ISABEL GRAPE BAGASSE AS A POTENTIAL BIOSORBENT OF ZINC IN THE EFFLUENTS TREATMENT

L. GELAIN, J.S. CRESPO, and M. GIOVANELA

Centro de Ciências Exatas e Tecnologia, Universidade de Caxias do Sul, 95070-560, Caxias do Sul, RS – Brazil
E-mail: mgiovan1@ucs.br

EXTENDED ABSTRACT

Effluent treatment has become important because of its possible environmental impact as well as its possible adverse effects on human health. Additionally, improvements in environmental laws are another element of pressure for paradigm changes. Due to these factors, investigations concerning efficient effluent treatments have greatly increased. Alternatively, inexpensive natural materials have also been proposed for this task, which can reduce overall costs, thus making both investigation and use of these materials to be of utmost importance. Different unconventional substrates generated as byproducts of the agricultural and food industries are being tested to evaluate their efficiency in the removal of metal ions. Because of their low-cost, these materials can be profitably used as alternatives or complements to the more commonly used methods for effluent treatment. However, the application of such materials to the real conditions of industrial effluent treatment requires knowledge of their reactivity and the content of their adsorption sites to optimize the retention processes. In view of these facts, the aim of this work was to describe the equilibrium and kinetics of the adsorption process of Zn^{2+} in aqueous medium, in order to demonstrate its potential for use in effluents treatment. In general, the Freundlich isotherm provided the better fit of the equilibrium experimental data, and the adsorption of Zn^{2+} by grape bagasse showed a value of $K_F$ and $n$ equal to 6.43 mg g$^{-1}$ and 1.45, respectively. The kinetics of the adsorption process, on the order hand, was better described by the pseudo-second order model and, furthermore, the removal percentage (~ 50%) was similar for all tested concentrations. Finally, the low cost, the availability of the agroindustrial waste, and the rapid adsorption promoted by the adsorbent, suggest that grape bagasse has great potential to be used in removal of zinc present in effluents.

Keywords: Isabel grape bagasse, adsorption, zinc, effluents treatment.

1. INTRODUCTION

The contamination by heavy metals from industrial wastewater has become a major problem for the environment. This occurs because these species are not biodegradable. Therefore, they can be accumulated in living tissue through the food chain, which increases the risk of intoxication (Srivastava et al., 2010).

Among the inorganic pollutants present at higher concentrations in effluents from pharmaceutical, galvanic, painting, insecticides, and cosmetic industries, zinc stands out. Although considered an essential element for life, to act as a micronutrient (Bhattacharya et al., 2006), zinc can be dangerous to human health from 12 mg day$^{-1}$ (Vaghiotti, 2009). Removal of metals from industrial wastewater has conventionally been accomplished mainly by precipitation, ion exchange, reverse osmosis, flotation, and electrolytic technologies (Febrianto et al., 2009). However, the low efficiency, the need of use of
expensive chemicals as well as accompanying problems with the disposal of the waste generated, are the major drawbacks of these methods (Satapathy and Natarajan, 2006).

The adsorption, on the other hand, offers a cleaner technology, free from sludge handling problems and produces a high quality effluent. It is a physicochemical process highly efficient, inexpensive and readily adaptable (Bhattacharya et al. 2006). Over the last few decades, it has gained importance as an effective purification and separation technique used in water and wastewater treatment. In this context, the most frequently applied adsorbent is currently activated carbon. However, this material is very expensive. Thus, there is growing interest in using low cost material for adsorption as alternatives to activated carbons. A wide variety of materials have been used for this purpose such as peat, lignite, diatomite, dolomite, kudzu, bone char, zeolites, and a range of other natural materials such as agroindustrial residues. The functional groups present in the structure of these residues are usually the main responsible for the interaction with the adsorbate (Farinella et al., 2007).

The grape bagasse is an agroindustrial residue produced in large quantities in southern Brazil, mainly in the State of Rio Grande do Sul. This residue is commonly employed as a fertilizer, but its use can lead to chemical changes in soil and plants (Deiana et al., 2009). Its accumulation in inappropriate places can also provide the proliferation of insects, rats, and other animals. Because of this, its employment as adsorbent material may an alternative to be evaluated for decreasing the stored amount of this residue in the wineries.

In view of these facts, the goal of this work was to evaluate the equilibrium and kinetics of adsorption of Zn(II) by Isabel grape bagasse (Vitis labrusca x Vitis vinifera), in a batch system, in order to verify the potentiality of using this biomass as adsorbent in the effluents treatment.

2. MATERIALS AND METHODS

2.1. Collection and processing of grape bagasse

Isabel grape bagasse that was generated from the wine production process was collected from the Waldemar Milani Winery (Rio Grande do Sul State, Brazil). The sample was then freeze-dried at -45°C before being crushed and sieved to a particle size less than 150 µm. After this procedure, the adsorbent was stored in glass bottles and was used without any physical or chemical pre-treatment.

2.2. Adsorption procedure

The adsorption experiments were carried out in a batch system, under mechanical stirring, using 50 mL of aqueous solutions containing Zn(II). Prior to these experiments, the parameters such as adsorbent mass (10, 20, 40, 60, 80, and 100 mg), initial pH of the solutions (2.0, 3.0, 4.0, 5.0 and 6.0), and stirring frequency of the adsorption process (100, 150, 200 and 250 rpm) were previously optimized. The initial concentration of Zn(II) (20, 50, 80, 100, and 125 mg L⁻¹) in the adsorption process was also evaluated. The pH of each solution was adjusted only at the beginning of each experiment, and the optimization of the adsorbent mass, stirring frequency and pH were performed using an initial concentration of 100 mg L⁻¹. All aqueous solutions of Zn(II) were prepared by dilution from a stock solution (1000 mg L⁻¹). Aliquots were periodically collected, filtered and diluted with Milli-Q water in order to be analyzed by atomic absorption spectrometry in a VARIAN PLUS 250 spectrometer.
2.3. Adsorption capacity

The amount of adsorbed material per unit mass of the adsorbent was calculated using the following expression (Vadivelan e Kumar, 2005):

\[ q_e = \frac{V}{m} (C_i - C_e) \quad (1) \]

where \( q_e \) represent the amount of Zn\(^{2+} \) adsorbed at equilibrium (mg g\(^{-1} \)); \( V \) is the total volume of the solution (L); \( C_i \) and \( C_e \) correspond to the initial concentration and the equilibrium concentration of the metal in solution (mg L\(^{-1} \)), respectively; and \( m \) is the adsorbent mass (g).

2.4. Equilibrium of adsorption process

The equilibrium of adsorption process was evaluated at 22 °C, using the Langmuir and Freundlich models. The linearized equation of the Langmuir is described below (Febrianto et al., 2009):

\[ \frac{C_e}{q_e} = \frac{1}{q_mK_L} + \frac{1}{q_m}C_e \quad (2) \]

where \( q_m \) is the maximum adsorption capacity corresponding to the total coverage of the surface of the adsorbent material by the adsorbate (mg g\(^{-1} \)), and \( K_L \) is the Langmuir constant (L mg\(^{-1} \)).

The linearized equation of the Freundlich can be represented by:

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3) \]

where \( K_F \) and \( n \) are constants which depend on the temperature and are related to the adsorption capacity and the extent of adsorption (Montanher, 2009), respectively. The value of \( \log K_F \) is equal to \( \log q_e \) when \( C_e \) is equal to 1.0. However, for other situations in which the value of \( n \) is different from 1.0, the unit of \( K_F \) depends upon the units in which \( q_e \) and \( C_e \) parameters are being expressed (Febrianto et al., 2009).

2.5. Kinetics of adsorption process

The kinetics of adsorption process was evaluated using the pseudo-first- and pseudo-second-order models. The linear form of pseudo-first-order model is given as (Chojnacka, 2008):

\[ \ln(q_e - q_t) = \ln(q_e) - k_1t \quad (4) \]

where \( q_t \) is the amount of solute adsorbed per unit mass of adsorbent (mg g\(^{-1} \)) at time \( t \) (min), and \( k_1 \) is the pseudo-first-order rate constant (min\(^{-1} \)). This model assumes that each ion binds to only one site of adsorption on the surface of the adsorbent (Chojnacka, 2008).

The linear form of pseudo-second-order model can be represented by:

\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t \quad (5) \]

where \( k_2 \) corresponds to the pseudo-first-order rate constant (g mg\(^{-1} \) min\(^{-1} \)). For this model, the rate of occupation of adsorption sites is proportional to the square of the
number of sites not occupied. Each ion is bonded to two adsorption sites (Chojnacka, 2008).

3. RESULTS

3.1. Effect of adsorbent mass on the adsorption process

Figure 1 shows the amount of zinc adsorbed by Isabel grape bagasse using different adsorbent masses. As can be observed, the amount of zinc removed from the solution employing 10 mg was very low (~ 15%) while for the other experiments (20, 40, 60, 80 and 100 mg), the removal values were similar (around 55% of the initial concentration), and for this reason the condition containing 20 mg of grape bagasse was chosen for the optimization of other parameters by generating less waste at the end of each experiment.

![Figure 1](image1.png)

**Figure 1.** Concentration of Zn(II) as a function of time by varying the adsorbent mass. $C_i$ of Zn(II) = 100 mg L$^{-1}$, stirring frequency = 150 rpm, and pH = 3.0.

3.2. Effect of stirring frequency on the adsorption process

Figure 2 shows the amount of zinc adsorbed by Isabel grape bagasse using different stirring frequencies. In general, the stirring frequencies of 200 and 250 rpm showed unsatisfactory adsorption profiles due to intense stirring of the solutions.

![Figure 2](image2.png)

**Figure 2.** Concentration of Zn(II) as a function of time by varying the stirring frequency. $C_i$ of Zn(II) = 100 mg L$^{-1}$, adsorbent mass = 20 mg, and pH = 3.0.

The experiments performed at 100 and 150 rpm, on the other hand, resulting in satisfactory adsorption profiles for the removal of zinc, because it was found that the concentration of Zn(II) decreased exponentially as a function of time. However, the
stirring frequency of 150 rpm provided a greater removal, being applied to the other experiments.

3.3. Effect of initial pH on the adsorption process

Table 1 presents the removal percentage of zinc by Isabel grape bagasse as a function of initial pH of the solutions used in the adsorption experiments. As can be seen, the lowest zinc removal occurs at pH = 2.0. This may be due to possible competition for active sites on the surface of the adsorbent between the Zn(II) and H₃O⁺ present in aqueous medium (Vaghetti et al., 2009). Moreover, it was also observed that the increase in pH (3.0 to 6.0) did not cause an increase in the removal percentage of zinc.

In a general way, the pH = 3.0 was found to provide the best adsorption profile since it was possible to follow the variation of Zn(II) concentration before the system reach the equilibrium (15 min). In contrast, the pH = 5.0 is an interesting option for larger scale processes due to the rapidity with which the system reaches equilibrium (3 min).

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Time required to reach equilibrium (min)</th>
<th>Removal of Zn(II) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>3</td>
<td>29</td>
</tr>
<tr>
<td>3.0</td>
<td>15</td>
<td>43</td>
</tr>
<tr>
<td>4.0</td>
<td>15</td>
<td>43</td>
</tr>
<tr>
<td>5.0</td>
<td>3</td>
<td>44</td>
</tr>
<tr>
<td>6.0</td>
<td>15</td>
<td>42</td>
</tr>
</tbody>
</table>

3.4. Equilibrium of the adsorption process

The Freundlich isotherm (Figure 3b) described the results of adsorption better than the Langmuir isotherm (Figure 3a), considering that the coefficient of determination for the first model was close to unity ($r^2 = 0.9090$).

The values of Freundlich constants ($n$ and $K_F$) were 1.45 and 6.43 mg g⁻¹, respectively. In general, an adsorption tends to have a favorable value for the constant $n$ between 1.0 and 10.0 (Febrianto et al., 2009). The result obtained for the constant $n$ suggests that the adsorption of Zn(II) by Isabel grape bagasse was favorable.

According to Montanher (2009), the $K_F$ parameter can be used to compare the adsorption of various adsorbates in the same adsorbent, or the adsorption of the same adsorbate on different adsorbents in order to establish which is the most efficiently system of adsorption. The value of $K_F$ can be defined as the adsorption coefficient that describes the amount of solute adsorbed by the adsorbent per unit concentration at equilibrium: the higher the value, the greater the adsorption capacity (Wang et al. 2006). The value of $K_F$
using the Isabel grape bagasse as adsorbent was higher than to other adsorbents from vegetable origin, as can be observed in Table 2. This shows the great potential of this agroindustrial residue as adsorbent for Zn(II).

### Table 2. Freundlich isotherm parameters for adsorption of Zn\(^{2+}\) by different adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH</th>
<th>T (°C)</th>
<th>(K_F) (mg g(^{-1}))</th>
<th>(n)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isabel grape bagasse</td>
<td>3.0</td>
<td>22</td>
<td>6.43</td>
<td>1.45</td>
<td>This study</td>
</tr>
<tr>
<td>Waste activated sludge</td>
<td>5.3</td>
<td>25</td>
<td>4.67</td>
<td>2.16</td>
<td></td>
</tr>
<tr>
<td>Plam leaves</td>
<td>5.5</td>
<td>25</td>
<td>3.01</td>
<td>3.23</td>
<td>Febrianto et al., 2009</td>
</tr>
<tr>
<td>Sea grapes</td>
<td>3.0</td>
<td>-</td>
<td>1.21</td>
<td>0.86</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 presents the parameters related to the Langmuir isotherm using different adsorbents. The results show that the value of maximum adsorption capacity \(q_m\) provided by Isabel grape bagasse in the adsorption of zinc is much higher than other adsorbents from vegetable origin.

### Table 3. Langmuir isotherm parameters for adsorption of Zn\(^{2+}\) by different adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH</th>
<th>T (°C)</th>
<th>(K_L) (L mg(^{-1}))</th>
<th>(q_m) (mg g(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isabel grape bagasse</td>
<td>3.0</td>
<td>22</td>
<td>0.0201</td>
<td>192.3</td>
<td>This study</td>
</tr>
<tr>
<td>Lignin</td>
<td>5.5</td>
<td>20</td>
<td>0.2046</td>
<td>11.25</td>
<td>Febrianto et al., 2009</td>
</tr>
<tr>
<td>Palm leaves</td>
<td>5.5</td>
<td>25</td>
<td>0.0560</td>
<td>14.60</td>
<td></td>
</tr>
<tr>
<td>Sea grapes</td>
<td>3.0</td>
<td>-</td>
<td>0.0201</td>
<td>1.37</td>
<td></td>
</tr>
</tbody>
</table>

3.5. Kinetics of the adsorption process

The removal capacity of Zn(II) by Isabel grape bagasse increased with the contact time, removing about 42-55% of the initial concentration of Zn(II), except for the condition of pH = 2.0 (removal percentage of 29%) and 10 mg of adsorbent (removal percentage of 15%). The results concerning the kinetics of the adsorption process are shown in Figures 4a and 4b, and in Table 4. As can be observed, the pseudo-second-order model showed the best fit to the experimental results presenting a value for \(r^2\) close to unity. Furthermore, the value of \(q_e\) obtained by this model was similar to that obtained experimentally.

**Figure 4.** (a) Pseudo-first-order model; (b) Pseudo-second-order model. Experimental conditions: adsorbent mass = 20 mg, \(C_i\) of Zn(II) = 80 mg L\(^{-1}\), pH = 3.0, and stirring frequency = 150 rpm.
The rapid adsorption early in the process probably occurs due to an increased concentration gradient between the adsorbate in solution and the adsorbate on the adsorbent as well as the number of sites available on the surface of the adsorbent at the beginning of the process (Sen and Arias, 2009).

Table 4. Kinetic parameters for the adsorption of Zn(II) by Isabel grape bagasse.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>(k_1) (min(^{-1}))</th>
<th>(r^2)</th>
<th>(q_e) (mg g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td></td>
<td>0.201</td>
<td>0.7488</td>
<td>71.39</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td></td>
<td>0.0323</td>
<td>0.9971</td>
<td>104.8</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

The adsorption capacity does not appear to depend upon the amount of adsorbent mass from 10 mg, but it was dependent on the initial concentration of the Zn\(^{2+}\) solution, contact time and stirring frequency of the system. The most suitable values for the mass of adsorbent, pH and stirring for studying the adsorption of Zn\(^{2+}\) by Isabel grape bagasse were 20 mg, 3.0 and 150 rpm, respectively. Concerning the equilibrium of the adsorption process, the Freundlich isotherm provided the better fit of the experimental data, and the value of the constant \(n\) indicates that the process studied is favorable. The kinetics of the adsorption process, on the other hand, was better described by the pseudo-second order model and, furthermore, the removal percentage (~ 50%) was similar for all tested concentrations. Finally, the low cost, the availability of the agroindustrial waste, and the rapid adsorption promoted by the adsorbent, suggest that Isabel grape bagasse has great potential to be used in the removal of zinc present in effluents.

5. ACKNOWLEDGEMENTS

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