This fact comes from the ability of certain organisms to adsorb and cumulate heavy metals from aqueous solutions (Baldantoni et al. 2004). Traditional wastewater treatment pathways involve at least one or more steps of neutralization, precipitation and filtration (Gaballah and Kilbertus 1998; Degremont 1989). An important factor that must not be overlooked is the volume or amount of wastewater per unit of time to be treated. This issue is directly connected with the costs of treatment operation. In consequence, the assessment of new low cost and efficient materials has lead to make the wastewater treatment cheaper. Low cost renewable biomass such as pine bark is a material assessed as adsorption surface in several both fundamental and applied studies, as well. (Gaballah et al. 1994c; Saarela et al. 2005). In fact many scientific reports have revealed that this material can adsorb and act simultaneously as biofilter for several types of pollutants, such heavy metals and organic products (Du Plessis et al. 2003; Bras et al. 2005).

This type of material at laboratory level has been evaluated successfully as substrate for heavy metal ions adsorption (Gaballah and Kilbertus 1998). Taking into account its low natural apparent density (ca. 0.35 kg/L) after particle size reduction (lower than 1 mm particle diameter) it is imperative to use low pulp density values which lead to higher amounts of metals removal from aqueous solution (removal referred to the unit of bark mass used). This contributes to making easier the subsequent recycling of the biomass. Other variables to be considered are pH, mean particle size and the eventual use of modified pine bark previous to wastewater treatment (Degremont 1989).

MATERIALS AND METHODS

Natural pine bark was reduced to a particle size lower than 1 mm. 1000 ml. Batch experiments were performed in duplicate to determine the kinetics of heavy metal extraction. The bark material was chemically activated by means of sulfuric acid, 0.2 mol/L at 20ºC, with a solid-liquid ratio equal to 1:10 in stirring conditions during 2 hours. Afterwards, the bark was washed with distilled water until reaching neutral pH.

Correspondence to: G. Montes-Atenas

The content of adsorbed metal was obtained by incinerating the raw and activated material. Afterwards, semi-quantitative X-ray fluorescence analysis (Phillips Model PW 2400, detection limit 0.007%, and average standard deviation 0.013%) was performed to determine the amount of different metals present in the bark structure.

To evaluate the surface distribution composition of bark charged with the metal, scanning electron microscopic (SEM) analysis was used.

Aqueous solutions of copper sulfate and lead nitrate were prepared separately to obtain solutions at 100 mg/L metal concentration. The adsorption studies were carried out at pH 5.0 and 20ºC, at different pulp densities: 1, 1.5, 3, 5, 10 g/L. Atomic absorption spectrophotometry (AAS) was performed to the aqueous solutions to determine after several reaction times the metal concentration. All reagents used to perform the experiments were of high purity (>99%), from Merck S.A.

RESULTS AND DISCUSSION

Bark activation is considered a first priority process since it allows an increase in the adsorption capacity and also to eliminate toxic tannins. However, the activation effects in acid media are quite variable depending on the nature of both bark and activating agents, their concentration and the temperature of the overall process (Gaballah et al. 1994; Seki et al. 1997). This fact explains the difficulties in finding the experimental conditions where the adsorption on modified bark is effective. Bibliographic data indicates that the activation process is usefully performed in a narrow range of pH (Gaballah and Kilbertus 1998) which confirms our results. The figure 1 shows the adsorption percentage of cooper from batch experiments.

The profile of the curves shows the heterogeneous energetic surface that can be related to the different acidity sites present at bark surface (polyphenolic groups: $K_a \sim 10^{-10}$- 10^{-11} ; secondary alcohols : $K_a \sim 10^{-18}$- 10^{-20}) (12) and the steric effect associated to each adsorption site. Figure 1 shows a strong increment on adsorption percentage if pulp density goes from 1.5 to 5 g/L. Nevertheless, it does not imply a significant decreasing on bark adsorption capacity. In fact, the adsorption capacity just shifts from 24.1 to 19.3 mg/g dry bark.

On the other hand, if it is assessed the adsorption kinetics considering the complex characteristics associated to bark surface, the following general equation may be written:

$$\frac{d\left[Cu^{+2}\right]}{dt} = -Ka\left[Cu^{+2}\right]^n$$

where "n" is the pseudo-partial order of cupric ions in dissolved state to be adsorbed, K is a kinetic constant that takes into account kinetics parameters and "a" is the specific surface related to a heterogeneous reaction at constant temperature. By assuming both chemical and physical properties are kept constant or the different experiences and bark samples utilized, the following data are obtained associated to an apparent global second order reaction (Table 1). This fact is not in agreement with other publications which reports pseudo-first order kinetics for the case of divalent metals such as Fe(II) (Acemioglu 2004). The latter reveals that when different metals are tested, the mechanisms involved might differ.

All results obtained showed a high reliability since fluctuations in the adsorbed quantities measured were less than 5% average.

In order to fix ideas, it can be established that two major processes are taking place in the system such as:
a.- Diffusion of divalent ions from the bulk of aqueous solution towards particle surface.
b.- Ions exchange at particle surface where other ions are released to the solution bulk.

The driving force for diffusion mechanism will be the gradient of concentration present in the solution while for surface reaction will be the difference of concentration at the interface with the available sites for ionic exchange.

Table 1. Kinetics parameters for Cu(II) adsorption over chemically treated radiata pine bark.

ρ_p (g/L)	K (L mg^{-1} min^{-1})	R^2, correlation coefficient
1.0	6.0×10^{-6}	0.842
1.5	1.0×10^{-5}	0.915
5.0	7.0×10^{-4}	0.956

Neglecting ions diffusion over solid surface, the overall mechanism might be written in terms of three subsequent steps: (i) mass transfer, (ii) charge transfer or ionic exchange and (iii) surface saturation. The stage (ii) represents the adsorption process and when stage (iii) is reached the overall adsorption process goes to other zones of bark surface harder to accomplish.

Since for charge transfer the main driving force is the gradient of concentration and available sites for ionic exchange, the ions closed to the bark surface will react quickly (strong increments on the adsorption capacity). When available sites will require diffusion inside the bark porous structure the adsorption percentage increases at that moment but much slower than the first stage. Then, the diffusion or mass transfer mechanism governs the whole process. This might explain the shape of the adsorption curves in time obtained experimentally.

From kinetics outcomes it can be deduced that the adsorption process is not only defined from diffusion mechanism (associated to order one). A parameter determining the effect on the different mechanisms present in the system is, among others, the ionic radius which takes into account if the metal ion is complexed or not (Shannon and Prewitt 1970; Gaballah et al. 1997).

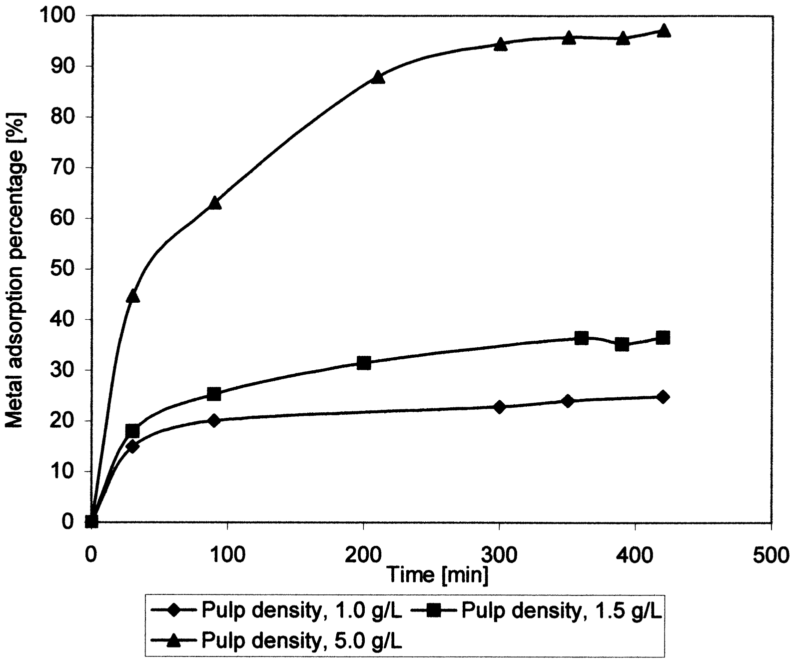

Figure 1. Kinetic adsorption curves of copper on activated radiata pine bark. Initial concentration of Cu(II). 100 mg/L. pH 5.0

Other variables are: metal concentration in solution, pulp density which determines the number of available sites for ionic exchange per unit of surface, steric effects and hydrodynamic of suspended fine solid particles.

From the point of view of aqueous speciation (Figure 2) although the cupric ions dominates at pH 5, the mono-hydroxilated specie reaches a maximum of concentration at same pH which allows to form surface mono-dentated species with acidic groups such as R-OH. The ratio $\left(\frac{[H^+]}{[Cu(II)]}\right)_{pH=5,T=20^{\circ}C}$ was 1.6.

The 1.6 value implies that cupric ions cannot only form bi-dentated surface species but also mono-dentated species, having the last ones mentioned less steric effect than Cu(II).

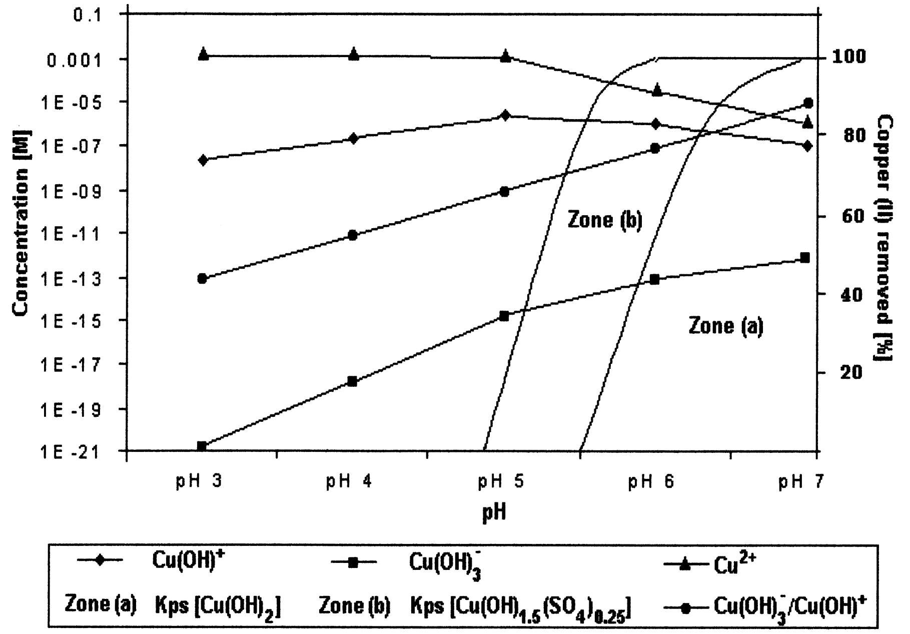

Figure 2. Copper (II) speciation diagram in aqueous solution versus pH. The coloured zone indicates the precipitation of the following species: (a) Cu(OH)$_2$, Kps = $1.26*10^{-20}$; (b) Cu(OH)$_{1.5}$(SO$_4$)$_{0.25}$, Kps = $7.08*10^{-18}$. (presented S. Montes, G. Montes-Atenas, TMS. Fall 2002. Extraction and Processing Division Meeting. June.Lulea,Sweden).

Figure 1 shows that apparently at higher times of reaction than 100 minutes and lower than 420 minutes, if pulp density is 1 g/L, the adsorption percentage is not considerably modified which actually happens at higher pulp densities. This is explainable by the reduced number of available sites for Cu(II) ionic exchange per unit of bark surface area related to the concentration of metal ions in aqueous solution.

When pulp density increases, the availability of sites with variable energy increases, for the same number of mol of ions in solution. This argument can explain the initial slope for each kinetic curve positive at reaction times between 100 and 250 minutes reaction. Certainly, also cationic radius and the stereochemistry of the exchanged surface site must be important for the ionic exchange process to go on at that stage.

Table 2 shows a completely opposite effect to that observed in Figure 1. In fact, the percentage and adsorption capacity increase significantly for a pulp density of 1 g/L (68.4%) going from 7 to 24 hrs. No changes were observed for pulp density 5 g/L, where if the maximum adsorption value assessed the saturation “plateau” is attained. In this latter case, the adsorption percentage gets near to 100%. The adsorption capacity practically does not change between 7 and 24 hrs reaction. These observed changes match well with the profiles of the curves showed in Figure 1.

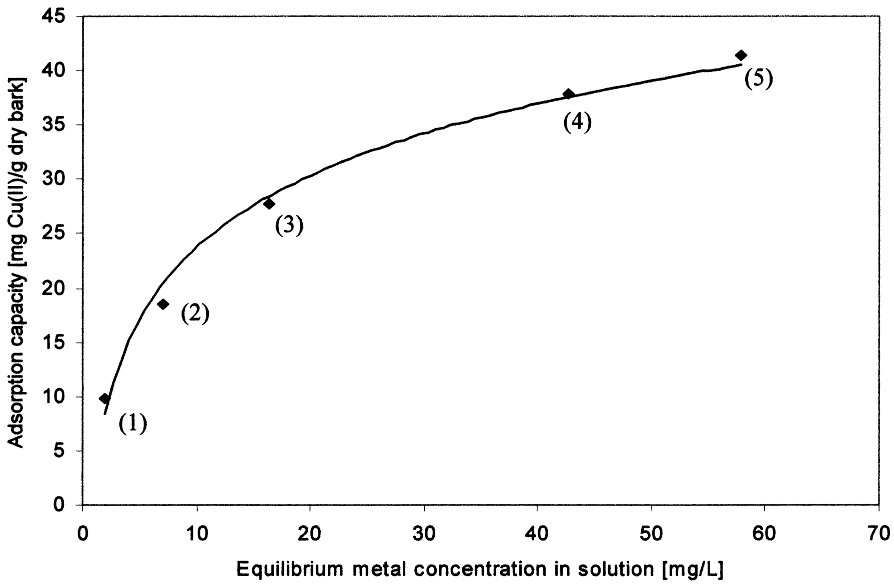

Figure 3. Copper adsorption isotherm at different pulp density values. Initial concentration of Cu(II) : 100 mg/L, pH 5.0, 20°C, (1) 10 g/L, (2) 5 g/L, (3) 3 g/L, (4) 1.5 g/L y (5) 1.0 g/L.

Figure 3 shows the adsorption isotherm of Cu(II) at pH 5 and 20°C from an aqueous solution containing 100 mg/L of the metal mentioned. The lowest value of adsorption capacity obtained was near to 40 mg/g dry bark at pulp density value lower than 1,5 g/L.

Table 2. Time effect on bark activated adsorption capability of Cu (II) ions during diffusion control mechanism. Initial concentration: 100 ppm. pH 5.0

Time [h]	7 h		24 h	
Pulp density [gL^{-1}]	Adsorption [%]	Adsorption Capability [mg/g dry bark]	Adsorption [%]	Adsorption Capability [mg/g dry bark]
1.0	25.0	25.0	42.1	42.1
1.5	36.6	24.4	57.4	38.3
5.0	97.2	19.4	93.0	18.6

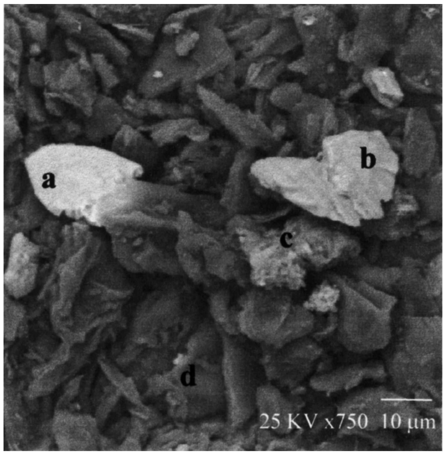

Figure 4. Original activated bark. (going from point "a" to point "c" the percentage of oxygen and silicon are reduced. It was also found a high content of Fe and Mg in "a"; "b" is rich in Ca and "c" is rich in Al.

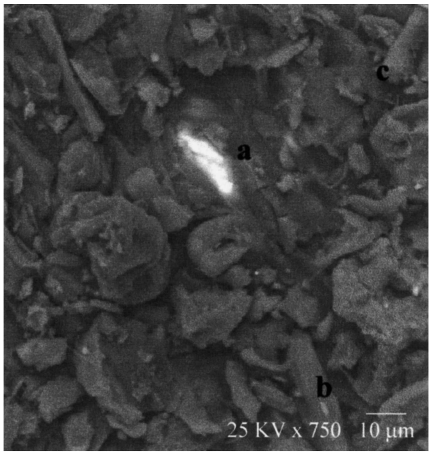

Figure 5. Activated bark charged with Cu(II). Pulp density: 1.5 g/L. For 3 grams of sample, the percentage of copper is near to 62%. At point "a" it was found a high content in Zn(II).

Table 3 shows the distribution of the chemical elements present in both raw and chemically treated bark. Most soluble species decrease in their amount due to the activation process. Furthermore, it is important to note that Mg, Ca and K are higher while the most insoluble metals such as Al and Si increase their content expressed as mg/gram dry bark. These outcomes can be compared with those given by SEM analysis (Figures 4 and 5) which present important differences in the element distribution per grain between activated bark with and without the metal.

Table 3. Semi- quantitative analysis of pine bark by X-ray spectroscopy fluorescence[a].

Sample	Ca	Fe	Na	Mg	Mn
Original Raw bark	12.8	4.80	0.98	2.40	0.57
Activated Bark	5.70	4.30	0.94	0.79	0.11

Sample	K	Al	Si	Ti	Cu
Original Raw bark	2.03	6.40	17.1	0.47	0.03
Activated Bark	1.08	7.00	21.3	0.46	0.04

[a] Values are given in mg/g dry bark

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