Adsorption Study on Moringa Oleifera Seeds and Musa Cavendish as Natural Water Purification Agents for Removal of Lead, Nickel and Cadmium from Drinking Water

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Adsorption Study on Moringa Oleifera Seeds and Musa Cavendish as Natural Water Purification Agents for Removal of Lead, Nickel and Cadmium from Drinking Water

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Abstract: The effectiveness of plant based materials Moringa oleifera (Moringa) seeds and Musa cavendish (banana peel) for removing heavy metals namely lead (Pb), nickel (Ni) and cadmium (Cd) from contaminated groundwater was studied. Tests were carried out with individual and combined biomass at neutral pH condition on synthetic groundwater samples. The optimum biomass doses were determined as 200 mg/L for single biomass and 400 mg/L (in the ratio of 200 mg/L: 200 mg/L) for combined biomasses and used for adsorption isotherm studies with contact time of 30 minutes. Results showed that combined biomasses was able to met the Pb, Ni and Cd WHO standards from higher Pb, Ni and Cd initial concentrations which were up to 40 µg/L, 50 µg/L 9 µg/L, respectively compared to individual biomass of Moringa seed and banana peel. Moringa seeds exhibited the highest removal of Pb (81%) while the combined biomasses was most effective in removing Ni (74%) and Cd (97%) over wider their initial concentration ranges. The experimental data were linearized with Langmuir and Freundlich adsorption isotherm models. Freundlich model described the Pb adsorption better than the Langmuir model for all the tested biomasses. However, the Langmuir model fit better with the experimental data of Ni adsorption by Moringa seeds. Both models showed negligible differences in the coefficient of determination (R2) when applied for Ni and Cd adsorption on banana peel and combined biomasses, suggesting that there were multiple layers on the biomass interacting with the metals. Chemisorption is suggested to be involved in Pb adsorption for all tested biomasses as the value of nF calculated was lower than one. This type of adsorption could explain the phenomenon of different behavior of Pb removal and the higher Pb adsorption capacity (represented by KF values) compared to Ni and Cd. The study demonstrates that Moringa seeds, banana peel and their combination have the potential to be used as a natural alternative to the other water treatment agents for removing the Pb, Ni and Cd from drinking water.

Keywords: Adsorption, cadmium, coagulation, drinking water, freundlich isotherm, langmuir isotherm, lead, moringa oleifera, musa cavendish, nickel.
1. Introduction
Most people living in remote areas of developing countries are largely dependent on groundwater as a source of drinking water. However, the groundwater can be contaminated with various pollutants such as heavy metals. Heavy metals are present in groundwater due to poor land use practices including excessive use of agrochemicals. Average lead (Pb) levels of 287 µg/L and 330 µg/L have been recorded in groundwater samples collected from some areas in India and Pakistan, respectively [1, 2]. [2] reported that the average level of nickel (Ni) in groundwater in Pakistan was up to 960 µg/L. In Sri Lanka, Cd average levels in groundwater have been recorded between 5 to 23 µg/L [3]. The concentrations of the heavy metals far exceeded those recommended by WHO drinking water quality standards (10 µg/L, 20 µg/L and 3 µg/L for Pb, Ni and Cd, respectively). Therefore, it is of extremely importance to remove these harmful substances from the drinking water to prevent the potential adverse effects to human health.

Poor economic situations in some developing countries require low-cost drinking water treatment solutions for the affected communities for which conventional/advanced drinking water treatment is not viable. Application of plant-based materials for drinking water treatment is environmentally sustainable, cost-effective as they are locally available, non-toxic, easy to prepare and the residual generated is easy to dispose.

Various natural-based materials have been studied as potential low-cost coagulants for water purification including Moringa oleifera (Moringa, MO) seed [4, 5]. MO seed is one of the popular natural materials investigated as it has shown ability in removing various pollutants such as copper, nickel, zinc and color from water and wastewater [6, 7]. MO is a vegetable that can be found widely in Asian countries, growing well in any tropical areas including many in Africa. Besides, Musa cavendish (banana peel, MC) was also reported to be a promising plant-based material for removing As, Pb and Cd [8, 9]. The use of MC in water purification fits well with the concept of environmental sustainability since the agricultural waste are recycled to minimize the wastes in an environmentally friendly way [10, 11].

Adsorption was regarded as a key removal mechanism when these types of biomass material were used for water treatment [12]. Despite considerable attention has been paid by current researchers on the application of natural materials as water purification agents to remove various kind of pollutants, understanding of the mechanism involved in the treatment process is still lacking. The removal mechanism for one heavy metal could be different to one another. Therefore, it is important to understand the mechanism that contributing to the removal of a specific heavy metal from the aqueous solution using the different type of biomass rather than just its application. The aim of this study was to examine whether the existing adsorption isotherm models can best describe the behavior and treatment efficiency in removing Pb, Ni and Cd with Moringa seeds (MO), Musa cavendish/banana peel (MC) and their combination (MO+MC) from contaminated groundwater and to understand the adsorption mechanism of particular heavy metal described by the presented models.

2. Methodology

2.1 Preparation of synthetic groundwater samples
Synthetic groundwater samples containing individual Pb, Ni and Cd of known concentrations were prepared with deionized water [13]. All chemicals used in the study, including lead carbonate, nickel carbonate and cadmium nitrate tetrahydrate were of analytical grade and obtained from Sigma-Aldrich (Australia). The chemical stock solutions with a concentration of 1000 mg/L of each heavy metal were prepared and then diluted to the target concentrations as per need for the experiments. The pH of the water samples was adjusted using either 0.1 M H2SO4 and 0.1 M of NaOH. Table 1 presents the initial concentrations of the contaminants in the synthetic groundwater samples. The initial concentration values in this study were based on the mean groundwater quality values reported in the literature [1, 2, 3].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Initial concentration (µg/L)</th>
<th>WHO drinking water quality standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>µg/L</td>
<td>5, 10, 20, 40, 60, 80, 100</td>
<td>10</td>
</tr>
<tr>
<td>Ni</td>
<td>µg/L</td>
<td>10, 20, 30, 40, 50, 80, 100</td>
<td>20</td>
</tr>
<tr>
<td>Cd</td>
<td>µg/L</td>
<td>1, 3, 5, 7, 9, 10, 11</td>
<td>3</td>
</tr>
<tr>
<td>pH</td>
<td>-</td>
<td>7.0</td>
<td>6.5-8.5</td>
</tr>
</tbody>
</table>
2.2 Preparation of biomass

2.2.1 Moringa oleifera (moringa seeds)
Moringa seeds (MO) were bought from Pacific Blue Consulting Pty. Ltd. (The Moringa Shop, Australia). High-quality seeds were selected and cleaned from debris. Husks and external coats were removed [14]. The selected MO seeds were then rinsed with deionized water and dried in an oven at 100ºC for 1 hour. The dried seeds were ground to a fine powder and sieved through a stainless steel mesh with an opening size of 300 μm to obtain MO particles of similar size. One gram of the MO seed powder was added to 1 L deionized water and stirred for 10 minutes using a magnetic stirrer to create active constituents to prepare an MO stock solution of 1000 mg/L.

2.2.2 Musa cavendish (banana peel)
Ripe bananas (MC) were purchased from a local market. The peels were gently separated from the fruits. The peels were cleaned and dried in an oven for 1 hour at 100ºC. Then, the dried peels were cut into small pieces, ground and sieved through a stainless steel mesh with an opening size of 300 μm [15]. One gram of powdered banana peel was added to 1000 mL deionized water and stirred for 10 minutes to generate active constituents making it a stock solution with the MC concentration of 1000 mg/L.

2.3 Batch experiments
A standard jar tester (Lovibond, Phipps & Bird) was used for batch tests for determining the removal of the target contaminants by the selected natural materials. All experiments were performed at room temperature (20ºC ± 1ºC) and were carried out with 1 L water samples in acrylic jars. The pH of each sample was adjusted to 7.0 with 0.1 M NaOH or 0.1 M H₂SO₄ prior to the batch experiment. The water sample was then mixed with the biomass of a required dosage. Then the sample was subjected to a rapid mixing at 150 rpm for 3 min, followed by the slow mixing at 30 rpm for 30 min [5]. The agitated solutions were permitted to settle for 30 min before the supernatant was taken for sampling. The samples were filtered through 0.45 µm fiberglass membrane filters (Advantec) prior to the analysis to determine the removal efficiency of the target contaminants. Pb, Ni and Cd concentrations were determined using Agilent 7700 series Inductively Coupled Plasma Mass Spectrometry (ICP-MS). pH measurement was carried out using Seven Easy Mettler Toledo pH meter. In the investigations with the combined biomass (MO+MC), two different biomasses were added to the water sample concurrently. The experiments were conducted in triplicate (N=3) to ensure the reproducibility, and the mean values were reported.

In previous studies [13, 16] evaluated the optimum biomass doses for removing arsenic (As), Pb, Ni, Cd, fluoride (F) and turbidity from single and multi-element synthetic groundwater samples. From the above studies, the optimum biomass concentrations which gave the best removal efficiencies were found to be 200 mg/L (for MO and MC, separately) and 200+200 mg/L (for combined MO and MC). Above biomass concentrations were therefore used in the adsorption isotherm studies.

2.4 Adsorption isotherms.
Adsorption isotherm studies were carried out by using batch experiments as described in the previous section. The adsorption data have been subjected to Langmuir [17] and Freundlich [18] isotherm models (Equations 1 & 2, respectively).

Langmuir theory assumed that the adsorption process takes place on a set of distinct localized adsorption sites within the natural material and no interactions between adsorbate molecules on adjacent sites. In linear form, it can be written as Equation 1.

\[
\frac{C_e}{Q_e} = \frac{1}{Q_m} + \frac{1}{K_L Q_m} C_e 
\]  

(1)

where \( Q_m \) and \( K_L \) are the Langmuir constants. \( Q_m \) is the monolayer adsorption capacity (mg/g), \( K_L \) is adsorption constant (L/mg), \( C_e \) is the equilibrium concentration of the heavy metal (mg/L) and \( Q_e \) is the amount of heavy metal adsorbed (mg/g) (Equation 3). The \( Q_m \) and \( K_L \) can be determined from the gradient and the intercept of the linear graph between \( \frac{C_e}{Q_e} \) and \( C_e \). The Freundlich isotherm accounts for a multiple sites adsorption for heterogeneous surfaces (Equation 2).
\[
\ln (Q_e) = \ln (K_F) + \left( \frac{1}{n_F} \right) \ln (C_e)
\]  
(2)

where \( K_F \) and \( n_F \) are Freundlich adsorption constants. \( Q_e \) and \( C_e \) are as defined earlier for Equation 1. \( n_F \) (dimensionless) and \( K_F \) (L/g) can be determined from the gradient and the intercept of the linear graph between \( \ln (Q_e) \) and \( \ln (C_e) \).

\[ Q_e = \frac{(C_0 - C_e)V}{m} \]  
(3)

where \( C_0 \) is the initial concentration of heavy metal in the solution (mg/L), \( V \) is the volume of the solution (L) and \( m \) is the mass of the biomass used (g). Percentage removal of heavy metal was calculated using Equation 4.

\[ \% \text{ Removal} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \]  
(4)

where \( C_0 \) and \( C_e \) are as defined earlier in Equation 3 and 1, respectively.

3. Result and Discussions

3.1 Effect of initial concentration of heavy metals

The initial concentrations for Pb, Ni and Cd of the synthetic groundwater samples were varied as shown in Table 1. Figure 1a depicts the relationship between initial Pb concentration and removal efficiency at fixed dosages of 200 mg/L for MO and MC, and 200+200 mg/L for MO+MC. For MO, the increase of initial Pb concentration from 5 µg/L to 60 µg/L increased the Pb removal from 65% to 81%. However, Pb removal remained unchanged (around 80% to 81%) for concentrations between 60 to 100 µg/L. Similar to MO, the removal percentage increased from 32% to 58% with MC until the Pb concentration is 60 µg/L. The removal of Pb did not increase with the increase of initial Pb concentration beyond 60 µg/L. The combined biomasses gave similar removal rates to MO alone. MC showed the least removal efficiency compared to MO and MO+MC.

In contrast to Pb, removal efficiencies decrease with the increase of Ni and Cd concentrations. Figure 1b shows that the removal efficiency decreased rapidly from 98% to 42% with MO when Ni concentration was increased from 10 to 30 µg/L. The rate of decrease in removal efficiency was lower with MC and MO+MC when the initial Ni concentrations were gradually increased. As depicted in Figure 1b the removal efficiency of Ni was improved by combining MO and MC.

Similar to Ni, MO+MC showed a better removal efficiency of Cd compared to MO and MC alone. There was a sudden drop in removal efficiency when the Cd concentration increased from 3 to 5 µg/L and further reduction was shown when Cd concentration was beyond 9 µg/L for MC and MO+MC (Figure 1c). [19] attributed this behavior to the saturation of adsorption sites on biomass’s surface. The % reduction of Cd with MO did not vary much (63% to 54%) when Cd initial concentration increased from 1 to 11 µg/L.
Figure 1. The relationship between removal efficiency of plant-based biomasses and initial concentrations of (a) Pb, (b) Ni and (c) Cd.

3.2 Adsorption Isotherms

Adsorption of Pb, Ni and Cd by MO, MC and MO+MC were modeled using the Langmuir (Equation 1) and Freundlich (Equation 2) isotherms with the quality of the fit assessed using the coefficient of determination ($R^2$).

The experimental plots of Pb adsorption by MO, MC and MO+MC (Figure 2), were best fitted with Freundlich model with $R^2$ values of 0.97, 0.99 and 0.99, respectively (Figure 2b). [12] also reported that Freundlich model showed a better fit for Pb adsorption experimental data on MO. This finding suggested that the Pb was interacting with multi-layer of the biomass’s sites for adsorption. Negative slopes and intercepts obtained for Pb adsorption on all tested biomasses (Figure 2a), suggesting that the adsorption behavior do not obey the Langmuir’s theory assumption (surface of biomass is energetically homogeneous). In nature, MO and MC may have heterogeneous available adsorption sites due to its abundant availability of functional groups, considering the origin of the materials used in this study being plant-based materials [11]. Therefore, in this case Pb might have chemical interactions with the specific functional groups present on the biomass’s surface. Such interactions could lead to the generation of new chemical bonds that could improve the adsorption capacity of the biomass.

Figure 2. (a) Langmuir and (b) Freundlich isotherms of Pb on the MO, MC and MO+MC.

The experimental plots of Ni adsorption on the MC and MO+MC were best fitted with Freundlich model with $R^2$ values of 0.97 and 0.99, respectively (Figure 3b). On the other hand, MO exhibited a better fitness with the Langmuir model ($R^2 = 0.96$) as shown in Figure 3a than with the Freundlich model ($R^2 = 0.74$), indicating that greater monolayer adsorption occurred rather than multilayer adsorption.
Based on Figure 4(a and b), the Freundlich model demonstrated a better fit than the Langmuir model for Cd adsorption by MO. Similar finding was reported by [20]. The difference between the \( R^2 \) values from both models were insignificant when adsorption by MC was considered, suggesting that there is a possibility that Cd adsorption onto these biomasses occurred in multilayers. This finding reinforces the conclusions made by [12] that the insignificant difference between \( R^2 \) values obtained for both models, indicating a possible existence of more than one type of adsorption site interacting with the metal.

In the Langmuir linearization of MO, MC and MO+MC for Ni adsorption, it was verified that MO+MC had a higher adsorption capacity of Ni (\( Q_m \)) compared to MO and MC alone. However, MO had the highest binding energy (\( K_L \)) with Ni. The binding energy (\( K_L \)) of Cd by MO+MC was significantly higher in the Langmuir linearization compared with MO and MC. This was likely the reason that the Cd removal efficiency was better achieved by MO+MC compared to MO and MC alone (Figure 1c).

Table 2 presents the model parameters and the coefficient of determination (\( R^2 \)) obtained by fitting Langmuir and Freundlich models (Equations 1 & 2) with the experimental data.

Negative values were obtained for \( Q_m \) (adsorption capacity) and \( K_L \) (binding energy) by fitting the Langmuir linearization model with MO, MC and MO+MC biomasses for Pb adsorption. This was due to the negative gradient of the linear graph as shown in Figure 2a. This result indicated that the adsorption behavior of the treatment did not follow the theory assumptions of Langmuir isotherm due to possibility to undertake a specific kind of adsorption mechanism (i.e. chemisorption) as the behavior of Pb removal was different when compared to Ni and Cd (Figure 1a).
Table 2. Parameters of equilibrium isotherm of Langmuir and Freundlich models for Pb, Ni and Cd adsorption of MO, MC and MO+MC.

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>Biomass</th>
<th>Langmuir isotherm model</th>
<th>Freundlich isotherm model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$Q_m$ (mg/g)</td>
<td>$K_L$ (L/mg)</td>
</tr>
<tr>
<td>Pb</td>
<td>MO</td>
<td>-0.540</td>
<td>-23.422</td>
</tr>
<tr>
<td></td>
<td>MC</td>
<td>-0.174</td>
<td>-17.563</td>
</tr>
<tr>
<td></td>
<td>MO+MC</td>
<td>-0.125</td>
<td>-37.191</td>
</tr>
<tr>
<td>Ni</td>
<td>MO</td>
<td>0.122</td>
<td>101.832</td>
</tr>
<tr>
<td></td>
<td>MC</td>
<td>0.195</td>
<td>49.712</td>
</tr>
<tr>
<td></td>
<td>MO+MC</td>
<td>0.239</td>
<td>28.222</td>
</tr>
<tr>
<td>Cd</td>
<td>MO</td>
<td>0.090</td>
<td>93.294</td>
</tr>
<tr>
<td></td>
<td>MC</td>
<td>0.032</td>
<td>974.905</td>
</tr>
<tr>
<td></td>
<td>MO+MC</td>
<td>0.015</td>
<td>4168.667</td>
</tr>
<tr>
<td></td>
<td>MO</td>
<td>0.368</td>
<td>2.093</td>
</tr>
<tr>
<td></td>
<td>MC</td>
<td>0.073</td>
<td>3.396</td>
</tr>
</tbody>
</table>

In the Freundlich linearization, the $K_F$ constants (adsorption capacity) obtained for Pb by all biomasses were much higher than those of Ni and Cd. This result was consistent with the increase of Pb removal with the increase in initial Pb concentration (Figure 1a).

The $n_F$ value in the Freundlich model represents the reactivity of biomass’s active sites. According to [21], if a value of $n_F = 1$, the adsorption is linear, for $n_F < 1$, the adsorption is chemisorption, and for $n_F > 1$ the adsorption is a favorable physical adsorption. Thus, analyzing the $n_F$ values (Table 2), adsorption of Pb onto MO, MC and MO+MC was much favored the chemisorption. In this case, adsorption of Pb on MO, MC and MO+MC was likely to generate new chemical bonds at the biomass’s surface which could lead to the improvement of the biomass adsorption capacity. This phenomenon could explain the reason of the increase of removal efficiency with the increase of initial Pb concentration and the higher values of $K_F$ (adsorption capacity) compared to Ni and Cd. On the other hand, physical adsorption was shown favorable for adsorption of Ni and Cd on MO, MC and MO+MC.

4. Conclusion
The adsorption of lead (Pb), nickel (Ni) and cadmium (Cd) by naturally occurring plant-based materials of Moringa oleifera (MO) seeds, Musa cavendish (MC) and their combination (MO+MC) was investigated and following conclusions are drawn from the study:

- MO showed the highest removal efficiency for Pb while MO+MC showed the highest removal for Ni and Cd compared to MO and MC alone.
- Freundlich model best described the Pb adsorption for all the tested biomasses. The experimental data with Pb did not obey the Langmuir’s model adsorption theory assumptions.
- Adsorption of Pb on MO, MC and MO+MC favored the chemisorption type of adsorption. This phenomenon could explain the reason of different behavior of removal Pb and higher adsorption capacity were obtained for Pb compared to Ni and Cd.
- Data linearization demonstrated the best fit by the Langmuir model for Ni adsorption on MO. Negligible difference between $R^2$ from both isotherms for Ni and Cd adsorption by MC and MO+MC, suggests that there were multiple layers on the biomass interacting with the metals.
- MO, MC and MO+MC show potential to be used as alternative treatment material for purification of drinking waters polluted with heavy metals such as Pb, Ni and Cd as they are available and low-cost in the affected developing countries.

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References


