



Adsorption of copper onto agriculture waste materials

Henrik K. Hansen*, Fernanda Arancibia, Claudia Gutiérrez

Departamento de Ingeniería Química y Ambiental, Universidad Técnica Federico Santa María, Casilla 110 V, Valparaíso, Chile

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ABSTRACT

Mining activities generate large amounts of wastewater, which contain heavy metals of elevated concentration according to legislative threshold values. Therefore, treatment is necessary, and there has been a recent focus on more environmentally friendly methods. One of these is biosorption, where heavy metals are adsorbed from the wastewater via materials of biological origin. In this work copper sorption capacity, kinetics and isotherms of different low-cost residual agricultural materials was studied. Seven different materials were investigated: peanut shells, nut shells, plum seeds, eucalyptus bark, olive pips, peach stones, and pine sawdust. The best sorption results were obtained in acidic pH for olive pips, peach stones and pine sawdust. Furthermore, it was observed that at higher pH, a longer duration of time is required before equilibrium is established. In general, the better biosorbents were found to be peach stones and pine sawdust with a sorption capacity at acidic pH around 10–15 mg Cu g⁻¹ biosorbent. In addition it was found, that the Ho and McKay second order model described the sorption kinetics very satisfactorily. Both Langmuir and Freundlich models described the equilibrium sorption isotherms well for the biosorbents studied – with the last model being slightly better.

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1. Introduction

Mining has crucial importance for the Chilean economy, since Chile is one of the world's largest copper producers – with more than 30% of the worldwide copper production [1]. During the concentration and processing of copper sulphide minerals considerable volumes of residues – either liquid or solid – are generated. The liquid residues – or wastewaters – produced by mining activities contain heavy metals, arsenic and other inorganic species in concentrations that exceed the local legal threshold values [2]. Different treatment alternatives exist such as chemical precipitation, electro dialysis, ion exchange, and adsorption. All of these technologies facilitate the removal of the inorganic compounds from the wastewater with either high or low efficiency but all are associated with important costs such as reagent addition, power consumption, limited life time of equipment, and general operational costs.

Lately, investigation has turned into the search for low-cost adsorbents [3–5]. These are typically residues from industry or agriculture, which have been used in the treatment of industrial wastewater or contaminated groundwater. Furthermore, research has also included the use of different organic or biological originated residues such as wood waste, seeds, and algae. The use of these residues has, in general, given the process the more common name of biosorption with the adsorbent nominated as biosorbent

[6,7]. Several inorganic contaminants have been removed by a variety of biosorbents – including to some extent copper, which is the main inorganic contaminant of Chilean copper smelter wastewaters. However, an optimal biosorbent has still to be found for copper removal from acidic wastewater. Table 1 shows copper adsorption capacities of a variety of agricultural by-products published lately [8–23]. As it can be seen from the table the adsorption capacity depends on the material and pH. Due to the large agricultural sector of Chile, a lot of by-products are produced, which mainly end as residues in land fills. Many of these by-products could eventually be used as alternative adsorbents due to the low-cost and abundances.

The objectives of this work are: (i) to evaluate the copper removal of seven different organic residues (of low-cost) used as biosorbents in the treatment of copper containing wastewater prepared synthetically, (ii) to determine the maximum adsorption capacity of these materials, (iii) to determine biosorption kinetics in order to fit the behaviour to existing models, (iv) to evaluate the behaviour of the different biosorbents varying the pH in the wastewater and the relation biosorbent mass/solution volume, and (v) to determine adsorption isotherms. Finally, the potential new use as biosorbents could add sustainable value to these residues.

2. Theoretical background

The trace metal adsorption efficiency of a biosorbent can be evaluated quantitatively by a simple series of experiments including the determination of adsorption capacity, isotherms and kinetics. Adsorption processes tend to be exothermic, which means that

* Corresponding author. Tel.: +56 322654030; fax: +56 322654278.
E-mail address: henrik.hansen@usm.cl (H.K. Hansen).

Table 1
Copper adsorption capacities for some residue-derived adsorbents reported in the literature ($T=298\text{ K}$).

Adsorbent	Adsorption capacity (mg Cu g ⁻¹ adsorbent)	Optimum pH	Reference
Apple wastes	10.8	5.5–7	[8]
Banana peel	4.75	6–8	[9]
Birch wood sawdust	4.9	5.5	[10]
Carrot residue	32.7	3–5	[11]
Cotton seed hulls	19.1	–	[12]
Dried activated sludge (<0.063 mm)	294	4	[13]
Litter of natural trembling poplar forest	19.5	4.5–5	[14]
Olive mill residue	13.5	5	[15]
Pine cone powder	5.76	3–5	[16]
Powdered waste sludge	117	4–6	[17]
Rubber leaves powder	15.0	4–5	[18]
Sour orange residue	21.7	4–6	[19]
Soybean hulls	38.7	–	[12]
Terrestrial moss	11.1	5.5	[10]
Tree fern	11.7	–	[20]
Waste beer yeast	0.51	5	[21]
Waste sugar beet pulp	28.5	4–4.5	[22]
Wheat shell	10.8	5	[23]

any analysis should be done at constant temperature. On the other hand, it has been shown that small variations in temperature do not affect the adsorption process severely [24]. Other parameters have more importance for the process – such as changes in pH.

The retention of a solute (e.g. metal ion) by a biosorbent can be estimated by a simple mass balance following the logic that metal removed from the solution is found in or on the solid biomass:

$$C_i (\text{mg L}^{-1}) V(\text{L}) = C_{\text{eq}} (\text{mg L}^{-1}) V(\text{L}) + q (\text{mg g}^{-1}) M(\text{g}) \quad (1)$$

$$q = \frac{V (C_i - C_{\text{eq}})}{M} \quad (2)$$

where C_i and C_{eq} (mg L⁻¹) are the initial and equilibrium concentrations of the solute, respectively, q is the metal retention by the biosorbent (mg g⁻¹ dry biosorbent), $V(\text{L})$ is the volume of the liquid phase, and $M(\text{g})$ is the mass of adsorbent.

In this context, it is necessary to stress that the retention is not only a function of the mass of biosorbent but it also depends on the shape and size of the biosorbent [24]. This means that biosorption results are quite different when using the biosorbent as fine particles and as pellets. Therefore, when characterizing the biosorption process and efficiencies, it is important to describe the actual shape of the biosorbent used.

The adsorption isotherms allow one to obtain the maximum metal retention by a biosorbent at a given equilibrium concentration. On the other hand, the form of the isotherms gives valuable information about the affinity of the biosorbent for a specific metal ion. For example, high initial slopes indicate high affinity between the biosorbent and the metal [24]. These isotherms can be adjusted mathematically to models, the most applicable models are either the Langmuir or Freundlich models. Both models are typically used for single component systems at constant temperature and pH. In addition to the equilibrium models, it is important to have kinetic data and models in order to scale up the process. Several models have been suggested – either of first or second order reaction. The commonly used kinetic models are the Lagergren first order model [25] and the second order Ho and McKay model [26].

2.1. Langmuir isotherm

This model is based on the assumption that active surface sites exist on the solid material, to which the metals are adsorbed. The ions are fixed on a monolayer on the surface. This means that there is no penetration of ions into the interior of the adsorbent. The model can be expressed in the following manner:

$$q_{\text{eq}} = \frac{q_m C_{\text{eq}}}{K_d + C_{\text{eq}}} \quad (3)$$

or

$$\frac{C_{\text{eq}}}{q_{\text{eq}}} = \frac{K_d}{q_m} + \frac{C_{\text{eq}}}{q_m} \quad (4)$$

where q_{eq} is the equilibrium concentration of the metal on the biomass (mg metal g⁻¹ dry biosorbent), q_m is the maximum concentration of the metal on the biomass (mg metal g⁻¹ dry biosorbent), K_d is an adsorption energy related constant (mg L⁻¹) and C_{eq} is the equilibrium concentration of metal in the solution (mg L⁻¹). q_m corresponds to the maximum quantity of metal that the biosorbent can adsorb. At this point, all the active sites have been occupied by ions, and the material cannot adsorb any further metal even if the concentration in the solution is increased. On the other hand, K_d is the dissociation coefficient of the solute–adsorbent complex, which represents the affinity between the solute and the adsorbent – meaning that a higher K_d value corresponds to a higher affinity.

2.2. Freundlich isotherm

This model is characterized by being an empirical equation, which is not limited to a finite adsorption capacity as the Langmuir model. Therefore, it is applicable for low and medium concentrations of solutes:

$$q_{\text{eq}} = k C_{\text{eq}}^{\frac{1}{n}} \quad (5)$$

or

$$\ln(q_{\text{eq}}) = \ln(k) + \frac{1}{n} \ln(C_{\text{eq}}) \quad (6)$$

where k is a constant related to the adsorption capacity, and $1/n$ is related to adsorption intensity.

2.3. First order kinetics: Lagergren model

One of the first and most used first order models to describe the sorption of metals onto biosorbents is the Lagergren model and is based on the function of the adsorbed mass over time in the following manner:

$$\frac{dq_t}{dt} = k_{\text{ad}} (q_{\text{eq}} - q_t) \quad (7)$$

where q_t (mg g dry sorbent) is metal adsorbed by the biosorbent at time t (min), q_{eq} (mg g) is adsorbed metal in equilibrium conditions, and k_{ad} is a first order adsorption constant. When Eq. (7) is integrated to a linear form, the following expression is obtained:

$$\log(q_{\text{eq}} - q_t) = \log(q_{\text{eq}}) - \frac{k_{\text{ad}} t}{2.303} \quad (8)$$

2.4. Second order kinetics: Ho and McKay model

This model assumes that the velocity of occupation of the available adsorption sites is proportional with the square of the number of not occupied sites, and that the number of occupied sites is

Table 2
Different residues used as biosorbents.

Biosorbent	Characteristics
1	Peanut shells Elongated, length: 3.0–4.5 cm, width: 1.0–1.5 cm.
2	Nut shells Roughly halves or quarters of hollow spheres, diameter: 3.0–3.5 cm
3	Plum seeds Flattened spherical shape, length: 0.8–1.0 cm, thickness: 0.5–0.7 cm.
4	Eucalyptus bark Strip shaped, length: 5.5–7.0 cm, thickness: 2.0–5.5 mm
5	Olive pips Elongated ellipsoidal shape, length: 4.0–6.0 cm, width: 1.2–1.5 cm
6	Peach stones Ellipsoidal shape, length: 3.0–3.5 cm, width: 2.0–2.5 cm
7	Pine sawdust Miscellaneous shaped, length and width: 0.5–1.0 cm

proportional to the fraction of metal ions adsorbed. The model describes the kinetics as:

$$\frac{dq_t}{dt} = k (q_{eq} - q_t)^2 \quad (9)$$

where k is a second order adsorption constant ($\text{g mg}^{-1} \text{min}^{-1}$). This expression can be integrated to:

$$\int \frac{dq_t}{(q_{eq} - q_t)^2} = \int k dt \quad (10)$$

$$\frac{t}{q_t} = \frac{1}{k_{ad}} + \frac{t}{q_{eq}} \quad (11)$$

3. Experimental

3.1. Reagents

The copper solutions were prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (analytical grade) in distilled water. In order to adjust pH either HCl or NaOH (both analytical grade) was used.

3.2. Analytical

Each liquid sample was filtered through a No 131 grade filter paper by a vacuum pump. The copper concentration in the filtrate was determined by Atomic Absorption Spectrophotometry in flame according to Chilean standard NCh 2313/10 Of. 96.

pH was measured with a Orion 370 pH meter with a combined pH electrode.

3.3. Preparation of adsorbents

Table 2 shows type, size and shape of the residues used in this work as biosorbents. Seven residues were chosen for this investigation due to abundance, easiness of pre-treatment/separation and expected adsorption capacity. The residues were decided to be used

without size reduction or shape deformation in order not to alter the properties of the materials. This is important when any practical use in full scale should be considered. Each material was collected separately, and was first washed several times in tap water and then in distilled water. Thereafter, they were dried until they had a constant weight at 105°C , cooled down and placed separately in sealed plastic bags.

3.4. Experimental plan

The different experimental conditions are summarized in Table 3. The analysed parameters were: (a) type of biosorbent, (b) initial copper concentration ($[\text{Cu}]_0$), (c) biosorbent mass-to-solution volume ratio (M/V), (d) solution pH, and (e) sorption time. These parameters were analysed in order to determine sorption capacity, kinetics and isotherms. From the sorption capacity experiments, the best three biosorbents were selected for sorption kinetics experiments. Furthermore, the best two biosorbent were chosen for the experiments evaluating the pH effect, the M/V ratio effect and the sorption isotherms determination.

The pH in the solution was kept constant by adding drops of either 37% HCl or 6 M NaOH solutions, assuring that the total liquid volume was not affected severely. The experiments were carried out without stirring and at ambient temperature ($21\text{--}24^\circ\text{C}$). It was decided that these small changes in temperature did not affect the sorption isotherms since all experiments were carried out in triplicate and an average was used. In general, the standard deviations were below 5% for all data points.

For the sorption capacity experiments either 800 or 240 mg Cu L^{-1} solutions were used, from which either 300 or 480 mL was poured into 500 mL beakers. Either 7.5 g or 4.8 g of biomass were added in each case in order to maintain similar biomass-to-copper ratios for both concentrations. After 30 h the solution was filtered and the copper content measured. On the other hand, for the sorption kinetics experiments, a 200 mg Cu L^{-1} solution was prepared, and 200 mL of the solution was poured into eight different 500 mL beakers and 5.0 g of biosorbent was added to each. At different times – according to Table 3 – the solution was filtered and the copper content measured. When determining the sorption isotherms, 200 mL of the copper containing solution was poured into different 500 mL beakers and 5.0 g of biosorbent was added to each. After 30 h the solution was filtered and the copper content measured. The experimental methodology when analysing the pH effect and the solid-to-liquid ratio was similar to the procedure when determining the isotherms.

4. Results and discussion

4.1. Biosorption capacity

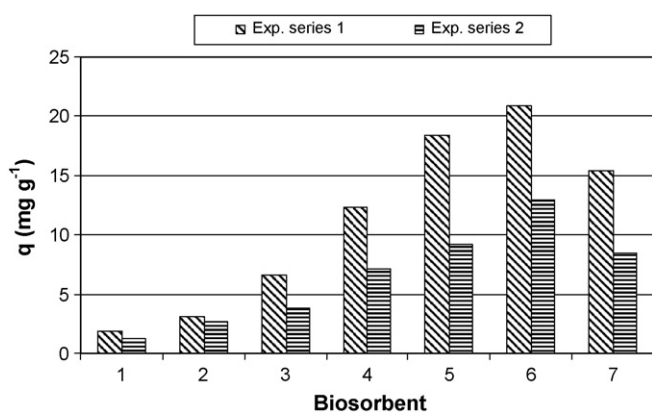
In this stage, a preliminary screening of the seven biosorbent was carried out in order to have a comparative measure of the

Table 3
Experimental biosorption conditions.

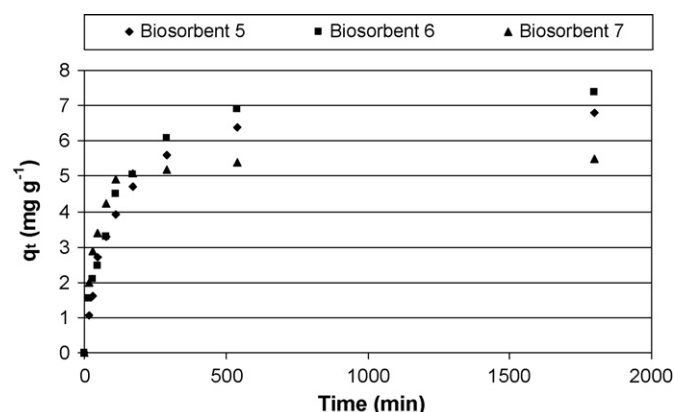
Experiment type	Biosorbent investigated	$[\text{Cu}]_0$ (mg L^{-1})	M/V (g mL^{-1})	pH	Time (min)
Biosorption capacity	1, 2, 3, 4, 5, 6 and 7	800	0.025	5.0	1800
		240	0.01	5.0	1800
Biosorption kinetics	5, 6 and 7	200	0.025	5.0	0, 15, 30, 45, 75, 110, 170, 290, 540 and 1800
Solid-to-liquid ratio variation	6 and 7	400	0.0025–0.05	5.0	1800
pH effect	6 and 7	400	0.025	1.5, 3.0, 5.0, 7.0 and 10.0	1800
Biosorption isotherms	6 and 7	50, 100, 200, 300, 400, 600 and 800	0.025	1.5, 3.0 and 5.0	1800

Table 4
Determination of adsorption capacity.

	Biosorbent						
	1	2	3	4	5	6	7
First series of experiments: <i>M</i> : 7.5 g, <i>V</i> : 300 mL, pH: 5.0, Time: 1800 min							
[Cu] ₀ (mg L ⁻¹)	764.6	764.6	764.6	764.6	764.6	764.6	764.6
[Cu] _f (mg L ⁻¹)	716.2	686.5	599.7	457.5	305.2	241.9	379.8
<i>q</i> (mg Cu g ⁻¹)	1.9	3.1	6.6	12.3	18.4	20.9	15.4
Second series of experiments: <i>M</i> : 4.8 g, <i>V</i> : 480 mL, pH: 5.0, Time: 1800 min							
[Cu] ₀ (mg L ⁻¹)	233.61	233.61	233.61	233.61	233.61	233.61	233.61
[Cu] _f (mg L ⁻¹)	221.12	206.14	195.14	162.17	141.19	104.72	148.68
<i>q</i> (mg Cu g ⁻¹)	1.2	2.7	3.8	7.1	9.2	12.9	8.5

**Fig. 1.** Biosorption capacity. Series 1 (*M* adsorbent: 7.5 g, *V*: 300 mL, pH: 4.6, Time: 1800 min) and series 2 (*M* adsorbent: 4.8 g, *V*: 480 mL, pH: 5.0, Time: 1800 min).

biosorption efficiency. Two experiments were carried out for each biosorbent, one experiment with an initial copper concentration of around 800 mg L⁻¹ and a solid-to-liquid ratio *M/V* of 0.025 g mL⁻¹, and one experiment with an initial concentration of 240 mg L⁻¹ and a solid-to-liquid ratio of 0.01 g mL⁻¹. Table 4 shows the copper biosorption results for the seven different biosorbents for the two cases. In order to evaluate the copper adsorption capacity – or copper retention – *q*, in each case, Fig. 1 compares the copper retention for the seven biosorbents. From Fig. 1 and Table 4, it can be observed that the adsorption capacity varies between the adsorbents. For both series of experiments, the three best copper biosorbents are 5 (olive pips), 6 (peach stones) and 7 (pine sawdust). Biosorbent 4 (Eucalyptus bark) is showing a fair biosorption capacity but still clearly lower than the three other materials mentioned. The remaining materials (biosorbent 1, 2 and 3) are not suitable as adsorbents for copper removal due to the low sorption capacity for copper. Biosorbents 5, 6 and 7 all show great potential for copper removal, compared to other biosorbents reported

**Fig. 2.** Biosorption kinetics: *q_t* versus time.

[4,5]. This corresponds well with the literature, where for example olive pomace has been reported efficient in the uptake of copper [15]. Therefore, these materials are chosen for further experimental analysis regarding kinetics, isotherms, *M/V* ratios and pH dependencies. Furthermore, in Fig. 1 it can be observed that by changing *M/V* and initial copper concentration, the overall behaviour of the different biosorbents is the same.

4.2. Biosorption kinetics

Table 5 shows the conditions and results for the study of sorption kinetics for biosorbents 5, 6 and 7. Fig. 2 shows *q_t* as a function of time. From table and figure it can be noted that the initial adsorption velocity is relatively high and nearly constant until a certain level. After this level the velocity drops considerably reaching zero at equilibrium. In Fig. 2, it can also be observed that biosorbent 7 has the highest initial velocity – even if the equilibrium uptake is lower. Therefore, this material is favourable for industrial use of the biosorbent, since the process equipment would be smaller. In

Table 5
Conditions and results for biosorption kinetics experiments.

Adsorption time (min)	Biosorbent 5		6		7	
	[Cu] _f (mg L ⁻¹)	<i>q_t</i> (mg g ⁻¹)	[Cu] _f (mg L ⁻¹)	<i>q_t</i> (mg g ⁻¹)	[Cu] _f (mg L ⁻¹)	<i>q_t</i> (mg g ⁻¹)
<i>M</i> adsorbent: 5.0 g, <i>V</i> : 200 mL, <i>M/V</i> : 0.025 g mL ⁻¹ , [Cu] ₀ : 200 g mL ⁻¹ , pH: 5.0						
0	233.60	0.00	233.60	0.00	233.60	0.00
15	207.12	1.06	195.14	1.54	183.65	2.00
30	193.62	1.60	181.15	2.10	161.67	2.88
45	166.15	2.70	171.65	2.48	148.68	3.40
75	151.66	3.28	151.67	3.28	128.19	4.22
110	136.17	3.90	121.20	4.50	111.21	4.90
170	115.85	4.71	107.21	5.06	106.71	5.08
290	93.70	5.60	81.24	6.09	103.72	5.20
540	74.10	6.38	61.10	6.90	98.60	5.40
1800	63.73	6.79	48.76	7.39	96.22	5.50

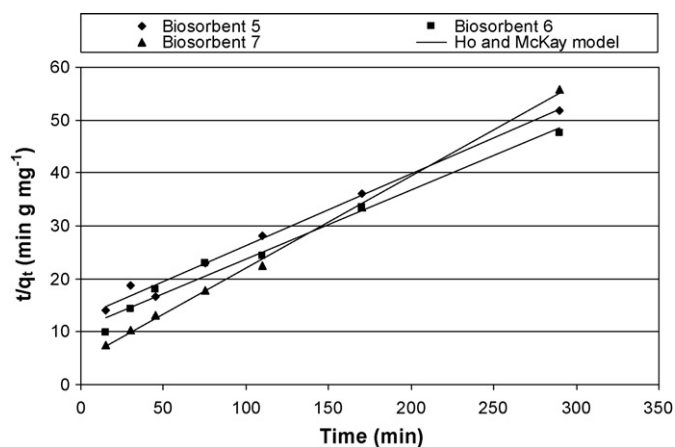


Fig. 3. Experimental biosorption data with time compared with Ho and McKay model fitting.

Table 6
Ho and McKay second order model parameters.

Biosorbent	Ho and McKay model	q_{eq} (mg g ⁻¹)	k_{ad} (mg g ⁻¹ min ⁻¹)
5	$\frac{t}{q_t} = 0.1335 t + 12.63$	7.49	0.079
6	$\frac{t}{q_t} = 0.1302 t + 10.72$	7.68	0.093
7	$\frac{t}{q_t} = 0.1734 t + 4.76$	5.77	0.210

general it can be concluded that the equilibrium has been reached before 1800 min (=30 h). According to Fig. 2, for biosorbent 7 the equilibrium is reached after around 500 min, whereas for the two other biosorbents it occurs after around 1000 min.

The kinetic data can be fitted to either Lagergren first order or Ho and McKay second order models. When fitting the data, for the Ho and McKay model, R^2 is higher than 0.98 for all biosorbents, whereas for the first order model, R^2 is considerably lower (0.7–0.92). Fig. 3 shows this fit for biosorbents 5, 6 and 7 – when considering the first 290 min of biosorption only. When applying the Ho and McKay model to the experimental data, the model specific parameters can be estimated, and Table 6 gives these parameters.

4.3. Variation of the M/V ratio

Above it was found that biosorbent 7 gave the highest initial adsorption velocity, whereas biosorbent 6 has the highest total copper uptake. Therefore, only these two materials were chosen for M/V effect analysis. The biosorption conditions and results when varying the M/V ratio are shown in Table 7.

As can be seen and expected from Table 7, the larger the amount of solid biomass, the lower the equilibrium concentration is after 1800 min. On the other hand, when depicting q_{eq} versus M/V, which is done in Fig. 4, one can observe that for both biosorbents, an optimal q_{eq} value is found. This optimum is for biosorbent 7 found at a

Table 7
Biosorption results with different M/V ratios.

Sample	Biosorbent 6			7		
	M/V (g mL)	[Cu] _{eq} (mg L)	q_{eq} (mg g)	M/V (g mL)	[Cu] _{eq} (mg L)	q_{eq} (mg g)
V: 200 mL, [Cu] ₀ : 396.3 mg L, pH: 5.0, Time 1800 min						
1	0.0051	382.3	2.75	0.0025	378.3	7.20
2	0.0076	257.4	18.28	0.005	287.4	21.78
3	0.0137	195.4	14.66	0.01	223.4	17.29
4	0.0246	147.5	10.11	0.025	134.5	10.47
5	0.0318	63.5	10.47	0.05	82.5	6.28

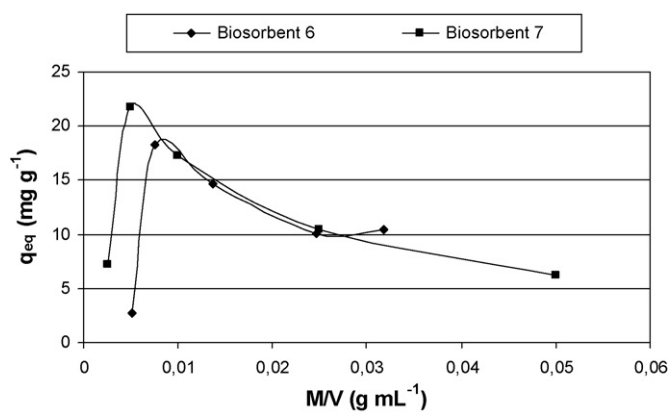


Fig. 4. Variation of q_{eq} at different M/V values.

M/V ratio of approx. 0.005 g mL⁻¹, and for biosorbent 6 at a M/V ratio around 0.0075 g mL⁻¹. The explanation could be that when using large amounts of biomass, one can obtain efficient metal removal from the solution but the biosorbent is not occupying all its active sites fully. In fact, at the optimal M/V ratio biosorbent 7 seems to be a better adsorbent than biosorbent 6 – in contrast to the initial experiments done analysing sorption capacity and kinetics.

4.4. Influence of pH on the biosorption

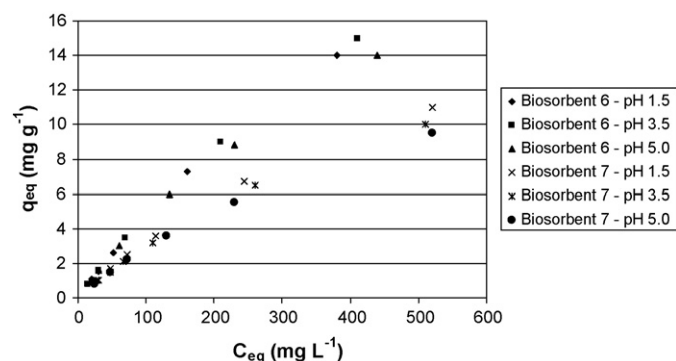
In order to evaluate the efficiency of the copper adsorption of the biosorbents over a large range of pH, a series of experiments were performed, varying the pH of the solution from 1.5 to 10. Normally, copper containing wastewater has an acidic to neutral pH but an alkaline solution was also analysed. Only biosorbents 6 and 7 were tested since they in general showed the best performance in the previous experiments. The results are summarized in Table 8. From the table it is easy to see that the adsorption is far better in acidic solutions. In alkaline solution, where the formation of copper hydroxides should also contribute to the overall copper removal, it is the worse case. In the pH range of 1.5 to 5, the copper biosorption phenomena are therefore expected to be similar and independent of pH with slightly better results (highest q_{eq} value) for the most acidic conditions. Many of the other agricultural by-products, as shown previously in Table 1, have typically their optimum pH a little higher than biosorbents 6 and 7 from this work. Therefore, biosorbents 6 and 7 complement well existing adsorbents. Nevertheless, copper smelter wastewater and general mining activity effluents have typically a pH below 4 (ref.), and that means that the two biosorbents would fit well as an alternative remediation tool.

4.5. Adsorption isotherms

A series of experiments were carried out for biosorbents 6 and 7, where the initial copper concentration was varied, and the cop-

Table 8
 q_{eq} versus pH.

pH	Biosorbent 6		7	
	[Cu] _{eq} (mg L ⁻¹)	q_{eq} (mg g ⁻¹)	[Cu] _{eq} (mg L ⁻¹)	q_{eq} (mg g ⁻¹)
V: 200 mL, M: 5.0 g, M/V: 0.025 g mL ⁻¹ , [Cu] ₀ : 396.3 mg L ⁻¹ , Time 1800 min				
1.5	60.55	13.43	104.3	11.68
3.0	95.05	12.05	107.8	11.54
5.0	134.5	10.47	147.5	9.95
7.0	225.4	6.84	200.4	7.84
10.0	290.4	4.24	323.3	2.92

**Fig. 5.** q_{eq} as a function of C_{eq} for biosorbent 6 and 7 at different pH.

per concentration in the solution was measured at equilibrium. M/V was maintained constant at 0.025 g mL⁻¹. With this, the goal was to find the best biosorbent in the best possible conditions, and therefore the analysis was divided in three parts. First the optimum biosorption pH was to be determined, second an isotherm comparison between biosorbent 6 and 7 was to be carried out, and finally the isotherms were adjusted to commonly used biosorption isotherm models.

Fig. 5 shows the biosorption isotherm for biosorbents 6 and 7 at various pH. The isotherms are shown as q_{eq} as a function of C_{eq} . The higher the curves are situated, the better the overall biosorption efficiency is expected to be. The tendency of these curves confirms that the most acidic pH gives the best results. Again, the behaviour of each biosorbent is similar, even if the origin and shape of the materials is quite different – larger peach stones (biosorbent 6) versus small pine sawdust particles (biosorbent 7). Confirming earlier

Table 9
Langmuir and Freundlich parameters representing biosorption isotherms of biosorbent 6 and 7 as a function of pH. R^2 values correspond to the linearized equations.

	Langmuir parameters			
	pH	q_m (mg g ⁻¹)	K_d (mg L ⁻¹)	R^2
Biosorbent 6	1.5	43.3	796.1	0.9902
	3.5	43.3	782.7	0.9941
	5.0	31.3	562.3	0.9911
Biosorbent 7	1.5	24.3	636.7	0.9966
	3.5	22.7	652.4	0.9925
	5.0	20.0	583.9	0.9941
	Freundlich parameters			
	pH	$1/n$	k (mg g ⁻¹)	R^2
Biosorbent 6	1.5	0.881	0.0783	0.9985
	3.5	0.880	0.0790	0.9986
	5.0	0.828	0.0967	0.9973
Biosorbent 7	1.5	0.811	0.0741	0.9961
	3.5	0.819	0.0649	0.9965
	5.0	0.808	0.0657	0.9953

discoveries in this work, biosorbent 6 seems to be somewhat better for copper removal than biosorbent 7.

The experimental isotherm data was adjusted to common models. Table 9 shows Freundlich and Langmuir parameters together with the fitting accuracy. It can be seen that both models fit the biosorption of copper by biosorbent 6 and 7 very well. This is useful for any practical use of the biosorption in real wastewater treatment. The next step must be to analyse the behaviour of the two biosorbents in real wastewater treatment. Comparing the estimated Langmuir maximum adsorption capacities with values found in the literature (Table 1), both biosorbent 6 and 7 are showing a quite high capacity – despite the fact that the biosorbents listed in Table 1 typically are pre-treated and size reduced. Biosorbents 6 and 7 therefore have a much lower surface area per volume. This is also shown by the rather slow biosorption compared to smaller biosorbents. Future work should include analysis of the effect of particle size distribution.

5. Conclusions

The efficiency and characteristics of seven organic waste materials as copper biosorbents were analysed. In general, the best materials found were olive pips, peach stones and pine sawdust. Pine sawdust presents the highest copper uptake velocity, whereas peach stones show the highest copper uptake in general. Other materials studied – peanut shells, nut shells, plum seeds, and eucalyptus bark – did not adsorb copper sufficiently efficient for any practical implementation.

When adjusting the copper uptake of pine sawdust, olive pips and peach stones over time to existing kinetic models, the second order model of Ho and McKay showed an excellent fit for the biosorbents studied. At pH 5, an optimal M/V ratio for copper uptake was found at 0.005 g mL⁻¹ and 0.0075 g mL⁻¹ for olive pips and pine sawdust, respectively. The best copper uptake was found at acidic pH, which is promising for real wastewater treatment, where pH is typically low.

It was found that both Langmuir and Freundlich models could describe the biosorption isotherms excellent for all pH levels studied (1.5–5) for the two biosorbents selected (pine sawdust and olive pips). The R^2 values were higher than 0.99 for all isotherms analysed.

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