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Biosorption of lead (II) from aqueous solution by a bacterial dead Streptomyces rimosus biomass

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Abstract

The lead biosorption capacity of a Streptomyces rimosus biomass treated with NaOH (0.1 M) was studied in the batch mode. After pretreatment of biomass at the ambient temperature, optimum conditions of biosorption were found to be: a biomass particle size between 50 and 160 μm, an average contact time of 3 h, a biomass concentration of 3 g/l and a stirring speed of 250 rpm. The equilibrium data could be fitted by Langmuir isotherm equation. Under these optimal conditions, 135 mg Pb²⁺/g biomass was obtained.

Keywords: Biosorption; Lead; Streptomyces rimosus; Waste-water treatment; Filamentous bacteria; Batch processing

1. Introduction

Many industries such as coating, automotive, aeronautical and steel industries generate large quantities of waste-water containing various concentrations of lead. These concentrations are usually too low to be treated by standard methods. Chemical precipitation leads to the production of toxic sludge. Solvent extraction techniques are not suitable for effluents containing less than 1 g/l of targeted heavy metals. On the other hand, ion exchange processes are too expensive due to the high cost of synthetic resins.

Antibiotic fermentation produces large amounts of semi-solid wastes which are normally disposed by incineration. Such semi-solid wastes, after granulation and heat treatment, have been used to recover and remove heavy metals from waste-water streams [1–4]. These researchers tested several filamentous fungi (Mucor rouxii, Penicillium chrysogenum, A. niger and Rhizopus arrhizus) and showed that R. arrhizus presented the best biosorption capacity of about 55.6 mg Pb²⁺/g biomass.

In the literature, the capability of either living or nonliving organisms fixing metal ions is widely described. Modak et al. [5] showed that nonliving A. niger biomass attached to wheat bran was selective for the extraction of copper and zinc. Guibal et al. [6] studied the biosorption of uranium by filamentous fungus Mucor and Gardea-Torresdey et al. [7] performed batch experiments with inactivated cells of Mucor rouxii for Cu²⁺ binding. Other studies were performed with different biomaterials as marine biomass [8–12], bacteria [13–21], chitosan [22]; humic substances [23] and sewage sludge [24,25]. All these studies were done to remove and recover heavy metals from dilute aqueous streams by biosorption.

In the present work, dead Streptomyces rimosus biomass treated with NaOH (0.1 M) was used in granulated form to remove Pb²⁺ from synthetic aqueous solutions. The effects of physical and chemical parameters on the performance of the biosorption were studied and the mechanism and the kinetics of the lead binding were determined.

2. Diffusion and sorption models

2.1. Sorption isotherms

The equilibrium of a solute separated between the liquid and solid phases is described by various models of sorption isotherms such as the Langmuir and Freundlich models. These models suggest a monolayer sorption, with lateral interactions between the sorbed molecules in the case of the Freundlich models: the energetic distribution of sites is heterogeneous, due to the diversity of sorption sites or the diverse nature of the metal ions sorbed, free or hydrolysed species. The Langmuir model supposes a monolayer sorption with a homogeneous distribution of sorption sites and
Sorption energies, without interactions between the sorbed molecules.

The Langmuir model is described by the following equation:

\[ q_e = \frac{q_m b C_e}{1 + b C_e} \]  

where \( q_e \) is the adsorbed metal ion quantity per gram of biomass at equilibrium (mg/g), \( q_m \) is the maximum amount of metal ion per unit weight of biomass to form a complete monolayer on the surface bound at high \( C_e \) (mg/l) and \( b \) is a constant related to the affinity of the binding sites (L/mg).

The Freundlich model equation is of the form:

\[ q_e = K C_e^{1/n} \]  

where \( k \) and \( n \) are the Freundlich’s constants characteristic of the system.

2.2. Diffusion models

Sorption kinetics are mainly controlled by various steps including diffusion processes. Three steps can be enumerated and applied to lead removal [26–31]:

- **Step 1**: Lead transfer from the boundary film bordering to the surface of the particle.
- **Step 2**: Transfer of the lead from the surface to the intraparticle active sites.
- **Step 3**: Uptake of metal ion on the active sites, via complexation, sorption and intraparticle precipitation phenomena.

Step 1 describes film mass transfer resistance. Step 2 is related to the intraparticle diffusion model. Step 3 is a rapid, nonlimiting phase.

Various models of diffusion have been examined, including single steps of diffusion external or intraparticle or combined phenomena [32–36]. The objective of this study was not to propose a new diffusion model but to select the main limiting step in the overall uptake mechanism.

2.2.1. External mass transfer diffusion model

This model, as an application of the Fick’s laws, describes the evolution of the solute concentration in the solution \( C \) (mg/l), as a function of the difference in the concentrations of the metal ion in the solution, \( C \) at the particle surface, \( C_s \) (mg/l) according to the following equation [37–39]:

\[ \frac{dC}{dt} = -\beta S(C - C_s) \]  

where \( \beta \) is the mass transfer coefficient (m/s) and \( S \) the surface area of the biomass per unit solution volume (m\(^{-1}\)).

The coefficients are determined after making some assumptions such as a surface concentration \( C_s \) negligible at \( t = 0 \), a concentration in solution tending to the initial concentration \( C_0 \) and also negligible intraparticle diffusion. So the previous equation can be simplified to

\[ \left[ \frac{dC}{dt} \right]_{t=0} = -\beta S \]  

The initial rate of sorption, \( -\beta S \) (s\(^{-1}\)), was obtained by polynomial linearisation of \( CC_0 \), and subsequent derivation at \( t = 0 \).

The surface area is approximated as the external surface area. Moreover, the particles are supposed spherical and \( S \) calculated as the external surface compared to the solid/liquid ratio in the solution:

\[ S = \frac{6m}{d \rho_{app}} \]

### Nomenclature

- **b**: Langmuir adsorption constant (L/mg)
- **C**: metal ion concentration in the solution (mg/l)
- **C_{biomass}**: biomass concentration (g/l)
- **C_e**: residual metal ion concentration at equilibrium (mg/l)
- **C_i**: metal ion concentration at the particle surface (mg/l)
- **C_{(Pb^{2+})}**: Pb^{2+} initial concentration (mg/l)
- **d_p**: particle size diameter (m)
- **D_i**: diffusion coefficient in the solid (m\(^2\)/s)
- **k_1**: rate constant of first-order biosorption (s\(^{-1}\))
- **k_2**: rate constant of second-order biosorption (g/mg s)
- **K_1**: diffusion coefficient in the solid (mg/g s\(^{1/2}\))
- **K_{m}**: sorbent mass concentration in the solution (g/m\(^3\))
- **PS**: biomass particle size (m)
- **q**: amount of adsorbed metal ion on the biomass at time \( t \) (mg/g)
- **q_e**: adsorbed metal ion quantity per gram of biomass at equilibrium (mg/g)
- **q_m**: maximum amount of metal ion per unit weight of biomass to form a complete monolayer on the surface bound at high \( C_e \) (mg/l) and \( b \) a constant related to the affinity of the binding sites (L/mg).
- **S**: surface area of the biomass per unit solution volume (m\(^{-1}\))
- **t**: time for biosorption (s)
- **T**: temperature (°C)

### Greek letters

- \( \beta \): mass transfer coefficient (m/s)
- \( \rho_{app} \): apparent volume mass of the sorbent (g/m\(^3\))
- \( \omega \): stirring speed (rpm)
where \( m \) is the sorbent mass concentration in the solution (g/m²), \( d_p \) the particle size diameter (m) and \( \rho_{app} \) the apparent volume mass of the sorbent (g/m³).

2.2.2. Intraparticle mass transfer diffusion model

In this work, the models chosen refer to theories developed by various authors [37,38,40].

According to the intraparticle diffusion model proposed by Weber and Morris [37], the initial rate of intraparticle diffusion is calculated by linearisation of the curve \( q = f(t) \):

\[
q = K_d t^{0.5}
\]

where \( q \) is the amount of adsorbed metal ion on the biomass at time \( t \) (mg/g), \( t \) the time (s) and \( K_d \) the diffusion coefficient in the solid (mg/g s¹/²).

Another kind of intraparticle diffusion model was proposed by Urano and Tachikawa [40]. In this model, the adsorption rate is considered as independent of the stirring speed, and external diffusion negligible relative to the low overall adsorption rate. The sorption kinetics are modelled according to the following equation:

\[
\log_{10} \left( 1 - \frac{q}{q_e} \right) = \log_{10} K_i + \frac{4 \pi D_i q_e}{3 M_p} \left( \frac{1}{t^2} \right)
\]

where \( D_i \) is the diffusion coefficient in the solid (m²/s).

### 2.3. Kinetic modelling

The first-order rate expression of Lagergreen [41], Ho and Mc Kay [42], Aksu [43], based on solid capacity is generally expressed as follows:

\[
\log_{10} \left( 1 - \frac{q}{q_e} \right) = \log_{10} k_1 + \frac{1}{2.3} \left( \frac{t}{q_e} \right)
\]

where \( k_1 \) is the rate constant of first-order biosorption (s⁻¹).

The pseudo second-order equation is also based on the sorption capacity of the solid phase [43–45]. The pseudo second-order kinetic rate is expressed as

\[
\frac{1}{q_e - q} = k_2 t + \frac{1}{q_e}
\]

where \( k_2 \) is the rate constant of second-order biosorption (g/mg s⁻¹).

### 3. Methods and materials

*S. rimosus* biomass produced during oxytetracycline antibiotic production was collected after fermentation. This biomass was washed with distilled water and dried at 50°C for 24 h. It was then crushed and sieved in order to select a fraction with particle diameters between 50 and 160 μm. This biomass was then treated with NaOH (0.1 M) for 30 min and once again dried and sieved to obtain the 50–160 μm particle size fraction. The physical and chemical properties of this biosorbent are shown in Table 1.

The biosorption tests were carried out in a closed system. A small quantity of Pb(NO₃)₂ was added to biomass solution until adsorption equilibrium was reached. Equilibrium and kinetic curves are plotted by monitoring the Pb²⁺ residual concentration as a function of time. A magnetic stirrer was used to homogenise the mixture. For all the experiments, initial Pb²⁺ and biomass concentrations were fixed at 100 mg/l and 3 g/l, respectively.

Pb²⁺ residual concentrations in solution were determined using a Unicam939 atomic absorption spectrophotometer with a wavelength at 217 nm.

All the experiments were carried out at unadjusted pH. Infrared Spectra were obtained with the help of a Perkin-Elmer FTIR1650.

### 4. Results and discussion

#### 4.1. IR spectral analysis

In order to find out which functions are responsible for the lead adsorption, IR analysis of the biomass was carried out. Figs. 1 and 2 show the IR spectra and the various functional groups corresponding to the absorption bands. The whole of the frequencies of vibrations and their corresponding groups are presented in Table 2.

#### 4.2. Lead biosorption kinetics

Lead biosorption kinetics was very fast suggesting very active surface phenomena of the biomass (Fig. 3). In fact, this biomass cell walls are made of large molecules (peptidoglycan) linked with teichoic acid and polysaccharides.

### Table 1

<table>
<thead>
<tr>
<th>Physical characteristic</th>
<th>Untreated biomass</th>
<th>NaOH-treated biomass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size (μm)</td>
<td>50–160</td>
<td>50–160</td>
</tr>
<tr>
<td>Humidity (%)</td>
<td>3.2</td>
<td>4.3</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.43</td>
<td>0.41</td>
</tr>
<tr>
<td>Specific area (m²/g)</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>Zeta potential (V)</td>
<td>−0.062</td>
<td>−0.082</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>IR absorption bands and corresponding possible groups</th>
<th>Frequency (cm⁻¹)</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3431.58</td>
<td>–OH, –SH</td>
</tr>
<tr>
<td></td>
<td>2919.49</td>
<td>–CH</td>
</tr>
<tr>
<td></td>
<td>2832.92</td>
<td>–CH</td>
</tr>
<tr>
<td></td>
<td>1623.90</td>
<td>–COO, –C=O</td>
</tr>
<tr>
<td></td>
<td>1398.58</td>
<td>–COO⁻</td>
</tr>
<tr>
<td></td>
<td>1111.81</td>
<td>–C=O, –C=N</td>
</tr>
<tr>
<td></td>
<td>696.29</td>
<td>–CH</td>
</tr>
</tbody>
</table>
These molecules possess functional groups which can adsorb heavy metals. These groups are of the type (\(-\text{NH}\)), carboxylate anions (\(-\text{COO}^\cdot\)), hydroxy (\(-\text{OH}\)) and others (\(-\text{C}–\text{N}\), \(-\text{C}–\text{O}\), \(-\text{C}–\text{H}\), \(-\text{C} = \text{O}\)) which present different affinities towards metallic ions. Fig. 3 shows adsorption kinetics of the biomass.

It can be seen that the limiting value of adsorbed Pb\(^{2+}\) ions on the NaOH-treated biomass after 3 h was 98%. This contact time of 3 h was thus selected as the equilibrium time for all the following experiments. After this length of time, the residual concentration was constant.

The chemical treatment of the biomass with NaOH (0.1 M) shows that in the sodium form, the ion exchange sites are more easily able to exchange this cation (Na\(^+\)) with Pb\(^{2+}\) than when the ion exchange sites are protonated.

### 4.3. Biosorption rate constant

In order to find out the Pb\(^{2+}\) biosorption kinetic parameters, many experiments were conducted under optimal conditions with NaOH-treated biomass.

Fig. 4 shows a plot of the function \(\log_{10}\left[q(t)/q_e - q\right]\) as a function of time for the NaOH-treated biomass. One can see that the adsorption kinetics was of first order. The rate constant was \(k_1 = 3.56 \times 10^{-4}\) (s\(^{-1}\)).

### 4.4. External mass transfer coefficient

By plotting the slope values at \(C = 0\) of the plot \((C/C_0)\) as a function of time, we can deduce the value of the external mass transfer coefficient \(\beta\). The corresponding value of the external mass transfer \(\beta = 2.16 \times 10^{-6}\) m/s.

The low values of the external mass transfer coefficient means that the resistance to external mass transfer is quite important (Fig. 5).

### 4.5. Intraparticle diffusion coefficient

The rate constant of intraparticle diffusion \(K_i\) has been determined by a plot \(q = f(t^{1/2})\) taking account only of the initial period according to Weber and Morris model [37].

The intraparticle diffusion coefficient \(D_i\) was computed by plotting \(-\log_{10}\left[1 - q(t)/q_e\right]^2\) as a function of time according to Urano and Tachikawa model [40] (Figs. 6 and 7).

Values of \(K_i\) and \(D_i\) are given in Table 3. The low values of \(K_i\) and \(D_i\) coefficients suggest that the intraparticle diffusion

<table>
<thead>
<tr>
<th>NaOH-treated biomass</th>
<th>(K_i) (mg/g s(^{1/2}))</th>
<th>(D_i) (m(^2)/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH-treated biomass</td>
<td>0.063</td>
<td>9.86 \times 10^{-13}</td>
</tr>
</tbody>
</table>
is negligible in comparison with the external mass transfer phenomena and the adsorption at the surface of the biomass.

4.6. Effect of initial pH on Pb\(^{2+}\) biosorption

As can be seen from Fig. 8, the initial pH did not affect the biosorption of Pb\(^{2+}\) ions onto the NaOH-treated biomass. This phenomena was observed in the biosorption of Pb\(^{2+}\) by P. laminosum biomass treated with NaOH (1 M) [46].

The metal biosorption depends on the protonation or unprotonation of the functional groups on the cell wall (i.e., carboxylic, hydroxyl and amino groups) [13,47,48]. The ionic forms of the metal in solution and the electrical charge of the biomass depend on the solution pH. After NaOH treatment of the biomass, we can suggest a H\(^+\)/Na\(^+\) interconversion on the cell wall of the biomass. Maximum Pb\(^{2+}\) sorption at different initial pH was observed.

Fig. 5. \((C/C_0)\) vs. time \((t)\) for NaOH-treated biomass according to the external mass transfer resistance model.

Fig. 6. \(-\log_{10}[1-(q/q_e)^2]\) vs. time \((t)\) for NaOH-treated biomass according to the Urano and Tachikawa model.

Fig. 7. \(q\) vs. \(t^{0.5}\) for NaOH-treated biomass according to the Weber and Morris model.

Fig. 8. Effect of initial pH on the Pb\(^{2+}\) adsorption capacity by the NaOH-treated biomass: \(\omega = 250\) rpm; \(C_0(\text{Pb}^{2+}) = 100\) mg/l; \(C_{\text{biomass}} = 3\) g/l; PS: 50–160 \(\mu\)m.

Fig. 9. Effect of stirring speed on the biosorption capacity of the NaOH-treated biomass: \(C_0(\text{Pb}^{2+}) = 100\) mg/l; \(C_{\text{biomass}} = 3\) g/l; PS: 50–160 \(\mu\)m.

(33.3 mg Pb\(^{2+}\)/g biomass). This result can be explained by the strong relation of biosorption to the Na\(^+\)/Pb\(^{2+}\) exchange.

4.7. Effect of stirring speed on Pb\(^{2+}\) biosorption

Optimal value of adsorption capacity was obtained for a stirring speed \(\omega = 250\) rpm (Fig. 9). This moderate stirring speed gave a better homogeneity to the mixture solution-biomass granulates. This stirring speed was used in all our experiments. At a high stirring speed, vortex phenomena occurred and the suspension was no longer homogenous which made the adsorption of Pb\(^{2+}\) difficult.

4.8. Influence of biomass concentration

Fig. 10 shows the metallic ions elimination in wt.% as a function of biomass concentration. This graph shows the growth of the elimination of the metal ions with the increase in the concentration of the biomass up to a concentration of 3 g/l. Starting from this optimal concentration in biomass of 3 g/l, the rate of elimination of the ions Pb\(^{2+}\) decreased and it could be attributed to the biomass granulates which are agglomerated.

4.9. Influence of the initial Pb\(^{2+}\) concentration

Many studies have shown that for low Pb\(^{2+}\) concentrations, the quantity of adsorbed Pb\(^{2+}\) per unit mass of
biosorbent was directly proportional to the ionic concentration in solution.

Fig. 11 shows that the quantity of adsorbed $\text{Pb}^{2+}$ per unit mass of biosorbent increased when the initial $\text{Pb}^{2+}$ ions concentration increased. In our study, initial $\text{Pb}^{2+}$ concentration varies from 10 to 800 mg/l. As can be seen from Fig. 11, the maximum quantity of adsorbed $\text{Pb}^{2+}$ on biomass was approximately 135 mg $\text{Pb}^{2+}$/g biomass. This value is higher than those obtained by Niu et al. [49] and Tobin et al. [50] who have tested, respectively, the $\text{Pb}^{2+}$ biosorption by $P$. chrysogenum and $R$. arrhizus. The best performance obtained for $\text{Pb}^{2+}$ biosorption capacity by $P$. chrysogenum and $R$. arrhizus were, respectively, 116 and 104 mg $\text{Pb}^{2+}$/g biomass.

In order to optimise the biosorption process parameters, we have modelised the equilibrium curve (Fig. 12). Both Langmuir and Freundlich models were tested. The isotherm curve shows a limiting biosorption capacity attained at $\text{Pb}^{2+}$ equilibrium concentration of about 195 mg/l. Figs. 13 and 14 are the transformed forms of these models which permit to calculate Langmuir’s constants ($q_m$ and $b$) and Freundlich constants ($k$ and $n$). Table 4 shows the values of the computed constants. Values of coefficients of correlation $R^2$ show that the Langmuir model, fitted best our experimental data.

### 5. Conclusion

$S$. rimosus dead biomass was found to be an efficient adsorbent of $\text{Pb}^{2+}$ in dilute solutions. Up to 135 mg of lead can be obtained by each gram of NaOH-treated biomass. The Langmuir model, fitted best our experimental data. The cell walls of this biomass contain anionic groups such as ($-\text{COO}$, $-\text{C-O}$, $-\text{NH}$, $-\text{C=O}$, $-\text{OH}$) whose adsorbent ability towards $\text{Pb}^{2+}$ ions was fairly high. Adsorption was influenced by various parameters such as initial $\text{Pb}^{2+}$ concentration, stirring speed, biomass concentration and the external mass transfer. The results obtained during this study show that this method of eliminating $\text{Pb}^{2+}$ ions is very promising and confirm the technical and economic interest compared to the conventional processes such as the ion exchange on resins.

### References


