Adsorption study of Ni(II) and Zn(II) by activated bone char residue
Daniel de A. Soares, Araceli A. Seolatto, Taísa de M. Campos and Uaitã P. do Nascimento

ABSTRACT
A large part of the chemical industry sectors, particularly industrial surface treatments, contributes to the contamination of water bodies with heavy metals. The environmental laws have been stringent regarding discharge of effluents containing these compounds. This study evaluated the removal of metals Ni(II) and Zn(II) by adsorption on activated bone char residue. To evaluate the adsorption capacity, experiments were performed using kinetics in a monocomponent system and adsorption isotherms in monocomponent and bicomponent systems. The models used to fit the isotherms were the Langmuir and Freundlich.

INTRODUCTION
Water contamination by heavy metals causes serious problems for humans and the environment (Doan et al. 2008). The metals Ni, Zn, Cr, Fe, and others are essential to the human body, but concentrations above the permissible limits can be toxic (Lalhruaitluanga et al. 2011). According to the World Health Organization (WHO), the maximum permissible concentration for the metals nickel and zinc in drinking water are 0.02 and 5 mg L\(^{-1}\), respectively (Kalavathy et al. 2010; Seolatto et al. 2009).

With the increase in environmental concerns, the laws have become more stringent with respect to wastewater containing heavy metals. The companies that generate high levels of these toxic metals in wastewater must treat the effluent so that their elimination is complete or within the limit permitted for the discharge (Boricha & Murthy 2009).

The most common methods used in the removal of heavy metals are precipitation, coagulation, flotation, adsorption, ion exchange, electrolysis and membrane techniques. But most of these methods generally have a high cost and are inefficient when the concentration of metals in the effluent is down to 100 ppm (Doan et al. 2008; Lalhruaitluanga et al. 2011; Weng & Huang 2004).

The solid–liquid adsorption is a treatment process that has been accepted around the world. This technique represents the ability of certain solids to concentrate substances from a solution on their surfaces. This principle is used for removing organic compounds and heavy metals from industrial effluents (Moreno-Piraján et al. 2010; Yang 2003).

Activated bone char has an enormous potential not yet studied. This material is a product of incinerating bovine bone at temperatures around 800 °C in an atmosphere of restricted oxygen. The adsorbent is composed mainly of hydroxyapatite (70–76 wt%), carbon (9.11 wt%) and calcium carbonate (9.7 wt%). This kind of material is being used as an adsorbent for clarification in the sugar syrup industry, and removal of organic compounds and heavy metals in wastewater. Granulometries out of specification are considered by manufacturers as industrial residue and it can be used in metal ions adsorption (Chen et al. 2008; Choy & McKay 2005). The adsorbent presents advantages over other adsorbents because it is relatively inexpensive since it is made from spent bone. The other advantage is that bone char has been demonstrated as a versatile adsorbent (Pan et al. 2009).

Many authors have studied adsorption of heavy metals in bone char. Cadmium, copper and zinc in aqueous solutions were studied in monocomponent and bicomponent systems (Choy & McKay 2005). Arsenic was analyzed in batch studies conducted as a function of pH, dosage of adsorbent, and contact time (Chen et al. 2008). The adsorption of Reactive Black 5 dye was evaluated by four different
adsorbents, including bone char (Ip et al. 2009). The removal of copper and zinc ions from wastewater by bone char has been studied in single component sorption systems (Cheung et al. 2000). Fluoride adsorption from water solution on bone char was interpreted by using a diffusional model as well as kinetic models (Levya-Ramos et al. 2010).

This study aims to evaluate the ability of activated bone char to absorb nickel and zinc in synthetic solutions, through kinetics and isotherms adsorption. This adsorption process is a low-cost alternative in the post-industrial wastewater treatment.

**METHODS**

**Adsorption kinetics**

The activated bone char used in these experiments is the residue of Company Bonechar do Brasil located in Maringá/PR, Brazil. The adsorbent was washed three times with deionized water and dried at 105 °C in a drying oven (Nova Ética – 400 ND) for 24 hours to remove impurities. Table 1 shows the composition of bone char.

The solutions of nickel and zinc were prepared using NiCl₂ 6H₂O (Isofar) and ZnCl₂ (Aldrich) dissolved in deionized water.

Kinetic tests were conducted in Erlenmeyer flasks with a capacity of 2 L, containing 1 L of solution and 1.5 g of adsorbent. For both metals, the initial concentrations were 50 and 150 mg L⁻¹. The pH was adjusted to 3.0 with dilute HCl (pH meter TECNAL TEC-5). The flasks were maintained at a temperature of 30 °C with agitation (100 rpm) on a shaker (TECNAL – 421 TE) for 24 hours. In intervals of predetermined time, 1 mL aliquots were removed with a micropipette. Then the samples were diluted with deionized water and the concentrations of nickel and zinc were determined by atomic absorption spectroscopy (GBC – 932AA). All tests were performed in duplicate.

The calculation of the percentage of metal removal by the adsorbent was performed by means of Equation (1) (Wang & Qin 2006; Seolatto et al. 2009):

\[
\text{% removal efficiency} = \left(\frac{C_i - C_f}{C_i}\right) \times 100
\]

where \(C_i\) is the initial concentration of metal (mg L⁻¹); \(C_f\) is the final concentration of metal (mg L⁻¹).

The adsorption capacity \(q\) was calculated by Equation (2):

\[
q = V \left(\frac{C_i - C_f}{M}\right)
\]

where \(q\) is the adsorption capacity (mg g⁻¹); \(V\) is the volume of solution (L); \(M\) is the mass of adsorbent (g).

**Modelling of the adsorption kinetics**

The kinetics of adsorption of Ni(II) and Zn(II) were modeled using the first order equation (of Langergren), and second order equation. The first order model is given by Equation (3) (Guzel et al. 2008; Pan et al. 2009):

\[
\frac{dq}{dt} = k_1(q_{eq} - q_t)
\]

where \(k_1\) is the first order kinetic constant (min⁻¹); \(q_{eq}\) and \(q_t\) (mg g⁻¹) are the quantity of metal ions adsorbed at equilibrium and at time \(t\), respectively.

The expression has the initial condition (Equation (4)):

\[
q(0) = 0
\]

**Table 1 | Physical and chemical properties of bone char**

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density</td>
<td>0.65 g cm⁻³</td>
</tr>
<tr>
<td>Carbon surface area</td>
<td>52 m² g⁻¹</td>
</tr>
<tr>
<td>Total surface area*</td>
<td>100.98 m² g⁻¹</td>
</tr>
<tr>
<td>Pore volume*</td>
<td>0.24 cm³ g⁻¹</td>
</tr>
<tr>
<td>Moisture</td>
<td>5 wt% max</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical composites</th>
<th>Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid insoluble ash</td>
<td>3 wt% max</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>7–9 wt%</td>
</tr>
<tr>
<td>Calcium sulfate</td>
<td>0.1–0.2 wt%</td>
</tr>
<tr>
<td>Carbon content</td>
<td>9–11 wt%</td>
</tr>
<tr>
<td>Calcium hydroxyapatite</td>
<td>70–76%</td>
</tr>
</tbody>
</table>

*Residue of bone char used in this work (Pan et al. 2009).
The solution of the differential equation represented by Equations (3) and (4) is given by the following expression (Equation (5)):

$$q(t) = q_{eq}(1 - e^{-kt})$$

(Equation 5)

The adjustment of the second order model is given by:

$$\frac{dq}{dt} = k_2(q_{eq} - q_t)^2$$

(Equation 6)

where $k_2$ is the second order kinetic constant (meq g$^{-1}$ min$^{-1}$).

The solution of the differential equation represented by Equation (6) is given by the expression:

$$q(t) = q_{eq} \frac{q_{eq}kt}{q_{eq}kt + 1}$$

(Equation 7)

### Adsorption isotherms

The monocomponent adsorption isotherms were measured at 30°C. To 80 mL of solution at concentrations of 50, 100, 150, 200, 300 or 400 mg L$^{-1}$ was added 0.1 g of bone char for both metals at pH 3. The samples were maintained in an orbital shaker at 100 rpm (TECNAL TE-421) for 24 hours. Aliquots were removed from each Erlenmeyer flask and diluted with deionized water. Reading the initial and final concentrations of the samples was performed by atomic absorption spectroscopy. All tests were performed in duplicate.

Experiments were conducted to obtain bicomponent adsorption isotherms. The procedures were the same as for the monocomponent systems, varying only in the preparation of the solutions. This analysis was performed in three different conditions:

- System (B1): 50% solution of nickel and 50% solution of zinc;
- System (B2): 75% solution of nickel and 25% solution of zinc;
- System (B3): 25% solution of nickel and 75% solution of zinc.

Two equations of equilibrium isotherms were used to discover the equilibrium concentrations of adsorbate in the liquid and solid phases. These isotherms are:

(a) Langmuir isotherm

$$q^* = \frac{(q_mB^*)}{(1 + bC^*)}$$

(Equation 8)

where $C^*$ is the equilibrium concentration in the liquid phase (mg L$^{-1}$); $q^*$ is the concentration of adsorbate on the solid phase (mg g$^{-1}$); $q_m$ and $b$ are coefficients representing the Langmuir equilibrium constants for the adsorbate-adsorbent and the ability to form monolayers.

(b) Freundlich isotherm

$$q^* = a(C^*)^n$$

(Equation 9)

where $a$ and $n$ represent Freundlich constants.

### RESULTS AND DISCUSSION

#### Adsorption kinetics

The adsorption kinetics generally includes two steps: rapid removal stage followed by a slow stage when equilibrium is established. Studies of adsorption kinetics are important to provide information about the mechanism of adsorption and consequently to improve process efficiency. Many models of the kinetics of adsorption of metal ions have been used. The first order model has been used for reversible reactions where there is an equilibrium established between the liquid and solid phases. The reaction rate is defined as the rate of concentration per time unit (Zhi-Rong et al. 2009).

The kinetics of adsorption of Ni(II) and Zn(II) were evaluated in two different concentrations at a temperature of 30°C. Figure 1 shows the curves of the adsorption kinetics of Ni(II) and Zn(II) on activated bone char.

The data obtained from adsorption capacity, per cent removal and first and second order kinetic models are shown in Table 2. The time of equilibrium between the adsorbent and the solution of Ni(II) with a concentration of 50 mg L$^{-1}$ was approximately 3 hours, and with a concentration of 150 mg L$^{-1}$ was 5 hours. The experiments for Zn(II) had the equilibrium time of about 4 hours for the solution of lowest concentration and 6 hours for a solution of higher concentration.

For the same mass of adsorbent, the removal percentage decreased when the concentration of ions increased from 50 to 150 mg L$^{-1}$. However, the quantity of ions
adsorbed per unit mass \((q)\), showed an increase for the highest concentration of both metals. For the concentration of 50 mg L\(^{-1}\), the ratio of the number of ions to the number of sites available is small and therefore the adsorption is independent of the initial concentration. But at the concentration of 150 mg L\(^{-1}\), the competition of ions for the active sites becomes greater. As a result, the potential for adsorption decreases considerably at higher concentrations per unit mass of adsorbent. These results were also obtained in previous studies (Gupta & Bhattacharyya 2006; Gupta et al. 2003).

The adsorption capacities of Ni(II) at both concentrations presented lower values than for Zn(II). All curves of adsorption kinetics were best fitted by second order kinetic models, since they have a higher value of \(R^2\). The model of the pseudo-second order assumes that in the sorption process the occupancy of sites is proportional to the square of the number of active sites (Pan et al. 2009).

The initial volume of 1 L was used in these adsorption kinetics experiments to ensure that samples collected did not influence significantly the total volume of the system. Table 3 shows the adsorption capacity of a few adsorbents utilized in the removal of Ni(II) and Zn(II). The bone char residue shows a performance comparable with other adsorbents cited in the table.

### Adsorption Isotherms

Equilibrium sorption data of individual nickel and zinc ions and also of bicomponent systems (at varying concentrations) were used to evaluate the performance of the sorption capacity of these metals by bone char. Data from equilibrium sorption of ions were represented by Langmuir and Freundlich isotherms. Figure 2 shows the Langmuir and Freundlich isotherms for aqueous solutions of Ni(II) and Zn(II) using bone char at 30 °C. Table 4 presents the data obtained for the Langmuir and Freundlich isotherms for the adsorption of Ni(II) and Zn(II) in monocomponent systems.

According to the results, both metals isotherms were best fitted by the Langmuir model. By analyzing the \(q_m\) values obtained by fitting Langmuir, it appears that both metal ions have practically the same amount adsorbed per unit weight of adsorbent. The parameter \(b\) represents the affinity between the sorbent and adsorbate, and could also be a value to distinguish the adsorption of the metals. But the difference between the amounts of Ni(II) and Zn(II) state is too small to determine which has the higher affinity for the active sites of the absorbent (Kalavathy et al. 2010). In this study, the \(b\) value obtained for Zn(II) is a little higher than Ni(II). In evaluating the data using the Freundlich model,
when the parameter $n$ is smaller than 1, it can be stated that removal of the compound is favorable (McCabe et al. 2005).

**Bicomponent systems**

Little attention has been given to adsorption studies containing more than one ion in solution. The application of activated bone char in electroplating effluent requires this kind of study because the residuals of this industry do not usually show only one type of metal trace. We evaluated the competition between metals Ni(II) and Zn(II) for the active sites of the adsorbent.

Figure 3 shows the graphs of the Langmuir isotherm and Freundlich adsorption of Ni(II) and Zn(II) bicomponent systems.

By analyzing the graph curves it can be seen that the adsorption of Zn(II) is favored in the competitive system.

**Table 3** | Comparison of adsorption capacity of various adsorbents for the removal of Ni(II) and Zn(II) from aqueous phase

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>Adsorbent</th>
<th>Adsorption $(mg \cdot g^{-1})$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td><em>Melocanna baccifera</em> activated char</td>
<td>52.91</td>
<td>Lalhruaitluanga et al. (2011)</td>
</tr>
<tr>
<td></td>
<td>Activated carbon</td>
<td>44.10</td>
<td>Ewecharoen et al. (2009)</td>
</tr>
<tr>
<td></td>
<td><em>Hevea brasiliensis</em> activated char</td>
<td>14.04</td>
<td>Kalavathy et al. (2010)</td>
</tr>
<tr>
<td>Ni</td>
<td>Bone char in oxidizing atmosphere</td>
<td>46.29</td>
<td>Moreno-Piraján et al. (2011)</td>
</tr>
<tr>
<td>Ni</td>
<td>Bone char in inert atmosphere</td>
<td>28.57</td>
<td>Moreno-Piraján et al. (2011)</td>
</tr>
<tr>
<td>Ni</td>
<td>Bone char (residue)</td>
<td>30.81</td>
<td>Present work</td>
</tr>
<tr>
<td>Zn</td>
<td>Bone char</td>
<td>33.03</td>
<td>Choy et al. (2004); Choy &amp; McKay (2005); Ko et al. (2004)</td>
</tr>
<tr>
<td>Zn</td>
<td>Bone char</td>
<td>34.66</td>
<td>Cheung et al. (2000)</td>
</tr>
<tr>
<td>Zn</td>
<td><em>Melocanna baccifera</em> activated char</td>
<td>40.49</td>
<td>Lalhruaitluanga et al. (2011)</td>
</tr>
<tr>
<td>Zn</td>
<td>Animal bones</td>
<td>11.55</td>
<td>Banat et al. (2000)</td>
</tr>
<tr>
<td>Zn</td>
<td>Coal</td>
<td>1.20</td>
<td>Karabulut et al. (2000)</td>
</tr>
<tr>
<td>Zn</td>
<td>Bone char (residue)</td>
<td>48.36</td>
<td>Present work</td>
</tr>
</tbody>
</table>

**Table 4** | Values of the constants of Langmuir and Freundlich isotherms of ions Ni(II) and Zn(II) for monocomponent systems

<table>
<thead>
<tr>
<th>Metal</th>
<th>$q_m$ $(mg \cdot g^{-1})$</th>
<th>$b$ $R^2$</th>
<th>$K$ $(mg \cdot g^{-1})$</th>
<th>$n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(II)</td>
<td>65.78</td>
<td>0.01</td>
<td>0.99</td>
<td>4.98</td>
<td>0.42</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>65.48</td>
<td>0.02</td>
<td>0.99</td>
<td>10.44</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Figure 2 | Adsorption isotherms of (a) Ni(II) and (b) Zn(II) in activated bone char.
Electronegativities are different. For Ni(II) the electronegativity is 1.91; for Zn(II) it is 1.65. The wheat straw presents oxygen on its surface due to the presence of phenolic and carboxylic groups. The electron clouds of these oxygen atoms tend to repel compounds with high electronegativity. Thus, the Ni(II) was repelled faster than Zn(II) by active sites of wheat straw. Therefore, the biosorption of Zn(II) was more favorable. As the Zn(II) is adsorbed more rapidly, this can represent a physical block for Ni(II). Furthermore, from the standpoint of mass transfer, the diffusivity of Zn(II) (\(7.016 \times 10^{-10} \text{m}^2 \text{s}^{-1}\)) was about 15% greater than the diffusivity of Ni(II) (\(6.132 \times 10^{-10} \text{m}^2 \text{s}^{-1}\)) (Anderko & Lenka 1998). Therefore, the rate of mass transfer of Zn(II) from solution to the surface of the biosorbent was greater than that of Ni(II); thus the biosorption of Zn(II) is favored (Doan et al. 2008).

When evaluating the data obtained in this work for the bone char, basically the same process occurs in wheat straw in studies obtained by Doan et al. (2008). It is known that the surface of the adsorbent is mainly composed of calcium hydroxyapatite, carbon and calcium carbonate. These compounds are randomly distributed on the surface. The hydroxyapatite has a good ability to remove inorganic cations due to the heterogeneity of the adsorption sites. (Pan et al. 2009; Ko et al. 2004).

Table 5 gives the data obtained for the Langmuir and Freundlich isotherms for the adsorption of Ni(II) and Zn(II) bicomponent systems.

When comparing the values of \(q_m\) for systems B1, B2 and B3 for Ni(II) it is apparent that there has been a considerable increase in adsorption when the metal is in higher concentration. When the metal is in lower concentration it is hardly adsorbed, obtaining an isotherm response as nearly linear. In the case of Zn(II) there was no significant variation in adsorption capacity, since the values obtained in the systems (B1 \(q_m = 50.41\), B2 \(q_m = 47.17\) and B3 \(q_m = 50.20\)), taking into account the error obtained for each value, are practically constant. That is, in competition with nickel, no matter the quantity of zinc added to solution, zinc will have a medium value of \(q\) equal to 50 mg g\(^{-1}\).

### CONCLUSIONS

According to the results, the adsorption process by activated bone char residue is efficient for removal of heavy metals from aqueous solutions, having a high removal rate of Zn(II). Removal of Ni(II) was lower.

In the study of isotherms, monocomponent systems of both metals were best fitted by the Langmuir model. The \(q_m\) values obtained indicate that the adsorbed ions were almost the same proportion. When the two metals are in the competitive system the Ni(II) does not interfere with the adsorption of Zn(II).

### REFERENCES


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