Biosorption of Arsenic by *Lessonia nigrescens* in Wastewater from Copper Smelting

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Abstract:

Conventional treatment methods for arsenic removal from copper smelting wastewaters create sludge that is difficult to handle. Biosorption of arsenic using algae as sorbent is an interesting alternative to the conventional methods. This work shows results from biosorption of arsenic (V) by *Lessonia nigrescens* at pH = 2.5, 4.5 and 6.5. The adsorption of arsenic could be explained satisfactorily both by the Freundlich and the Langmuir isotherms. Maximum adsorption capacities were estimated to 45.2 mg/g (pH = 2.5), 33.3 mg/g (pH = 4.5), and 28.2 mg/g (pH = 6.5) indicating better adsorption at the lower pH. These values are high in comparison with other arsenic adsorbents reported. The sorption kinetics of arsenic by *Lessonia nigrescens* could be modelled well by Lagergren’s first order rate equation. The kinetics were observed to be independent of pH during the first 120 minutes of adsorption with the Lagergren first order rate constant of around $1.07 \cdot 10^{-3}$ min⁻¹.

Keywords: water treatment, adsorption isotherms, arsenic, algae, kinetics

Introduction

Copper smelting generates large amount of wastewater containing considerable amounts of inorganic compounds such as heavy metals and arsenic species. These wastewaters originate from sulphuric acid plants, which treat the SO₂ containing gases from the smelter. In order to maintain a high quality of fresh water resources these effluents have to be treated before the water can be returned to the ecosystems. Existing treatment methods such as sulphide or hydroxide precipitation create sludge that is difficult to handle. Furthermore, these methods consume considerable amounts of reagents in order to precipitate, coagulate and flocculate the contaminants (1,2).
During the last decades the use of biosorbents has become interesting due to high adsorption capacities, low costs and regenerability of the sorbent (3,4). Algae have been used for pharmaceutical reasons for detoxification of heavy metals in the human body due to a very efficient adsorption of the contaminants (ref), and this effect could be used to remove heavy metals from industrial wastewaters. Different algae have been applied to wastewater treatment during the last decade (5-7). One of the interesting algae that could be used to remove heavy metals from these contaminated waters is the \textit{Lessonia nigrescens}, which is abundant all along the coast of Chile.

The objective with this work is to test the sorption capacities and kinetics of arsenic (V) of air-dried and size reduced algae \textit{Lessonia nigrescens}. It will be analysed if the biosorption of arsenic follows the first order Lagergren model, which often can be used to simplify the sorption kinetics. Finally, it will be evaluated if either the Freundlich or Langmuir isotherms can describe the arsenic biosorption capacity of \textit{Lessonia nigrescens}.

\section*{Theoretical background}

The knowledge of the kinetics of any adsorption process is crucial in order to be able to design industrial scale separation processes. For biosorption is simplified approach given by Lagergren can often be applied with success especially in the first phase of the biosorption. The Lagergren first order rate model is given by the following expression:

\begin{equation}
\log (q_e - q) = \log q_e - k_{ad} t / 2.303
\end{equation}

where \( q \) is the quantity of adsorbed material [mg/g] in a given time \( t \) [min], and \( q_e \) is quantity of adsorbed material [mg/g] at equilibrium, and \( k_{ad} \) [min\(^{-1}\)] is the adsorption rate constant.

In order to be able to estimate maximum capacities of adsorbents it is necessary to know the quantity of adsorbed metal as a function of metal concentration in solution. Typically two models can be applied - the Freundlich and Langmuir isotherms.

\textbf{Freundlich:}

\begin{equation}
q = K \cdot C^n
\end{equation}

or

\begin{equation}
\log q = \log K + n \cdot \log C
\end{equation}

where \( q \) (mg/g) and \( C \) (mg/ml) are the equilibrium concentration of solute in solid and liquid phases, respectively. The Freundlich constants \( K \) (mg/g) and \( n \) (value between 0 and 1) represent the adsorption capacity and adsorption intensity of the adsorbent, respectively. The Freundlich equation serves as a practical tool for simulating adsorption processes.
Langmuir:

\[ q = \frac{q_{\text{max}} C}{(C + K_d)} \]  

(4)

Constant \( q_{\text{max}} \) (mg/g) and \( K_d \) (mg/ml) are the Langmuir parameters. The constant \( q_{\text{max}} \) represents the maximum adsorption capacity and \( K_d \) is the dissociation coefficient of the solute-adsorbent complex, which represents the affinity between the solute and the adsorbent.

The Langmuir isotherm has been widely accepted as a practical method for integrating experimental data of adsorption processes. Rearranging equation 4, a linear expression can be derived as a function of \( C \):

\[ \frac{C}{q} = \frac{K_d}{q_{\text{max}}} + \left(\frac{1}{q_{\text{max}}}\right) C \]  

(5)

Experimental

Preparation of adsorbent

The *Lessonia nigrescens* samples were collected in the bay of Valparaiso, Chile, and Figure 1 shows a general view of the algae. Only the leaves were used in this work. After sampling, the algae was washed several times in tap water and then in distilled water in order to remove any salt present. Thereafter it was dried at 50 °C for 48 hours. The dry alga was cut into small pieces by a food processor, size fractioned by a gravimetrical sieve procedure, and the size fraction between 150 – 212 μm was chosen for biosorption experiments due to recommendations by (7).

Determination of adsorption kinetics

The experimental wastewater solutions (pH = 2.5, 4.5 and 6.5) were prepared in the laboratory and contained 200 mg As(V)/L. The arsenic solution was prepared from analytic grade sodium arsenate. pH was adjusted to 2.5 or 4.5 by adding drops of concentrated HNO₃. The solution fixed at pH 6.5 did not need initial adjustment. 500 mL of the solution was poured into a conical flask with mechanical stirring (100 rpm). 2.0 g of algae was added, and a 1 mL sample was taken from the solution (t=0). 1 mL samples were taken successive after 10, 20, 40, 60, 80, 100, 120, 150, 200, 250, 300, 420, 1200, and 1580 minutes of contact time between the algae and the arsenic containing solution. The pH was measured again in the solution, and it did not change more than 0.2 in comparison with the initial value. Therefore the initial value was taken as experimental pH value. The temperature was not controlled during experiments but the room temperature was 20 °C.

The difference in volume in the adsorption cell due the samples removed was corrected during calculations. The concentration of arsenic in the samples was measured by AAS in flame. Each adsorption kinetics experiment was carried out twice, and the average was used in this work.
Determination of adsorption capacity

The experimental wastewater solutions (pH = 2.5, 4.5 and 6.5) were prepared in the laboratory and contained 50, 100, 200, 300, 400 and 600 mg As(V)/L. pH was adjusted to 2.5 or 4.5 by adding drops of concentrated HNO$_3$. The solution fixed at pH 6.5 did not need initial adjustment. 500 mL of the solution was poured into a conical flask with mechanical stirring (100 rpm). 2 g of algae was added, and a 1 mL sample was taken from the solution (confirmation of initial concentration). Another sample was taken after 24 hours of contact time between the algae and the arsenic containing solution, since the results from the kinetic experiments showed that no further adsorption occurred at that point. It was therefore assumed at equilibrium was reach.

The concentration of arsenic in the samples was measured by AAS in flame. Each adsorption capacity experiment was carried out in triplicate, and the average was used in this work.

The q values are estimated in the following manner:

\[ q = \left( C_{\text{initial}} - C \right) \cdot \frac{V}{M} \quad (6) \]

where \( C_{\text{initial}} \) [mg/L] is the initial concentration of arsenic in the solution, \( V \) [L] is the volume of the liquid phase, and \( M \) [g] is the mass of adsorbent.
Results and discussion

Figure 2 shows the biosorption by *Lessonia Nigrescens* taken as the percentage of arsenic adsorbed from a 200 mg/L solution as a function of time for three different initial pH values: 2.5, 4.5 and 6.5. It is seen that after around 300 minutes the maximum biosorption is reached for all experiments. That the adsorption capacity is depending on pH can be seen from the figure since most arsenic could be adsorbed at the lowest pH.

Figure 3 shows the adsorption results during the first 120 minutes. Analysing the kinetics, it can be seen that the Lagergren first order kinetics describes well the arsenic sorption during the first two hours. The rate calculated rate constants, $K_{ad}$, for the three experiments can be estimated to: $1.069 \times 10^{-3}$ (pH = 2.5), $1.071 \times 10^{-3}$ (pH = 4.5) and $1.077 \times 10^{-3}$ (pH = 6.5). These values are nearly identical, which means that the adsorption kinetics are independent of pH.

Table 1 shows the concentration of arsenic in the wastewater solution after 20 hours of biosorption by *Lessonia Nigrescens* with different initial concentrations and at different pH values. After this time it was assumed that the adsorption equilibrium was reached. These values can used to analyse if the biosorption follows either the Langmuir or Freundlich isotherms. Figure 4 shows the Freundlich behaviour of the adsorption and Figure 5 the Langmuir isotherm. It can be seen from the figures that a straight line would fulfil both of the isotherms. This is the case here where it can be concluded that both the Freundlich and the Langmuir isotherms can be used to characterize the biosorption of arsenic by *Lessonia Nigrescens* satisfactorily for the three pH values studied.

![Figure 2. Arsenic sorbed by *Lessonia Nigrescens* at different pH as a function of time.](image-url)
Figure 3. Lagergren first order rate model predictions during the first 120 minutes of biosorption.

Table 1. Equilibrium concentration of arsenic after 20 hours of adsorption by *Lessonia Nigrescens* depending on pH and initial concentration.

<table>
<thead>
<tr>
<th>pH</th>
<th>Initial conc. 50 ppm</th>
<th>Initial conc. 100 ppm</th>
<th>Initial conc. 200 ppm</th>
<th>Initial conc. 300 ppm</th>
<th>Initial conc. 400 ppm</th>
<th>Initial conc. 600 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>12 ppm</td>
<td>41 ppm</td>
<td>93 ppm</td>
<td>180 ppm</td>
<td>265 ppm</td>
<td>450 ppm</td>
</tr>
<tr>
<td>4.5</td>
<td>16 ppm</td>
<td>48 ppm</td>
<td>122 ppm</td>
<td>210 ppm</td>
<td>298 ppm</td>
<td>489 ppm</td>
</tr>
<tr>
<td>6.5</td>
<td>18 ppm</td>
<td>52 ppm</td>
<td>130 ppm</td>
<td>220 ppm</td>
<td>310 ppm</td>
<td>502 ppm</td>
</tr>
</tbody>
</table>

Figure 4. Freundlich isotherm behaviour for the *Lessonia Nigrescens* biosorption.
Table 2 gives the constants for the Freundlich and the Langmuir isotherms as defined in equation 2 and 4 for pH = 2.5, 4.5 and 6.5. The values of Freundlich constants K and n represent the adsorption capacity and adsorption intensity of the adsorbent, respectively. The constant $K_d$ in the Langmuir model reflects the adsorption bond energy, and the constant $q_{\text{max}}$ estimates the maximum adsorption capacity, and this last value can be used when comparing the biosorption capacity of Lessonia Nigrescens to other adsorbents. Table 3 compares the adsorption capacity of Lessonia Nigrescens with some other adsorbents for arsenic removal, and it can be seen that the capacity of the algae is high. Especially at pH = 2.5 the biosorption is good, which is promising when considering the remediation of wastewater from copper smelting. These wastewaters origin from the sulphuric acid plant, and here pH normally is in the range from 2 – 4. Typical copper smelting wastewater contains 400 – 1000 ppm of As. These concentrations do not seem to be a problem for the arsenic biosorption.
Table 3. Maximum sorption capacity for arsenic by *Lessonia Nigrescens* compared with other adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH</th>
<th>Maximum capacity [mg As/g adsorbent]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Lessonia Nigrescens</em></td>
<td>2.5</td>
<td>45.2</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>33.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.5</td>
<td>28.2</td>
<td></td>
</tr>
<tr>
<td>Activated carbon</td>
<td>-</td>
<td>0.82-1.02</td>
<td>(8)</td>
</tr>
<tr>
<td>Activated alumina</td>
<td>6.0</td>
<td>15.56</td>
<td>(9)</td>
</tr>
<tr>
<td>Iron(III) oxide/silica</td>
<td>7.0</td>
<td>11.3</td>
<td>(10)</td>
</tr>
<tr>
<td><em>Penicillium purpurogenum</em></td>
<td>5.0</td>
<td>35.6</td>
<td>(11)</td>
</tr>
<tr>
<td>Hematite</td>
<td>4.5 – 6.5</td>
<td>0.4</td>
<td>(12)</td>
</tr>
</tbody>
</table>

The arsenic speciation in copper smelting wastewaters is a mixture of As(III) and As(V). In this work only As(V) was studied. Future work should include the biosorption of As(III) as well.

**Conclusions**

The results shows that the arsenic biosorption capacity by *Lessonia nigrescens* is pH dependent with the best arsenic sorption at low pH (2.5). At pH 4.5 and 6.5 the adsorption capacity was slightly lower. Maximum arsenic sorption capacities were 45.2 mg/g (pH = 2.5), 33.3 mg/g (pH = 4.5), and 28.2 mg/g (pH = 6.5). These values are quite high in comparison with other arsenic adsorbents reported, and this is promising for further work on optimisation of the biosorption process.

The adsorption of arsenic could be explained satisfactorily both by the Freundlich and the Langmuir isotherms.

The sorption kinetics of arsenic by *Lessonia nigrescens* could be modelled well by Lagergren’s first order rate equation during the first 120 minutes of adsorption. The kinetics were observed to be independent of pH during the first 120 minutes of adsorption with the Lagergren first order rate constant of $1.07 \times 10^3$ min$^{-1}$.

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