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Sorption of Cd(II) and Pb(II) from aqueous solutions onto *Agave americana* fibers

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ABSTRACT

The potential of *Agave americana* fibers as biosorbent was investigated in batch Pb(II) and Cd(II) removal as a function of pH, initial metal concentration and temperature. Metal sorption followed pseudo-second-order kinetics with excellent correlation. The Langmuir model was successfully applied to describe the sorption isotherms. Under optimum conditions (20 °C, pH 5.0, contact time of 30–60 min and 5 g L^{-1} biomass concentration), the maximum sorption capacity of *A. americana* fibers was 40.0 mg g^{-1} for Pb and 12.5 mg g^{-1} for Cd, respectively. The results obtained at different temperatures allowed estimating the thermodynamic parameters (ΔG°, ΔH° and ΔS°) from the sorption equilibrium constants. The positive ΔH° value obtained for sorption of both metals indicates the endothermic nature of the process. *A. americana* fibers were also analyzed by IR-FT spectroscopy and scanning electron and metallographic microscopy, with the aim of investigating the interactions of biomass functional groups with cations and evaluating the mechanisms involved in metal sorption.

1. Introduction

Heavy metal pollution is a problem in the areas of intensive industrialization. Metal plating, finishing and processing industries as well as excess or incorrect application of pesticides [1] and fertilizers [2] in agriculture were considered to be the largest sources of heavy metals pollution.

Cadmium and lead are toxic to humans and aquatic life [3,4]. There has been a noteworthy increase in the use of Cd and Pb for several industrial applications [5]. Therefore, the presence of these ions in industrial wastewaters, even at very low concentrations, causes hazardous problems to the aquatic ecosystem and raises possible risks for humans related to their high toxicological and carcinogenic potential [6].

The most common methods used to remove heavy metals from wastewater are ion-exchange, reverse osmosis and chemical precipitation, but all these methods are too expensive [7,8]. Although more attention has recently been paid to the sorption onto activated carbon [9], numerous studies were conducted to search for alternative sorbents making use of less expensive natural biomass. Among these materials, cellulosic biomass is of great concern as sorbent because of its low cost and abundance, including Pecan nutshell [10], olive stone [11], orange waste [12] and sawdust of *Pinus sylvestris* [13].

Agave is the genus name that identifies a group of desert plants belonging to the monocotyledonous family called Agavaceae [14]. Plants belonging to this genus are characterized by spiny-leaves yielding various types of fibers and do not need tender care. According to Vieira et al. [15], *Agave* fibers are mainly composed of about 80% cellulose, 15% lignin and 5% hemicellulose. *Agave americana* is scientifically identified as a desert plant of North American origin, which is also abundant in South of Africa and the Mediterranean area [16]. This material was previously shown to be an effective sorbent to remove dyes from wastewaters [17,18].

The aim of the present work was to confirm such a sorption potential of *A. americana* fibers (AAF) also in the removal of heavy metals from aqueous solution, specifically Cd(II) and Pb(II). The effect of some operating conditions, specifically the initial pH and concentration of metal solution and temperature, was investigated. The kinetic data were fitted with pseudo-first-order and pseudo-second-order kinetic models. The Langmuir and Freundlich models were used to describe the equilibrium isotherms.

2. Materials and methods

2.1. Biosorbent and sorbates preparation

Agave americana was collected at Hergla in the region of Sousse (Eastern coast of Tunisia). Their leaves were submitted to a salt hydrolysis at 80 °C for 8 h, beaten with a mallet and thrashed energetically with a scraper in order to separate the fibers [17]. The *A. americana* fibers were washed abundantly with distilled water to

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remove non-cellulosic compounds, cut to pieces with uniform size of 2 cm, and then oven-dried at 70 °C to constant weight (about 24 h). Stock solutions of sorbates [Cd(II) or Pb(II)] were prepared by dissolving $CdSO_4 \cdot 3H_2O$ or $Pb(NO_3)_2$ in distilled water to give a concentration of either salt of 1000 mg L^{-1} and diluting when necessary.

2.2. Sorption tests and analytical methods

Batch sorption experiments were carried out in 250 mL-Erlenmeyer flasks by adding 0.5 g of AAF to 100 mL of metal solution with the selected concentration, at the desired temperature (20–50 °C) and pH (1–5). Apart the tests carried out to investigate the influence of temperature on sorption, all the other effects were investigated at 20 °C. Temperature was controlled by a thermo-regulated water bath, mod. SWB25 (Enco, Spinea, Venice, Italy), operating at 80 oscillations min^{-1}, while pH was adjusted at the selected initial value by addition of HCl 1.0N. After sorption, Cd(II) and Pb(II) residual concentrations were determined using an atomic absorption spectrophotometer, model AA240FS (Varian, Palo Alto, CA).

The calculation of the point zero of charge (pzc) of AAF biomass was determined by potentiometric titrations of solutions containing 5 g L^{-1} of biomass in 0.01, 0.1 and 1.0 M NaCl, using 0.1 M HCl as a titrant [19].

At the end of the sorption tests, the AAF were collected, dried, crushed and mixed with KBr, which is a compound transparent to IR radiation in the range 4000–400 cm^{-1}. The mixture was pressed in self-supporting disks for analyses. Biomass samples taken either before or after metal sorption were analyzed with a Nicolet 6700 FT-IR instrument (Thermo Fisher, Waltham, MA) equipped with DTGS-KBr detector and OMNIC^{TM} acquisition software. The acquisition was 100 scans for each spectrum and the resolution 2 cm^{-1}.

2.3. Sorption kinetics

For kinetic studies, 3.0 mL of the heavy metal solution were taken periodically and then analyzed for metal concentration as described in the previous section. All experiments were conducted in duplicate, and the percentage error was always less than 6%.

The capability of the selected material as sorbent was evaluated either in terms of sorption capacity at equilibrium (q_e), expressed in mg g^{-1}:

$$q_e = (C_o - C_e)\frac{v}{w} \tag{1}$$

where C_o and C_e are the initial and equilibrium liquid-phase metal concentrations (mg L^{-1}), respectively, v is the volume of the solution (L) and w is the weight of dry fiber used (g), or in terms of metal removal efficiency (Y_R), expressed in %:

$$Y_R = \frac{C_o - C_e}{C_o} \times 100(\%) \tag{2}$$

The model of Lagergren [20] and the pseudo-second-order equation of Ho and McKay [21] were used to fit the experimental data of metal sorption before the achievement of equilibrium.

The linearized form of the model of Lagergren [22]:

$$\ln(q_e - q) = \ln\ q_e - \frac{k_1}{2.303}t \tag{3}$$

where q is the amount of heavy metal sorbed (mg g^{-1}) at a given time, was used in plots of $\ln(q_e - q)$ versus time, t, to estimate the first-order-rate constant of sorption, k_1 (min^{-1}).

The pseudo-second-order model of Ho and McKay [21], based on the sorption capacity of the solid phase and consistent with the chimiosorption mechanism, is described by the equation:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

which was used in t/q plots versus time at different initial heavy metal concentrations to estimate the second-order-rate constant of sorption, k_2 (mg min g^{-1}).

2.4. Evaluation of thermodynamic parameters

The standard change of the Gibbs free energy of the sorption process was calculated by the equation:

$$\Delta G^\circ = -RT\ \ln\ K_c \tag{5}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T the absolute temperature (K) and K_c the sorption equilibrium constant, defined according to Yurtsever and Şengil [23] as:

$$K_c = \frac{C_a}{C_e} \tag{6}$$

C_a being the concentration of sorbed metal (mg L^{-1}).

The values of the standard changes of enthalpy (ΔH°) and entropy (ΔS°) were calculated from the slope and intercept of the plot of $\ln K_c$ versus $1/T$.

2.5. Evaluation of equilibrium isotherms

The equilibrium data were firstly fitted by the well-known linearized isotherm equation of Langmuir [24]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{7}$$

where q_m is the maximum sorption capacity (mg g^{-1}) and K_L the Langmuir equilibrium constant (L mg^{-1}).

Afterwards, further fitting was done by the linearized form of the isotherm of Freundlich [25]:

$$\ln\ q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{8}$$

where K_F ($mg^{1-1/n}$ g^{-1} $L^{1/n}$) and $1/n$ (dimensionless) are constants for a given sorbate and sorbent at a particular temperature, which are related to the sorption capacity and intensity, respectively.

The parameters and constants appearing in both equations were estimated by linear regression, by plotting C_e/q_e versus C_e in the former case and $\ln q_e$ versus $\ln C_e$ in the latter.

2.6. Microscopic analysis

The surface structure of AAF was analyzed either before or after metal sorption by scanning electron microscope (SEM), model SS40 (ISI, Tokyo, Japan). For this purpose, samples were covered with a 200 nm-thick layer of gold. A second set of samples, either before or after sorption, were soaked into 0.1 M ammonium sulfide solution and then observed by metallographic microscope, model DMLM (Leica, Wetzlar, Germany).

3. Results and discussion

3.1. Effect of pH

Firstly, the point of zero charge (pzc) of AAF was determined and illustrated in Table 1. The pzc is a concept relating to the phenomenon of sorption, expressing the pH at which the electrical charge density on a biomass surface is zero. The pzc of AAF was found to be 2.6, a value almost coincident with that (2.58) reported for *Agave lechuguilla* biomass [19]. This result demonstrates that

Table 1
Acidic dissociation constants (pK_1 and pK_2) of *Agave americana* fiber biomass and point zero of charge determined as their average at variable NaCl concentration.

NaCl concentration (M)	pK_1	pK_2	pH
1.0	3.5	2.09	2.80
0.1	3.1	1.89	2.50
0.01	2.9	2.12	2.51
$(pH_{pzc})_{average}$			2.60

the biomass surface of this sorbent has negative charge at pH values higher than the pzc and thus should be able to sorb cations.

Because the net charges present on the sorbent surface greatly depend on the initial pH (pH_o), this is perhaps the most important parameter influencing the sorption process; therefore, its influence on the sorption of both metals onto *A. americana* fibers was widely investigated in the first part of this study. For this purpose, pH_o was varied from 1.0 to 5.0, whereas no experiment was carried out at higher pH_o because both metals precipitate under these conditions forming insoluble hydroxides [26]. No significant variation of pH was observed during the adsorption tests.

The results of Fig. 1 indicate, for both metals, that the sorption was ineffective at $pH_o < 3$ and that the maximum sorption capacity was found at pH_o 5.0 (17.1 and 30.4 mg L^{-1} for Cd and Pb, respectively). Such a 9–13-fold raise in sorption capacity with increasing the initial pH from 1.0 to 5.0 can reasonably be ascribed to a decreased H^+ concentration in the solution and, consequently, to an increased number of negative charges on the fiber surface. This situation could have promoted electrostatic attraction and sorption of positively charged Cd(II) and Pb(II) ions and then increased the amount of metals sorbed [27]. Similar trend was observed for the sorption of Cd(II) and Pb(II) onto others cellulosic biomass [13,26,28]. On the other hand, because of the above-mentioned precipitation of insoluble hydroxides at $pH_o > 5$ (results not shown), this optimum pH value (5.0) was used in all the further experiments carried out to explore the effects of the other operating variables.

3.2. Effect of temperature

It is well known that temperature is an additional factor greatly influencing any sorption process. Therefore, additional experiments were carried out at high concentrations of either metal (C_o = 80 and 160 mg L^{-1}) and different temperatures (20, 30, 40 and 50 °C).

The time evolution of the amounts of Cd(II) and Pb(II) sorbed onto dried AAF used at an initial level of 160 mg L^{-1} is shown in Fig. 2. It is noteworthy that the equilibrium was achieved within 20–30 min and that a progressive increase in temperature from 20 to 50 °C not only accelerated the sorption of both heavy metals, but also increased the sorption capacity of AAF at equilibrium from 12.7 to 14.9 mg g^{-1} for Pb(II) and from 25.0 to 27.2 mg g^{-1} for Cd(II), respectively. This result suggests that the process can be considered as an endothermic one. Similar trend has been observed for the sorption of textile dyes onto AAF [17] and Pb(II) onto *Candida albicans* biomass [26].

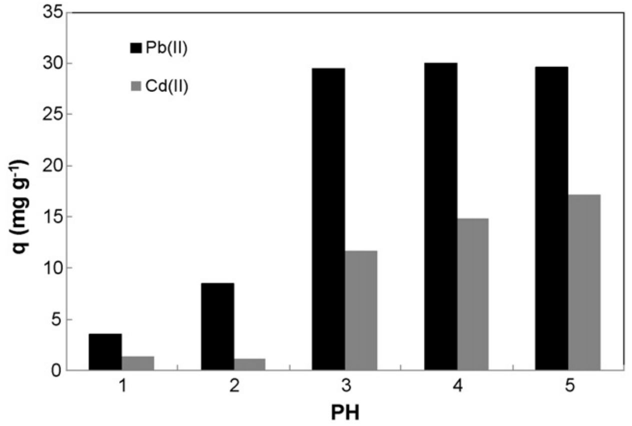

Fig. 1. Effect of pH on Cd(II) and Pb(II) sorption onto AAF. Conditions: T = 20 °C; C_o = 160 mg L^{-1} for both metals.

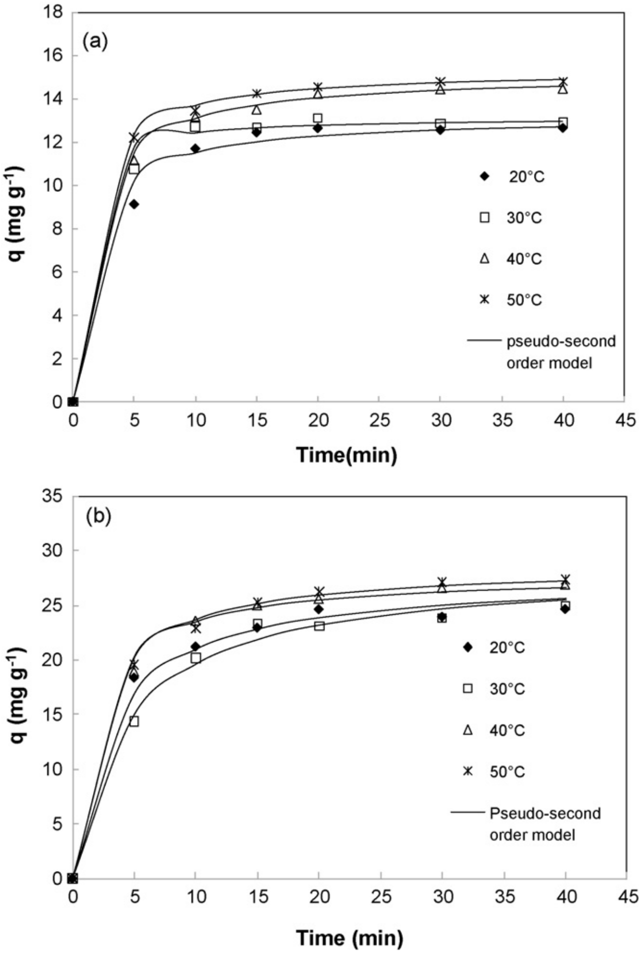

Fig. 2. Effect of temperature on Cd(II) (a) and Pb(II) (b) sorption by AAF along the time. Conditions: C_o = 160 mg L^{-1} for both metals, pH 5.0.

3.3. Thermodynamic study

For environmental engineering practice, knowledge of the relevant thermodynamic parameters is needed to establish if the removal process would be able to occur spontaneously or not. Hence, the standard changes of Gibbs free energy, ΔG° (kJ mol^{-1}), enthalpy, ΔH° (kJ mol^{-1}), and entropy, ΔS° (J mol^{-1} K^{-1}), were estimated for concentrations of 80 and 160 mg L^{-1} as described in Section 2.4 and listed in Table 2.

The feasibility and spontaneity of the removal of Pb(II) by AAF are demonstrated by the negative values of ΔG° of its sorption, varying from −7.77 to −5.16 kJ mol^{-1} and from −10.72 to −8.37 kJ mol^{-1} at 160 and 80 mg L^{-1}, respectively. Moreover, being these values within the range −20 to 0 kJ mol^{-1}, this process should not be considered a pure chemical sorption, but also a physical sorption or "physiosorption" [29]. On the other hand, the positive values of ΔG° for Cd(II) sorption suggest a low affinity of *A. americana* fibers as a sorbent for Cd(II) ions at the higher metal concentration (160 mg L^{-1}). Moreover the negative values of ΔG°

Table 2
Thermodynamic parameters estimated for Cd(II) and Pb(II) sorption onto AAF at initial metal concentrations (C_o) of 80 and 160 mg L^{-1}.

Metal	C_o (mg L^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	Temperature (°C)			
				0	30	40	50
				ΔG° (kJ mol^{-1})			
Cd(II)	80	5.01	22.61	−1.64	−1.81	−2.09	−2.30
	160	7.54	28.59	0.98	0.80	0.26	0.42
Pb(II)	80	13.65	75.48	−8.37	−9.41	−9.89	−10.72
	160	18.34	81.50	−5.16	−7.02	−6.08	−7.77

at the lower concentration of both metals (80 mg L^{-1}) pointed out the spontaneity of sorption.

Finally, the positive values of ΔH° and ΔS° for the sorption of both heavy metals indicate the endothermic nature of this process along with an increased randomness at the system solid/liquid interface. These results demonstrate the significance of temperature on sorption kinetics.

3.4. *Effect of initial Cd(II) and Pb(II) concentrations*

Kinetics of Cd(II) and Pb(II) sorption onto AAF was investigated at different initial levels of either metal, ranging from 20 to 160 mg L^{-1} for Cd(II) and from 20 to 300 mg L^{-1} for Pb(II). The highest concentrations of these ranges were suggested, ongoing work, by the different affinity of AAF for each metal.

The sorbed amount of both metals progressively increased with their respective initial concentrations at pH 5.0 and 20 °C, either before or after the achievement of equilibrium (Fig. 3). Within the first 15 min, a rapid increase in heavy metal sorption took place because of the large number of sites available for the sorption, and no less than 80% of total metal was removed. After this period, owing to a reduction in the number of available sites, the heavy metal ions took more time to access the least accessible sites [17]; so, the sorption decelerated and reached the equilibrium approximately after 30 min. A similar trend was observed with similar systems [13,30].

The sorbed amount of Cd(II) at equilibrium raised from about 3.5 to 12 mg g^{-1} and that of Pb(II) from about 4 to 37 mg g^{-1} as a result of the progressive C_o increase.

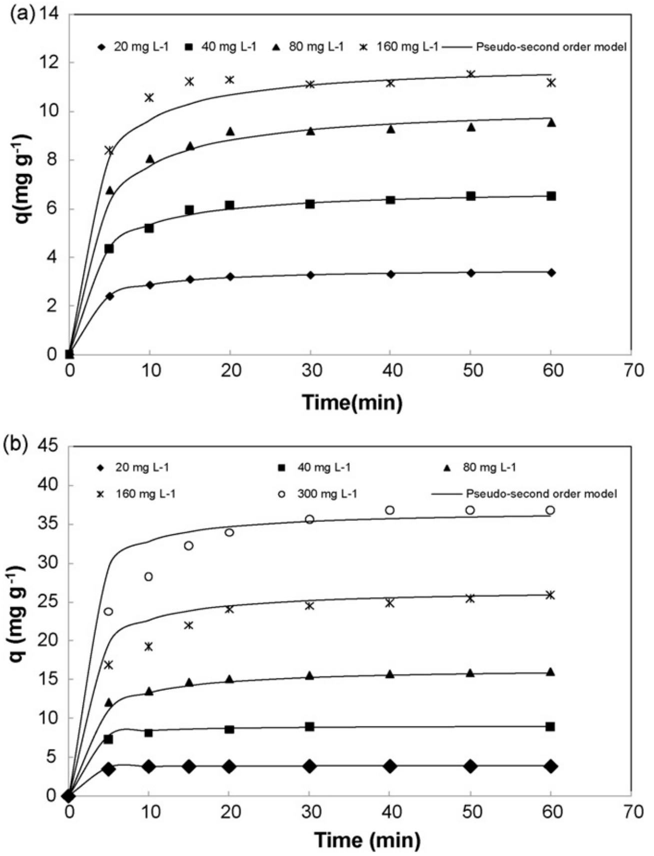

Fig. 3. Effect of initial metal concentration on Cd(II) (a) and Pb(II) (b) sorption by AAF along the time. Conditions: T = 20 °C, pH 5.0.

3.5. *Sorption isotherms modeling*

The sorption process was evaluated and mathematically described under equilibrium conditions at 20 °C. For this purpose, equilibrium isotherm equations are usually employed to fit the experimental sorption data, because the related constants are often able to give some insight into the sorption process, the surface proprieties and the affinity of the sorbent for the sorbate.

The equilibrium data were fitted in the present study by the isotherm expressions of Langmuir [24] and Freundlich [25] in their linearized forms. Table 3 shows the correlation coefficient (r^2), and Fig. 4 clearly shows that the former model fitted the equilibrium data better (r^2 = 0.999 for Cd and 0.995 for Pb) than the latter (r^2 = 0.940 for Cd and 0.962 for Pb), thus confirming the poor applicability of Freundlich isotherm for this type of sorption process. On the basis of these results, one should infer the occurrence of monolayer coverage of Cd(II) and Pb(II) on AAF predicted by the Langmuir isotherm.

Table 3 also lists the values of the constants appearing in the Freundlich and Langmuir models at 20 °C. It should be noticed that the maximum sorption capacity, q_m, of AAF was 12.5 mg g^{-1} for Cd(II) and 40.0 mg g^{-1} for Pb(II), respectively. The comparison of these results with those reported in the literature for other biomaterials and the same metals (Table 4) suggests that AAF is a quite promising alternative biosorbent for heavy metals removal.

Table 3
Isotherm parameters of Langmuir and Freundlich models referred to the sorption of Cd(II) and Pb(II) onto AAF at 20 °C.

Metal	Langmuir			Freundlich		
	q_m (mg g^{-1})	K_L (L mg^{-1})	r^2	K_f (mg$^{1-1/n}$ g^{-1} L$^{1/n}$)	n	r^2
Cd(II)	12.5	0.19	0.999	3.68	3.53	0.940
Pb(II)	40.0	0.15	0.995	8.91	3.09	0.962

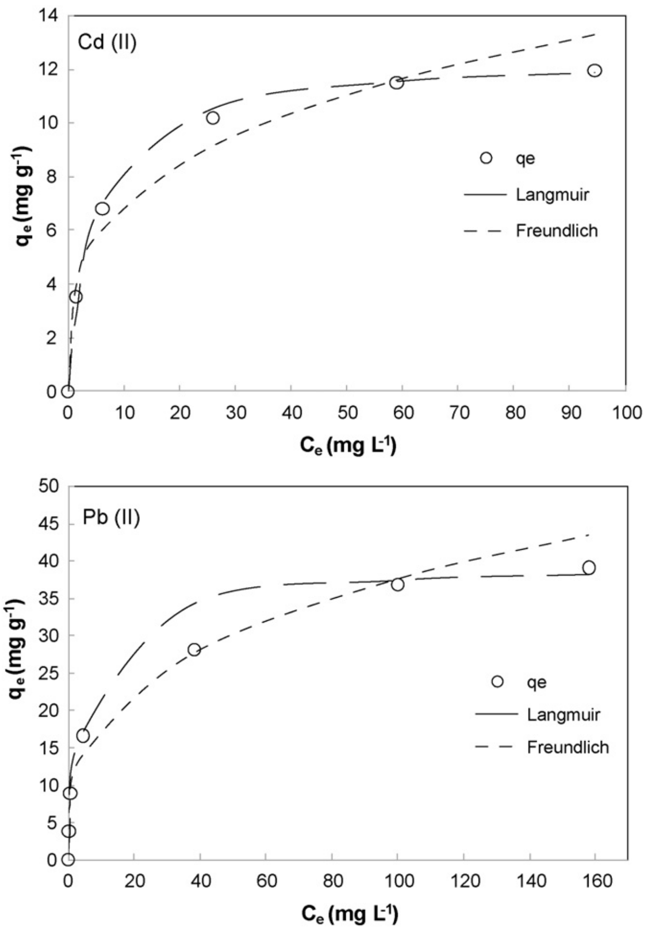

Fig. 4. Isotherms of Cd(II) (a) and Pb(II) (b) sorption onto AAF at 20 °C and pH 5, and fitting with Langmuir and Freundlich models.

3.6. Sorption kinetic modeling

In order to shed further light on the mechanisms of this sorption process, the kinetics of both metals uptake was investigated, before reaching equilibrium, by the above two kinetic models.

The rate constants, the experimental and calculated equilibrium sorption capacities and the linear regression coefficients were obtained at all temperatures tested, and only the satisfactory results referring to the second-order model are summarized in Table 5. Whereas the correlation coefficients obtained by the Lagergren model were found to be less than 0.864, those of the second-order model were higher than 0.99 at all temperatures and initial metal concentrations explored. These results, which are consistent with those previously reported by some of the authors for Cd sorption by dried and reydrated *Spirulina platensis* biomass [31], demonstrate that only the latter model is able to satisfactorily describe the kinetic behavior of Cd(II) and Pb(II) sorption by AAF.

Table 4
Comparison of the maximum AAF sorption capacity (q_m) with those reported in the related literature for other sorbent materials at pH 5.0.

Metal	Biosorbent	Temperature (°C)	q_m (mg g^{-1})	Reference
Cd(II)	Sawdust of *Pinus*	25	15.3	[13]
	Amanita rubensis	20	27.3	[34]
	tree fern	25	16.3	[20]
	AAF	20	12.5	This study
Pb(II)	Sawdust of *Pinus*	25	15.8	[13]
	Amanita rubensis	20	38.4	[34]
	Pinus sylvestris	25	22.22	[13]
	AAF	20	39.7	This study

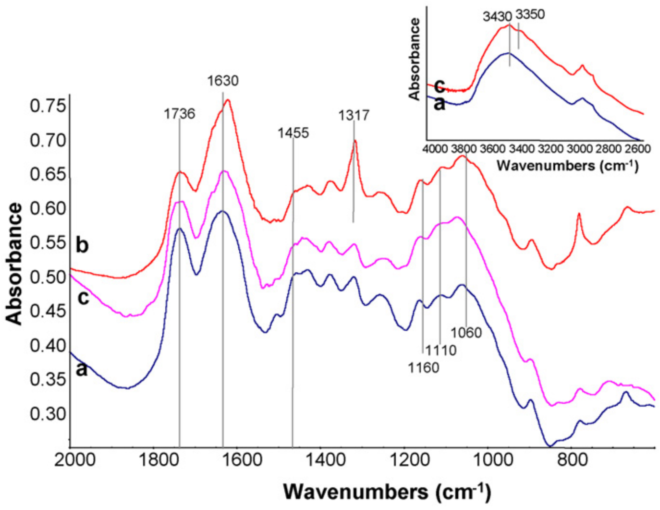

Fig. 5. FT-IR spectrum of AAF biomass (a) before and after sorption of (b) Cd(II) and (c) Pb(II).

3.7. FT-IR analysis

Fig. 5 (line a) illustrates the spectrum of the AAF before sorption. The main IR bands detectable are due to C=O stretching mode of ester and carboxylate (free COOH) functional groups (1736 cm^{-1}, broad), whose corresponding C–O stretching falls at 1257 cm^{-1}, and to amide I (1630 cm^{-1}, broad), amide II (1505 cm^{-1}, weak) and amide III (1380 cm^{-1}) of protein components [32,33]. The asymmetric and symmetric stretching modes of COO– groups likely overlapped with the bands at 1630 cm^{-1} and showed a maximum around 1430 cm^{-1}. The complex band with maxima at 1162, 1110 and 1006 cm^{-1} can be attributed to CO and CC stretching mode of polysaccharides. In the high frequency-region of the spectrum, a broad absorption centered at 3400 cm^{-1} and tailing towards lower frequencies was due to OH stretching modes of H-bonded hydroxy groups, while several weak bands between 2960 and 2850 cm^{-1} can be assigned to saturated CH stretching modes [34].

From the spectra recorded after metal sorption (Fig. 5, lines b and c), it appears that several functional groups of the dried biomass are involved in the sorption process.

Following Pb sorption, peaks at 1736 and 1630 cm^{-1} were not shifted in frequency, and the relative intensity of the former band seems to be slightly lowered (Fig. 5, line c). At the same time, the weak band at 1257 cm^{-1} in the spectrum of AAF before sorption shifted to lower frequency (1250 cm^{-1}), thus confirming an interaction with the COO group, likely due to coordination with the oxygen lone pairs. On the other hand, bands due to CO/CC stretching modes (1110–1006 cm^{-1}) shifted towards higher frequencies, pointing out an interaction with polysaccharides components [35]. Pan et al. [36] ascribed the progressive disappearance of the band at 1455 cm^{-1} (NH bending, mainly) also to the involvement of amino groups in Pb(II) sorption. This effect was also detected in our case, although we rather observed a weakening of the band.

Cd sorption led to a spectrum (Fig. 5, line b) whose features are even better defined and stronger with respect to the raw biomass spectrum. In particular, the amide band shifted from 1630 to 1620 cm^{-1} and became sharper and stronger. The decrease in band intensity at 1736 cm^{-1} could have been due to the interaction of Cd(II) with carboxylate species. Moreover, comparison of the spectra before (line a) and after (line c) Cd(II) sorption shows a prominent band at 1317 cm^{-1} and new bands at 3430

Table 5
Second-order kinetic parameters estimated by the model of Ho and McKay [21] for the sorption of Cd(II) and Pb(II) onto AAF at different temperatures.

T (°C)	Cd(II)				Pb(II)			
	q_e (mg g^{-1})[a]	k_2 (mg min g^{-1})[b]	q_c (mg g^{-1})[c]	r^2	q_e (mg g^{-1})[a]	k_2 (mg min g^{-1})[b]	q_c (mg g^{-1})[c]	r^2
20	14.1	0.058	14.2	0.999	29.4	0.010	28.1	0.999
30	15.1	0.089	15.1	0.999	29.2	0.006	29.4	0.999
40	15.9	0.041	16.0	0.999	29.3	0.015	28.5	0.999
50	15.8	0.046	15.9	0.999	30.1	0.011	29.8	0.999

[a] Experimental sorption capacity at equilibrium.
[b] Pseudo-second-order kinetic constant.
[c] Calculated sorption capacity at equilibrium.

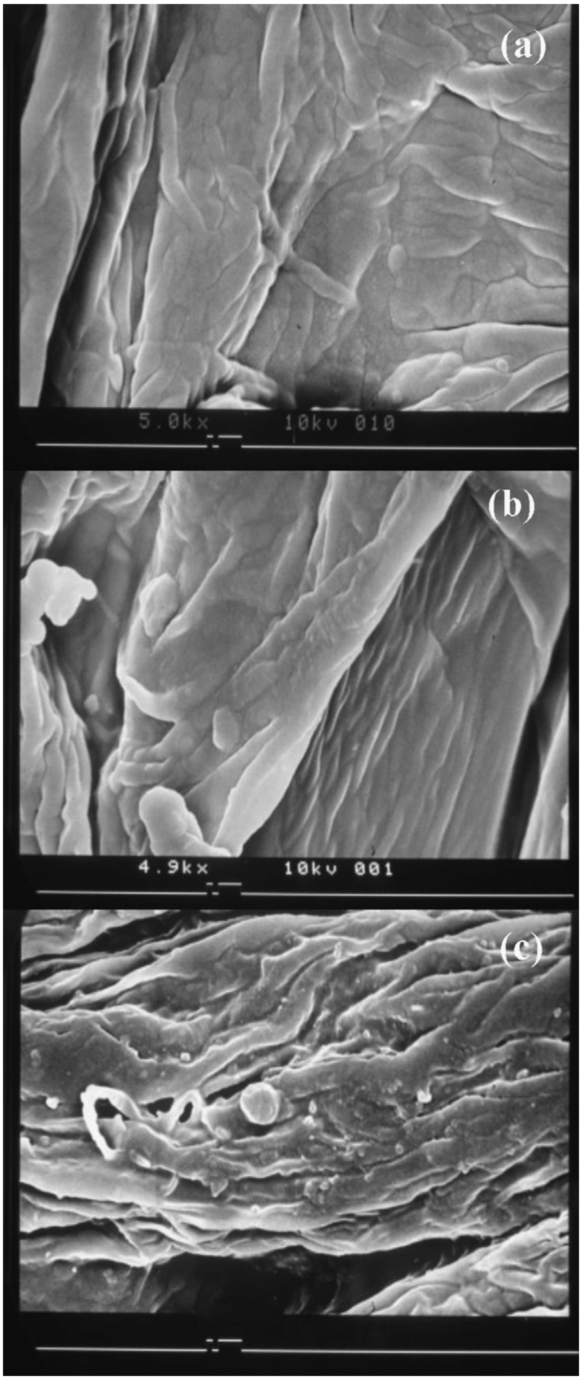

Fig. 6. SEM micrographs of AAF (a) before (5000×) and after (4900×) sorption of (b) Cd(II) and (c) Pb(II).

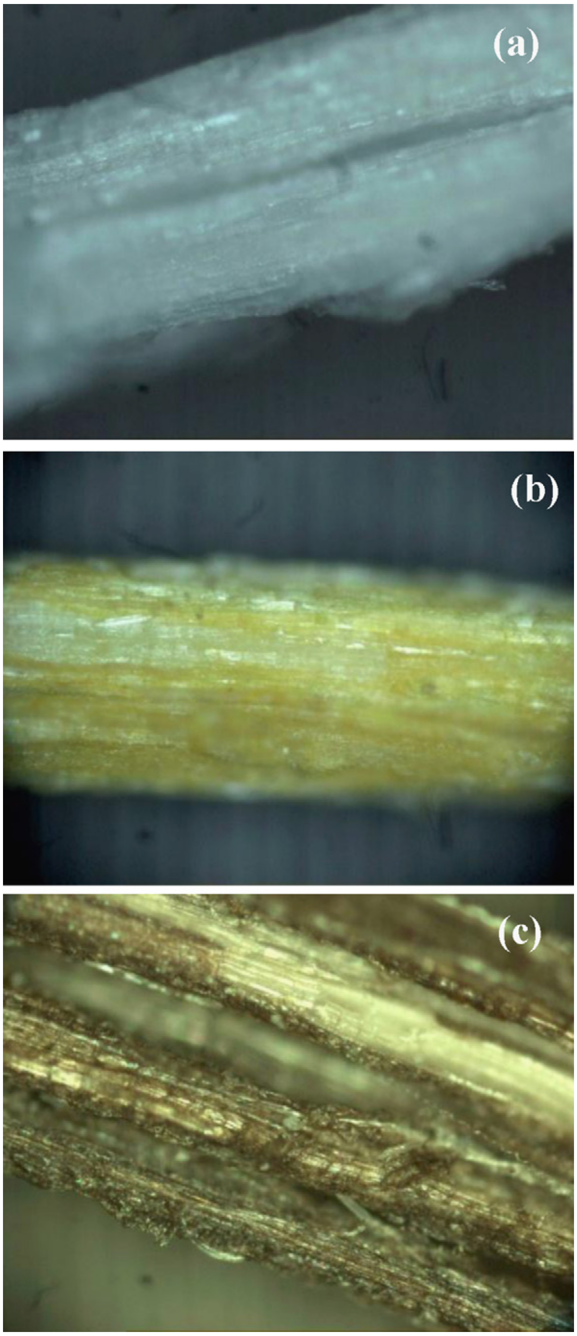

Fig. 7. Metallographic micrographs of AAF (50×) (a) before and after sorption of (b) Cd(II) and (c) Pb(II).

and 3350 cm^{-1} (Fig. 5, inset), i.e., in the NH stretching frequency range. This effect can be due partly to the selected acidic environment (pH 5.0) that allowed for partial hydrolysis of amide and ester groups. However, Romero-Gonzalez et al. [37] and Xu and Liu [38] reported similar findings for Cd sorption on different types of biomass. These results suggest that Cd(II) sorption could have mainly occurred through ion-exchange with the hydrogen atoms of non-ionized carboxyl groups [35], which are characterized by the band at 1736 cm^{-1} and whose intensity did in fact decrease. On the other hand, the sharp band at 1317 cm^{-1}, assigned to CO stretching mode [37], should be related to a not clearly defined-Cd(II) binding site other than the carboxylate.

Finally, the effects illustrated by the spectra of AAF after sorption were stronger and clearer for Pb than for Cd, which is consistent with the results obtained with different biomass in the removal of the same metals [35]. Moreover, these findings are in agreement with the spontaneity of Pb sorption and low affinity of AAF for Cd already evidenced by the thermodynamic parameters estimated in this study.

3.8. Microscopic analysis of AAF

Scanning electron micrographs were carried out on AAF samples either before or after sorption of Cd(II) and Pb(II) (Fig. 6) to shed light on the type of aggregates formed by metal sorption. However, the difference in the surface fiber structure before and after metal loading is not clear. Anyway, we can certainly exclude any crystalline formation as a consequence of sorption of both metals. Based on these results, metallographic microscopy was also performed on the same samples after treatment with ammonium sulfide, so as to highlight the difference in color between AAF (white) (Fig. 7a) and metal sulfides deposited on its surface, specifically yellow color for CdS (Fig. 7b) and black color for PbS (Fig. 7c). These micrographs provide a confirmation of metal sorption onto AAF surface. The observation of different color intensity in this figure suggests an inhomogeneous distribution of Cd and Pb loading into AAF. This result could have been due to the well-known heterogeneous composition of the sorbent (lignin and cellulose), and then to variable sorption propriety.

4. Conclusions

Batch sorption tests were performed using *A. americana* fibers (AAF) as biosorbent under different conditions of pH, temperature and initial metal concentrations. It was shown an increase in the amounts of sorbed Cd(II) and Pb(II) along the time, and the equilibrium conditions were almost achieved after 30–60 min. The highest effectiveness of heavy metals removal was detected at pH 5.0. The equilibrium data of both Cd(II) and Pb(II) sorption were satisfactorily fitted by the Langmuir isotherm, and the kinetic ones referring to the period preceding the occurrence of equilibrium by the second-order-rate model. Finally, the related thermodynamic parameters demonstrated that the sorption of both heavy metals is an endothermic process, even if AAF appeared to have low affinity for Cd(II) ions at least at the high metal concentrations selected for this work.

Infra-red spectroscopy demonstrated that several functional groups were involved in Pb(II) and Cd(II) binding on AAF. Lead sorption implied coordination to ester, hydroxy and amino groups, while cadmium binding seemed to be related mainly to ion-exchange with hydrogen atoms of non-ionized carboxyl groups. Scanning electron and metallographic micrographs provided a confirmation of metal sorption onto AAF surface.

The results of this investigation taken as a whole demonstrate the excellent capacity of the AAF to remove Pb(II) and Cd(II) from aqueous solutions, which may then be proposed as a low-cost sorbent material, in substitution of the expensive commercial sorbents presently used to reduce the impact of these heavy metals on the environment.

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