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Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestris*

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Abstract

Fixation of heavy metal ions (Cd(II) and Pb(II)) onto sawdust of *Pinus sylvestris* is presented in this paper. Batch experiments were conducted to study the main parameters such as adsorbent concentration, initial adsorbate concentration, contact time, kinetic, pH solution, and stirring velocity on the sorption of Cd(II) and Pb(II) by sawdust of *P. sylvestris*. Kinetic aspects are studied in order to develop a model which can describe the process of adsorption on sawdust. The equilibrium of a solution between liquid and solid phases is described by Langmuir model. Scanning electronic microscopy (SEM) coupled with energy dispersive X-ray analysis (EDAX) and X-ray photoelectron spectroscopy (XPS) shows that the process is controlled by a porous diffusion with ion-exchange. The capacity of the metal ions to bind onto the biomass was 96% for Cd(II), and 98% for Pb(II). The sorption followed a pseudo-second-order kinetics. The adsorption of these heavy metals ions increased with the pH and reached a maximum at a 5.5 value. From these results, it can be concluded that the sawdust of *P. sylvestris* could be a good adsorbent for the metal ions coming from aqueous solutions. Moreover, this material could also be used for purification of water before rejection into the natural environment.
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Keywords: Sawdust; Lead; Cadmium; Adsorption; Kinetic

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1. Introduction

The removal of toxic heavy metals ions from sewage, industrial and mining waste effluents has been widely studied in recent years. Their presence in streams and lakes has been responsible for several health problems with animals, plants, and human beings. Numerous metals such as Sb, Cr, Cd, Pb, Mn, Hg, etc. have toxic effects on man and his environment. The consumption of food containing traces of these elements may lead to various diseases, for example, the consumption of (i) rice containing high concentrations of cadmium (0.37 at 3.6 mg l^{-1}) led to a surge in the Itaï-Itaï disease in Japan in 1955 [1,2], and (ii) fish contaminated with methylmercury led to Minamata disease [3]. For these reasons, the legislation is progressively becoming more stringent; for example, the maximum concentrations of metals in drinking water according to guideline values are now: 0.01 mg l^{-1} for Pb(II) and 0.02 mg l^{-1} for Cd(II) [4]. However, these values are higher due to accumulation phenomena observed when the spreading operations are used instead of direct overflowing into rivers.

Among the many methods available to reduce heavy metals concentrations from wastewater, the most common are chemical precipitation, ion-exchange, and reverse osmosis. Precipitation methods are particularly reliable but require large settling tanks for the precipitation of voluminous alkalines sludges and a subsequent treatment is needed [5]. Ion-exchange has the advantage of allowing the recovery of metallic ions, but it is expensive and sophisticated. This has encouraged research into discovering materials that are both efficient and cheap. The by-products and wastes from the agricultural and forest industries were studied as these materials could be assumed as low-cost since they (i) require little processing and (ii) are abundant in nature. Commonly, it concerns vegetal materials, then the term of biosorption is used to designate the fixation of contaminants onto biomaterials. The low-cost adsorbent used in our study is the sawdust of *Pinus sylvestris*, a by-product of the wood industry. It contains various organic compounds (lignin, cellulose, and hemicellulose) with polyphenolic groups that might be useful for binding heavy metals ions [6].

The objective of this preliminary study was to investigate the feasibility of metallic ions removal from aqueous solution by sawdust of *P. sylvestris*. The kinetics of the process was determined, especially in relation to the effects of various factors on the removal. The factors investigated included aqueous metallic concentration, stirring, contact time, pH of solution, and adsorbent concentration. The mechanism of metallic ions adsorption at sawdust–solution interface was also studied.

2. Materials and methods

2.1. Adsorbate

All the compounds used to prepare reagent solutions were of analytic reagent grade. The mother solution of Cd(II) and Pb(II) (1000 mg l^{-1} for each ion) is prepared by dissolving a weighed quantity of the respective nitrate salts in twice distilled water. The concentrations of metals solutions ranged from 1 to 10 mg l^{-1}. Before mixing with the sawdust, the pH of each solution was adjusted to the required value for the sorption of Cd(II) and Pb(II) ions,

by adding 0.1 M NaOH or 0.1 M HNO_3. Constant ionic strength (0.01 M NaCl) was used in all experiments.

2.2. Adsorbent

The sawdust of *P. sylvestris* used as adsorbent was provided by the Société d'Exploitation Forestière Barillet, Châteauneuf-sur-Loire 45, France. For the laboratory studies only, the sawdust was washed several times with twice distilled water to remove surface impurities. The process was followed by air drying at 110 °C for 24 h. The sawdust was ground and sieved into three sizes: 0.1–0.16, 0.16–0.2, and 0.2–0.25 mm.

For laboratory scale experiments and to prevent the elution of phenolic compounds, which would stain the treated water, the ground sawdust was treated with formaldehyde in an acidic medium [7] under conditions previously optimized by Vázquez et al. [8]: a 1:4 (v/v) mixture of 37% formaldehyde and 0.2 M H_2SO_4 was heated to 50 °C, 4 g of sawdust per 10 ml of formaldehyde were then added and stirred at 50 °C for 2 h. The sawdust was filtered off, washed with distilled water until the pH of the washing was 6 and finally air-dried. In the case of industrial waste, it was shown that this treatment was not necessary [9].

To identify the active sites on the sawdust surface, the biomass was characterized by different methods such as IR, XPS, MEB coupled with EDAX, potentiometric and conductimetric titrations. Identification of the active sites is a way to find the mechanisms possibly involved in the process (physical adsorption, complexation, ionic exchange, and surface micro-precipitation). Analysis of these experimental results showed the influence of pH on the deprotonation of functional groups of sawdust. These results will be discussed in Section 3.3.

2.3. Analysis of Pb(II) and Cd(II) ions

A Hitachi Z8270 (Perkin-Elmer, France) atomic Absorption Spectrophotometer equipped with a Zeeman atomizer and a SSC-300 autosampler was used to determine the concentration of unadsorbed Pb(II) and Cd(II) ions in the effluent. Zeeman effect correction and pyrolytic graphite-coated tubes were used for AAS measurements. All the instrumental conditions were optimized for maximum sensitivity as indicated by the manufacturer.

The surface structure of sawdust was analyzed by scanning electronic microscopy (SEM) coupled with energy dispersive X-ray analysis (EDAX) using the Cambridge-Leo system at 15 kV with background subtraction with a summation of 240 scans. For these analyses sawdust samples were mounted on a stainless steel stab using a double-stick tape, coated with a thin layer of gold.

The evaluation of the surface characteristics was performed by X-ray photoelectron spectroscopy (XPS) using an ESCA-Auger system (Perkin-Elmer, Physical Electronics Division). XPS spectra were taken before and after lead and cadmium sorption to identify the groups involved in the sorption.

2.4. Batch sorption experiments

The experiments were performed in a batch reactor at 20.5 ± 0.5 °C with continuous stirring fixed at 400 rpm. Biosorbent particles (0.1–2 g) were left in contact with 100 ml of

each solution (1–50 mg l^{-1}) during 1 h; the initial pH value of the solution was adjusted with nitric acid (0.1 mol l^{-1}) or sodium hydroxide (0.1 mol l^{-1}). The pH value was chosen so that the metallic species were present in their divalent form.

Aliquots of supernatant were withdrawn at different time intervals and the amount of metallic ions in the solution was estimated by atomic absorption. In order to obtain the sorption capacity, the amount of ions adsorbed per mass unit of biomass (q_e in milligram of metal ions per gram of sawdust) was evaluated using the following expression (1):

$$q_e = \frac{C_0 - C_e}{m} \times V \tag{1}$$

where C_0 is the initial metal ions concentration (mg l^{-1}), C_e the equilibrium metal ions concentration (mg l^{-1}), V the volume of the aqueous phase (l), and m is the amount of the sawdust used (g). Sorption efficiency (ε) is considered in percentage as

$$\varepsilon = 100 - 100 \times \frac{C_e}{C_0} \tag{2}$$

For each condition, three experiments were performed and the deviation (Δq_e) of q_e, during the investigations, was calculated from Eq. (3) as follows:

$$\Delta q_e\,(\%) = \frac{\sum_{i=1}^{N} |[(q_e, i)_{cal} - (q_e, i)_{exp}]/(q_e, i)_{exp}|}{N} \times 100 \tag{3}$$

where the subscripts "exp" and "cal" show the experimental and calculated values of q_e and N is the number of measurements.

2.5. Diffusion models

Kinetics studies of sorption are significant since (i) the data can be used for determining the time required to reach equilibrium, (ii) the rate of adsorption can be used to deduce predictive models for column experiments, and (iii) these studies can be used in understanding the influence of variables on the sorption of solutes.

It is important to study the rate at which metallic ions can be removed from aqueous solutions in order to apply adsorption to wastewater treatment. There are essentially four stages in the adsorption process by porous adsorbents [10]: (i) solute transfer from the bulk solution to the boundary film bordering the polymer surface, (ii) solute transport from boundary film to the sorbent surface, (iii) solute transfer from the sorbent surface to the intraparticular active sites, and (iv) interactions of the solute molecules with the available sites on the internal surface.

One or more of the four above-mentioned steps may control the rate at which the solute is adsorbed and the amount of solute that is adsorbed onto the solid particles; at low stirring speeds, the boundary layer resistance will be significant and step (ii) will be important in the rate controlling process.

External mass transfer is characterized by the initial rate of solute sorption [10]. It can be calculated from the initial slope of the curves C_t/C_0 versus time. Intraparticular diffusion is characterized by the relationship between specific sorption (q_t) and the square root of

time ($\sqrt{t}$). This relation was given by Weber and Morris as cited in [11,12]:

$$q_t = \frac{k_w}{m} t^{1/2} \tag{4}$$

where m is the mass of adsorbent (g), q_t the amount of metal ions adsorbed at time t (mg g^{-1}), and k_w is the initial rate of intraparticular diffusion (mg l^{-1} s$^{-0.5}$).

3. Results and discussion

3.1. Effect of biomass pre-treatment on Cd^{2+} and Pb^{2+} sorption

The effect of the treatment on the sorption was examined by using the experimental procedure previously described. The solution with an initial concentration of 100 mg l^{-1} was stirred with 1 g l^{-1} of treated sawdust. Another experiment was carried out with untreated sawdust. The pH of each solution was regulated by adding dilute NaOH or HNO_3. Table 1 shows the retention capacities of treated sawdust and untreated sawdust for lead and cadmium ions sorption after a contact time of 1 h.

The results show that the removal yield for the metals studied is not modified by a preliminary treatment of the biomass. But this processing favors the stabilization of the extractable compounds of wood. Chemical treatment induces a stabilization of the hydrosoluble compounds of wood by creating covalent bonds on the constitutive units, and makes the biosorbent able to adsorb metal cations without an increase in COD that is due to the release of the polyphenolic compounds.

3.2. Effects of contact time and initial metal ion concentration

To establish an appropriate contact time between the biomass and metallic ions solution, sorption capacities of metal ions were measured as a function of time. As shown in Figs. 1 and 2, lead and cadmium were rapidly removed by sawdust (less than 20 min). This is rather good as compared with the results obtained with other adsorbents referred to other papers (Table 2). For the following experiments, the contact time was maintained for an hour to ensure that equilibrium was really achieved.

The equilibrium sorption capacity of the biomass for Cd(II) and Pb(II) ions increased with a rise in the initial ions concentration from 80 ± 1.8% up to 95 ± 0.5% for Cd(II) and 84 ± 1.8% up to 98 ± 0.5% for Pb(II), as it also is shown in Table 3. Ion removal is highly concentration-dependent. On the contrary, it may be noticed from Figs. 1 and 2 that time to reach equilibrium is concentration-independent.

Table 1
Effect of biomass pre-treatment on Cd^{2+} and Pb^{2+} sorption after 1 h of contact time

Adsorbent	COD (mg O_2 l^{-1})	Removal of Cd^{2+} (%)	Removal of Pb^{2+} (%)
Untreated sawdust	28	96.2	97.5
Sawdust treated with H_2SO_4 and HCHO	8	96.0	97.6

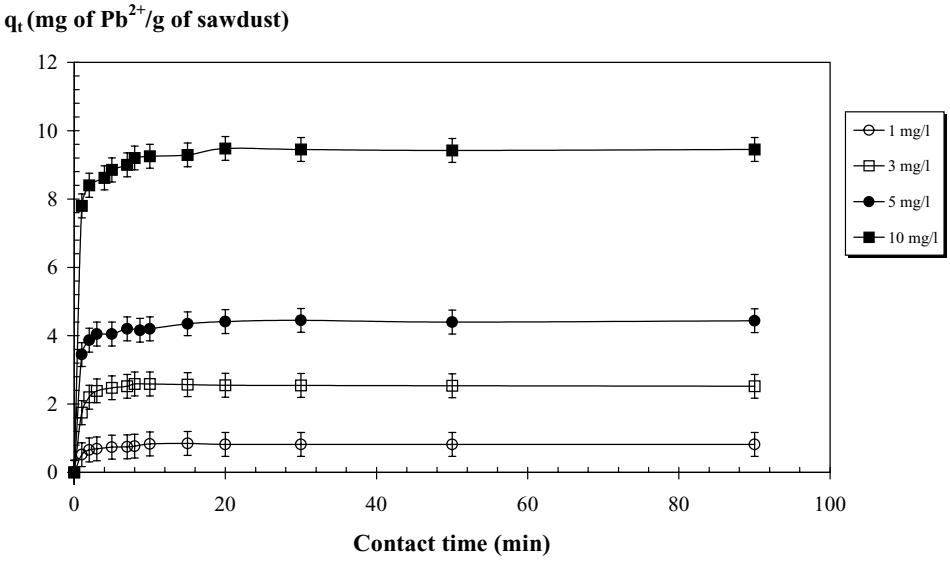

Fig. 1. Influence of contact time on the sorption capacity of Pb(II) onto sawdust of *Pinus sylvestris* at different initial concentrations (*T*, 25 °C; stirring speed, 400 rpm; pH, 5.5; *m*, 0.1 g of sawdust).

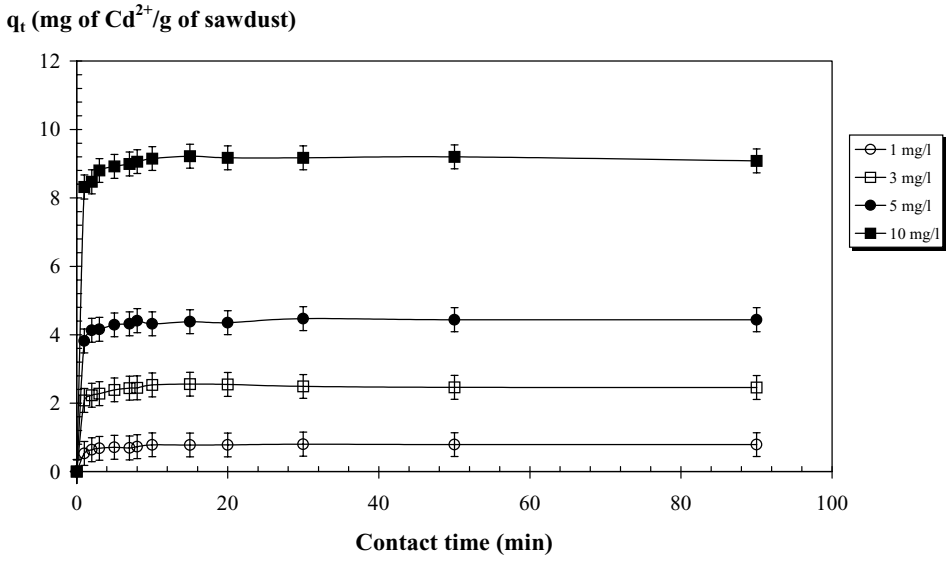

Fig. 2. Influence of contact time on the sorption capacity of Cd(II) onto sawdust of *Pinus sylvestris* at different initial concentrations (*T*, 25 °C; stirring speed, 400 rpm; pH, 5.5; *m*, 0.1 g of sawdust).

Table 2
Contact time for different adsorption systems

Metallic ions solution	Adsorbent	Contact time (min)	References
Pb(II)	Polyacrylamide grafted sawdust	180	Raji and Anirudhan [13]
Cd(II), Hg(II)	Treated *Pinus pinaster* bark	120	Vázquez et al. [14]
Cu(II)	Sawdust from India	60	Vaishya and Prasad [15]
Cd(II)	Poly(vinylalcohol)-coated/cibacron blues F3GA-attached polypropylene hollow fiber membranes	40	Büyüktuncel et al. [16]
Cd(II)	Actinomycetes	5	Kefala et al. [17]
Fe(III)	*Zoogloea ramigera* and *Rhizopus arrhizus*	15	Sa and Kutsal [18]
Cr(III), Cr(IV), Ni(II)	Industrial biomass with reference to environmental control	30	Sekhar et al. [19]
Cd(II), Pb(II), Fe(III)	*Schizomeris leibleinii*	25	Özer et al. [20]
Pb(II), Cu(II), Ni(II)	Low cost natural polysaccharides	20	Gérentes et al. [21]
Pb(II)	*Streptomyces pilosus*	5	Sadowski et al. [22]

This increase in loading capacity of the biosorbent with relation to metal ions concentration is probably due to a high driving force for mass transfer. In fact, the more concentrated the solution is, the better the adsorption is. At 20 °C, when the initial metal ions concentration was increased from 1 to 10 mg l^{-1}, the loading capacity of dried sawdust increased from 0.84 ± 0.13 to 9.49 ± 0.2 mg of Pb per gram of sawdust (Fig. 1) and 0.80 ± 0.13 to 9.29 ± 0.2 mg of Cd per gram of sawdust, respectively (Fig. 2).

It is well known [23,24] that the rate of the sorption process is modified by several parameters such as stirring speed, the structural properties of the adsorbent (i.e. porosity, specific area, particle size, etc.), the properties of the metallic ions (ionic radius, number of coordination, and speciation), metallic ions concentration, chelates formation between metallic ions, and the adsorbent, etc. This is why intraparticular diffusion was also studied in this work. The model chosen refers to the theory reported by Weber and Morris [24]. Temperature and stirring speed were constant for all experiments. The experimental results of this model demonstrated a non-linear distribution of points. The double nature of the plots (*curved and linear*) was obtained for the sorption process at different initial concentrations (Fig. 3); this indicated the existence of an intraparticular diffusion in this process. The initial

Table 3
Sorption capacity of metallic ions at different initial concentrations

Initial concentration (mg l^{-1})	Sorption capacity of Pb(II) (%)[a]	Sorption capacity of Cd(II) (%)[a]
1	84	80
3	86	84
5	89	88
10	98	95

Conditions: T, 25 °C; stirring speed, 400 rpm; pH, 5.5; m, 0.1 g of sawdust.
[a] The sorption capacity was calculated according to Eq. (2).

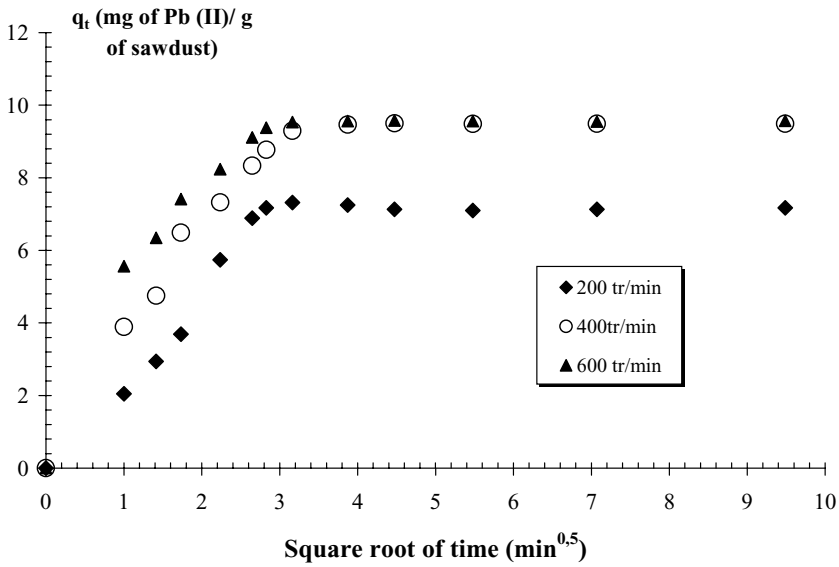

Fig. 3. Effect of stirring speed on the sorption capacity of Pb(II) onto sawdust of *Pinus sylvestris* (particular size, 0.1–0.16 mm; T, 25 °C; pH, 5.5; C_0, 10 mg l^{-1}; m, 0.1 g of sawdust).

portion represents the film diffusion. The subsequent linear portion is characteristic of an intraparticular diffusion. Similar results were found by Gaid et al. [25], Saucedo et al. [26], and Ho et al. [11]. These results also show that the biosorbent can easily replace the physical adsorbent.

3.3. Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process [27]. Thus, the effect of hydrogen ion concentration was examined from solutions at pH ranging from 2 to 9. Fig. 4 summarizes the uptake of Cd(II) and Pb(II) onto sawdust of *P. sylvestris* at various pH values. The maximum uptake of these ions was obtained at about pH 5.5.

At lower pH values, the H_3O^+ ions compete with the metal ions for the exchange sites in the sorbent. There is an increase in metal ions uptake as the pH value increases from 2 up to 5. One of the reasons for the metal ions adsorption behavior of the biosorbent is that the sawdust surface contains a large number of active sites. The metal uptake depends on these active sites as well as on the nature of the metal ions in solution. In fact, at pH lower than pH_{zpc} values (pH at zero point charge), complexation phenomena can also occur, especially for the carboxylic groups. In other respects, the property of the sawdust to uptake metal ions can also be explained by the carbonyl groups (C=O) or the hydroxyl groups (OH) of polyphenols. The oxygen of each carbonyl and hydroxyl group is considered as a strong Lewis base because of the presence of its vacant doublet electrons. Thanks to this

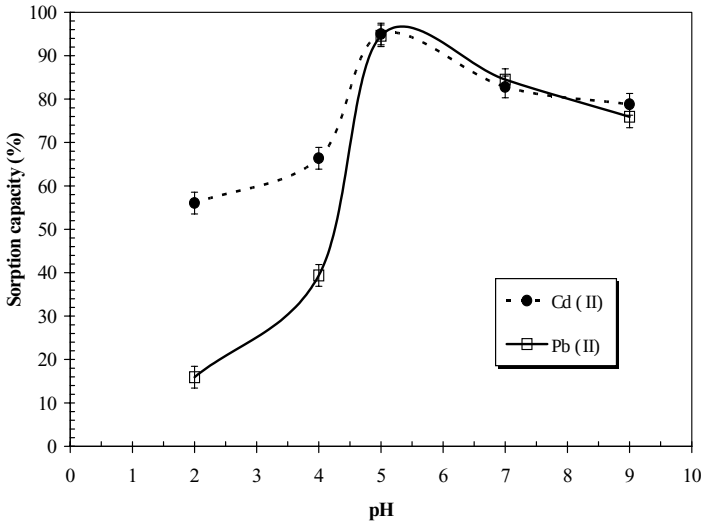

Fig. 4. Uptake of Cd(II) and Pb(II) onto sawdust of *Pinus sylvestris* at various pH values (C_0, 5 mg l^{-1}; T, 25 °C; m, 0.1 g of sawdust). The pH was regulated with a minimal amount of 0.1 M of NaOH or HNO_3.

doublet, the oxygen base makes a complex of coordination with the chemical entities low in electrons (metal ions, for example) (Fig. 5).

When pH increases from acid value to a neutral value, various species are noticeably present (for example, at pH 6, different sorts of species are present in each solution, i.e. $Pb(OH)^+$ and Pb^{2+} for the solution of lead and only Cd^{2+} for the solution of cadmium as suggested by Stumm and Morgan [28]). The affinities of the surface sites of sawdust depend on the nature of ions. This may be further explained in relation to a competition effect between the H_3O^+ and metal ions. At low pH values, the concentration of H_3O^+ ions is largely superior to that of the metal ions, hence the former ions occupy the binding

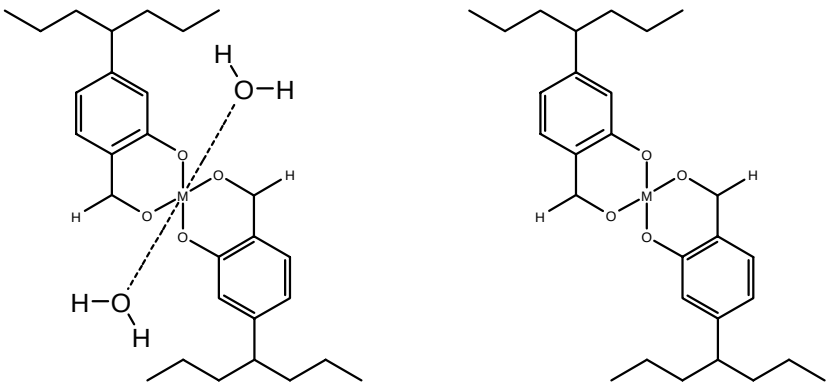

Fig. 5. Formation of metal complexes with the functional groups on the sawdust surface.

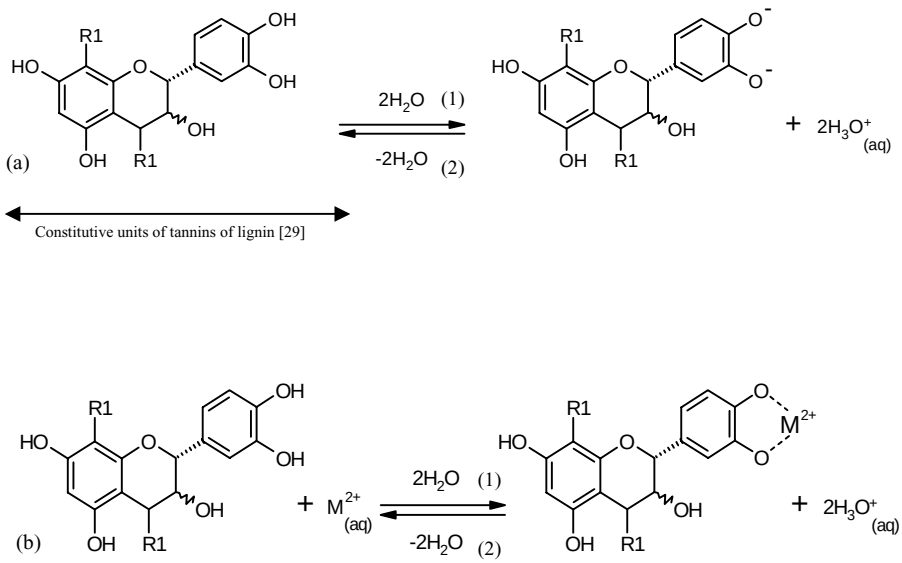

Fig. 6. Mechanism of biosorption: (a) represents the first stage of ion-exchange (deprotonation), while (b) shows the attachment (adsorption) of the metal cations onto the deprotonated active sites on the sawdust surface [29]. The symbol M is a metal ion of charge 2+.

sites on the sawdust, leaving metal ions free in solution. When the pH is increased, the concentration H_3O^+ ions decreases, and the sites on the sawdust surface mainly turn into dissociated forms (Fig. 6a) and can exchange H_3O^+ ions with metallic ions in solution (Fig. 6b). For all subsequent experiments, a pH of 5.5 was used in order to ensure that Cd(II) and Pb(II) do not precipitate as hydroxide.

3.4. Sorption isotherm

Since solution pH has a significant effect on adsorption equilibrium, the Langmuir model [30] was applied to the sorption equilibrium at different pH in order to establish the maximum metal sorption capacity. The equilibrium removal of the Pb(II) and Cd(II) ions can be mathematically expressed by the adsorption isotherms, according to the Langmuir model (5).

$$q_e = q_m \frac{bC_e}{1 + bC_e} \tag{5}$$

or its linearized form (6)

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \tag{6}$$

where C_e is the equilibrium aqueous metal ions concentration (mg l^{-1}), q_e the amount of metal ions adsorbed per gram of sawdust at equilibrium (mg g^{-1}), q_m and b the Langmuir

Table 4
Langmuir adsorption constants obtained from the isotherms of solutions of Pb(II) and Cd(II) at different initial pH

pH	Langmuir constants									
	Pb(II)					Cd(II)				
	q_e (mg g^{-1})	q_m (mg g^{-1})	b (l mg^{-1})	R_L	R^2	q_e (mg g^{-1})	q_m (mg g^{-1})	b (l mg^{-1})	R_L	R^2
4	7.17	15.77	0.058	0.63	0.92	6.29	15.27	0.054	0.65	0.95
5	9.78	22.22	0.052	0.66	0.91	9.29	19.08	0.057	0.64	0.93
7	3.90	8.45	0.077	0.56	0.99	5.5	6.72	0.105	0.49	0.99

R^2 is the correlation coefficient.

constants related to the maximum adsorption capacity and energy of adsorption, respectively. The values of b and q_m can be determined from the linear plot of C_e/q_e versus C_e. The main characteristic of Langmuir isotherm is its dimensionless constant separation factor (equilibrium parameter), R_L, defined by $R_L = 1/(1 + bC_0)$ [31].

The sorption isotherms were determined at different pH values for a concentration range of 1–50 mg l^{-1}. All solutions contained a fixed mass of sawdust (1 g of sawdust per liter of solution). The q_m, b, and R_L values calculated from isotherms at different initial pH values are presented in Table 4. The plots of C_e/q_e versus C_e obtained for two metals are linear (Figs. 7 and 8) according to the Langmuir model.

The values of q_m and b were determined from Eq. (6) and found to be 22.22 mg of Pb per gram of sawdust and 19.08 mg of Cd per gram of sawdust, under optimum adsorption conditions.

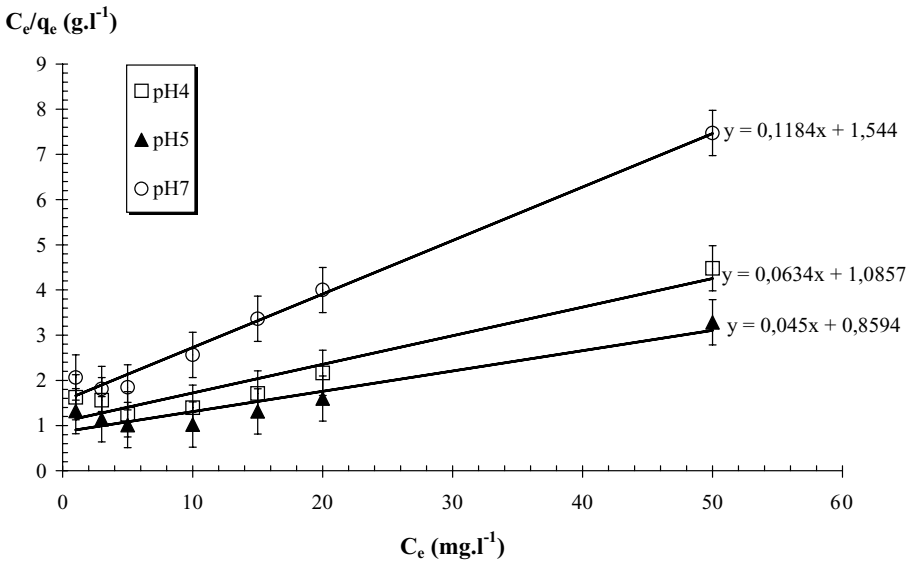

Fig. 7. Equilibrium isotherms at different pH for adsorption of Pb(II) ions onto sawdust of *Pinus sylvestris* (T, 25 °C; m, 0.1 g of sawdust; stirring speed, 400 rpm).

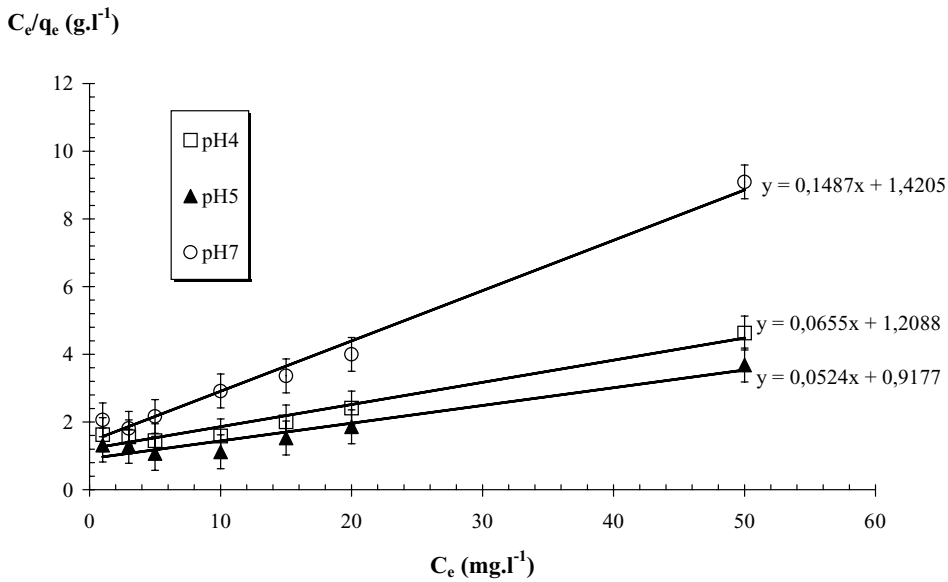

Fig. 8. Equilibrium isotherms at different pH for adsorption of Cd(II) ions onto sawdust of *Pinus sylvestris* (*T*, 25 °C; *m*, 0.1 g of sawdust; stirring speed, 400 rpm).

The sorption of Pb(II) and Cd(II) ions onto sawdust may be due to the development of a free negative charge on the surface. Besides, sorption of the above-mentioned metals may be due to ion-exchanges at the surface level or attachment through hydrogen bonding. The more electronegative a metal is, the better its sorption is. Sawdust exhibited better sorption capacity for Pb(II) (1.55 on Alfred and Rochow scale) than for Cd(II) (1.46 on Alfred and Rochow scale) [32].

However, q_e has smaller values than q_m. This shows that the adsorption of Cd(II) and Pd(II) ions onto sawdust is a monolayer type one that does not fully cover the surface of the sawdust [33]. Moreover, the R_L values obtained range from zero to one in the range of zero and one. According to McKay [31] and Battacharya and Venkobachar [34], this indicates that the sorption of Pb(II) and Cd(II) onto sawdust is feasible at the concentrations studied. The results also show the variation of *b* according to pH. This variation underlines the fact that the affinity of metal ions onto sawdust is pH-dependent.

3.5. Sorption kinetics

In order to determine the sorption kinetics of Pb(II) and Cd(II) ions, the first-order and second-order kinetics models were checked. The first-order rate expression of Lagergren [32] based on solid capacity is generally expressed as follows:

$$\frac{dq_t}{dt} = k_{1,ad}(q_e - q_t) \tag{7}$$

where q_e and q_t are the amounts of metal ions adsorbed onto the sawdust (mg g^{-1}), respectively, at equilibrium and at time t and $k_{1,ad}$ is the rate constant of first-order (min^{-1}). After integration in boundary conditions ($t = 0$ to t and $q_t = 0$ to q_e), Eq. (7) becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_{1,ad}}{2.303}t \tag{8}$$

In most cases, the first-order equation of Lagergren did not apply well throughout the whole range of contact times and is generally applicable over the initial 20–30 min of the sorption process. The plotting of $\log(q_e - q_t)$ versus "time" (curves not shown) deviated considerably from the theoretical data after a short period. The plots and intercepts of curves were used to determine the first-order constant $k_{1,ad}$ and equilibrium capacity q_e. The calculated values of q_e (Table 5) from the first-order kinetics model are lower than the experimental ones. So the sorption system does not follow a first-order reaction.

The pseudo-second-order equation, which is based on the sorption capacity of solid phase, was also used. If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetics rate equation is expressed as [35]:

$$\frac{dq_t}{dt} = k_{2,ad}(q_e - q_t)^2 \tag{9}$$

where $k_{2,ad}$ is the rate constant of second-order biosorption (g mg^{-1} min^{-1}). For boundary conditions ($t = 0$ to t and $q_t = 0$ to q_e), Eq. (9) becomes

$$\frac{t}{q_t} = \frac{1}{k_{2,ad}q_e^2} + \frac{1}{q_e}t \tag{10}$$

Using Eq. (10), t/q_t was plotted versus t at different adsorbent concentrations and second-order sorption rate constant ($k_{2,ad}$) and q_e values were determined from the slopes and intercepts of the plots (Figs. 9 and 10). The correlation coefficients for the linear plots are superior to 0.999 in all the systems. The values of these parameters and the deviation are presented in Table 5. The theoretical q_e values agree perfectly with the experimental q_e values. This suggests that the sorption system is not a first-order reaction and that a pseudo-second-order model (Eq. (10)) can be considered. The latter is based on the assumption that the rate limiting step may be a chemical sorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate. It provides the best correlation of the data.

3.6. Effect of stirring speed

The quality of the dispersion of the solid in adsorption on a batch reactor is a significant factor as in all processes of mass transfer. Stirring influences the distribution of the aqueous solution and can also act on the formation of an external film of separation. Table 6 shows the various values of the constants of diffusion according to stirring velocity (Spahn and Schlünder coefficient, k_s [36] is assigned to external diffusion and the k_w coefficient to intraparticular diffusion, according to Morris and Weber [24]). The results show that an increase in stirring speed from 200 to 600 rpm does not significantly modify the coefficient of diffusion of metal ions on the sawdust. It can be assumed

Table 5
Comparison of the first- and second-order adsorption rate constants, for calculated ($q_{e,cal}$) and experimental ($q_{e,exp}$) values at different adsorbent concentrations[a]

Metallic ion	Adsorbent concentration (g/100 ml)	First-order kinetic model				Second-order kinetic model		
		$q_{e,exp}$ (mg g^{-1})	$k_{1,ad}$ (min^{-1})	$q_{e,cal}$ (mg g^{-1})	Deviation (%)	$k_{2,ad}$ (g mg^{-1} min^{-1})	$q_{e,cal}$ (mg g^{-1})	Deviation (%)
Cd(II)	0.1	9.29	0.007	0.18	98.0	1.22	9.10	2.1
	0.5	1.95	0.015	0.13	93.4	10.89	1.94	0.1
	1	0.99	0.024	0.06	94.2	18.31	0.98	0.4
Pb(II)	0.1	9.49	0.010	0.09	99.0	0.51	9.45	0.4
	0.5	1.97	0.012	0.06	97.1	8.53	1.96	0.5
	1	1.00	0.035	0.03	97.3	9.27	0.99	0.5

[a] The deviation was calculated according to Eq. (3).

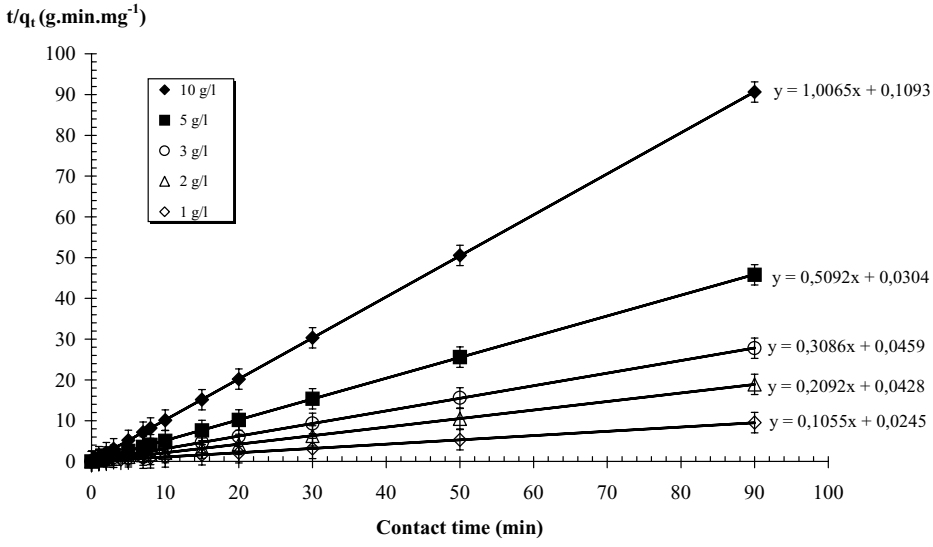

Fig. 9. Plot of Pb(II) for the pseudo-second-order kinetic model at different adsorbent concentrations (T, 25 °C; stirring speed, 400 rpm; pH, 5.5; C_0, 10 mg l^{-1}).

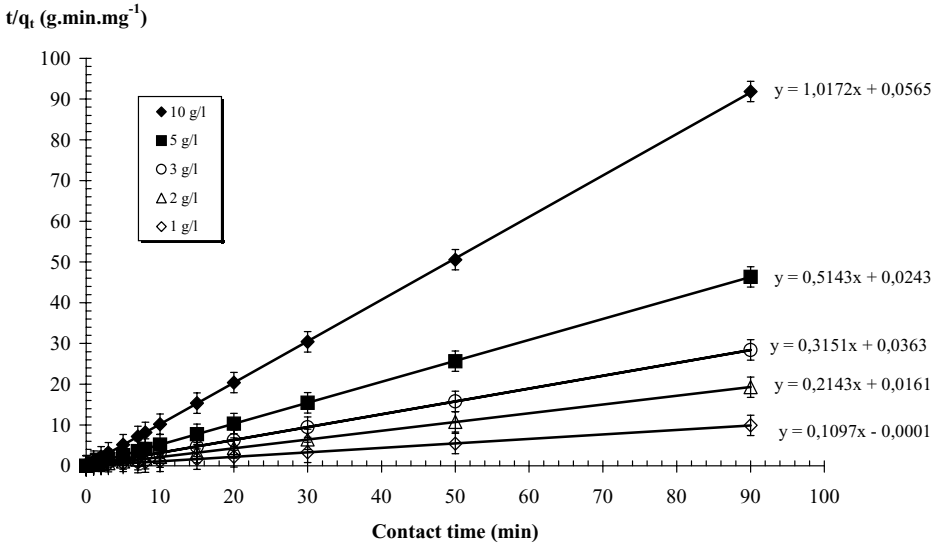

Fig. 10. Plot of Cd(II) for the pseudo-second-order kinetic model at different adsorbent concentrations (T, 25 °C; stirring speed, 400 rpm; pH, 5.5; C_0, 10 mg l^{-1}).

Table 6
Effect of stirring speed on diffusion coefficients k_w and k_s

Stirring speed (rpm)	Constant of external diffusion[a], k_s ($\times 10^{-8}$ m s^{-1})	Constant of intraparticular diffusion[b], k_w (mg g^{-1} s$^{-0.5}$)
Cadmium		
200	1.89	0.31
400	4.33	0.41
600	4.33	0.45
Lead		
200	1.95	0.30
400	3.03	0.36
600	3.03	0.39

[a] This diffusion coefficient was calculated from $C_t/C_0 = f(t)$ according to Spahn and Schlünder models [36].
[b] This diffusion coefficient was calculated from $q_t = f(\sqrt{t})$ according to Weber and Morris models [24].

that the rate of adsorption is controlled by the diffusion of the solute inside the biomass [24].

However, the coefficient of external diffusion is rather different in the case of Pb(II). Therefore, the effect of stirring is obscured by the effect of an external resistance to mass transfer inside the solid particle.

3.7. Analysis of sawdust by SEM, EDAX, and XPS

Electron micrographs and EDAX spectra of the sawdust before and after sorption with 100 mg l^{-1} of solution, which contained Pb(II) and Cd(II), are shown in Figs. 11–15. These

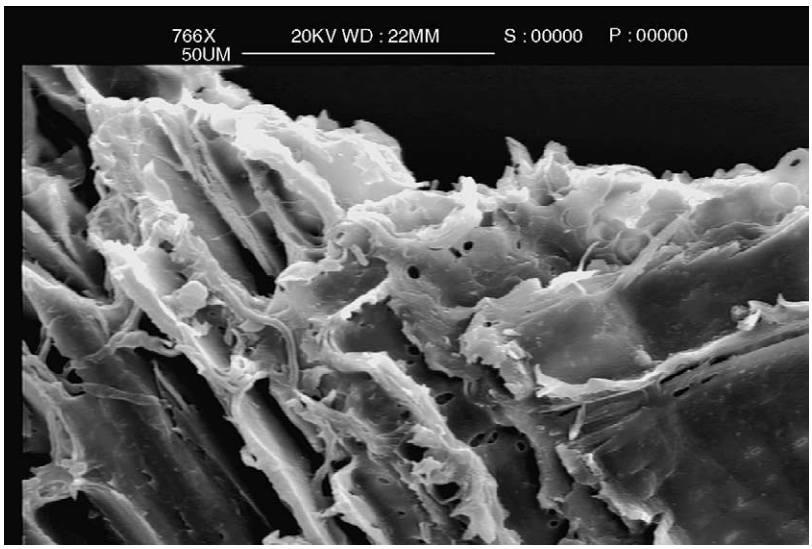

Fig. 11. Typical SEM micrograph of virgin sawdust of *Pinus sylvestris*.

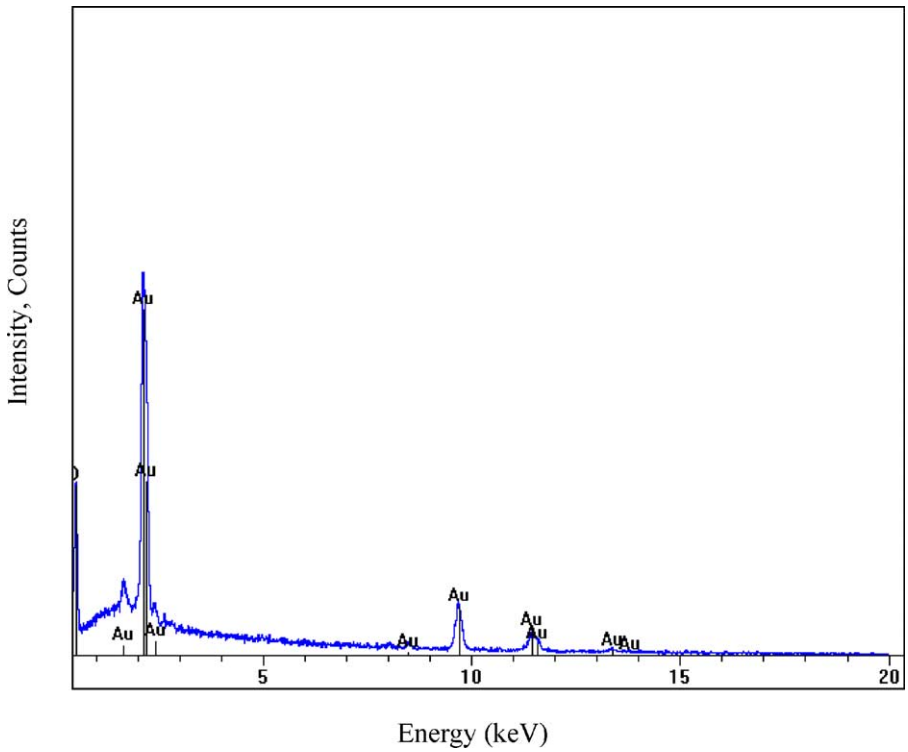

Fig. 12. Corresponding EDAX spectrum of virgin sawdust of *Pinus sylvestris*.

micrographs reveal clearly the apparition of pellets on the sawdust particles (Figs. 13 and 14), whereas these pellets were absent on the sawdust before loading it with metallic ions solution (Fig. 11). Some modifications can be observed on the sawdust particles after adsorption with: (i) a strong density of pellets on the sawdust particles (Fig. 13), (ii) pellets inside layers of sawdust particles (Fig. 14), and (iii) two types of crystals looking like "rice seeds" (Fig. 13) and "billiard balls" (Fig. 14).

The density of pellets observed in SEM was also characterized by EDAX. The EDAX analysis reveals Pb(II) and Cd(II) signals on the surface of the sawdust after adsorption by a metallic ions solution (Fig. 15). The presence of gold peaks in all spectra results from the gold purposely settled to increase the electric conduction and to improve the quality of the micrographs.

The XPS spectra obtained before (a) and after (b) Pb(II) biosorption onto sawdust are presented in Figs. 16 and 17. Fig. 16 shows that doublets characteristic of lead appear, respectively, at 138.5 eV (assigned to Pb $4f_{7/2}$) and at 143.85 eV (assigned to Pb $4f_{5/2}$) after loading sawdust with Pb(II) solution. The peak observed at 138.5 eV agrees with the 138.0 eV value reported for PbO [37]. This shows a fixation of lead onto sawdust during the process. A similar mechanism was also made for the cadmium uptake. There is also a significant difference between the oxygen peaks before (a) and after (b) lead biosorption

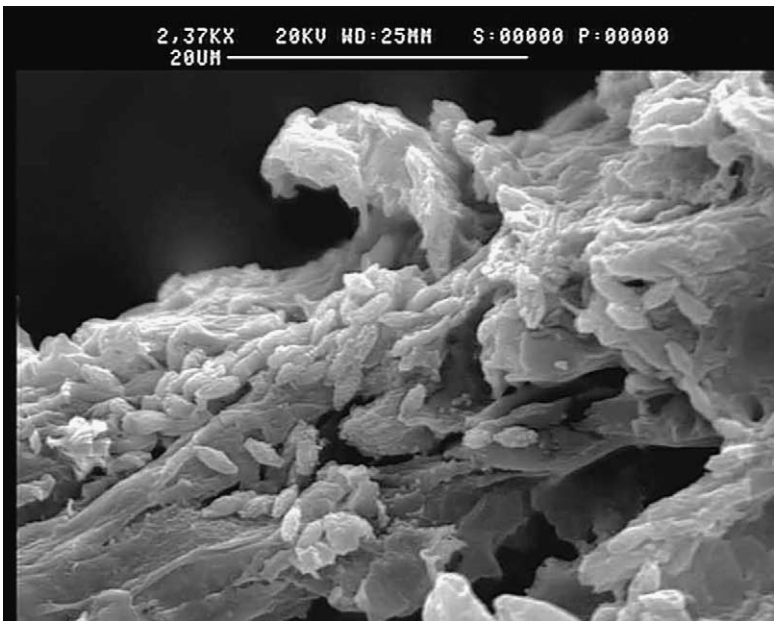

Fig. 13. Typical SEM micrograph of sawdust of *Pinus sylvestris* after loading with synthetic metallic nitrate solution of lead and cadmium.

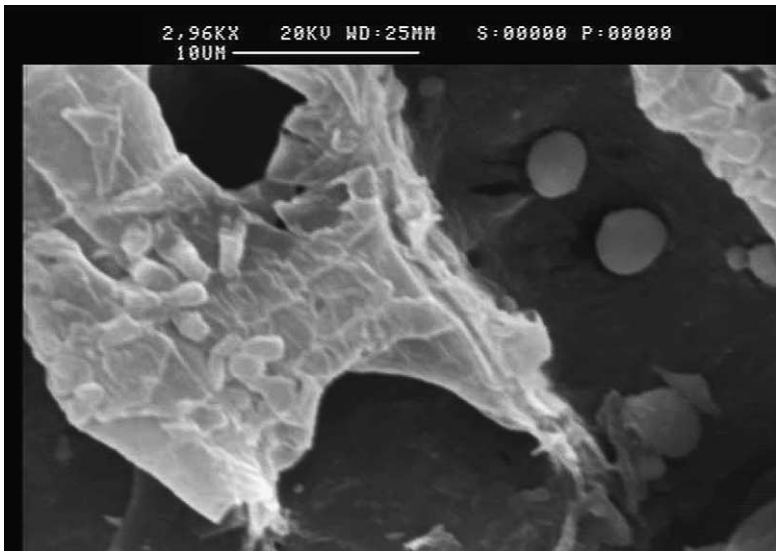

Fig. 14. Typical SEM micrograph of sawdust of *Pinus sylvestris* after loading with synthetic metallic nitrate of lead and cadmium.

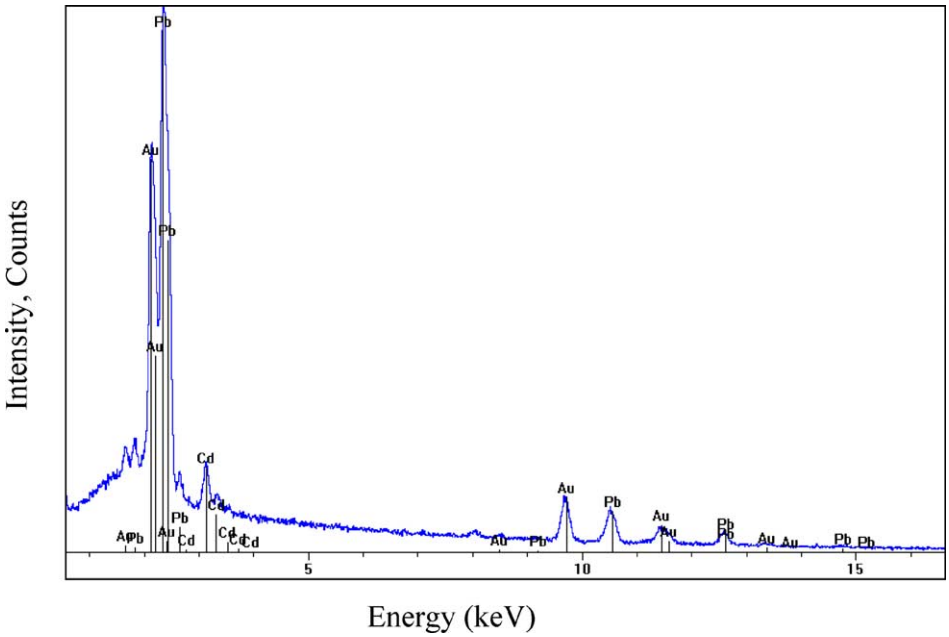

Fig. 15. Corresponding EDAX spectrum of loaded of sawdust of *Pinus sylvestris* after loading with synthetic metallic nitrate of lead and cadmium.

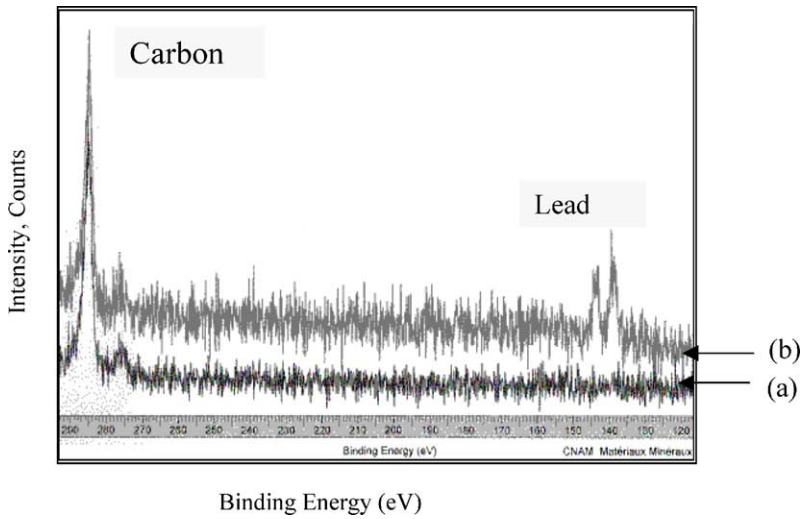

Fig. 16. XPS analysis spectra of *Pinus sylvestris* biomass: (a) before and (b) after lead uptake.

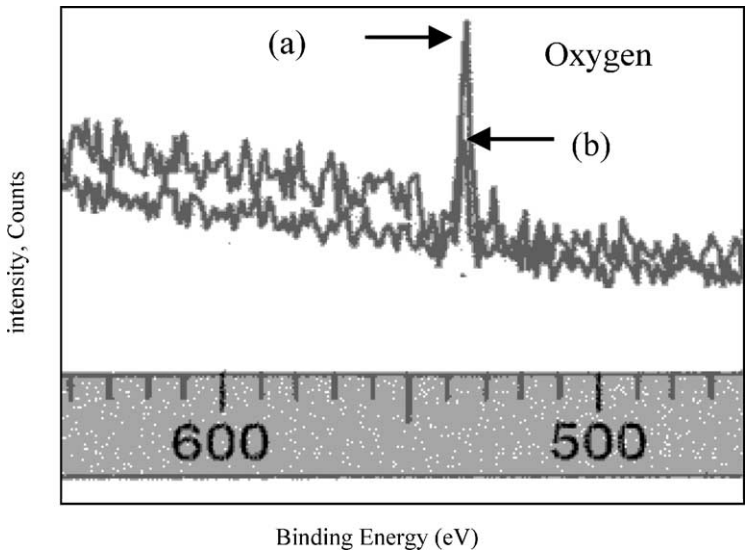

Fig. 17. High resolution oxygen XPS spectra of *Pinus sylvestris* biomass (a) before and (b) after lead uptake.

(Fig. 17). The atomic concentration of oxygen after lead biosorption decreases. Hence, lead biosorption is accompanied by a change in oxygen binding, providing evidence that the oxygen of carboxylic group takes part in lead biosorption. The oxygen peak was shifted by 0.73 eV after lead biosorption (Fig. 17). This shift could have been expected since $Pb(OH)_2$ pellets cover the sawdust surface (Figs. 13 and 14), it suggests that the oxygen of lignines reacts with the metallic ions. Similar results were reported by Kuyucak and Volesky [38].

4. Conclusion

The present study clearly establishes that sawdust of *P. sylvestris* is an effective adsorbent for Pb(II) and Cd(II) removal from aqueous solutions. The results obtained show that the sorption of lead is higher than that of cadmium. Moreover, both sorption capacity and sorption rate are strongly dependent on the initial concentration in heavy metals, initial pH of solution, and sawdust concentration.

Adsorption equilibrium can be simulated by Langmuir isotherms. These isotherms are influenced by the pH of initial metal ions concentrations as adsorption is essentially a phenomenon of surface.

The kinetics of sorption can be described by a model of a pseudo-second-order because of the strong correlation of the experimental results obtained with Ho and McKay's linearization. Two models of transfer were examined: external diffusion and intraparticular diffusion. The experimental data show that intraparticular diffusion is significant in the determination of the sorption rate. However, external diffusion has only a weak effect, all the weaker as stirring velocity hardly influences equilibrium in the stirring field explored.

It can be concluded that the use of *P. sylvestris* sawdust as an adsorbent may be an alternative to more costly materials such as activated carbon for the treatment of liquid wastes containing metal ions. Moreover, the rapid uptake allows to consider carrying out the sorption of heavy metals on column filled with this sawdust because the contact time between the metal solution and the adsorbent is generally short in this process. These results were confirmed working with some industrial sewage and the development on a pilot scale is now being studied.

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