

This article was downloaded by: [Univ Politec Cat]

On: 31 December 2011, At: 05:03

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Chemistry and Ecology

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gche20>

A homogeneous and low-cost biosorbent for Cd, Pb and Cu removal from aqueous effluents

Diego A. Grassi^a, Mariana Galicio^a & Alicia Fernández Cirelli^a

^a Centros de Estudios Transdisciplinarios del Agua FVET, Universidad de Buenos Aires, Buenos Aires, Argentina

Available online: 26 Apr 2011

To cite this article: Diego A. Grassi, Mariana Galicio & Alicia Fernández Cirelli (2011): A homogeneous and low-cost biosorbent for Cd, Pb and Cu removal from aqueous effluents, *Chemistry and Ecology*, 27:4, 297-309

To link to this article: <http://dx.doi.org/10.1080/02757540.2011.565750>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

A homogeneous and low-cost biosorbent for Cd, Pb and Cu removal from aqueous effluents

Diego A. Grassi, Mariana Galicio and Alicia Fernández Cirelli*

Centros de Estudios Transdisciplinarios del Agua FVET, Universidad de Buenos Aires, Buenos Aires, Argentina

(Received 28 August 2010; final version received 21 February 2011)

Heavy metal pollution of aqueous effluents is a matter of widespread concern. The use of low-cost materials for the adsorption of heavy metals seems to be a suitable choice for waste water treatment. *Polyporus tenuiculus*, easily cultivated on lignocellulosic waste, was assayed for Cu, Pb and Cd removal from aqueous solutions. Pb was removed more efficiently. Kinetics studies suggested a *pseudo*-second-order reaction and equilibrium was reached in ~ 30 min in all cases. The metal-sorption data were analysed according to several two-parameter isotherms. Data better fitted the Langmuir model for the three metals. A great dependence of metal adsorption with pH was observed. Characterisation of both the biomass and the complex metal-biomass was performed by FT-IR and SEM-EDX. Results suggest an ion exchange mechanism.

Keywords: biosorbent; *Polyporus tenuiculus*; heavy metal removal; adsorption isotherms; pH dependence

1. Introduction

Heavy metal pollution of aqueous effluents is a matter of widespread concern in the world. In particular, Cd(II) and Pb(II) are toxic elements; Pb(II) affects the central nervous system, especially of children, whereas Cd(II) is toxic to the kidney and liver. Cd(II) and Pb(II) pollution arise mostly from anthropogenic activities. The main uses of cadmium are in battery manufacturing, and as stabilisers for plastics and nonferrous alloys. Electroplating industries are a great source of cadmium pollution. The use of lead in several commercial products, such as paints, gasoline and pesticides has been prohibited in order to reduce environmental pollution. However, there exist several industrial wastes containing lead, for example, those generated in mining, electroplating and battery manufacture.

Considerable efforts have been made for their removal because of to the hazards they pose to human health, their accumulation in biota and, in general, their dangerous effects on ecosystems. In the case of cadmium, recovery is highly attractive not only because for its high toxicity, but also because reserves are becoming depleted. Common methods for the removal of toxic metals from water are: ion exchange, reverse osmosis, precipitation, solvent extraction, membrane technologies, electrochemical treatment and sorption. Carbon adsorption is by far the most widely

*Corresponding author. Email: afcirelli@fvet.uba.ar

used. However, the use of activated carbon is expensive, and there has been considerable interest in the use of other sorbent materials, particularly biosorbents. Reports on the use of inexpensive biological materials such as algae, fungi, bacteria and macrophytes have increased considerably since the pioneering work of Volesky [1,2].

In previous studies in our laboratory, dead macrophytes, such as *Lemna minor*, *Spirodela intermedia* and *Pistia stratiotes*, have proved to be efficient for the simultaneous removal of Pb, Cd, Ni, Cu and Zn [3].

Biosorbents of natural occurrence have the advantage of accessibility and low cost. Nevertheless, they may be heterogeneous in their composition depending on the environment where they have developed [4]. In some cases, they may have also accumulated heavy metals. However, cultivated fungus may be an alternative source of biosorbents.

Polyporus tenuiculus is a naturally occurring macroscopic mushroom from Central and South America with big fructification bodies. *P. tenuiculus* may be easily cultivated on wheat straw and sawdust [5].

Very few studies using *Polyporus* species for metal sorption have been reported [6,7]. The aim of our study was to investigate the use of dead biomass of *P. tenuiculus* for heavy metal removal from aqueous solutions.

Use of this biosorbent may have advantages over others reported in the literature: on the one hand, *P. tenuiculus* is cultivated on lignocellulosic materials, which would otherwise constitute waste; on the other hand, it has been reported that the chemical composition of the fungi wall strongly depends on the presence or absence of nutrients in the environment where they have grown [8–10]. In that way, use of a cultivated biosorbent ensures a constant chemical composition over time and thus the reproducibility of removal performance.

Therefore, these studies may be useful for low-cost industrial wastewater treatment.

Because pollution problems with Cd, Cu and Pb have been reported in some ecosystems of Argentina and bordering countries, these metals were chosen for these studies [11,12].

Equilibrium, kinetic and spectroscopic studies were performed to assess the operating mechanism from the prospect of metal recovery.

2. Materials and methods

2.1. Biosorbent

The fungal *P. tenuiculus* was kindly provided by Alejandra Omarini (Instituto Nacional de Tecnología Industrial, Buenos Aires, Argentina). Fungi were lyophilised and grounded. Samples were stored protected from light and atmospheric moisture.

2.2. Experimental techniques

2.2.1. Materials

All reagents used were analytical grade or better. Stock standard solutions of Pb^{2+} , Cu^{2+} and Cd^{2+} ($1000 \text{ mg}\cdot\text{L}^{-1}$) were prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ (Sigma-Aldrich), $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (Mallinckrodt) and CdCl_2 (Fluka) in milliQ water (Millipore).

Experiments were carried out in batch mode in 250 mL conical flasks under magnetic stirring. In all cases, the temperature was controlled at $25 \pm 2^\circ\text{C}$. Experiments were performed in duplicate. In each case, 100 mL of metal solution was placed in the flask and 200 mg of biomass were added under stirring; pH was registered (or adjusted) using a Hanna pH210 potentiometer (Hanna Instrument). The natural pH of the mixture was 5.0.

Once the experiment was complete, samples were filtered through 0.45- μm nylon disc filters (Pall), and diluted with HNO_3 0.2% (v/v) as a preservative and matrix modifier for atomic spectrometric determinations.

Spectrometric determinations were performed by inductively coupled plasma–optical emission spectroscopy (ICP–OES) using a Perkin–Elmer Optima 2000 DV. Instrumental conditions were set to obtain a robust plasma [13]: power, 1400 W; Ar nebuliser flow, 0.5 $\text{mL}\cdot\text{min}^{-1}$; Ar plasma flow, 15 $\text{mL}\cdot\text{min}^{-1}$; Ar auxiliary flow, 0.7 $\text{mL}\cdot\text{min}^{-1}$; and sample flow rate, 1.2 $\text{mL}\cdot\text{min}^{-1}$. The atomic lines used were: Cu 324.752 nm, Cd 228.801 nm, Pb 220.353 nm, Na 589.592 nm, K 766.490 nm, Ca 317.933 nm and Mg 285.213 nm.

For calibration of the instrument, a set of standards was prepared from a multimetallic standard solution of 100 $\text{mg}\cdot\text{L}^{-1}$ with a certificate of traceability (Perkin–Elmer). Peak integration was performed with a multicomponent spectral fitting (MSF) algorithm [14].

Metal uptake was determined as:

$$q_e = \frac{(C_0 - C_e) \times V}{m}, \quad (1)$$

Where q_e is metal uptake in mg of metal per g of biomass. C_0 is the initial concentration of the metal, C_e is the metal equilibrium concentration, both in $\text{mg}\cdot\text{L}^{-1}$. V (L) is the volume of the metal solution and m (g) is the mass of biosorbent.

Percentage removal was calculated as:

$$R(\%) = \frac{(C_0 - C_e) \times 100}{C_0}. \quad (2)$$

Fitting was evaluated using the coefficient of determination R^2 :

$$R^2 = 1 - \frac{\sum_i (y_i - \hat{y}_i)^2}{\sum_i (y_i - \bar{y})^2}, \quad (3)$$

where y_i are y-axis values, \hat{y}_i are model estimate and \bar{y} is the mean of y values.

2.2.2. Kinetics

A kinetic study was carried out to determine the equilibrium time required for the uptake of metals from a liquid solution. Experiments were performed with an initial metal concentration of 10 $\text{mg}\cdot\text{L}^{-1}$. The contact time between the metal solutions and the biosorbent ranged between 1.5 and 60 min. Liquid samples were withdrawn at different times to cover the whole period.

Pseudo-first-order kinetics [15] are described by Equation (4).

$$\frac{dq_t}{dt} = K_1 \times (q_e - q_t), \quad (4)$$

where K_1 (min^{-1}) is the *pseudo*-first-order equilibrium rate constant and q_t ($\text{mg}\cdot\text{g}^{-1}$) is the mass of adsorbed of solute per unit mass of adsorbent at time t .

Because Equation (4) is a differential equation, the next expression is used for linear fitting:

$$\text{Ln}(q_e - q_t) = \text{Ln}(q_e) - K_1 \times t. \quad (5)$$

According to Wang and Chen [16], initial sorption rate for *pseudo*-first-order kinetics is expressed as:

$$v_{0,1} = K_1 \times q_e. \quad (6)$$

Equation (7) describes a *pseudo*-second-order kinetic equation [17]:

$$\frac{dq_t}{dt} = K_2 \times (q_e - q_t)^2, \quad (7)$$

where K_2 is the *pseudo*-second-order equilibrium rate constant in $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$. Its integrated form was used for linear fitting:

$$\frac{t}{q_t} = \frac{1}{q_e^2 \times K_2} + \frac{t}{q_e}. \quad (8)$$

The initial sorption rate for *pseudo*-second-order kinetics is:

$$v_{0,2} = K_2 \times q_e^2. \quad (9)$$

2.2.3. pH dependence

Sorption processes are strongly dependent on solution pH [18,19]. Several experiments were performed to analyse the variation of metal uptake due to variation in the pH of the solution.

Experiments were conducted for 60 min, twice the contact time needed to reach equilibrium, working with a metal concentration of 10 mg L^{-1} . pH was adjusted by addition of 1 M NaOH or HCl during the experiment to obtain different equilibrium pH. Higher pH values (> 8) were avoided to prevent metal precipitation [20].

2.2.4. Adsorption isotherms

Equilibrium adsorption processes are described by isotherms governing the distribution of a given sorbate between the liquid phase and the sorbent. There are many isotherms to describe sorption. Langmuir, Freundlich and Temkin isotherms were used to fit the experimental data in this study.

The Langmuir isotherm [21] assumes monolayer sorption onto a surface containing a finite number of identical sorption sites, and once the adsorption site is occupied, no further adsorption can take place at that site, Langmuir equation is represented as:

$$q_e = \frac{q_m \times K_L \times C_e}{1 + K_L \times C_e}, \quad (10)$$

where q_m is the amount of sorbate needed to form a complete monolayer per mass of sorbent in mg g^{-1} and K_L is the Langmuir equilibrium constant in $\text{L}\cdot\text{mg}^{-1}$.

The linear form of the Langmuir isotherm used was:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m \times K_L}. \quad (11)$$

The Freundlich isotherm [22] supposes that the ratio between the amount of adsorbed sorbate and the concentration of sorbate in the liquid phase is not a constant at different concentrations. The Freundlich isotherm does not assume monolayer adsorption and, thus, infinite sorbate uptake is predicted mathematically. This equation has an implicit exponential distribution of active sites and their energies [20].

$$q_e = K_F C_e^{1/n}, \quad (12)$$

where K_F ($\text{mg}^{(1-1/n)}\cdot\text{L}^{1/n}\cdot\text{g}^{-1}$) is the biosorption equilibrium constant, representative of the sorption capacity, and n is a constant indicative of biosorption intensity [16].

The linear form of the Freundlich isotherm used was:

$$\text{Ln}(q_e) = \text{Ln}(K_F) + \frac{1}{n}\text{Ln}(C_e), \quad (13)$$

Temkin is another important isotherm that was developed assuming an heterogeneous surface [23], and is described by:

$$q_e = A \times \ln(B \times C_e), \quad (14)$$

where B is the Temkin adsorption potential in $\text{L}\cdot\text{mg}^{-1}$ and A is the Temkin constant in $\text{mg}\cdot\text{g}^{-1}$, related to heat of sorption.

The linear form of the Temkin isotherm used was:

$$q_e = A \times \ln(B) + A \times \ln(C_e). \quad (15)$$

Langmuir, Freundlich and Temkin are two-parameter isotherms and can be compared for fitting experimental data.

Contact time to reach equilibrium was 60 min and experiments were performed at pH 5.

2.3. FT-IR spectroscopy

Fourier transform infrared spectroscopy (FT-IR) was performed on both biomass and biomass after treatment with heavy metals. Sample preparation was as follows: 2 mg of dried biomass was grounded with 125 mg of dried KBr (Anedra) in an agate mortar, and a translucent disk was obtained in a hand press (Spectra-Tech). Spectra were recorded in a Shimadzu IRAffinity-1 in the range $400\text{--}4000\text{ cm}^{-1}$, using Happ-Ganzel apodisation, a resolution of 4 cm^{-1} and 25 scans.

2.4. SEM-EDX analysis

In order to characterise biomass and metal sorbates, electronic micrographs were performed in a scanning electron microscope (SEM). In addition, elemental spectra and a semi-quantitative analysis of samples with and without adsorbed metal were obtained by energy dispersive X-ray (EDX). Analyses were performed in a Philips XL30 ESEM instrument. For measurement, samples were dried in a desiccator, grounded in an agate mortar and placed in an aluminium-supporting plate for direct analysis without any further treatment. For each sample, EDX spectra were obtained in different places to confirm sample homogeneity.

2.5. Ion-exchange capacity

To investigate possible mechanisms involved in heavy metal sorption, batch experiments were performed using Pb^{2+} as the sorbate. The release of Na^+ , K^+ , Ca^{2+} and Mg^{2+} was measured. Initial and final pH were determined to estimate the amount of H^+ exchanged. Experiments were performed in triplicate and proper blanks were used.

2.6. Desorption of heavy metal

To test for the possibility of recovery of the sorbed metal, lead-treated biomass was centrifuged; the precipitate was washed twice with distilled water and subsequently treated with 0.1 M hydrochloric acid. The lead concentration in the resulting solution was measured by ICP.

3. Results and discussion

The metal-removal capacity of *P. tenuiculus* was previously evaluated in batch experiments at pH 5 to assess its potential use as a biosorbent. Overall, a removal capacity of $37 \pm 3\%$, $64 \pm 3\%$

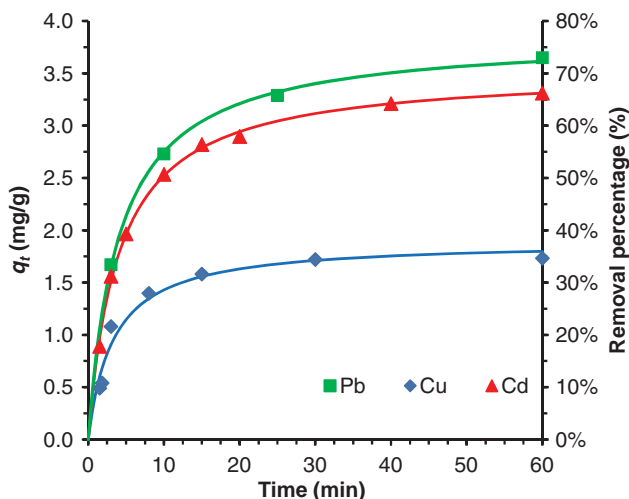


Figure 1. Time evolution of metal uptake for Cu^{2+} , Pb^{2+} and Cd^{2+} ions.

and $74 \pm 4\%$ was found for Cu, Cd and Pb, respectively. These earlier results obtained for Cd and Pb using this homogeneous material were promising and prompted us to study the mechanisms involved to analyse the possible recovery of these metals.

3.1. Kinetics

Kinetics experiments were performed to determine the contact time required to reach equilibrium, and the operating processes that may be involved.

The results obtained for Cu^{2+} , Cd^{2+} and Pb^{2+} are shown in Figure 1. In all cases, equilibria were reached in ~ 30 min, when q_e is $\sim 90\%$ of $q_{e,\text{max}}$, indicating a very fast metal uptake.

Kinetic parameters obtained from linear fitting are shown in Table 1, and the corresponding plots are shown in Figure 2 a and b, for a *pseudo*-first-order and *pseudo*-second-order model, respectively. The experimental data may be better described by a second-order kinetics, taking into account r^2 values. In the *pseudo*-second-order model the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites, and the number of occupied sites is proportional to the fraction of the metal ion adsorbed. Similar results were found for another fungal biomass [24].

The initial adsorption rate ($v_{0,2}$) follows the order $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+}$, suggesting that *P. tenuiculus* is more suitable for Pb and Cd removal than for Cu removal.

Table 1. *Pseudo*-first and *pseudo*-second-order parameters obtained for the adsorption of Cu^{2+} , Pb^{2+} and Cd^{2+} on *Polyporus tenuiculus*.

		Cu^{2+}	Cd^{2+}	Pb^{2+}
<i>Pseudo</i> -first order	K_1 (min^{-1})	0.068 ± 0.011	0.034 ± 0.008	0.033 ± 0.015
	q_e ($\text{mg}\cdot\text{g}^{-1}$)	1.15 ± 0.17	1.37 ± 0.19	1.42 ± 0.33
	$v_{0,1}$	0.079 ± 0.017	0.047 ± 0.013	0.046 ± 0.023
	R^2	0.989	0.971	0.978
<i>Pseudo</i> -second order	K_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$)	0.18 ± 0.09	0.070 ± 0.007	0.060 ± 0.011
	q_e ($\text{mg}\cdot\text{g}^{-1}$)	1.84 ± 0.11	3.53 ± 0.05	3.90 ± 0.09
	$v_{0,2}$	0.59 ± 0.32	0.87 ± 0.09	0.92 ± 0.17
	R^2	0.998	0.999	0.999

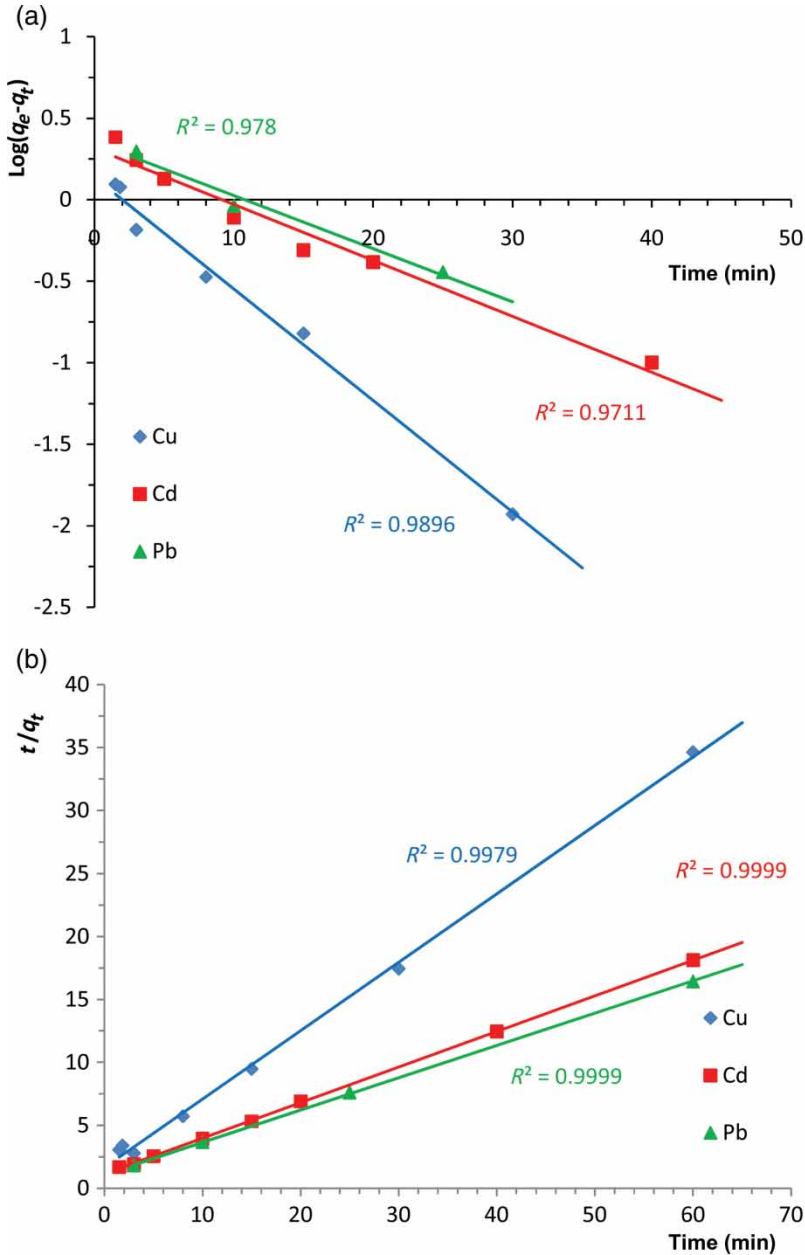


Figure 2. Linear plots for kinetic experiments. pH = 5.0, metal initial concentration $10 \text{ mg} \cdot \text{L}^{-1}$ and 0.2 g of biomass: (a) *pseudo*-first order fitting; (b) *pseudo*-second order fitting.

3.2. Influence of pH

Batch studies were performed using Cu^{2+} , Cd^{2+} and Pb^{2+} ions, at different equilibrium pH. Figure 3 shows results which evidence a great dependence of metal adsorption on pH. Metal uptake increases strongly with pH and decreases at lower values.

Data were fitted to curves using a sigmoideal equation with an inflexion point of 5.2 ± 1.2 , 4.35 ± 0.55 and 4.31 ± 0.75 for Cu^{2+} , Cd^{2+} and Pb^{2+} , respectively. A similar trend is observed

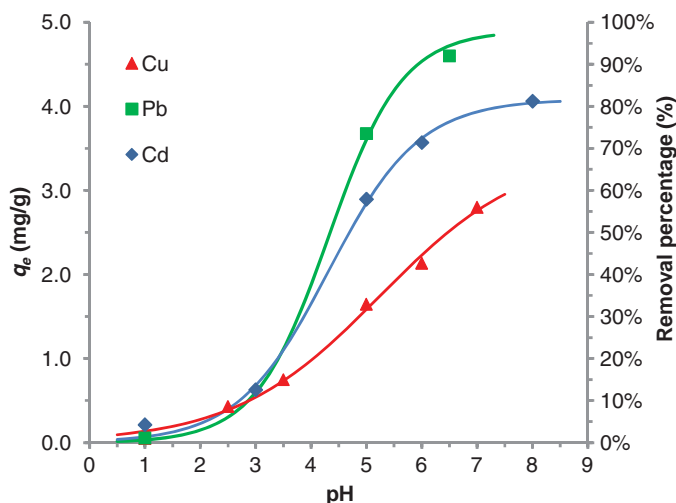


Figure 3. Effect of pH on Cd^{2+} , Pb^{2+} and Cu^{2+} adsorption capacity, at a metal level of $10 \text{ mg} \cdot \text{L}^{-1}$.

for chemical species in the cell wall due to deprotonated carboxylic acid with $\text{p}K_a$ values of 3.5–5 [25]. These results suggest that metal complexation or ion exchange between metal ions and the biosorbent is the main mechanism for heavy metal removal. At low pH, acid groups are in protonated form and low adsorption of heavy metals is observed, as already reported for other biosorbents [25–29].

3.3. Sorption isotherms

The experimental data were adjusted using Langmuir, Freundlich and Temkin models. The sorption isotherms for Cu, Cd and Pb are shown in Figure 4. The parameters for the three models as well as the coefficients of determination are shown in Table 2, and linearised plots are shown in

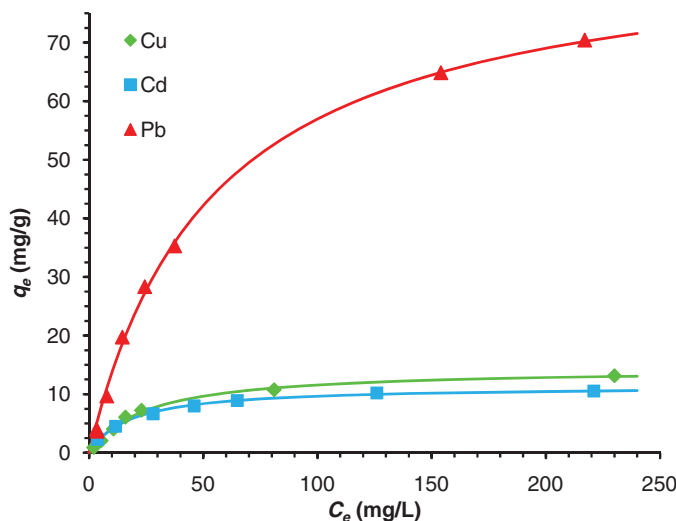


Figure 4. Adsorption isotherm of Cu^{2+} , Cd^{2+} and Pb^{2+} on *Polyporus tenuiculus*.

Table 2. Isotherm parameters for sorption of Cu, Cd and Pb on *Polyporus tenuiculus*.

		Cu ²⁺	Cd ²⁺	Pb ²⁺
Langmuir	K_L (L·mg ⁻¹)	0.036 ± 0.007	0.057 ± 0.012	0.015 ± 0.004
	q_m (mg·g ⁻¹)	14.7 ± 0.84	11.4 ± 0.42	92 ± 13
	R^2	0.998	0.999	0.992
Freundlich	K_F	0.90 ± 0.41	1.7 ± 0.6	2.2 ± 0.7
	n	1.8 ± 0.8	2.7 ± 0.9	1.42 ± 0.43
	R^2	0.896	0.938	0.942
Temkin	A	6.3 ± 1.1	4.92 ± 0.76	37 ± 6
	B	0.76 ± 0.16	0.92 ± 0.15	0.59 ± 0.11
	R^2	0.983	0.987	0.978

Figure 5. In all cases, the experimental data fitted the Langmuir isotherm better ($R^2 > 0.98$), in agreement with previous studies carried out with another dead fungal biomass [30–32].

Therefore, it may be concluded that metal removal of divalent heavy metals ions by *P. tenuiculus* is a monolayer process.

The q_m of the Langmuir model is assumed to be the number of ions which form a complete monolayer on the surface of the biosorbent. Maximum surface coverage was found to be 14.7 ± 0.3 mg·g⁻¹ for Cu, 11.4 ± 0.4 mg·g⁻¹ for Cd and 92 ± 13 mg·g⁻¹ for Pb respectively, following the order $Pb^{2+} > Cu^{2+} > Cd^{2+}$.

The Langmuir equilibrium constant K_L is related to the affinity of metal ion by the biomass. In the present case, the affinity follows this order: $Cd^{2+} > Cu^{2+} > Pb^{2+}$, in spite of the removal capacity which follows the following order $Pb^{2+} > Cd^{2+} > Cu^{2+}$.

3.4. Characterisation

FTIR spectra of *P. tenuiculus* before and after treatment with copper, cadmium and lead ions at pH 5.0 are shown in Figure 6. The spectra reveal a complex chemical structure in sorbent. Because a disagreement in functional groups band assignment is found in the literature, our assignments were carried out in accordance with previous studies [29,33–35].

The main difference between untreated and metal-treated biomass is in the region of ~ 1700 cm⁻¹. A peak can be seen at 1710 – 1714 cm⁻¹ for metal-treated biomass, and this peak is not visible in the untreated biomass spectrum, where a shoulder overlapping the amide I peak (1650 cm⁻¹) is observed. This signal corresponds to C–O stretching in carboxylic acids. These facts agree with metal complexation binding or ionic exchange of heavy metals, carboxylate groups being responsible for metal uptake.

With the aim of further characterising the sorption mechanism, SEM-EDX analysis was performed on biomass and on solid samples obtained after metal uptake. The EDX analyses are shown in Figure 7.

No great differences were observed in the morphology of the biomass after metal uptake (micrographs not shown). In general, metal-loaded samples show a slight roughness that is not observed for untreated biomass, suggesting surface modification. However, EDX analysis shows significant differences. The presence of metals is confirmed by characteristic lines. An important fact is that untreated biomass shows the presence of potassium, whereas all metal-treated samples do not evidence it. This suggests that ionic exchange took place between heavy metals and potassium in the biomass. Nevertheless, because EDX analysis is semiquantitative and the sensitivity of light elements such as sodium are so small, complementary experiments must be necessary to ensure if the ion exchange is the main mechanism for heavy metal sorption.

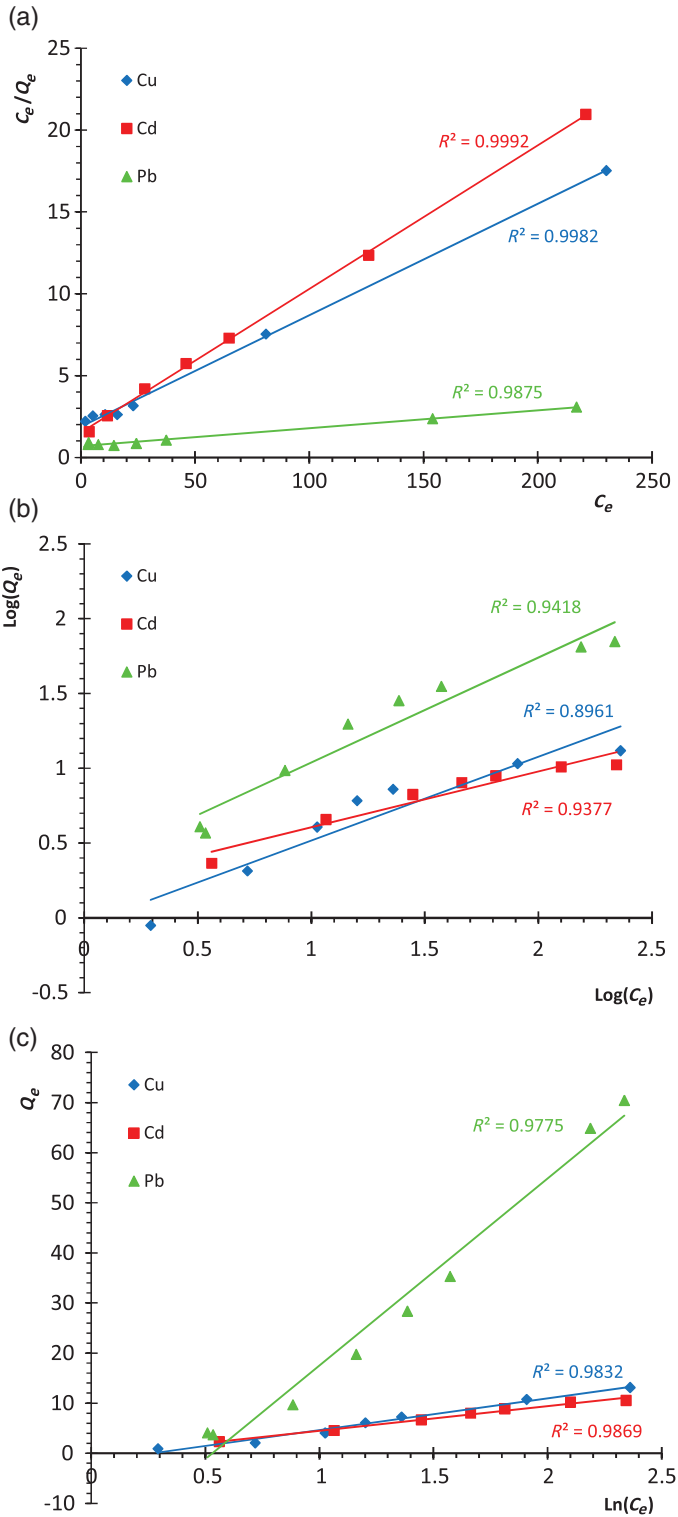


Figure 5. Linear plots for adsorption isotherms: (a) Langmuir model; (b) Freundlich model; (c) Temkin model.

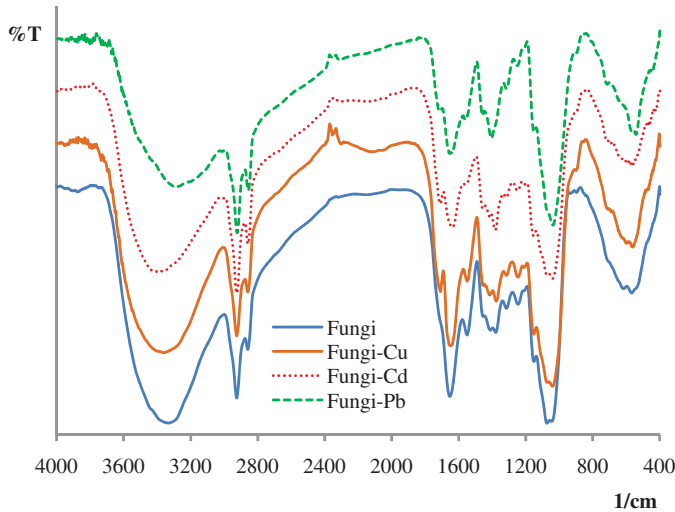


Figure 6. FTIR spectra of metal treated and untreated *Polyporus tenuiculus*.

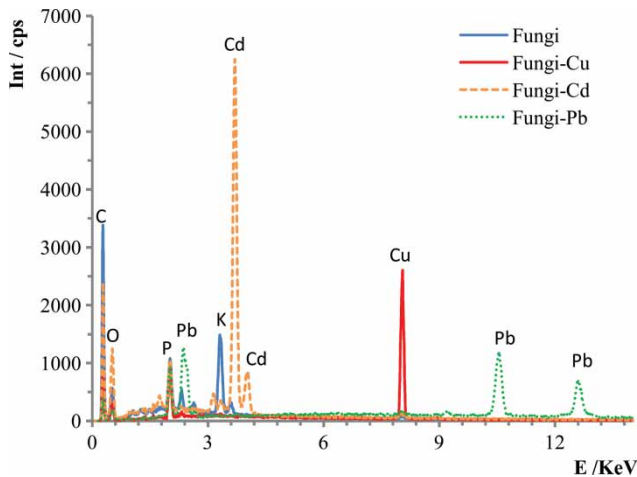


Figure 7. EDX analysis of *Polyporus tenuiculus*, Cu, Cd and Pb treated biomass.

3.5. Ion-exchange mechanism

It has been reported in the literature, that in biosorbents showing an ion-exchange mechanism, the sorbed metal is exchanged by alkali and alkaline earth metals [20,36].

For this reason, equivalents sorbed and released by the biomass were measured by ICP-OES. The results are shown in Table 3, revealing the release of a significant amount of K^+ and Na^+ . However, release of alkaline earths was not significant because the ICP analysis showed no detectable amounts of Ca and Mg. The equivalent of H^+ released was negligible. The total amount of lead sorbed was $0.039 \pm 0.002 \text{ mEq}\cdot\text{g}^{-1}$ and total metal released was $0.035 \pm 0.011 \text{ mEq}\cdot\text{g}^{-1}$. The confidence interval obtained for the release and sorption amounts overlapped, indicating that ion exchange between heavy metal and sodium and potassium in took place in the biosorbent.

However, desorption of Pb^{2+} from Pb-loaded *P. tenuiculus* was performed with 0.1 M HCl obtaining a 99% recovery of the sorbed lead, thus confirming that the main mechanism for heavy metal sorption is ion exchange.

Table 3. Release of alkali, alkaline earth metal cations and proton due to sorption of Pb^{2+} on *Polyporus tenuiculus*.

Pb^{2+} sorbed ($\text{mEq}\cdot\text{g}^{-1}$)	Amount of cations released ($\text{mEq}\cdot\text{g}^{-1}$)					Sum of equivalents released ($\text{mEq}\cdot\text{g}^{-1}$)
	Na^+	K^+	Ca^{2+}	Mg^{2+}	H^+	
0.039 ± 0.002	0.011 ± 0.004	0.024 ± 0.010	<0.00025	<0.00008	<0.000005	0.035 ± 0.011

4. Conclusions

This study confirms the potential use of low-cost *P. tenuiculus* as a metal adsorbent. The biosorbent presented in this study ensures reproducibility of the results over time, because of its invariable source. The rapid kinetics of the adsorption process has significant practical importance, ensuring efficiency and economy.

Ion exchange between the metals in solution and potassium and sodium in the fungus is the main mechanism of heavy metal sorption. In addition, chelation reactions between metals and carboxyl groups or another functional group in the cell wall are also possible. Carboxyl groups seem to be the main functional groups involved in the biosorption process.

The principal advantages of use this biosorbent are: (1) reproducibility; (2) the low cost; (3) the recovery of metals in concentrated solution, which makes its use as a metal-recovery agent attractive because ion exchange has been proved to be the main mechanism involved; and (4) its high efficiency at low metal concentrations.

It should be noted that the effect of other compounds present in waste water (other metal ions, surfactants, sequestering agents) was not considered in this study. Therefore, there are ongoing studies to determine the capability of *P. tenuiculus* for removing heavy metals from a multi-element solution as well as from effluent.

Acknowledgements

The authors kindly acknowledge UBA and CONICET for financial support, Alejandra Omarini (Instituto Nacional de Tecnología Industrial, Colectora Av. General Paz 5445 – Parque Tecnológico Miguelete) for providing the fungus and Jenck S.A. for FTIR measurements.

References

- [1] B. Volesky, *Biosorbent materials*, Biotechnol. Bioeng. Symp. Ser. 16 (1986), pp. 121–126.
- [2] B. Volesky, *Biosorbents for metal recovery*, Trends Biotechnol. 5(4) (1987), pp. 96–101.
- [3] P. Miretzky, A. Saralegui, and A.F. Cirelli, *Simultaneous heavy metal removal mechanism by dead macrophytes*, Chemosphere 62 (2006), pp. 247–254.
- [4] P. Miretzky, A. Saralegui, and A.F. Cirelli, *Aquatic macrophytes potential for the simultaneous removal of heavy metals*, Chemosphere 57(6) (2004), pp. 997–1005.
- [5] A. Omarini, B.E. Lechner, and E. Albertó, *Polyporus tenuiculus: a new naturally occurring mushroom that can be industrially cultivated on agricultural waste*, J. Ind. Microbiol. Biotechnol. 36 (2009), pp. 635–642.
- [6] F.B. Dilek, A. Erbay, and U. Yetis, *Ni(II) biosorption by Polyporus versicolor*, Process Biochem. 37 (2002), pp. 723–726.
- [7] O. Genc, N. Şatiroglu, Y. Yalçınkaya, A. Denizli, M.Y. Arıca, and S. Bektas, *Application of NaOH treated Polyporus versicolor for removal of divalent ions of Group IIB elements from synthetic wastewater*, Process Biochem. 38 (2002), pp. 65–72.
- [8] G.M. Gadd, J.M. Tobin, and C. White, *Metal accumulation by fungi: applications in environmental biotechnology*, Biomed. Life Sci. 13(2) (1994), pp. 126–130.
- [9] F.M. Klis, P. Mol, K. Hellingwerf, and S. Brul, *Dynamics of cell wall structure in Saccharomyces cerevisiae*, FEMS Microbiol. Rev. 19(3) (2002), pp. 239–256.
- [10] N. Ohno, R. Tada, N. Nagi-Miura, and Y. Adachi, *The influence of culture conditions on vasculitis and anaphylactoid shock induced by fungal pathogen Candida albicans cell wall extract in mice*, Microb. Pathogen. 44(5) (2008), pp. 379–388.

- [11] J.R. Miller, K.A. Hudson-Edwards, P.J. Lechler, D. Preston, and M.G. Macklin, *Heavy metal contamination of water, soil and produce within riverine communities of the Río Pilcomayo basin, Bolivia*, *Sci. Total Environ.* 320(2/3) (2003), pp. 189–209.
- [12] A.M. Gagneten and J.C. Paggi, *Effects of heavy metal contamination (Cr, Cu, Pb, Cd) and eutrophication on zooplankton in the lower basin of the Salado River (Argentina)*, *Water Air Soil Pollut.* 198(1–4) (2009), pp. 317–334.
- [13] J. Dennaud, A. Howes, E. Poussel, and J.-M. Mermet, *Study of ionic-to-atomic line intensity ratios for two axial viewing-based inductively coupled plasma atomic emission spectrometers*, *Spectrochim. Acta B* 56 (2001), pp. 101–112.
- [14] J. Nölte, *Minimizing spectral interferences with an array ICP emission spectrometer using different strategies for signal evaluation*, *Atom. Spectrosc.* 20(3) (1999), pp. 103–107.
- [15] S. Lagergren, *Zur theorie der sogenannten adsorption gelöster stoffe*. *Kungliga Svenska Vetenskapsakademiens, Fin. Lakaresällsk. Handl.* 24 (1898), pp. 1–39.
- [16] J. Wang and C. Chen, *Biosorbents for heavy metals removal and their future*, *Biotechnol. Adv.* 27 (2009), pp. 195–226.
- [17] Y.-S. Ho, *Review of second-order models for adsorption systems*, *J. Hazard. Mater.* B136 (2006), pp. 681–689.
- [18] T.A. Kurniawana, G.Y.S. Chana, W.-h. Loa, and S. Babelb, *Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals*, *Sci. Total Environ.* 366(2/3) (2006), pp. 409–426.
- [19] P. Yin, Q. Yu, B. Jin, and Z. Ling, *Biosorption removal of cadmium from aqueous solution by using pretreated fungal biomass cultured from starch wastewater*, *Water Res.* 33(6) (1999), pp. 1960–1963.
- [20] A. Saeed, M. Iqbalb, and W.H. Hölla, *Kinetics, equilibrium and mechanism of Cd²⁺ removal from aqueous solution by mungbean husk*, *J. Hazard. Mater.* 168(2/3) (2009), pp. 1467–1475.
- [21] I. Langmuir, *The adsorption of gases on plane surfaces of glass, mica and platinum*, *J. Am. Chem. Soc.* 40(9) (1918), pp. 1361–1403.
- [22] H. Freundlich, *Ueber Die Adsorption in Loesungen*, *Z. Phys. Chem* 57 (1907), p. 385.
- [23] X. Wang and Y. Qin, *Equilibrium sorption isotherms for of Cu²⁺ on rice bran*, *Process Biochem.* 40 (2005), pp. 677–680.
- [24] X. Li, Q. Xu, G. Han, W. Zhu, Z. Chen, X. He, and X. Tian, *Equilibrium and kinetic studies of copper(II) removal by three species of dead fungal biomasses*, *J. Hazard. Mater.* 165(1–3) (2009), pp. 469–474.
- [25] P.X. Sheng, Y.-P. Ting, J.P. Chen and L. Hong, *Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms*, *J. Colloid Interface Sci.* 275(1) (2004), pp. 131–141.
- [26] D.R. Crist, R.H. Crist, and J.R. Martin, *A new process for toxic metal uptake by a kraft lignin*, *J. Chem. Technol. Biotechnol.* 78(2/3) (2003), pp. 199–202.
- [27] R.H. Crist, J.R. Martin, and D.R. Crist, *Heavy metal uptake by lignin: comparison of biotic ligand models with an ion-exchange process*, *Environ. Sci. Technol.* 36(5) (2002), pp. 1485–1490.
- [28] X. Guo, S. Zhang, and X.-Q. Shan, *Adsorption of metal ions on lignin*, *J. Hazard. Mater.* 151(1) (2008), pp. 134–142.
- [29] M. Kacurakova, P. Capek, V. Sasinkova, N. Wellner, and A. Ebringerova, *FT-IR study of plant cell wall model compounds: pectic polysaccharides and hemicelluloses*, *Carbohydr. Polym.* 43(2) (2000), pp. 195–203.
- [30] A. Kapoor, T. Viraraghavan, and D.R. Cullimore, *Removal of heavy metals using the fungus Aspergillus niger*, *Bioresour. Technol.* 95–104 (1999), pp. 95–104.
- [31] R. Han, H. Li, Y. Li, J. Zhang, H. Xiao and J. Shi, *Biosorption of copper and lead ions by waste beer yeast*, *J. Hazard. Mater.* 137(3) (2006), pp. 1569–1576.
- [32] M.Y. Arica, Ç. Arpab, A. Ergenea, G.B. Luc, and Ö. Genç, *Ca-alginate as a support for Pb(II) and Zn(II) biosorption with immobilized Phanerochaete chrysosporium*, *Carbohydr. Polym.* 52(2) (2003), pp. 167–174.
- [33] Y.N. Mata, M.L. Blázquez, A. Ballester, F. González, and J.A. Muñoz, *Characterization of the biosorption of cadmium, lead and copper with the brown alga Fucus vesiculosus*, *J. Hazard. Mater.* 158(2) (2008), pp. 316–323.
- [34] B. Stuart, *Infrared Spectroscopy: Fundamentals and Applications*, Wiley, New York, 2004.
- [35] R. Balasubramanian, S.V. Perumal, and K. Vijayaraghavan, *Equilibrium isotherm studies for the multicomponent adsorption of lead, zinc, and cadmium onto Indonesian peat*, *Ind. Eng. Chem. Res.* 48(4) (2009), pp. 2093–2099.
- [36] M. Martinez, N. Miralles, S. Hidalgo, N. Fiol, I. Villaescusa, and J. Poch, *Removal of lead(II) and cadmium(II) from aqueous solutions using grape stalk waste*, *J. Hazard. Mater.* 133 (2006), pp. 203–211.