Bioadsorbents of heavy metals from coal mines area in Mozambique

Estevao A. Jr. Pondja1,2*, Raed Bashitialshaaer1, Kenneth M. Persson1 and Nelson Pedro Matsinhe2

Abstract: Mozambique is one of the largest coal exporters in Africa. Usually mining activities generate polluted water that is discharged into the Zambezi river basin in the Moatize area without treatment, increasing the risk both to the local environment and to public health because of this water containing significant amounts of metals and metalloids. At the same time, Mozambique is one of the largest producers of cassava peels, most of which are wasted. The aim of the present investigation was to study the use of discarded cassava peels to treat the polluted mine water from Moatize by means of adsorption. The effects both of the pH and of the contact time between the adsorbent, the adsorbate and the adsorption isotherms were examined. For calcium, magnesium, cobalt, mercury and manganese, an equilibrium was attained in less than 50 min, the removal efficiency of calcium, magnesium, and mercury being greater under alkaline conditions and being greatest for cobalt at pH 4 and for manganese at pH 7.5. The correlation coefficients of the experimental data were very high for the calcium, magnesium and manganese metals as compared with the Langmuir and Freundlich isotherms. For the Langmuir isotherms, it was found that the adsorption of calcium, magnesium, cobalt, mercury, and manganese by the cassava peels was favorable for adsorption generally, whereas for the Freundlich isotherms it was only manganese that was found to be not favorable for adsorption.

ABOUT THE AUTHORS

Estevao A. Jr. Pondja, PhD, is a lecturer in the Department of Chemical Engineering at Eduardo Mondlane University in Mozambique. His research is focus on: mine water treatment and environmental aspects of mining. The author is a member of International Mine Water Association (IMWA) and expert of greenhouse gas for United Nation Framework Convention on Climate Change (UNFCCC).

Raed Bashitialshaaer is a senior researcher in the Department of Water Resources of Lund University. He is also a member of International Desalination Association (IDA).

Kenneth M Persson is a professor in the Department of Water Resources of Lund University and Director of research at Sydvatten-Lund, Sweden.

Nelson Pedro Matsinhe is a professor in the Department of Civil Engineering at Eduardo Mondlane University in Mozambique.

PUBLIC INTEREST STATEMENT

The present study focused on the need of investigating the use of cassava peels as bioadsorbent in the treatment of mine water from coal mines area. This type of wastewater normally contains metals and metalloids that need to be removed before discharging to the environment, because presence of these metals presents risk, both for public health and biodiversity. The use of low-cost bioadsorbent such as cassava peels is under investigation around the world because commercial adsorbents are expensive. The present study analyzed the possibility of cassava peels to remove metals from mine water under different conditions.
1. Introduction

Mozambique is one of the largest cassava producers in Africa. According to Food and Agricultural Organization (FAO, 2012), the country was ranked in this regard 5th in Africa and 8th in the world in 2012 (FAO, 2012). The cassava waste generated in Mozambique is now wasted, whereas it could be used for the treatment of mine water by adsorption so as to reduce the amounts of metals and metalloids that are present in it.

Mozambique is one of the largest coal producers in Africa, at the same time as very large amounts of polluted water are generated by the coal mines there, specifically those in Moatize in the center of the country. This polluted water is discharged directly into the environment without treatment of any sort (Pondja, 2013). The coal mines are located within the Zambezi river basin, which is one of the most important sources of water in southern Africa. The local communities there rely on the water resources of the Zambezi river basin for their agriculture, their fishing, and drinking water (NEPAD, 2012). There is a risk of the basin becoming polluted if the coal mines continue to discharge untreated mine water. Using the low-cost cassava peels that are readily available in the area for treating this water by means of adsorption could be a promising and cheap solution to the problem of polluted mine water in Mozambique.

Chemical and physical methods such as those of chemical precipitation, ion exchange, reverse osmosis, sedimentation, filtration, flotation, oxidation, electrochemical treatment (Ahmadi, Heidarzadeh, Mokhtar, & Darezereshki, 2014), membrane filtration, ozonation, photochemical, Fenton reagents, and biological treatment (Ariffin et al., 2017) have been used for the treatment of wastewater contaminated by metals and metalloids. Some of these methods, however, have high operational and capital costs, as well as low removal efficiency at low metal concentrations, thereby also generating toxic sludge and not being easy to operate (Matouq, Jildeh, Qtaishat, Hindiyeh, & Al Syouf, 2015). Adsorption is a promising technology that, due to its high selectivity, low operational costs, high level of efficiency, and minimal degree of generation of toxic sludge, is used frequently nowadays for metal removal (Kurniawan et al., 2011). Use of commercial activated carbon as an adsorbent makes the adsorption process expensive. In efforts to overcome this limitation, use of low-cost adsorbents, such as agricultural wastes are under investigation (Kurniawan et al., 2011). Biodorsorbents such as modified rice husks (Agrafioti, Kalderis, & Diamadopoulos, 2014), modified sugarcane bagasse (Ahmad, Wan Ahmad, Karim, Santhana Raj, & Zakaria, 2013), modified orange peels (Marín et al., 2010), modified sawdust (Politi & Sidiras, 2012), coffee residue (Azouaou, Sadaoui, Djaafri, & Mokaddem, 2010), rice husks (Akhtar, Iqbal, Kausar, Bhanger, & Shaheen, 2010), and yeast biomass (Cojocaru, Diaconu, Cretescu, Savić, & Vasić, 2009) have also been used to remove metals and metalloids from wastewater. In addition, the adsorption of metals and of metalloids through use of agro-waste materials has proved to be effective, cheap, and easy to handle (De Gisi, Lofrano, Grassi, & Notarnicola, 2016). The use of cassava peels as an adsorbent has been investigated by several researchers (e.g. Horsfall, Abia, & Spiff, 2005; Kurniawan et al., 2011; Schwantes et al., 2016; Simate & Ndlovo, 2014). Their studies have shown that cassava peels can be employed as adsorbents for removing metals that are present in wastewater in an efficient way. Also, various studies in the literature that are referred to here have used cassava peels to remove metals from aqueous solutions containing few metals.

Mine water contains many metals and metalloids. The treatment of water of this type by adsorption is a challenging task. There appears to be no published studies in which cassava peels have been used to treat mine water. Generally speaking, cassava peels have virtually no economic value. Using them as an adsorbent could create a market for them and thus benefit many local farmers who produce cassava.
The aim of the present study was to evaluate the use of cassava peels as an adsorbent in order to appreciably reduce the presence of metals and metalloids in mine water, account being taken in particular of the fact that the country of Mozambique is one of the largest producers of cassava peels and one of the major exporters of coal in Africa. In order to investigate this, we had to run a number of lab-scale experiments aimed at achieving a better understanding of the polluted water contained in the coal mines there (polluted e.g. by Ca, Mg, Co, Hg and Mn). It was important in this connection to compare the experimental results obtained with those obtained for other isotherms, such as Langmuir and Freundlich.

2. Materials and methods

2.1. Materials employed

As raw materials for the adsorption study, use was made of cassava peels, coal mine waste (overburden), deionized water, nitric acid at a concentration of 0.3 M, and both sulfuric acid and sodium hydroxide at a concentration of 0.1 M. The cassava peels were used as adsorbents, and both overburden and deionized water were employed to produce synthetic mine water. The nitric acid was used to activate the cassava peels for the adsorption process. Both sulfuric acid and sodium hydroxide were employed to adjust the pH of the solution.

2.1.1. Preparation of cassava peels for use as adsorbents

The cassava peels used in the study were obtained at local markets in Maputo, Mozambique. The fresh cassava were washed in clean water, and the peels were removed. Since cassava peels normally contain cyanide, they were soaked in water for 5 h to remove the cyanide. They were then exposed to the sun for about 7 days to dry. The dried cassava peels were chopped and milled then to increase the surface area so as to improve the adsorption process. The dried and milled cassava peels were activated by soaking 500 g of them in 0.3 M of nitric acid (HNO₃) for 24 h. They were then filtered, the liquid part being discarded, the residue that remained being washed in deionized water until a pH of 7 was achieved. After the cassava peel material had been air dried, it was ready for use as an adsorbent.

2.2. Methods used

A lab-scale experiment was designed for studying the mine water adsorption process that took place in Moatize coal mines with coal wastes (or overburden) consisting of rock materials. The experiment carried out can be described as follows: a hollow column made of glass, open at the top, and having an external diameter of 10 cm, an inner diameter of 5 cm, and a height of 15 cm was used for generating what corresponded to mine water. The column was filled and overburdened with particles less than 4 mm in diameter. Deionized water was then recirculated in the column for 72 h by a peristaltic pump at a flow rate of 1.5 l/h, the room temperature being about 25°C (see Figure 1). After 72 h, samples were collected, part of them being reserved for adsorption and the rest being sent to a laboratory at the Department of Biology of Lund University for analysis of the metal concentrations prior to treatment.

2.2.1. The adsorption process

The adsorption process began by 100 mL of mine water being poured into six Erlenmeyer flasks having a capacity each of 250 mL. Thereafter, 2 g of activated cassava peel material was put into each flask, the resulting solution being mixed then, and its pH value being determined. The pH of the solution was adjusted to values of between 3 and 10 by use of a solution of 0.1 M of NaOH or 0.1 M of H₂SO₄. The flasks containing the mixtures were filled inside of a shaking water bath (Grant OLS 200) at a temperature of 30°C and at a rotation speed of 150 rpm. Every 15 min, one of the flasks was removed from the shaker, samples being collected for analyzing the metal ion concentrations involved. The effects of the contact time between the adsorbent and the adsorbate, as well as of the pH of the system were investigated.
The equilibrium of the isotherms was analyzed by introducing 2 g of cassava peel material into six different flasks, each containing 100 mL of mine water but differing in the initial concentration involved. The pH was adjusted to 7 in each of the flasks. After two hours, which was sufficient for an equilibrium concentration ($C_e$) to be reached, the resulting sample was collected from each flask, the metal concentrations being analyzed to determine the $C_e$ for each flask. The pH was measured in each case, using a pH meter of the Orion Research Microprocessor Ionanalyzer Model 901 type. The metal ions were analyzed using the ICP-OES Optima 8300 from Perkin Elmer.

2.2.2. Calculations concerning the adsorption process

The effectiveness of the cassava peels in adsorbing metal ions was determined in each case by use of Equation (1),

$$\text{Removal (\%)} = \frac{C_o - C_e}{C_o} \times 100\%$$  \hspace{1cm} (1)

where $C_o$ is the initial metal ion concentration and $C_e$ is the equilibrium concentration of metal ions expressed in mg/L. To determine the quantity of metal ions adsorbed per unit time ($q_t$), use was made of Equation (2),

$$q_t = \frac{(C_o - C_t) \times V}{m}$$  \hspace{1cm} (2)

where $C_o$ and $C_t$ are the concentrations of metal ions in the solution before and after sorption (in mg/L), respectively, $m$ is the mass of the cassava peel involved (in g), and $V$ is the volume of the solution (in L).

For determining the adsorption isotherms, it was necessary to first determine the equilibrium concentrations of the various samples, these differing in their initial metal ion concentrations. The quantity of the metal ions adsorbed at equilibrium ($q_e$), expressed in mg/g, was determined using Equation (3),

$$q_e = \frac{(C_o - C_i) \times V}{m}$$  \hspace{1cm} (3)

where $C_i$ is the equilibrium metal ion concentration in mg/L.
3. Results and discussion

Use of the cheap cassava peel material that was available in the study area provided an excellent means of cleaning the polluted coal mine water there. The two major reasons for cleaning it were for the sake of people’s health in Moatize and for protecting the local water resources.

Results obtained during the generation of synthetic coal mine water in the hollow column are presented in Table 1. Only metal ions that showed considerable removal efficiency were presented. The mine water was found to contain high concentrations of calcium (Ca) and magnesium (Mg). The concentrations of cobalt (Co), mercury (Hg), and manganese (Mn), in contrast, were rather low. The high concentrations of Ca and Mg in the mine water that was produced can be explained in terms of the dissolution of the carbonates and the dolomites that were available having neutralized the acidic water generated in the column. The pH of the solution was neutral, indicating that the acid was buffered by the neutralizing materials (carbonates and dolomites) (see Table 1).

3.1. Adsorption process

3.1.1. Effects of the contact time
To determine how the adsorption of metal ions on the surface of the cassava peels was affected by the contact time involved, the quantity of metal ions adsorbed per unit time (q_t) was determined, the results being presented in Figures 2 and 3. It was found that a state of equilibrium was achieved for Ca after 50 min and for Mg after 20 min (Figure 2), whereas for Hg and Co it was achieved after 15 min and for Mn after 40 min (Figure 3).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ca</th>
<th>Co</th>
<th>Hg</th>
<th>Mg</th>
<th>Mn</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum</td>
<td>151.00</td>
<td>0.041</td>
<td>0.064</td>
<td>67.50</td>
<td>2.50</td>
<td>8.0</td>
</tr>
<tr>
<td>Minimum</td>
<td>53.00</td>
<td>0.009</td>
<td>0.030</td>
<td>21.00</td>
<td>0.51</td>
<td>7.2</td>
</tr>
<tr>
<td>Mean</td>
<td>95.033</td>
<td>0.021</td>
<td>0.046</td>
<td>42.00</td>
<td>1.315</td>
<td>7.5</td>
</tr>
<tr>
<td>SD</td>
<td>38.140</td>
<td>0.001</td>
<td>0.013</td>
<td>15.04</td>
<td>0.694</td>
<td>0.339</td>
</tr>
</tbody>
</table>

Figure 2. Effects of the contact time on the removal of Ca and Mg ions by the cassava peels.
3.1.2. Effects of the pH
The pH is a highly important parameter in the adsorption of metal ions when use to this end is made of natural products such as cassava peels. Numerous acid functional groups are found in the surface layers of cassava peels. Manipulation of the pH of the system can result in a dissociation of these groups, which in turn can result in a significant improvement or worsening of the efficiency of the removal of metal ions that are present, such as those found in coal mine water (Ndlovu et al., 2012). This occurs since under acidic conditions the concentration of hydrogen ions (H+) is high, their filling up the binding sites on the surface of the cassava peel, resulting in a decrease in the removal of cations, since these compete with H+ for the binding sites located on the surface of the cassava peels (Awokoya et al., 2016).

As can be seen in Figure 4, the pH value has a considerable impact on events taking place in the system. The removal efficiency for Ca, Mg, and Hg increases with an increase in pH until alkaline conditions are reached. For Ca, Mg and Hg, alkaline conditions appear to provide good results in terms of adsorption on the cassava peels. For Co, the removal efficiency is at a maximum at pH 4 and starts then to decrease as the pH value becomes higher probably due to the generation of certain complex compounds that precipitate. For Co, it appears too that adsorption is favored at lower pH values. For Mn, the maximum removal efficiency is at pH 7.5, with a rise in pH value above that level the removal efficiency beginning to decrease. This can be explained by the fact that at lower pH values the availability of dissolved manganese (Mn^{2+}) is greater with a rise in pH value solid compounds (e.g. Mn(OH)_{2}) being formed, these precipitating in the solution, resulting in a decrease in the availability of dissolved Mn, this reducing the adsorption removal efficiency (Hem, 1963).

3.2. Adsorption isotherms
The relationship between the quantity of the metal ions adsorbed and the concentration of the ions at a state of equilibrium can be described by an adsorption isotherm. Fitting experimental data to a specific isotherm model is highly important, since useful information can be obtained from the
analysis and the comparisons involved. In the present study, the experimental data obtained were compared with two isotherms, those provided by the Langmuir and the Freundlich model, respectively.

3.2.1. Langmuir adsorption isotherms
The Langmuir adsorption model is based on the monolayer adsorption theory, in terms of which the amount of ions adsorbed corresponds to the number of active centers on the surface of the adsorbent. Equation (4) is the Langmuir equation,

\[ q_e = \frac{q_{\text{max}} \times b \times C_e}{1 + b \times C_e} \]  

(4)

where \( q_{\text{max}} \) is the maximum adsorption capacity for a particular adsorbent (mg/g) and \( b \) is the adsorption equilibrium constant (L/mg). To determine values for \( b \) and \( q_{\text{max}} \), it was necessary to plot \( 1/q_e \) vs. \( 1/C_e \), from the slope and the intercept obtained \( b \) and \( q_{\text{max}} \), being determined then, as presented in Table 2. The dimensionless separation factor \( R_L \), calculated as shown in Equation (5) was used to characterize the Langmuir isotherms,

\[ R_L = \frac{1}{1 + b \times C_0} \]  

(5)

where \( C_0 \) is the highest initial concentration of the metal ions (mg/L). The value of \( R_L \) indicates whether the type of isotherm involved is unfavorable (\( R_L > 1 \)), linear (\( R_L = 1 \)), favorable (\( 0 < R_L < 1 \)), or irreversible (\( R_L = 0 \)) (Bhatt et al., 2012).
3.2.2. Freundlich adsorption isotherms
When the adsorption process takes place on adsorbents having a heterogeneous structure, use is made of Freundlich’s isotherm model, described in Equation (6),

\[ q_e = K_F \times C_e^n \]  

where \( K_F \) is the Freundlich constant, which is related to the bonding energy (L/g) involved, \( n \) being an empirical constant used to characterize the heterogeneity of the process that takes place (g/L). Thus, if \( n < 1 \), the adsorption that occurs is unfavorable, and if \( 1 < n < 10 \), the adsorption is favorable. The values of \( K_F \) and \( n \), as presented in Table 2, were determined by plotting \( \ln(q_e) \) vs. \( \ln(C_e) \) and obtaining the intercept and the slope.

3.2.3. Comparison of adsorption isotherms
The results of the adsorption of Ca, Mg, Co, Hg, and Mn for the Langmuir and the Freundlich isotherms, respectively, are presented in Table 2. The equilibrium adsorption isotherms obtained and the fitting of the models to the experimental data are presented in Figure 5, in which only the adsorption isotherms of Ca, Mg, and Mn are shown, because of only these having high values for the correlation coefficient \( (R^2) \) involved. The close fit of the experimental data to the Langmuir isotherms

### Table 2. Langmuir and Freundlich isotherm constants for Ca, Mg, Co, Hg and Mn ions adsorbed into cassava peels

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Langmuir isotherms</th>
<th>Freundlich isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_{\text{max}} ) (mg/g)</td>
<td>( b ) (L/mg)</td>
</tr>
<tr>
<td>Ca</td>
<td>18.868</td>
<td>0.006</td>
</tr>
<tr>
<td>Mg</td>
<td>2.597</td>
<td>0.0175</td>
</tr>
<tr>
<td>Co</td>
<td>0.0083</td>
<td>8.186</td>
</tr>
<tr>
<td>Hg</td>
<td>( 5 \times 10^{-4} )</td>
<td>225.850</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0818</td>
<td>0.9892</td>
</tr>
</tbody>
</table>

Figure 5. Fitting experimental data to the Langmuir and the Freundlich isotherm model, respectively, to obtain equilibrium results for (a) calcium, (b) magnesium and (c) manganese.
for Ca, Mg, and Mn is confirmed by the high values of the respective correlation coefficients of 0.9885, 0.9987, and 0.9970, respectively. The separation factor $R_L$ for Ca, Mg, Co, Hg, and Mn, respectively, is between 0 and 1, which means that the adsorption is favorable. The highest maximum adsorption capacity was found for Ca ions, which had a value of 18.868 mg/g and for the Mg ions, which had a value of 2.597 mg/g. The other ions had very low values for $q_{\text{max}}$. The explanation of this could be the fact that the content of Hg, Co, and Mn in the sample was very low.

The respective correlation coefficients in the Freundlich model for Ca, Mg, and Mn are very high, showing the model to have fitted very well. In contrast, the model is poorly fitted to the experimental data for Hg and Co. The values of $n$ are in the interval $1 < n < 10$ for Ca, Mg, Co, and Hg, indicating that for these the adsorption is favorable. The value of $n$ for Mn is 0.78, i.e. less than 1.0 ($n < 1$), which means that there the adsorption is unfavorable.

4. Conclusion
In the present study, cassava peels were used successfully as bioadsorbents to remove metals (e.g. Ca, Mg, Co, Hg and Mn) from mine water from Moatize coal mines. The main outcomes of the present study are as follows:

- The removal efficiency of Ca, Mg, and Hg was found to be high under alkaline conditions,
- For Co, the maximum removal efficiency (65%) was obtained at pH 4, the efficiency starting to decrease then as the pH increases, due to the generation then of metal complexes that precipitate in the solution, this reducing the availability of the Co to be adsorbed by the cassava peels,
- For Mn, the maximum removal efficiency (70%) was obtained at pH 7.5, its then starting to decrease with a rise in the pH value through this precipitating formation of the manganese complex.

In general, it can be concluded that cassava peels can remove metals from the mine water quite efficiently. Also, from the comparisons made between the isotherm models of Langmuir and of Freundlich, respectively, on the basis of the experimental data collected here, important information regarding the maximum adsorption capacity and the correlation coefficients involved was obtained. Such information can be highly useful in connection with both models in the future.

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Author details
Estevao A. Jr. Pondja1,2  
E-mail: estevao.pondja@tvrl.lth.se  
ORCID ID: http://orcid.org/0000-0002-6094-4770  
Raed Bashitialshaaer1  
E-mail: Raed.Alshaaer@tvrl.lth.se  
ORCID ID: http://orcid.org/0000-0001-6370-5508  
Kenneth M. Persson1  
E-mail: kenneth_m.persson@tvrl.lth.se  
Nelson Pedro Matsinhe2  
E-mail: tinjombo@gmail.com

1 Department of Building and Environmental Engineering, Division of Water Resources, Lund University, Lund, Sweden.  
2 Department of Chemical Engineering, Eduardo Mondlane University, Maputo, Mozambique.

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References
https://doi.org/10.1016/j.jenvman.2014.07.029  
https://doi.org/10.1016/j.ibiod.2013.01.008  
https://doi.org/10.1016/j.gexplo.2014.10.005  
https://doi.org/10.1016/j.colsurfb.2009.08.025  


