Removal of lead (II) ions from synthetic and real effluents using immobilized *Pinus sylvestris* sawdust: Adsorption on a fixed-bed column

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Abstract

The purpose of this work was to evaluate the potential of *Pinus sylvestris* sawdust, in a continuous flow removal of lead (II) ions from synthetic and industrial aqueous effluents. The kinetic parameters obtained in a batch process were used to scale-up the process on a mini-column and to choose the breakthrough model. The column experimental data concerning the volumes treated were correlated using the bed depth service time model. These experimental data closely fitted the bed depth service time model at 10% of the breakthrough curve.

The results from the bed depth service time model on the mini-column were then used to design a pilot plant adsorption unit. The performance of the pilot plant column accurately agreed with that obtained from the mini-column. The experiments carried out in a dynamic reactor allowed to bring out the influence of various parameters on the efficiency of the *P. sylvestris* sawdust. In addition, the process was checked for the treatment of industrial aqueous effluents on a pilot plant scale and the results were in accordance with those obtained from synthetic effluents.
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1. Introduction

The removal of toxic heavy metal contaminants from aqueous waste streams is currently one of the most important environmental issues being researched. Although this issue has been studied for many years, effective treatment options are still limited. Chemical precipitation, ion exchange, reverse osmosis and solvent extraction are the methods most commonly used for removing heavy metals ions from dilute aqueous streams [1]. Studies carried out to look for new and innovative treatment technologies have focused attention on the metal binding qualities of various types of biomass [2,3]. It was shown that some microorganisms and biomass are able to adsorb toxic and heavy metals from dilute aqueous so-lutions. The factors affecting the metal binding qualities of these biomaterials or their affinity for a metal dissolved in aqueous media include: (i) the chemical nature of the metal ions (e.g. size, valence, electron orbital structure, stability of the chemical forms in nature) and that of the biomass (e.g. charge density and structure of the polymer chain, functional groups), (ii) medium conditions (e.g., pH, temperature, ionic strength, presence of competing organic or inorganic metal chelators). Biosorptive processes are generally rapid and theoretically suitable for extracting metal ions from large volumes of water [4].

Results obtained in previous studies carried out on a batch reactor showed that the removal of lead and cadmium through their binding onto *Pinus sylvestris* sawdust is possible. The latter biomaterial contains various organic compounds such as lignin (with polyphenolic groups), cellulose (with numerous hydroxyl functions) and hemicelluloses (with carboxylic

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and hydroxyl groups). These functional groups may be useful for binding ions of heavy metals [5]. Although various types of reactors, e.g. batch, continuously stirred tank reactors and fluidized-bed columns can be used, adsorption on packed-bed columns presents numerous advantages. It is simple to operate, gives high yields and can be easily scaled up from a laboratory process.

The purpose of this study was to investigate the influences of bed depth, linear flow rate and concentrations of feed metal ions on the performance of lead (II) adsorption onto *P. sylvestris* sawdust immobilized in a packed-bed column. This work was firstly carried out on a mini-column and the results were then checked on a pilot scale unit.

2. Methods and materials

2.1. Methods

In this work, studies were starting from the mass balance of the packed-bed reactor. The variation of this balance during the reaction can be illustrated by Fig. 1, where u is the linear flow rate, which is the average rate of the liquid flow when the column is empty. The equation of mass balance material is: input flow = output flow + flow inside pores volume + matter adsorbed onto sawdust. For this system, the balance can be expressed according to the following equation

$$Q_v C_0 = Q_v C + V_p \frac{dC}{dt} + m \frac{dq}{dt} \tag{1}$$

where Q_v is the volumetric flow of the solution in the column ($l\,min^{-1}$), Q_0 and C, respectively, the inlet and outlet solute concentrations ($mg\,l^{-1}$), $Q_v C_0$ the inlet flow of solute in the column ($mg\,min^{-1}$), $Q_v C$ the outlet flow of solute leaving the column ($mg\,min^{-1}$), V_p the porous volume (l) ($V_p = \frac{1}{1-\varepsilon} V_a$ where V_a is the bulk volume and ε the porosity), $V_p \frac{dC}{dt}$ the flow rate through the bed depth column ($mg\,min^{-1}$) and $m \frac{dq}{dt}$ the amount of solute adsorbed onto sawdust ($mg\,min^{-1}$) where m is the mass of sawdust and $\frac{dq}{dt}$ the adsorption rate.
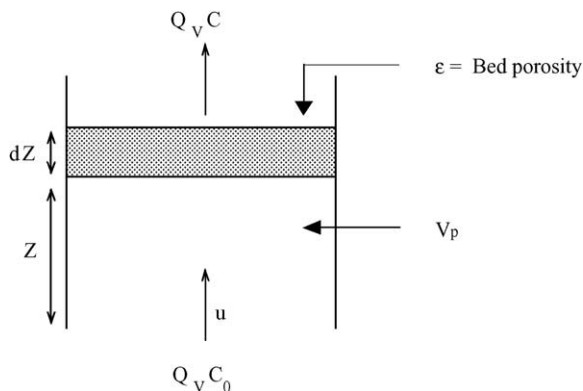

Fig. 1. Schema of bed depth [6].

According to relation (1), the determining factors of the balance for a given bed depth of the column are the linear flow rate ($u = \frac{Q_v}{S_c}$, where S_c is the column section, m^2), the initial solute concentration, the adsorption potential and the porous volume even if previous studies showed that the latter parameter may be neglected. Therefore, in order to optimize the adsorption process in a packed-bed column, it is necessary to examine these parameters and to estimate their influence. Several types of reactors were used for the adsorption processes in a continuous system: adsorption within a fixed-bed column and adsorption with a fluidized-bed column. It is necessary to note that the fixed-bed regime presents numerous advantages in a pilot plant notably its precision and bed performance, whereas in the industrial scale-up the fluidized bed is more advantageous particularly as it seals out the biomass and also reduces the risks of saturation in the columns.

2.1.1. Design of the adsorption column based on bed depth service time

Adsorption within a packed-bed column is a process in which a continuous mass transfer occurs between two phases (the mobile phase containing the solute and the solid phase of the packed bed). The solute concentration in both phases is a function of the contact time and the depth of the adsorption zone. A mathematical model based on mass balance is often used to explain the adsorption phenomena and to find out the characteristic variables of the process. Several models can be used. This work aims to study the effect of various experimental conditions on the bed depth service time (BDST) model and then to compare the obtained results with those of previous studies [6].

The BDST model describes a relation between the service time of the column and the packed-bed column. The original work on the BDST model was carried out by Bohart and Adams [7] on the adsorption, in dynamic system, of the chlorine onto activated charcoal and those of Thomas [8] on the adsorption of the ions by zeolites.

Working on the model, the authors supposed that intraparticular diffusion and external mass resistance are negligible and the adsorption kinetics is controlled by the surface chemical reaction between the solute in the solution and the adsorbent not yet used [9]. The authors demonstrated that the system agrees with Eq. (2) [9,10]:

$$\ln\left[\frac{C_0}{C_b} - 1\right] = \ln\left(e^{(k_{ads} N_0/u)z} - 1\right) - k_{ads} C_0 t_b \tag{2}$$

In this relation $e^{(k_{ads} N_0/u)z} \gg 1$, thus $\ln(e^{(k_{ads} N_0/u)z} - 1) \cong \frac{k_{ads} N_0}{u} Z$, that is the reason why Hutchins [11] proposed the following linear relation between the column bed depth (Z) and the service time (t_b):

$$t_b = \frac{N_0}{C_0 u} Z - \frac{1}{k_{ads} C_0} \ln\left(\frac{C_0}{C_b} - 1\right) \tag{3}$$

where t_b is the service time at breakthrough point (min), N_0 the dynamic bed capacity ($mg\,l^{-1}$), Z the packed-bed

column depth (m), u the linear flow rate (m min^{-1}) defined as the ratio of the volumetric flow rate Q_v (m^3 min^{-1}) to the cross-sectional area of the bed S_c (m^2), C_0 and C_b are, respectively, the inlet and the breakthrough metal ions concentration (mg l^{-1}) and k_{ads} the adsorption rate constant (l mg^{-1} min^{-1}). Eq. (3), known under the name of bed depth service time (BDST) can be determined for a given adsorbent depth and is a straight line:

$$t_b = m_x Z - C_x \qquad (4)$$

where m_x (min m^{-1}) is the slope of the BDST line and represents the time required for the adsorption zone to travel a unit length through the adsorbent [10]. It is used to predict the performance of the bed. C_x is the abscissa intercept in the BDST plot.

The dynamic bed capacity (N_0) and the adsorption rate constant (k_{ads}) can be evaluated from the slope and intercept of the plot of t_b versus Z. The bed depth (Z_0), which represents the theoretical depth of adsorbent able to prevent the adsorbent concentration from exceeding C_b, is obtained when $t_b = 0$, according to the following equation:

$$Z_0 = \frac{u}{k_{ads} N_0} \ln\left(\frac{C_0}{C_b} - 1\right) \qquad (5)$$

By varying the column bed depth (Z), the plot of Eq. (3) allows to calculate the value of N_0 and thus to estimate the value of Z_0. If there is a change in the initial solute concentration C_0 to a new value C_0', the new values of m_0' and C_x' can be, respectively, obtained from the slope and the intercept according to the relations proposed by Hutchins [11]:

$$m_x' = m_x \left(\frac{C_0}{C_0'}\right) \qquad (6)$$

$$C_x' = C_x \left(\frac{C_0}{C_0'}\right) \frac{\mathrm{Ln}\left(\frac{C_0'}{C_b} - 1\right)}{\mathrm{Ln}\left(\frac{C_0}{C_b} - 1\right)} \qquad (7)$$

where C_0 is the inlet solute concentration (mg l^{-1}) and C_0' the new inlet value (mg l^{-1}). When the linear flow rate is changed from u to u', the new value of the slope (m_x') is obtained by Eq. (8) [11]. However the intercept remains unchanged because it depends on the inlet solute concentration C_0:

$$m_x' = m_x \left(\frac{u}{u'}\right) \qquad (8)$$

2.1.2. Mass transfer zone

The mass transfer zone (MTZ) is the active surface of the sawdust bed in which adsorption occurs (Fig. 2). The fluid flowing into the column gets through a virgin bed. The top of the adsorbent in contact with the fluid quickly adsorbs the pollutant during the first contact. Thus the fluid leaving the column is practically free of metallic ions (points P1, P2 and P3 in Fig. 2). As the volume of polluted fluid getting through the bed column increases, an adsorption zone of mass transfer (MTZ) gets defined. In this MTZ, adsorption is complete and the concentration of pollutant in the bed column varies from 100% of C_0 (corresponding to total saturation) to approximately 0% of C_0 (corresponding to the virgin adsorbent). This adsorption zone then moves downwards through the bed column in relation to time until the breakthrough occurs. When this zone reaches the bottom of the bed the pollutant dissolved in the solution cannot yet be adsorbed any longer. This moment is called "breakpoint". The plot obtained after this point gives the concentration history and is called breakthrough profile or breakthrough curve.

From a practical point of view, this point allows to determine the solute concentration in the effluent and the volume treated (V_b). For most adsorbent–pollutant systems, the breakthrough curve is obtained after an effluent concentration of 50% has been reached. To facilitate the calculations of the bed adsorption capacity, the breakthrough curve is often fixed at 50% (P4, Fig. 2), sometimes at 10% (P3, Fig. 2) of the inlet concentration according to the target quality of the final effluent [12]. When the mass transfer zone leaves the bed column (P5, Fig. 2), the bed is completely saturated,
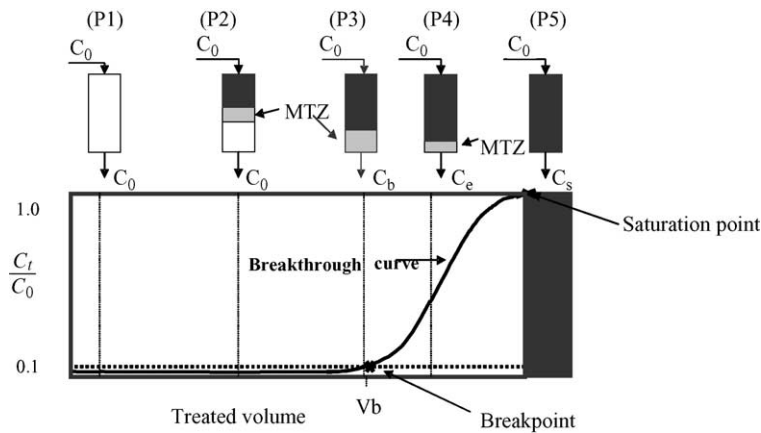

Fig. 2. Typical breakthrough curve for activated carbon showing the movement of the mass transfer zone according to the throughput volume [12] (MTZ: mass transfer zone).

adsorption in the bed does not occur and the effluent which leaves the column has the same concentration as the one that enters. The quantity of adsorbed pollutant at breakpoint (q_b in mg g^{-1}) can be obtained from the following relation [13]:

$$q_b = \frac{Q_v t_{10\%} C_0}{m_c} \tag{9}$$

where $t_{10\%}$ is the service time (min) obtained when the outlet concentration is 10% of the inlet one, C_0 the inlet metal ions concentration (mg l^{-1}), Q_v the effluent volumetric flow rate (l min^{-1}) and m_c the amount of sawdust (g).

2.2. Materials

2.2.1. Adsorbate

All the compounds used to prepare reagent solutions were of analytic reagent grade. The mother solution of lead (1000 mg l^{-1}) was prepared by dissolving a weighed quantity of nitrate lead salt in twice distilled water. This mother solution was then diluted and the concentrations of metal ions solutions ranged from 1 to 10 mg l^{-1}. Before the solution letting through the column packed with the sawdust, the pH of the solution was adjusted to the required value for the adsorption of lead (II) ions (which was 5.5 according to previous batch study [6]), by adding sodium hydroxide 0.1N or nitric acid 0.1N. Ionic strength was kept constant at 0.01 M value by adding a sodium chloride solution.

The adsorbing potential of sawdust was checked on real effluents supplied by the STCM Company from its industrial site based in Bazoches-les-Gallerandes (45 France). Beside the metal ion (lead at 1.07 mg l^{-1}) chosen as a model other metal ions (cadmium at 1.73 mg l^{-1}; nickel at 0.30 mg l^{-1} and zinc at 4.70 mg l^{-1}) were found.

2.2.2. Adsorbent

The sawdust of *P. sylvestris* used as an adsorbent was provided by the Société d'Exploitation Forestière Barillet, Châteauneuf-sur-Loire (45 France).

2.2.3. Analysis of lead (II) ions

A Hitachi Z8270 (Perkin Elmer, France) Atomic Absorption Spectrophotometer (AAS) equipped with a Zeeman atomizer and an SSC-300 autosampler was used to determine the concentration of unadsorbed lead (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 in a previous study [6].

2.3. Preliminary test on a mini-column

With the purpose of studying the efficiency of packed-bed columns in the treatment of a liquid effluent containing lead (II) or other metallic ions, preliminary experiments were carried out on a laboratory scale with a mini-column of 15 mm

internal diameter (i.d.). The design of the process is shown in Fig. 3.

The aim of this step was to improve the process conditions, to minimize the outlet metal ions concentration of the treated effluent, and thus to obtain lower metal ions concentrations than those set by law before dumping. That is why, the effects of some parameters influencing the adsorption process (bed depth, linear flow rate through the bed and inlet solute concentration) were studied separately. The results from these experiments were then transposed on a pilot plant scale.

This experimental was carried out with three different packed beds, respectively, 65, 85 and 130 mm in depth. The column was loaded with dried sawdust, then a 5 mm thick layer of glass cotton was placed at the bottom of the column to prevent any loss of biomaterial. Another one was set at the top of the bed to prevent sawdust dispersion while the solution flowed through the column. The sawdust particle size used in the fixed-bed study was inferior to 0.5 mm. The pH of the feed tank solution was adjusted to 5–5.5 value before feeding the column. The experiments were carried out at constant room temperature (about 25 °C). The column was packed vertically while being subjected to vertically directed vibrations to facilitate particle settling and prevent size segregation near the tube walls. The bottom of the column was connected to a detection cell (DC) equipped with a conductimetric probe (CP), a pH-meter probe (PMP) and a temperature probe (TP). The equilibrium concentration evolution of the solute was monitored by comparing the initial and measured pH values as well as the specific conductivity in the release tanks.

Before letting the solution flow through the bed depth, the column was conditioned with a 0.1 M NaHSO$_3$ solution at a pH value of 5.1 contained in the tank (PS), the peristaltic pump (PP2) delivered the latter solution through the bed for 2 h, at a volumetric flow rate of 5 ml min^{-1}. This 2-h pretreatment was necessary to fix the water-soluble compounds of the sawdust and to prevent its extractible polyphenolic compounds from staining the treated water. The column was then washed for 24 h with distilled water (DW) to clean excess of pre-treatment solution. The column experiments were carried out by feeding a solute solution in down flow mode through the fixed-bed with a peristaltic pump (PP1). Samples collected periodically from the effluent were analyzed by AAS to obtain concentration.

2.4. Pilot plant layout

To compare the bed performance of this process with those of other packed-bed processes, we considered a continuous system able to treat in 4 h a volume of 100 l of solution containing 1 mg of lead per liter of polluted solution. Fig. 4 shows the pilot plant column used for these studies. The PVC column (10 cm i.d., 100 cm height with a section of 78.5 cm^2) was used in vertical position. Experiments were carried out with a bed depth of 56 cm. The conditions of application for the experiment were the following ones: (i) the column was filled up in the same way as the mini-column, (ii) the column
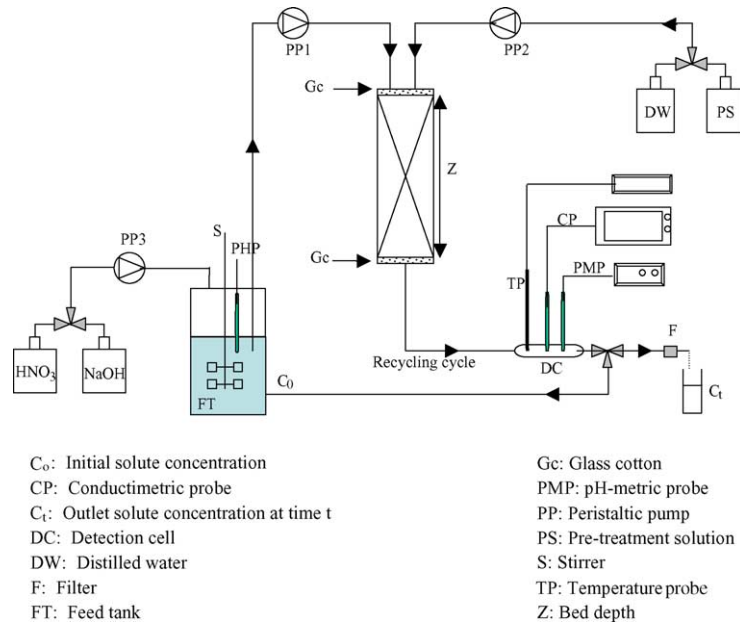
Fig. 3. Schematic design of column unit for laboratory scale experiments.

C_o: Initial solute concentration
CP: Conductimetric probe
C_t: Outlet solute concentration at time t
DC: Detection cell
DW: Distilled water
F: Filter
FT: Feed tank

Gc: Glass cotton
PMP: pH-metric probe
PP: Peristaltic pump
PS: Pre-treatment solution
S: Stirrer
TP: Temperature probe
Z: Bed depth

was fed from top to bottom by a centrifugal pump (Kripsol, KS 75 type delivered by Kripsol, Toledo, Spain) equipped with a filter. This pump delivered $25\,l\,h^{-1}$ equivalent to a linear flow rate of $5.66\,cm\,min^{-1}$. The height of the bed, being of 56 cm, a contact time of about 10 min was estimated to be necessary considering the height of that columns and the lower flow rate. All the experiments were carried out at room temperature (20–25 °C). The breakthrough concentration was defined as the concentration acceptable in view of the limits ($10\,\mu g\,l^{-1}$) set by the authorities applying to industrial waste before dumping. Samples of 5 ml were regularly taken to monitor the evolution of the metal ions concentration in the outlet solution. They were directly analyzed by AAS without preliminary dilution.

3. Results and discussion

3.1. Mini-column scale

The results of lead (II) adsorption onto *P. sylvestris* sawdust are presented in the form of breakthrough curves where

C: Column
FI: Flow indicator (20 to $200\,l\,h^{-1}$)
FT: Feed tank (150 l)
P: Pump

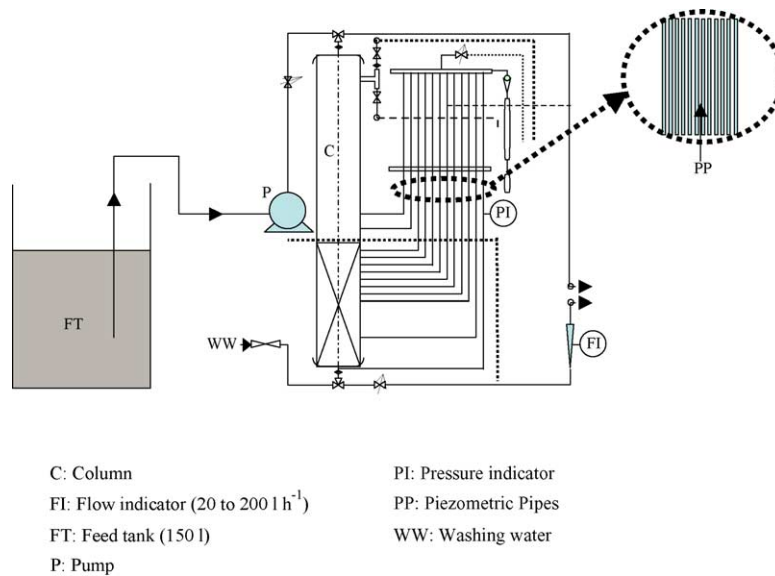PI: Pressure indicator
PP: Piezometric Pipes
WW: Washing water

Fig. 4. Pilot plant setup for industrial wastewater treatment.

Fig. 5. Effect of bed depth on the breakthrough curves of lead (II) ions ($u = 1.42\,\mathrm{cm\,min^{-1}}$; $C_0 = 10\,\mathrm{mg\,l^{-1}}$).

Fig. 6. Effect of initial concentration onto the breakthrough curves of lead (II) ions ($Q_v = 10\,\mathrm{ml\,min^{-1}}$; $Z = 13\,\mathrm{cm}$; $u = 5.66\,\mathrm{cm\,min^{-1}}$).

the concentration ratio C_t/C_0 is plotted versus time. Several parameters were studied.

3.1.1. Effect of bed depth

The breakthrough curves obtained for lead (II) ions adsorption are illustrated in Fig. 5 for different bed depth of *P. sylvestris* sawdust (6.5, 8.5, and 13.0 cm), at a constant linear flow rate of $1.42\,\mathrm{cm\,min^{-1}}$. They follow the characteristic "S" shape profile produced in ideal adsorption systems. Results indicate that the breakthrough volume varies with bed depth. This displacement of the front of adsorption with the increase in depth can be explained by mass transfer phenomena that take place in this process. When the bed depth is reduced, axial dispersion phenomena predominate in the mass transfer and reduce the diffusion of metallic ions. The solute (metallic ions) has not enough time to diffuse into the whole of the adsorbent mass. Consequently an important reduction 2580–1110 ml in the volume of solution treated at the breakthrough point is observed when the bed depth in the column decreases from 13.0 to 6.5 cm (Fig. 5 and Table 1). Moreover, an increase in the bed adsorption capacity (q_b) is noticed at the breakthrough point with the increase in bed depth (Table 1). This increase in the adsorption capacity with that in the bed depth can be due to the increase in the specific surface of the adsorbent which supplies more fixation binding sites. Then it follows that a delayed breakthrough of the pollutant leads to an increase in the volume of solution treated. The increase in adsorption with that in bed depth was due to the increase in adsorbent doses in larger beds which provide greater service area (or adsorption sites). Studies of experi-
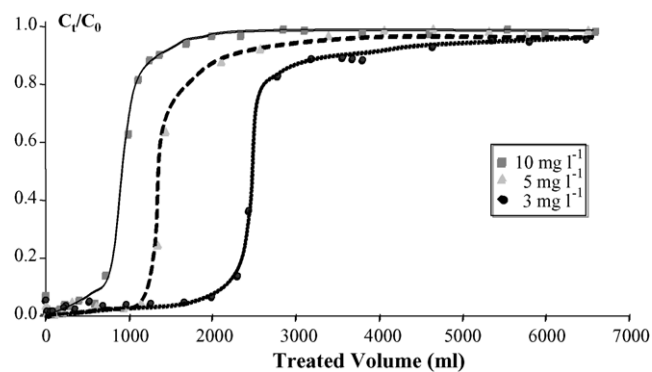
mental conditions (i.e. linear flow rate, bed depth and inlet solute concentration) on the fixation of the metal ions show that the breakthrough time (t_b) depends on Z, $1/u$ and $1/C_0$ according to Eq. (3). The breakthrough time also increased with the height of the bed. Breakthrough time is therefore the determining parameter of the process. The larger it is, the better the intra-particulate phenomena and the bed adsorption capacity are (Table 1).

3.1.2. Effect of inlet concentration

The effect of a variation from 3 to $10\,\mathrm{mg\,l^{-1}}$ of the inlet concentration of the solution used with a linear flow rate of $5.66\,\mathrm{cm\,min^{-1}}$ is shown in Fig. 6. Other results obtained with volumetric flow rates of 1.42 and $2.83\,\mathrm{cm\,min^{-1}}$ showed that the trends of the breakthrough curves were similar. However, the breakthrough points were totally different.

The effect of the initial concentration onto the breakthrough curves with column bed depth set at 13 cm is shown in Fig. 6. It can be seen that a rise in the inlet metal concentration reduces the volume treated before the packed bed gets saturated as shown in Table 2. A high metal concentration may saturate the sawdust more quickly, thereby decreasing the breakthrough time. Similar results were also obtained for the sorption of copper and cadmium ions onto bone char [13] and sorption of copper and zinc by the residual biomass of the alga *Sargassum* sp. [14]. These results demonstrate that an increase in the concentration modifies the adsorption rate through the bed and increases the bed adsorption capacity (Table 2). Therefore the diffusion process depends on the inlet concentration [13,15]. Nevertheless, the saturation of the adsorbent requires much more time. However the breakthrough

Table 1

Adsorption breakthrough data for mini-column scale for the sorption of lead (II) ions on different bed depth columns ($C_0 = 10\,\mathrm{mg\,l^{-1}}$; $u = 1.42\,\mathrm{cm\,min^{-1}}$; $Q_v = 2.51\,\mathrm{ml\,min^{-1}}$; $S_c = 1.77\,\mathrm{cm^2}$)

Bed depth Z (cm)	Adsorbent mass (g)	Treated volume V_b (ml)[b]	Breakthrough time t_b (min)[a]	Adsorption bed capacity q_b (mg g^{-1})[b]
6.5	1.96	1110	443	5.7
8.5	2.53	1625	648	6.4
13.0	3.92	2580	1030	6.6

[a] Obtained experimentally from Fig. 5.
[b] Calculated according to Eq. (9).

Table 2
Adsorption capacity of sawdust at different initial metal concentrations ($Z = 13$ cm; $m_c = 3.92$ g; $u = 5.66$ cm min^{-1}; $Q_v = 10$ ml min^{-1}; $S_c = 1.77$ cm^2)

Initial concentration C_0 (mg l^{-1})	Treated volume V_b (ml)[a]	Breakthrough point t_b (min)[a]	Adsorption bed capacity q_b (mg g^{-1})[b]
3	2200	220	1.7
5	1210	121	1.6
10	850	85	2.2

[a] Obtained experimentally from Fig. 6.
[b] Calculated according to Eq. (9).

Table 3
Effect of the linear flow rate on the sorption of lead (II) ions ($C_0 = 10$ mg l^{-1}; $Z = 13$ cm; $m_c = 3.92$ g; $S_c = 1.77$ cm^2)

Linear flow rate u (cm min^{-1})	Treated volume V_b (ml)[a]	Breakthrough time t_b (min)[a]	Adsorption bed capacity q_b (mg g^{-1})[b]
1.42	2580	1030	6.6
2.83	1450	289	3.7
5.66	640	64	1.6

[a] Obtained experimentally from Fig. 7.
[b] Calculated according to Eq. (9).

is reached before all the active sites of the sawdust are occupied by the metallic ions. Although, the value of q_b obtained in this study was slightly inferior to those obtained in batch system (at a pH value of 5, it was found that q_e were 7.14 and 6.29 mg g^{-1} for Pb(II) and Cd(II), respectively). However, *P. sylvestris* showed in this study a high affinity for lead cations under these experimental conditions.

3.1.3. Effect of the linear flow rate

The fact that the section area of the column is uniform implies that the linear flow rate through the bed, u, is directly proportional to the overall volumetric flow rate through the packed bed ($u = Q_v/S_c$). To examine the effect of the linear flow rate through the bed depth, the initial solute concentration and bed depth were kept constant ($C_0 = 10$ mg l^{-1}, $Z = 13$ cm) while the linear flow rate varied from 1.42 to 5.66 cm min^{-1}. Results are given in Fig. 7 and show that the uptake of metal ions onto the biomaterials decreases when the linear flow rate through the bed increases. An increase in the linear flow rate reduces the volume treated efficiently until breakthrough point and therefore decreases the service time of the bed. This is due to the decrease in contact time between the metal ions and the sawdust at higher linear flow rates. As the adsorption rate is controlled by intra-particulate diffusion, an early breakthrough occurs leading to a low bed adsorption capacity (Table 3). These results are also in agreement with those referred to the literatures [14,16]. When the linear flow rate decreases the contact time in the column
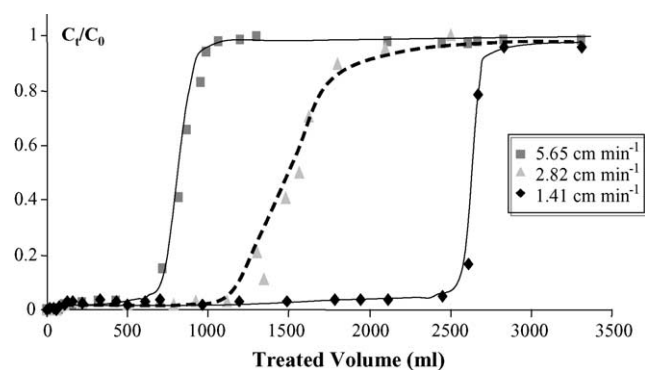
is longer, intra-particulate diffusion then becomes effective. Thus the metallic ions have more time to diffuse amidst the particles of sawdust and a better adsorption capacity is obtained (Table 3). At a higher linear flow rate, the biosorbent gets saturated early, certainly because of a reduced contact time, a larger amount of ions adsorbed on the sawdust and a weak distribution of the liquid into the column, which leads to a lower diffusivity of the solute amidst the particles of the biomaterials [17]. This shows an increase in the uptake of the metallic ions due to the intra-particulate phenomena. Therefore the volume treated, the breakthrough time and the bed adsorption capacity were reduced and a wide volume of solution is purified with an efficient elimination. As can be seen in Table 3, 2580 ml of solution were treated at a low linear flow rate of 1.42 cm min^{-1} while 640 ml were treated at a high linear flow rate of 5.66 cm min^{-1}. Similar effect by studying the elimination of copper using the calcium alginates [18] and gold using microorganisms were also presented [19].

3.1.4. Application of the BDST model with variations in the initial solute concentration

The effect of the inlet initial concentration on bed performance was studied through the BDST model. The results obtained are presented in Fig. 8 by a plot of service time versus bed depth at a constant linear flow rate. They show that an increase in slope when the inlet metal ions concentration decreases, allowing to treat a larger volume of solution. The
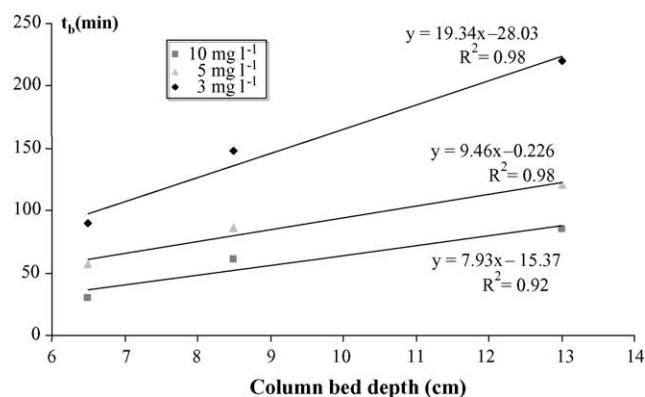

Fig. 7. Effect of the linear flow rate onto the breakthrough curves of lead (II) ions ($Z = 13$ cm; $C_0 = 10$ mg l^{-1}).

Fig. 8. Effect of inlet concentration onto the sorption of lead (II) ions: BDST modelling ($u = 5.66$ cm min^{-1}).

Table 4
Effect of inlet concentration on the BDST parameters ($u = 5.65$ cm min^{-1}; $S_c = 1.77$ cm^2; $m_c = 3.92$ g)

Inlet concentration C_0 (mg l^{-1})	Adsorption capacity q_b (mg g^{-1})[a]	Constant k_{ads} (l mg^{-1} min^{-1})[b]	Dynamic capacity N_0 (mg l^{-1})[c]	R^2
3	1.7	0.026	328	0.98
5	1.6	1.944	268	0.98
10	2.2	0.014	449	0.92

For all experiments the ratio C_0/C_b was 10. R^2 is the Correlation coefficient.
[a] Calculated according to Eq. (9) (Table 2).
[b] Obtained according to the abscissa intercept in BDST plot (Fig. 8 and Eq. (3)).
[c] Obtained according to the slope in BDST plot (Fig. 8 and Eq. (3)).

Table 5
Constants of BDST model calculated and obtained experimentally ($u = 5.65$ cm min^{-1}; $S_c = 1.77$ cm^2)

Inlet concentration C_0 (mg l^{-1})	Analyze	Slope m_x (min cm^{-1})	Intercept, C_x (min)	Dynamic capacity N_0 (mg l^{-1})	R^2
3	Experimental	19.34[a]	−28.03[a]	328	0.99
5	Experimental	9.46[a]	−0.23[a]	268	0.98
10	Experimental	7.93[a]	−15.37[a]	449	0.92
10	Calculated	7.02[b]	−13.20[b]	399	1.00

R^2 is the correlation coefficient.
[a] Obtained experimentally from Fig. 8.
[b] Obtained according to Eqs. (6) and (7), respectively, for m_x and C_x.

variation of inlet concentration also affects the BDST parameters. The adsorption capacity values, calculated according to Eq. (3), slightly increase with inlet concentration (Table 4) and the dynamic bed capacity of the column (N_0) increases by about 36% when the inlet concentration varies from 3 to 10 mg l^{-1}. These results are in correlation with those observed when studying the breakthrough curves and explain the lower performance obtained when concentration is raised. Correlation coefficients calculated by the linearization of experimental data are superior to 0.92 (Table 4).

Table 5 gives the results obtained from slopes and intercepts at constant linear flow rate and particle size, by calculations from Eqs. (4) and (5). These results were compared with those obtained experimentally. The predicted BDST parameters calculated from the slope and intercept of the median for the highest and lowest inlet concentrations, using Eq. (4), show a good agreement with those obtained experimentally with a correlation coefficient superior to 0.98. The experimental error was around 11%. Therefore, from these results we could conclude that the BDST model can produce accurate prediction for the variations of inlet concentration in a dynamic process for lead or other metallic ions–sawdust systems. This model was also successfully used for the prediction of the breakthrough curves in the elimination of lead [10] and cadmium [20] and were in agreement with the previous studies.

The results obtained in the above described experiments were very encouraging and suggested *P. sylvestris* sawdust offers real potentialities as an ionic-exchanger for an application of the process in industrial plants for the treatment of real liquid effluents as reported previously [21]. An application of the process on a pilot plant was then considered to validate the process and to find the optimal conditions.

3.2. Pilot plant scale

For the model building of systems using biomaterials as adsorbents in continuous systems, residence time is an important parameter. The longer the residence time is, the better the bed performance is. In our system we can reach the highest residence time in two ways: (i) by increasing the height of the column, which allows increasing the contact time; (ii) by decreasing the linear flow rate through the column, which increases the contact time. The linear flow rate through the bed depth was chosen according to the mini-column results.

For scale-up experiments we increased the internal diameter (D_i) as well as the bed depth (H) while keeping constant the ratio D_i/H at a value of 0.18. This value corresponds to the 85 mm high mini-column of 15 mm in internal diameter and the linear flow rate through the column was maintained constant at 5.3 cm min^{-1} (corresponding to a volumetric flow

Table 6
Data of parameters used for laboratory and pilot experiments

Parameters	Mini-column	Pilot column	Scale-up ratio
Geometric			
Internal diameter (cm)	1.5	10	6.7
Section (cm^2)	1.77	78.5	44.4
Height (cm)	15	100	6.7
Operating			
Linear flow rate (cm min^{-1})	5.6	5.3	0.95
Inlet concentration (mg l^{-1})	10	10	1
Volumetric flow (l h^{-1})	0.6	25	41.7
Height of sawdust bed (cm)	8.5	56	6.6
Adsorbent weight (g)	3.9	1000	256

Table 7
Comparison of the dynamic data predicted from the BDST model with those obtained experimentally

Effluent	Treated volume (l)	Calculated service time t_b (h)	Predicted service time (h)		Deviation (%)	Uptake (%)
			$C_0 = 3\,\text{mg}\,\text{l}^{-1}$	$C_0 = 10\,\text{mg}\,\text{l}^{-1}$		
Industrial	NS	NS	45	45	NS	99.9[a]
Synthetic	1150	46	48	48	4	99.9[a]

NS: not specified.

[a] Corresponds approximately to 1.25–2 g of lead (II) per kg of sawdust starting from the initial concentration of 1.07 mg l^{-1}.

rate of 25 l h^{-1}). Comparison of geometric and operating parameters used with mini and pilot columns are indexed in Table 6. BDST parameters, k_{ads} (adsorption rate constant) and N_0 (dynamic adsorption capacity), calculated from mini-column experiments were used to predict the service time of the column for the scale-up experiment.

The experimental results about the breakthrough curves of the adsorption of lead (II) obtained by measuring the outlet lead (II) ions concentrations are shown in Fig. 9 which presents the $\frac{C_t}{C_0} f(t)$ function. Initially, the concentration of metal ions adsorbed by the bed and that of the solution leaving the column are equal to 0. However, after a contact time of 45 h, which corresponds to 10% of the breakthrough point, the metal begins to flow through the column outlet. This time agrees with the service time of the sawdust. Then the concentration increases gradually until $C_t = C_0$; at this moment the bed is saturated. The service time of the column defined at 10% of breakthrough point is given in Table 7. Results show that the service times (t_b) deduced from the BDST model and those obtained experimentally are of the same order. In spite of the presence of other metal ions in the industrial effluent, the breakthrough curves (Fig. 9) evolve in the same way. This experiment was not carried on until saturation was reached because the firm could not supply any more effluent. According to the results obtained, it was noticed that the BDST model applied to 10% of breakthrough point allows to simulate or to predict the experimental breakthrough time with a relatively weak abnormality with regard to the theoretical value.
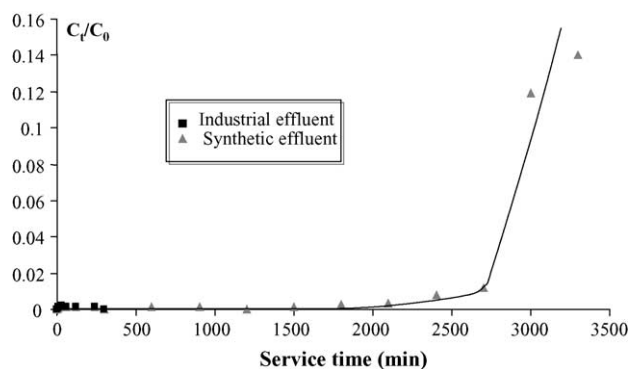

Fig. 9. Adsorption breakthrough data for lead (II) ions removal on a pilot plant scale at height 56 cm, concentration 1.40 mg l^{-1}, volumetric flow rate 25 l h^{-1}, column diameter 10 cm.

4. Conclusion

Adsorption of lead (II) ions through sawdust in a packed bed column is an economically feasible technique for removing metal ions from a solution. The process allows treatment of a given volume of effluent by using a minimal mass of adsorbent which concentrates maximal content of metal.

The adsorption breakthrough curves obtained at different flow rates indicate that an increase in flow rate decreases the volume treated until the breakthrough point and therefore decreases the service time of the bed. Lower removal capacities were observed, probably due to the fact that contact times were insufficient for the adsorption equilibrium to develop between the sawdust and the metal ions. This process was applied to industrial effluents containing some lead in the presence of other metallic ions (nickel, copper, cadmium, zinc, iron). The application of the BDST model at 10% of breakthrough point gave satisfactory results with an error of around 4% with regard to the theoretical service time.

This model was used to scale-up the process from a 0.6 l h^{-1} output ($u = 5.6$ cm min^{-1}) with the mini-column to a 25 l h^{-1} one ($u = 5.3$ cm min^{-1}) with the pilot column (Table 6). Moreover we were able to increase the flow rate to 100 l of solution per hour, which indicated that sawdust adsorption could successfully reduce the metallic ion concentration of outlet industrial effluents in packed bed columns. The results obtained with the pilot show that the process can decontaminate 1200 l of effluent containing 1 mg l^{-1} of lead (II) with only 1 kg of sawdust, before the pollutant gets released. Thus, the process can adsorb approximately 1.25–2 g of diluted lead (II) per kilogram of sawdust, with a 99% removing efficiency. Moreover, the pollutant adsorbed on the cheap material can be then captured since the polluted sawdust can be burnt in industrial furnaces and lead can be recovered from the ashes after a chemical treatment. Inexpensive, effective, readily available materials can be used in place of activated carbon or ion-exchange resins for the removal of heavy metals from solution. Therefore, comparisons of the adsorbents are difficult because of inconsistencies in data presentation. However, from the literature reviewed [22], the sorbent used in this study was compared in term of cost with those that stand out for high absorbency such as activated carbon, fungi biomass, ion-exchange resins, marine algae (Table 8). Although, improved sorption capacity may compensate the cost of additional processing it was noticed that the sawdust presented a better option with a complete

Table 8
Comparative purchase price of stand out adsorbents [22]

Adsorbent	Purchase price (€ t^{-1})
Ion-exchange resins	15000–31000
Cultivated algae	15000–18000
Activated carbon	2000–5000
Fungi biomass	1000–5000
Marine algae	1000–2000
Sawdust	10–50

reusability, lower purchase price, biodegradable, by-product and easy handling.

Acknowledgements

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