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# Adsorption of Cu(II), Zn(II), Cd(II) and Pb(II) by dead *Avena fatua* biomass and the effect of these metals on their growth



COLLOIDS AND SURFACES B

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# ABSTRACT

The biosorption of copper(II), zinc(II), cadmium(II) and lead(II) from aqueous solutions by dead *Avena fatua* biomass and the effect of these metals on the growth of this wild oat were investigated. Pseudo-first- and second-order and intra-particle diffusion models were applied to describe the kinetic data and to evaluate the rate constants. The adsorption kinetics of all the metals follows a pseudo-second-order model.

The adsorption capacity was determined, and the Freundlich and Langmuir models were applied. The experimental data obtained for all the metals are best described by the Langmuir model. *A. fatua* was characterized using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and zeta potential. The results obtained evidence the presence of Zn(II), Cu(II), Cd(II) or Pb(II) on the surface of the weed.

The growth of *A. fatua* was affected by the presence of all metals. The decrease in the growth rate with increasing metal concentration was more noticeable for zinc.

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# 1. Introduction

Natural clean water sources have been diminished in the past decades due to anthropogenic activities. Pollution by heavy metals, such as cadmium(II), lead(II), zinc(II) and copper(II), has become a vital issue due to the adverse impact of these metals on the environment and also on human health [1,2]. The increasing pollution of natural water sources has prompted scientists to develop new alternative technologies to clean effluents before they are discharged into natural waters. Different chemical, biological, biochemical, biosorptive and physico-chemical techniques have been used to remove heavy metals from wastewaters [3] and groundwater [4]. However, as previously reported by Lodeiro et al., [5] many of these techniques are not useful when the metals are present at concentrations between 1 and  $100 \text{ mg L}^{-1}$ .

Metal biosorption, which is the capacity of certain biomass to bind heavy metals from solutions, is a feasible and economical option for the removal of heavy metals from polluted waters. Some of the adsorbents reported in the literature include bacteria [6,7], seaweeds [8,9], macrophytes [10], maze bran [11], yeast [12], nut shells [13] and tobacco dust [14], etc. Therefore, it is possible to remove and recover toxic metals from wastewaters by using different types of inexpensive biomass.

Avena fatua is one of the most troublesome weeds in temperate climates, and it primarily infests spring cereals [15]. This weed can grow in different types of soils, and it has no economic interest. Therefore, wild oats can be used as a natural biosorbent because they grow easily and are found in large amounts in the countryside.

The objective of the present work is to investigate the biosorption of copper(II), zinc(II), cadmium(II) and lead(II) in solutions by dead *Avena fatua* biomass and the effect of these metals on the growth of this wild oat.

# 2. Materials and methods

# 2.1. Biomass and pretreatment

*A. fatua* was collected from the experimental field of the School of Agriculture of Buenos Aires University, Argentina.

The weed seeds were separated and stored in a desiccator. The stems, roots and leaf blades were first carefully washed with tap water, then with monodistilled water and finally with Milli-Q water to remove the salt, sand and microorganisms that were attached to them, which could overestimate the adsorption results. The material was then dried overnight at 60 °C and subsequently grinded into

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finer particles using a homogenizer. A standard stainless steel sieve was used to obtain particles with sizes between 1 and 2 mm. The resulting material was stored in closed containers in a dry environment and at room temperature until it was used in the biosorption experiments.

#### 2.2. Solutions preparation

All the chemicals were of analytical reagent grade and were used without further purification. All solutions and weed suspensions were prepared using Milli-Q water.

Stock solutions of Cu(II), Zn(II), Cd(II) and Pb(II) were prepared by dissolving CuSO<sub>4</sub>.5H<sub>2</sub>O, ZnSO<sub>4</sub>.7H<sub>2</sub>O, Cd(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O and Pb(NO<sub>3</sub>)<sub>2</sub>, respectively, in Milli-Q water. The concentrations of all solutions ranged from 0.1 mM to 7 mM.

# 2.3. Experimental procedure

#### 2.3.1. Batch experiments

The adsorptions of Cu(II), Zn(II), Cd(II) and Pb(II) by dead *A. fatua* biomass were evaluated using batch sorption experiments with 0.1 g of pretreated biomass suspended in 100 ml of the stock metal solutions.

The suspensions were kept in constant agitation at fixed and constant pH, ionic strength and at room temperature. The pH was adjusted throughout the experiments using small aliquots of HCl or NaOH solutions (0.1 M), and the ionic strength was maintained at a constant value of 0.1 M using KNO<sub>3</sub>.

The weed biomass was separated from the metal solutions by filtration with cellulose nitrate membrane filters with a pore size of 0.45  $\mu$ m. The final concentrations of metals in the filtered solutions were determined using different quantification methods, and the metal uptake (*q*) was calculated from kinetics experiments using the following mass balance equation [16]:

$$q_t = \left[\frac{(C_i - C_t) * V}{m}\right] \tag{1a}$$

where  $q_t$ ,  $C_i$ ,  $C_t$ , V, and m are the surface coverage at a given time t, the initial metal concentration (mM), the metal concentration at a given time (mM), solution volume (L) and weight of the dry weed (g), respectively.

For equilibrium adsorption isotherms the following mass balance equation was used:

$$q = \left[\frac{(C_i - C_{eq}) * V}{m}\right]$$
(1b)

where  $C_i$ ,  $C_{eq}$ , V, and m are the initial metal concentration (mM), equilibrium metal concentration (mM), solution volume (L) and weight of the dry weed (g), respectively.

Control experiments in the absence of adsorbents were performed to determine if there had been any adsorption of Cu(II), Zn(II), Cd(II) or Pb(II) on the container walls.

#### 2.3.2. pH effect

The pH dependence of the metal uptake by A. fatua was investigated using batch isotherm experiments in a pH range from 2 to 5.5 with a weed concentration of  $1 \text{ g L}^{-1}$  and different initial concentrations of Pb(II), Cd(II), Cu(II) and Zn(II) (mM) at a constant ionic strength of 0.1 M KNO<sub>3</sub>.

The pH was measured using a Metrohm 644 pH-meter with a combined glass microelectrode, and the pH was adjusted throughout the experiments using 0.1 M HCl or 0.1 M NaOH. The biosorption experiments were performed in triplicate, and there were no significant differences among replicates (p < 0.01). The expressed values represent the average of the obtained results.

# 2.4. The effect of metals on the growth of A. fatua

A. fatua seeds were germinated (Fig. S1) at  $10 \,^{\circ}$ C for 10 days in petri dishes that were coated with blotting paper soaked in 2 ml of a 0.200 mM gibberellin solution.

The sprouted seeds were planted in groups of 10 in pots that contained 500 g of soil free of copper, zinc, cadmium and lead. The pots were watered for 45 days with water (control) or solutions of different concentrations (10, 20, 50 and 100 ppm) of Zn(II), Cu(II), Cd(II) or Pb(II). The irrigation water volume was the same in all pots, and it was calculated in order to avoid drainage. Thus, we ensure that there is no loss of metals leading to an underestimation of the results.

The growth was linear during the first 12 days, and the daily growth rates ( $GR_d$ ) of the weeds were calculated (Eq. (2)) based on the growth data obtained during this period.

$$GR_d = \frac{G_t}{12} \tag{2}$$

where  $G_t$  is the total growth of the weeds after 12 days.

The metal transfer rate (*TR*) was evaluated using the following equation [17]:

$$TR = \frac{C_w}{C_s} \tag{3}$$

where  $C_w$  is the final metal concentration in the weeds (mg kg<sup>-1</sup> dry weight) and  $C_s$  is the final metal concentration in soils (mg kg<sup>-1</sup> dry weight).

All experiments were performed in triplicate.

#### 2.5. Metal quantification

A Shimadzu 6800 spectrophotometer with a GF-6501 graphite oven, ASC-6000 Hamamatshu autosampler and lead(II) and cadmium(II) hollow cathode lamps were used to determine the concentrations of cadmium(II) and lead(II) in the soils, weeds and solutions. The concentrations of zinc(II) were measured spectrophotometrically at a wavelength of 620 nm using Zincon (2carboxy-2'-hydroxy-5'-sulphoformacylbenzol) as a chromogenic reagent [18].

The concentrations of copper(II) were measured spectrophotometrically at 440 nm using a Shimadzu-Pharmaspec UV-1700 double-beam UV-Vis spectrophotometer with 1g of sodium diethyldithiocarbamate (DDTC) dissolved in ethanol–water 50% v/v and H<sub>2</sub>SO<sub>4</sub>,  $10^{-3}$  M, as a reagent [19].

## 2.6. Zeta potential

Zeta potential measurements were performed with a Zeta Plus Zeta Potential Analyzer from Brookhaven Instruments Corporation, using  $1.0 \text{ g L}^{-1}$  dispersions in  $10^{-3}$  M KCl as inert electrolyte. HCl or KOH were used to adjust the dispersion pH.

# 2.7. Reproducibility and data analysis

Unless otherwise indicated, all of the presented data are the mean values from three replicate experiments. The standard deviations were less than 5%.

The statistical data analyses were performed using the SigmaPlot software package and the Durbin–Watson statistical parameter, which is a measure of the serial correlation between the residuals. When the independent variable is time, the residuals are often correlated, and the deviation between the observation and the regression line at one time is related to the deviation at the previous time.

For interpreting the results of the growth of weeds exposed to different metal concentrations, one-way ANOVA analysis was performed using the GraphPad Prism 5.0 for Windows software package. The assumptions of normality were verified using the Kolmogorov–Smirnov test, and the homocedacea assumptions were verified using the Bartlett test.

# 3. Results and discussion

#### 3.1. Biosorption kinetics

It is important to assess how the sorption rates vary with aqueous free metal concentrations and how they are affected by the sorption capacity or by the sorbent character in terms of kinetics [20]. Fig. 1 presents all metal uptakes by *A. fatua* versus time at pH 5.5 and room temperature. The initial metal concentrations of Zn(II), Cu(II), Cd(II) and Pb(II) were 0.81, 0.80, 0.65 and 0.30 mM, respectively. The metal uptake equilibrium was reached in less than 5 h. The adsorption profile over time for all metals is represented by the solid lines that reach the plateau corresponding to equilibrium, which suggests a possible monolayer coating of metal on the surface of *A. fatua*.

The uptakes of the metals were calculated using Eq. (1a), and the maximum experimental values  $(q_{exp})$  for copper, zinc, cadmium and lead were 0.063, 0.070, 0.100 and 0.110 mmol g<sup>-1</sup>, respectively.

# 3.1.1. Kinetic models

The extent of biosorption depends on the initial and final equilibrium states. Sorption kinetics may be controlled by several independent processes, such as chemical binding reactions of the sorbate and transport from the bulk to the surface.

The formation of a surface complex with metal ions involves the coordination of the metal ions with donor oxygen atoms that compose the cell walls of the biomass, which is followed by the release of protons from the surface, as depicted in Eq. (4):

$$\equiv \text{SOH} + \text{Me}^{2+ \underset{k_{h}}{\overset{k_{f}}{\longleftrightarrow}}} \equiv \text{SOMe}^{+} + \text{H}^{+}$$
(4)

where  $Me^{2+}$  is the concentration of the sorbate in solution,  $\equiv$ SOH is the sorbent surface site that is susceptible to coordination,  $\equiv$ SOMe<sup>+</sup> is the sorbate concentration in the sorbent at any time, and  $k_f$  and



**Fig. 1.** Biosorption kinetics of metal uptake at pH 5.5 and room temperature for  $(\bullet)$ : Cu(II);  $(\blacksquare)$ : Zn(II);  $(\blacksquare)$ : Pb(II) and  $(\bullet)$ : Cd(II) biosorbed onto *Avena fatua*. Solid lines were calculated using the binding ligand kinetics model with the parameters shown in Table 1. All data shown are the mean values from three replicate experiments. Relative Standard deviations were below 5% in all cases.

 $k_b$  are the kinetic constants for the forward and backward reaction steps, respectively [9].

The transport process in the bulk solution and the film diffusion through the boundary layer of the bioadsorbent are generally considered fast processes. Therefore, intra-particle diffusion or chemical binding reactions are the controlling steps of the adsorption mechanism.

3.1.1.1. *Pseudo-first-order model.* The most widely used kinetic model for biosorption is the reversible first-order kinetic model that was previously reported by [21]. This model is based on the solution concentration and on the cadmium(II) sorption by establishing a balance between the liquid phase and solid biomass.

This kinetic model is based on a Lagergren pseudo-first-order rate expression

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

where  $k_1$  is the pseudo-first-order sorption rate constant,  $q_e$  is the amount of metal ions adsorbed at equilibrium by the biomass and  $q_t$  is the amount of metal ions adsorbed at any time t. Both  $q_e$  and  $q_t$  are expressed in units of mmol  $g^{-1}$ . The overall rate constant  $k_1$  (Table 1), in  $h^{-1}$ , was calculated from the slope by plotting  $\ln(q_e - q_t)$  versus t (Fig. S2.A). The determination coefficients obtained using the Lagergren model at all of the initial concentrations investigated were greater than 0.9 for all of the studied metals except for Cd(II). The experimental  $q_{exp}$  values agree with the calculated data ( $q_e$ ).

*3.1.1.2. Pseudo-second-order model.* Several systems respond to a second-order kinetics model for sorption reactions. In this model, the rate at which the adsorption sites are covered is proportional to the square of the number of unoccupied sites, and the number of occupied sites is proportional to the fraction of the adsorbed metal ion. This model is represented by Eq. (6) [22]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{6}$$

where  $k_2$  is the pseudo-second-order adsorption rate constant, and  $q_e$  and  $q_t$  are the amount of metal ion adsorbed at equilibrium and at given time, respectively. The sorption rate can be calculated as the initial sorption rate when t approaches 0. Integration of Eq. (6) gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(7)

To calculate the second-order rate constant,  $k_2$ , and the equilibrium adsorption capacity,  $q_e$ , a linear plot of  $t/q_t$  against time (t) was constructed (Fig. S2.B).

The fitting parameters for both the pseudo-first- and the pseudo-second-order equations are listed in Table 1. The determination coefficients of the pseudo-second-order kinetics model varied between 0.993 and 0.999, which reveals that the pseudo-second-order model accurately represents the experimental behavior.

In all cases, the linear regression coefficients obtained from the fit of the pseudo-second-order model to the data are greater than those obtained from the fit of the pseudo-first-order model.

The pseudo-second-order kinetic constant parameters obtained for the metal adsorption by *A. fatua* are not comparable to others found in the literature for other biosorbents [9,23–25].

3.1.1.3. Intra-particle diffusion model. The intrinsic adsorption on a mineral particle suspended in water is often faster than the transport to the interface. The thickness of the boundary layer that surrounds the particle should be minimal, the agitation speed

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# Table 1

Intra-particle diffusion, pseudo first order and pseudo second order kinetic parameters for four metals at room temperature and pH 5.5. *q*<sub>eq</sub>: maximum coverage concentration, *k*<sub>1</sub>: pseudo first order constant, *k*<sub>2</sub>: pseudo second order constant, *k*<sub>id</sub>: intra-particle diffusion constant.

Metal		Zn(II)	Cu(II)	Pb(II)	Cd(II)
Pseudo-first order	$q_e \ ( ext{mmol } g^{-1}) \ k_1 \ ( ext{h}^{-1}) \ R^2$	$0.070 \pm 0.005$ $1.58 \pm 0.18$ 0.928	$0.063 \pm 0.005$ $0.75 \pm 0.04$ 0.957	$\begin{array}{c} 0.110 \pm 0.005 \\ 4.56 \pm 0.35 \\ 0.988 \end{array}$	$\begin{array}{c} 0.100 \pm 0.057 \\ 11.11 \pm 4.19 \\ 0.799 \end{array}$
Pseudo-second order	$q_e \ (\text{mmol } g^{-1}) \ k_2 \ (\text{g } h^{-1} \ \text{mmol}^{-1})$	$0.080 \pm 0.002$ $20 \pm 4$	$0.063 \pm 0.001$ $16 \pm 3$	$0.120 \pm 0.002$ $18 \pm 4$	$0.1000 \pm 0.0007$ $48 \pm 13$
Intra-particle diffusion	$R^2 k_{\rm id} \ (\rm mmol \ h^{-1} \ g^{-1}) R^2$	$\begin{array}{c} 0.993 \\ 0.063 \pm 0.007 \\ 0.926 \end{array}$	$\begin{array}{c} 0.994 \\ 0.034 \pm 0.003 \\ 0.942 \end{array}$	$\begin{array}{c} 0.998 \\ 0.169 \pm 0.006 \\ 0.997 \end{array}$	$\begin{array}{c} 0.999 \\ 0.180 \pm 0.027 \\ 0.954 \end{array}$

should be fast enough and the boundary layer resistance or film diffusion should not be the rate-controlling step [26].

The rate constant for intra-particle diffusion  $(k_{id})$  is given by

$$q_t = k_{\rm id}(t)^{1/2} \tag{8}$$

where  $q_t$  is the amount of metal adsorbed at time t, which is the sorption time. Plots of q versus  $t^{1/2}$  for lead(II), zinc(II), cadmium(II) and copper(II) are shown (Fig. S2.C). An initial portion with a steep slope that corresponds to intra-particle diffusion, followed by the plateau at equilibrium, is observed in this figure. The initial segment of the curve with a sharp slope (from 0 to 1 h) is attributed to surface adsorption, where the intra-particle diffusion is the rate-controlling step followed by a plateau that corresponds to equilibrium. The same behavior was observed by Areco and dos Santos Afonso [26] for the same metals adsorbed by *Gymnogongrus torulosus*. The intra-particle diffusion rate was obtained from the slope of the linear region of the curve.

The determination coefficient ( $R^2$ ) obtained ranged between 0.926 and 0.997. The curves passed through the origin, which indicates that diffusion through the pores is the limiting factor. However, the linear regression values were lower than those obtained for the pseudo-second-order model. The results suggest the existence of a chemically controlled reaction mechanism [27], although we cannot exclude some degree of an intra-particle diffusion contribution.

The determination coefficients for the pseudo-second-order kinetic model were greater than those for the intra-particle diffusion model (Table 1), which suggests a chemical reaction mechanism [27]. This result would indicate that the sorption of metal cations is a complex mixture of surface chemisorption on the boundary layer of the weed particle and intra-particle diffusion [26].

# 3.2. Sorption batch models

The relationship between the metal uptake and the sorbate equilibrium concentration at constant temperature is known as the adsorption isotherm. The quality of a certain biomass is related to its adsorbent capacity, and is based on the system material balance adsorption: the sorbate that disappears from solution must be in the adsorbent. Using this assumption, the  $q_{max.exp}$  (Eq. (1b)) values for the adsorption of copper, zinc, cadmium and lead by *A. fatua* were calculated (0.27, 0.25, 0.73 and 0.84 mmol g<sup>-1</sup>, respectively). There are a considerable number of expressions that describe adsorption isotherms. Here, the Langmuir and Freundlich, models were applied to the equilibrium data.

## 3.2.1. Langmuir model

The Langmuir isotherm model indicates a reduction of the available interaction sites as the metal ion concentration increases [28]. The Langmuir isotherm assumes monolayer adsorption and is determined by using the following equation:

$$q = \frac{q_{\max L} * K_L * C_{eq}}{(1 + K_L * C_{eq})}$$
(9)

where  $q_{maxL}$  is the maximum metal uptake (mg g<sup>-1</sup> or mmol g<sup>-1</sup>) which reflects the maximum surface sites on the solid phase occupied by the adsorbate,  $C_{eq}$  (mmol L<sup>-1</sup>) is the metal concentration at equilibrium in the aqueous media and  $K_L$  (L mmol<sup>-1</sup>) is the Langmuir equilibrium constant, which is related to the free energy of the reaction.

The adsorption isotherms of *A. fatua* fitted by the Langmuir model (Eq. (9)) of copper, zinc, cadmium and lead are depicted (Fig. S3.A), and the resulting parameters are presented in Table 2. The maximum coverage,  $q_{maxL}$ , follows the sequence Pb > Cd > Cu ~ Zn. The obtained values are similar to those obtained experimentally (Table 2). The maximum adsorption capacities are greater than some cited in the literature for other biosorbents [29,30].

#### 3.2.2. Freundlich model

The Freundlich model predicts multilayer adsorption on the surface of the adsorbent. The process is represented by Eq. (10):

$$q_e = K_{\rm F} C_{\rm eq}^{1/n} \tag{10}$$

where  $K_F$  is the Freundlich constant that reflects the adsorption capacity and 1/n is the index or degree of heterogeneity. Linear regression analysis was used for treating the isotherm data (Fig. S3.B). Eq. (11) shows the linear form of the Freundlich isotherm used:

$$\ln q_e = \ln K_{\rm F} + \left(\frac{1}{n}\right) \ln C_{\rm eq} \tag{11}$$

The values of  $K_F$ , 1/n and the determination coefficient ( $R^2$ ) of the Freundlich isotherm are given in Table 2.

The obtained degree of heterogeneity (1/n) for each of the metals ranged between 0 and 1, which indicates that this model could be used for interpreting the data; however, the obtained determination coefficients were less than those obtained using the Langmuir model (Table 2).

The experimental results revealed that the biosorption isotherms of the *A. fatua* series is Pb > Cd> Zn ~ Cu, and the same sequence was obtained for the  $K_L$  values (Table 2). The maximum coverage values obtained for copper and zinc were similar. This result may indicate that the affinities of both metals for the functional groups of the cell wall of the weed are also similar. However, the affinity for lead is greater than that for cadmium, and the maximum coverage follows a similar behavior. This result could indicate that lead and cadmium are adsorbed onto the same type of sites on the cell walls of the weed. However, the bonding energy for the formations of the complexes on the surface is higher for lead than for cadmium.

#### Table 2

Fitting parameters for Langmuir and Freundlich isotherm equations and thermodynamics parameters for the adsorption of Zn(II), Cu(II), Pb(II) and Cd(II) on Avena fatua at pH 5.5, constant ionic strength and room temperature.

Me	$\frac{\text{Langmuir}}{q = \frac{q_{\max} * K_L * C_e}{(1 + K_L * C_e)}}$				$\frac{\text{Freundlich}}{q = K_{\text{F}} C_{\text{e}}^{1/n}}$			
	$q_{ m max}~ m mmolg^{-1}$	$K_{\rm L}  {\rm L}  {\rm mmol}^{-1}$	$\Delta G^_{\rm L}~{\rm kJ}~{\rm mol}^{-1}$	R <sup>2</sup>	$K_{\rm F} \operatorname{mmol}^{(n-1)/n} \mathrm{L}^{1/n} \mathrm{g}^{-1}$	1/ <i>n</i>	$R^2$	
Zn	$0.36\pm0.04$	$0.36\pm0.04$	-14.58	0.958	$0.10\pm0.009$	$0.47\pm0.07$	0.918	
Cu	$0.36\pm0.09$	$0.36\pm0.06$	-14.58	0.950	$0.09\pm0.008$	$0.44\pm0.06$	0.941	
Pb	$1.02\pm0.14$	$2.50\pm0.95$	-19.38	0.882	$0.59\pm0.009$	$0.58\pm0.10$	0.857	
Cd	$0.94\pm0.06$	$0.93\pm0.07$	-16.93	0.967	$0.16 \pm 0.01$	$0.48\pm0.05$	0.945	

Among the two isotherm models used, the Langmuir model shows the best determination coefficients and a better description of the experimental results.

Stumm and Morgan [31] have suggested that the tendency of alkaline and alkaline earth cations to be adsorbed increases with the ionic radius of the ion. Essentially, the 2+ oxidation state complexes of the first transition series become more stable as the size of the metal ion decreases, although there are other effects that arise from crystal/ligand field theory. The stability of coordination complexes increases from calcium to copper and subsequently decreases for zinc, which indicates that the coordination complexes of zinc are less stable than copper complexes. The tendency to form surface complexes, such as those formed between weeds and metals, may be compared with the tendency to form corresponding inner-sphere solute complexes [31]. K<sub>I</sub> and the formation constants of aqueous metal sulfate and/or carboxylate complexes [31] showed a similar increasing trend. However, for hydroxyl groups, an inverse behavior is observed when  $K_{\rm L}$  is compared to the formation constants of aqueous metal hydroxyl complexes [31]. These results indicate that sulfated and/or carboxylated groups are the main coordination centers on cell walls.

#### 3.3. pH influence

The influence of the solution pH on the adsorption of copper, zinc, cadmium and lead by *A. fatua* was studied. The uptake of metal is maximal at pH values greater than 5. Under acidic conditions, the majority of the binding sites are occupied by protons, which means that the functional groups of the cell walls are protonated. As a consequence, the biosorbent capacity of the weed for metals decreases. The metal biosorption dependence on pH is also related to the chemical speciation of the metals in solution [26].

The adsorption of Cu(II), Zn(II), Cd(II) and Pb(II) by *A. fatua* is pH dependant because they increase with pH (Fig. 2). Although industrial effluents can have a wide range of pH values, in nature, the acidic conditions of waters and streams are controlled by the minerals in the basin, by atmospheric acid gas dissolution (CO<sub>2</sub>) and by some chemical species with acid–base properties present in natural waters, which could facilitate the metal adsorption by natural weeds. Furthermore, the optimal pH for metal adsorption is determined by the metal salts solubility and the precipitation of (hydr)oxide and other slightly soluble salts.

#### 3.4. Cu(II), Zn(II), Cd(II) and Pb(II) effects on A. fatua growth

The presence of heavy metals in natural environments generates disturbances in both the environment and human health. Plants, including weeds, are susceptible to different contaminants, such as heavy metals; they produce metabolic changes that affect respiration, photosynthesis, stomata opening and growth [32].

The effect of different concentrations of Cu(II), Zn(II), Cd(II) and Pb(II) on the growth of *A. fatua* at pH 5.5 is shown (Fig. S4).

The effects of metals on the growth of *A. fatua* were statistically evaluated using Kolmogorov–Smirnov and Bartlett tests and were finally analyzed using one-factor ANOVA.

The growth rate of the plants irrigated with 10 and 50 ppm of Cu(II) did not present significant differences with respect to the control, although those irrigated with 100 ppm of Cu(II) were significantly different (p < 0.05) from the control (Fig. S4.A).

The results demonstrate that copper affects the growth of *A. fatua*, although in this case, the effects on the growth of the weeds are only detectable at high concentrations of copper.

The weeds irrigated with 10 ppm of Zn (II) (Fig. S4.B) did not exhibit significant differences with respect to the growth of the control weeds, although the growth of the weeds irrigated with 50 ppm (p < 0.01) and 100 ppm (p < 0.001) differed significantly with those irrigated with tap water (control). These results indicate that the presence of Zn(II) also affects the growth of the weeds, and the effect increases with the increase of the zinc concentration.

The growth of *A. fatua* was also evaluated in the presence of Cd(II). In this case, the adverse effects were significant (p < 0.01) with respect to the control, only at low metal concentration (10 ppm) among the tested concentrations (Fig. S4.C). High Cd(II) irrigation concentrations make the levels of metals in the weeds and soils increase (Table S1), but the growth of *A. fatua* is only affected at low Cd(II) irrigation concentrations.

Different Pb(II) concentrations do not appear to affect the growth of *A. fatua* (Fig. S4.D). The final Cd(II) and Pb(II) concentrations in soils and weeds increases as the concentrations of metals increases in the irrigated water (Figs. S4.C and D and Table S1). These metals are accumulated in soils, and the final concentrations reached are similar to those observed in contaminated soils in nature [33,34]. The amounts of Cd(II) and Pb(II) retained by *A. fatua* are considerably greater than those reported in the literature for other types of biomass [17,32,35,36].

*A. fatua* absorbs more lead than cadmium under the same experimental conditions (Table S1). This result may be due to the uptake of heavy metals by plants from soils, which depends on whether they are present in a chemical species that can be absorbed by the plants. Furthermore metals can be strongly attached to soil particles, which make the translocation of the metals to the plants difficult. The mineral composition of the soils, the pH, the redox potential, the temperature and the humidity also affect the absorption of metals by plants. [32].

The cadmium and lead transfer rates from the soils to the weeds were calculated from the data in Table S1, using Eq. (3).

The transfer rates obtained were 6.91, 2.78 and 4.06 for watering cadmium concentrations of 10 ppm, 50 ppm and 100 ppm, respectively, and 22.60, 13.80 and 7.98 for watering lead concentrations of 10 ppm, 50 ppm and 100 ppm, respectively.

The lead transference rate decreases when the watering metal concentration increases; this may be due to the metal interactions with the soil particles, which would explain why the weed growth is not affected by an increase in the lead concentration of the irrigation water.



Fig. 2. Cu(II), Zn(II), Cd(II) and Pb(II) adsorption isotherms at pH 2: ( ); 3: ( ); 4: ( ); 4: ( ); All data shown are the mean values from three replicate experiments. Relative Standard deviations were below 5% in all cases.

The obtained TR values were greater than those reported in the literature for other plants [32,36,37].

The volume of irrigation water is very small with respect to the soil volume; therefore, almost all of the metal added to the pot is retained by the soils and fails to reach the equilibrium conditions,  $Q \neq K$  and Q < K. Therefore, the amount of bioavailable metal to be absorbed by the plant is always the same.

# 3.5. Surface characterization

Scanning electron microscopy (SEM) images were used for the surface analysis of *A. fatua*, as shown in Fig. S5. The SEM images were collected by applying 5 kV of voltage with different magnifications to clarify the surface. These figures reveal the fibrous superficial structure of the weed biomass where the metal cations could be adsorbed. The energy-dispersive X-ray spectroscopic (EDS) images for the weed before and after adsorption are presented in Fig. 3. *A. fatua* does not present any metal adsorbed on the surface before being treated with metals. The images collected after the adsorption experiments reveal the presence of the different metals used in the experiments, which indicates that the metal cations are adsorbed on the surface of the weed and is further evidence for the adsorption of Zn(II), Cu(II), Cd(II) and Pb(II) by *A. fatua*.

Also, EDS of *A. fatua* (Fig. 3) do not show the presence of S, N or P on the cell wall, since the dispersive energies of these elements are 2.30, 0.40 and 2.01 keV, respectively.

The zeta potential curves for the A. fatua samples with and without Cu(II) are shown in Fig. 4. A pH dependent curve was observed for all the samples. For A. fatua aqueous suspension the zeta potential value obtained was increased from -10 mV for pH around 3 till -23 mV for pH near 6. The zeta potential is a measured of the net surface charge that is a balance between positive and negative surface sites. The point of zero charge (pzc) is around 2.8 pH units for *A. fatua* showing that the functional groups in the cell wall were highly deprotonated and negatively charged, indicating that the major binding sites are acidic groups. The binding groups with  $pK_a$  values below 4.7 are the carboxyl (-COOH,  $pK_a = 1.7-4.7$ ), sulfonate ( $-SO_3$ ,  $pK_a = 1.3$ ), phosphonate ( $-PO(OH)_2$ ,  $pK_a = 0.9-2.1$  and 6.1–6.8) and phosphodiester (–POOH,  $pK_a = 1.5$ ) [38]. However as EDS do not show evidence of the presence of S, or P on the surface, the main binding group present in the cell wall of A. fatua could be the carboxyl group.

At constant pH, the zeta potential value became more positive with the increase in copper concentration (Fig. 4). This indicates that copper surface coordination is by electrostatic attraction between the negative charge on the biomass and positive metal cations and/or by ionic exchange mechanism where a copper ion is replacing a proton from the surface of the cell wall as is outlined in Eq. (15).

$$\equiv \mathbf{R} - \mathbf{COOH} + \mathbf{Cu}^{2+} \rightleftharpoons \equiv \mathbf{R} - \mathbf{COOCu}^{+} + \mathbf{H}^{+}$$
(15)

As a consequence of that, a positive remaining charge could be located on the surface, being the zeta potential value more positive.



**Fig. 3.** *A. fatua* EDS images of: (A) before treatment; (B), (C), (D) and (E) after Zn(II), Cu(II), Cd(II) and Pb(II) adsorption, respectively.



**Fig. 4.** Zeta potential curves for copper adsorption on *A. fatua* at 100 ppm: ( $\blacklozenge$ ); 50 ppm: ( $\Box$ ) and the control without copper: ( $\blacklozenge$ ).

#### 4. Conclusions

A. fatua can be used as an efficient adsorbent for heavy metals such as Zn(II), Cu(II), Cd(II) and Pb(II) and the differences in the metal adsorption are due to the different affinities of the metals for the functional groups present in the weed cell wall.

The pH plays a significant role in biosorption. The process is enhanced at pH values close to the physiological values rather than at acidic pH values probably due to a competition between protons and metal ions for the binding sites present in the cell wall of the weeds.

As the majority of metal with ecological relevance are hydrophilic, their transport through the biological membranes are mediated by specific proteins [39]. In any case, the adsorption processes in the absence of biological activities cannot be underestimated.

Another important consequence of biosorption is the bioaccumulation of the adsorbed metals in the weed and along the trophic chain; however, to determine these types of effects, it is necessary to measure the amount of metals present in the roots, stems and leaves to evaluate the translocations rates of metals from the roots to the leaves and then use this data to evaluate if it is possible to transfer the metals to the food chain via herbivory.

The presence of zinc, copper and cadmium in soils affects the growth of *A. fatua* at different concentration levels. Thus, *A. fatua* can grow in soils contaminated with heavy metals, and because of its capacity to adsorb these metals it can be used as an indicator for the presence of heavy metals in soils and as a remediation technique.

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.colsurfb.2013.04.035.

### References

- [1] Z. Aksu, G. Egretli, T. Kutsal, Process Biochem. 33 (1998) 393.
- [2] C.H. Colangelo, H.N. Abbiatti, Contaminación Ambiental: Análisis Multidisciplinario, Ediciones Praia, Buenos Aires, 2003.
- [3] f. Fu, Q. Wang, J. Environ. Manage. 92 (2011) 407.
- [4] M.A. Hashim, S. Mukhopadhyay, J.N. Sahu, B. Sengupta, J. Environ. Manage. 92 (2011) 2355.
- [5] P. Lodeiro, J.L. Barriada, R. Herrero, M.E. Sastre de Vicente, Environ. Pollut. 142 (2006) 264.
- [6] F. Beolchini, F. Pagnanelli, L. Toro, F. Veglio, Int. J. Environ. Pollut. 34 (2008) 325.
- Y.H. Wu, S.X. Feng, B. Li, X.M. Mi, World J. Microbiol. Biotechnol. 26 (2010) 249.
   Y.M. Wumbu, H. Hushen, D. M. Laushin, J. Microbiol. 200 (2020) 245.
- [8] V. Murphy, H. Hughes, P. McLoughlin, J. Hazard. Mater. 166 (2009) 318.
  [9] M.M. Areco, S. Hanela, J. Duran, M. dos Santos Afonso, J. Hazard. Mater. 213–214 (2012) 123.
- [10] P. Miretzky, A. Saralegui, A. Fernandez Cirelli, Chemosphere 62 (2006) 247.
- [11] K.K. Singh, S.H. Hasan, M. Talat, M.V.K. Singh, S.K. Gangwar, J. Chem. Eng. 151 (2009) 113.
- [12] Y.S. Zhang, W.G. Liu, M. Xu, F. Zheng, M.J. Zhao, J. Hazard. Mater. 178 (2010) 1085.
- [13] P. SenthilKumar, S. Ramalingam, V. Sathyaselvabala, S.D. Kirupha, S. Sivanesan, Desalination 266 (2011) 63.
- [14] B.C. Qi, C. Aldrich, Bioresour. Technol. 99 (2008) 5595.
- [15] A. Stoklosa, A. Janeczko, A. Skoczowski, J. Kiec, Thermochim. Acta 441 (2006) 203.
- [16] T.A. Davis, B. Volesky, R.H.S.F. Vieira, Water Res. 34 (2000) 4270.
- [17] M. Greger, T. Malm, L. Kautsky, Eur. J. Agron. 26 (2007) 257.
- [18] J.A. Platte, V.M. Marcy, Anal. Chem. 31 (1959) 1226.

- [19] E.B. Sandell, Colorimetric Determination of Trace Metals, Interscience Publishers, New York, 1959.
- [20] Y.S. Ho, A.E. Ofomaja, J. Hazard. Mater. 129 (2006) 137.
- [21] A.K. Bhattacharya, C. Venkobachar, J. Environ. Eng.-ASCE 110 (1984) 110.
- [22] Y.S. Ho, G. McKay, Process Biochem. 34 (1999) 451.
- [23] R.A.K. Rao, M.A. Khan, Colloids Surf., A 332 (2009) 121.
- [24] P.L. Homagai, K.N. Ghimire, K. Inoue, Bioresour. Technol. 101 (2010) 2067.
- [25] F. Ge, M.-M. Li, H. Ye, B.-X. Zhao, J. Hazard. Mater. 211–212 (2012) 366.
- [26] M.M. Areco, M. dos Santos Afonso, Colloids Surf., B 81 (2010) 620.
  [27] Y.S. Ho, G. McKay, Process Biochem. 38 (2003) 1047.
- [28] P. Solari, A.I. Zouboulis, K.A. Matis, G.A. Stalidis, Sep. Sci. Technol. 31 (1996) 1075.
- [29] X. Guo, S. Zhang, X. Shan, J. Hazard. Mater. 151 (2008) 134.
- [30] M. Akhtar, S. Iqbal, A. Kausar, M.I. Bhanger, M.A. Shaheen, Colloids Surf., B 75 (2009) 149.
- [31] W. Stumm, J.J. Morgan, Chemistry of the Solid-Water Interface, John Wiley & Sons, USA, 1992.
- [32] M. Malandrino, O. Abollino, S. Buoso, A. Giacomino, C. La Gioia, E. Mentasti, Chemosphere 82 (2011) 169.
- [33] A. Ronco, C. Camilión, M. Manassero, Environ. Geochem. Health 23 (2001) 89.
  [34] M.C. Camilión, M.J. Manassero, M.A. Hurtado, A.E. Ronco, J. Soil. Sediment. 3 (2003) 213.
- [35] C. Paris, H. Hadad, M.A. Maine, N. Suñe, N. Limnetica 24 (2005) 237.
- [36] T. Li, M.J. Liu, X.T. Zhang, H.B. Zhang, T. Sha, Z.W. Zhao, Sci. Total Environ. 409
- (2001) 1069. [37] A.I. Smical, V. Hotea, V. Oros, J. Juhasz, E. Pop, J. Environ. Eng. Manag. 7 (2008)
- 609. [38] B. Volesky, Sorption and Biosorption, BV, Sorbex, Inc., Montreal, Canada, 2003.
- [39] I. Worms, D.F. Simon, C.S. Hassler, K.J. Wilkinson, Biochimie 88 (2006) 1721.