Adsorption Isotherm and Kinetic Studies of Cd (II) and Pb (II) Ions Bioremediation from Aqueous Solution Using Unmodified Bambara Groundnut Husk (Vigna Subterranean)

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Citation

Abstract
The global need to clean-up heavy metal contaminated environment cannot be over emphasized. In this study, the adsorption potential of Bambara Groundnut Husk (BGH) with respect to Cd(II) and Pb(II) ions, was studied in order to consider its possible application in the treatment of heavy metal contaminated wastewater. Functional group elucidation was done using Fourier Transform Infrared (FTIR) spectrometer. The samples were prepared by diluting the adsorbent to 5% KBr and cast into disks for analysis. Similarly, Scanning Electron Microscopy (SEM) was carried out to examine the morphology of the adsorbent. Characterization of the treated biomass was done before and after adsorption. The results of the FTIR spectra showed that there was participation of carbonyl, carboxylic and hydroxyl groups of BGH as major sites for the binding of Cd(II) and Pb(II) ions during adsorption. SEM analysis also revealed the porosity of the adsorbent. Equilibrium batch experimental parameters significantly (p>0.05) influence the overall adsorption process. However, the equilibrium isotherm modeling of data obtained was best fitted to the Langmuir model than the other isotherm models base on the R² values of 0.997 and 0.910 for Cd(II) and Pb(II) ions respectively. The monolayer sorption capacity (qe) of Cd (II) was found to be 6.944 mg/g while that of Pb(II) was 13.51 mg/g. The separation factor (RL) was between zero and one (0<RL<1) indicating a favourable adsorption experiment. The low apparent energy of adsorption (<8 kJ/mol) of the D-R isotherm model and the low Langmuir constant (KL) values, suggests that the adsorption process was largely due to physisorption mechanism. Kinetic modeling result followed the pseudo-second order model due to the high linear regression values (R²) obtained and the closeness of the calculated sorption capacity (qcal) to the experimental sorption capacity (qex). In conclusion, the study generally show that bambara groundnut husk (BGH) is a potential low cost and efficient adsorbent that could be explore for the bioremediation of heavy metal contaminated industrial wastewater.
1. Introduction

The global need for a pollution free environment has continued to be abortive, due to incessant release of toxic heavy metal ions from industrial effluents that are detrimental to both flora and fauna. Heavy metals are high priority pollutants because of their relatively high toxic and persistent nature in the environment, although they also occur naturally but rarely at toxic levels [1, 2]. It has been reported that their toxicity due to discharges into the environment from industries such as automobile, battery, pharmaceutical, mining, electroplating, soap and detergents, textile, paint, breweries and electroplating industries et c. far exceeds the combined total toxicity of all radioactive and organic waste [3, 4]. Although small amounts of many heavy metals are necessary in normal biological cycles, most become toxic at high concentrations [5, 6]. These metals in the form of inorganic compounds from natural and anthropogenic sources continuously enter the aquatic ecosystem where they could pose serious threat as they are passed along the food chain. Heavy metals enter the body system through food, air and water and bio-accumulate over a period of time [7, 8]. Excess heavy metal accumulation in the environment has toxicological implication in humans and other animals [9, 10].

Several industrial activities are important sources of environmental pollution due to their high content of several heavy metal ions. Metals such as lead, nickel, cadmium, manganese, chromium, copper, mercury and zine are known to be significantly toxic [11]. In particular, Cd(II) and Pb(II) are common metal ions found in effluents of a large number of industries. However, a chronic exposure to Cd(II) and Pb(II) is detrimental for human health. The toxicological profile of this pollutant has been well documented in literature and their presence in water and wastewaters is a potential risk for the environment and public health [2, 7, 12].

Several techniques have been employed for the remediation of heavy metal contaminated effluents, such as oxidation, coagulation–flocculation, membrane filtration, sedimentation, solvent extraction, ion exchange, reverse osmosis, evaporation, reduction and adsorption [13, 9]. Most of these processes, however, are expensive, inefficient and inapplicable to a wide range of pollutants and generate toxic wastes that are difficult to treat [9, 14].

Adsorption is a generally preferred method for removing heavy metal ions in terms of initial cost, flexibility and simplicity of design, ease of operation, insensitivity to toxic pollutants and the availability of different adsorbents [15, 16]. Furthermore, it does not result in the formation of harmful waste product, a problem with most other methods. Although activated carbon has been the adsorbent of choice for treating wastewater containing heavy metals, because of its favourable adsorption properties [17, 18], it is however very expensive, which limits its widespread use. As a result, many scientists have sought cheaper alternative. Various low-cost adsorbents, derived from agricultural waste, industrial by-product, natural material, or modified biopolymers, algae, clay, zeolites, soil, sawdust [19, 20], and the use of natural and modified forms of montmorillonite have been recently developed and applied for the removal of heavy metals from metal-contaminated wastewater [16, 21].

The increased biomass level of bambara groundnut husk (BGH) and sorghum husk (SH) in the environment through dumping as a refuge due to high consumption rates of these agricultural products has become an environmental concerned due to their land space occupation and subsequent pollution problems. Hence the need for the recycling of this agro-waste for use adsorbent in treatment of heavy metal contaminated wastewater. This will not only be economical but will also help to maintain the quality of the environment. This agricultural wastes is a promising clean up agents that could be harnessed and utilized for treatment of heavy metal contaminated wastewater due to their availability, potential cost-effectiveness, metal binding potential, non-hazardous nature and ease of disposed by incineration [22, 23]. In this study, the adsorption potential of bambara groundnut husk has been investigated.

2. Experimental Methods

2.1. Adsorbent Preparation

The bambara groundnut husk (BGH) was collected from a local farm in Wukari local government area, Taraba State, Nigeria, and then washed with distilled water in a pretreated plastic container with appropriate stirring. The mixture was then filtered through a 500μm mesh sieve and the filtrate was kept for 24 h to settle. Excess water was decanted from the top of the filtrate, and the residue obtained was sun dried for 7 days, oven dried at 105℃ for 4 h, then pulverized to obtain unmodified BGH.

2.2. Characterisation of Adsorbent

Functional group elucidation of the adsorbent was carried out using fourier transformed infrared (FTIR) spectrophometer. The samples were prepared by diluting the adsorbents to 5% KBr and cast into disks for analysis. While scanning electron microscopy (SEM; Hitachi S4800) was carried out to assess the morphology of the adsorbents. Characterisation of the pretreated biomass was done before and after adsorption.

2.3. Preparation of Stock Solution

All the reagents used in the study were of analytical grade obtained from Sigma–Aldrich and were used without further purification. A binary stock solution of 1000 mg/L of Cd(II) and Pb(II) ions was prepared by dissolving appropriate amounts of CdCl₂ and PbCl₂ in 1 L of double-distilled water. Working solutions of 50–500 mg/L were prepared from the stock solution by serial dilution. The pH of each solution was adjusted by drop-wise addition of 0.1 mol/L HCl or NaOH.
2.4. Batch Equilibrium Adsorption Study

Batch adsorption studies were performed by addition of 0.1 g of the adsorbent to 50 mL of a solution of metal ions in a 100mL pretreated plastic bottle at a room temperature of 25±2°C. The effects of the operating conditions pH (2.0–9.0), adsorbent dose (0.1–1g), particle size (<250–500 μm), contact time (20–180 min) and initial metal ion concentration (50–500 mg/L) were investigate [9]. In each experiment, one parameter was varied while the others were kept constant. The solution was filtered at the end of a given contact time, and the concentration of metal ions remaining in the filtrate was determined by atomic absorption spectrophotometer. Each experiment was performed twice and the mean value was computed to minimize error. The amount of metal ions adsorbed was calculated from the following equations adopted from Akpomie and Dowodu, [9]:

\[ q_e = V (Co - Ce) / m \]  \hspace{1cm} (1)

\[ \% Removal = 100 \times [(Co - Ce) / Co] \]  \hspace{1cm} (2)

where \( q_e \) (mg/g) is the adsorption capacity of the adsorbent for the adsorbate at equilibrium, \( Co \) (mg/L) and \( Ce \) (mg/L) are the initial and equilibrium concentrations of metal ions in solution, respectively, \( m \) (g) is the mass of adsorbent, and \( V \) (L) is the volume of solution used.

3. Results and Discussion

3.1. FTIR and SEM Analysis

The FTIR spectra of unmodified bambara groundnut husk (BGH) was determined to identify the surface functional groups responsible for binding of Cd(II) and Pb(II) ions. FTIR spectra for BGH before and after sorption are shown in figures 1 and 2. A broad peak at 3320.57 cm\(^{-1}\) is the indication of –OH and –NH groups. The stretching of the -OH groups bound to methyl radicals is attributed to a signal at 2928.04 cm\(^{-1}\). The peaks at 1653.05 and 1539.26 cm\(^{-1}\) are characteristic of carboxyl group stretching from aldehydes and ketones. The presence of -OH group, along with carboxyl group, is attributed to the presence of carboxylic acid groups in the adsorbent. The peak observed at 1050.28 cm\(^{-1}\) is due to C-O bonds. After sorption there was a shift and broadening of adsorption peaks. The shift of the -OH peak from 3320.57 to 3413.15 cm\(^{-1}\) indicates the involvement of the hydroxyl groups in the adsorption of Cd(II) and Pb(II). While shifting of the carbonyl group peak from 1420.62 to 1428.34cm\(^{-1}\) also show involvement of carboxyl groups in the sorption process. Similar spectra have seem reported for adsorption studies of metal ions using groundnut hull [24], cashew nut shells [25] and palm nut shells [26]. SEM analysis images of unmodified bambara groundnut husk are shown in Fig. 3A&B reveal the porous nature of BGH before sorption. After sorption the adsorbate tends to block the pores decreasing the size.

3.2. Effect of pH

The percentage removal and equilibrium sorption capacity of metal ions is strongly affected by pH [27]. At the same time, the state of chemically binding sites is changed by the solution pH [9]. At low pH, higher concentration and mobility of H\(^+\) ions favour H\(^+\) sorption compared to metal ions, this creates a competition between the protons and metal ions for the binding sites of the adsorbent. According to Onundi et al. [26] metal ions are more soluble in solution at lower pH values and this reduces their sorption. The low sorption of Cd(II) and Pb(II) ions at low pH in this study as shown in figure 4 was therefore due to saturation of binding sites of BGH with hydrogen ions. However, an initial metal sorption observed with increase in pH was due to a decrease in competition between hydrogen ions and metal ions for the adsorbents surface binding sites and also due to decrease in positive surface charge, which resulted in less electrostatic repulsion between the surface and metal ions before ion exchange which is the major mechanism of metal uptake [28]. As the pH of the solution increases, more negatively charged surface becomes available thus facilitating greater metal sorption. Giri et al. [29] reported a similar trend on studies of the effect of pH on the removal of Cr(VI) using Eichhornia crassipes root activated carbon. However, at higher pH metal ions tend to precipitate out of solution. Therefore the removal of metal ions at higher pH values was due to the formation of metal ion precipitates rather than sorption [30].

3.3. Effect of Initial Metal Ion Concentration

The amount of metal ions sorbed is a function of the initial concentration of the metal ion, making it an important factor in effective adsorption. The sorption capacity of BGH for Cd(II) and Pb(II) ions in this study increased with increasing metal ion concentration from 50 to 200mg/l, resulting to an increase metal ion concentration gradient that overcomes the resistance to mass transfer of metal ions between the aqueous phase and the adsorbent [31]. A higher concentration in a solution implies a higher concentration of metal ion to be fixed on the surface of the adsorbent [17]. The high sorption capacity of BGH for Cd(II) and Pb(II) ions as shown figure 5 is possibly attributed to its surface porosity as shown by the SEM images, better still may be due to its larger surface area and good cation exchange capacity. Dowodu and Okpomie, [9] reported a similar observation on simultaneous adsorption of Ni(II) and Mn(II) ions from aqueous solution onto a Nigerian kaolinite clay. A more higher metal concentration saturated the adsorbent sites more quickly thereby decreasing the overall percentage metal removal. A similar trend was observed by [32].

3.4. Effect of Particle Size

The particle size of an adsorbent has a tremendous effect on the sorption process [33]. The increase in the percentage removal of Cd(II) and Pb(II) ions with decreasing sorbent particle size in this study from 1000μm to < 250μm as shown
in figure 6 is attributable to an increase in the surface area of the adsorbent, thus increasing available sites for metal ions binding. The breaking up of larger particles into smaller ones tends to open tiny cracks and channels on the adsorbent surface area, resulting in greater accessibility and better diffusion of the metal ions [9]. Similar results have been reported previously [3, 17, 31].

3.5. Effect of Dosage

Adsorbent dosage has proved to be a useful parameter for determining the capacity of an adsorbent for a given initial metal ion concentration. The percentage removal of Cd(II) and Pb(II) ions in this study, increased with increasing adsorbent dosage from 0.1-1g, due mainly to an increase in the number of available exchangeable binding sites for metal ion sorption [33]. However, the equilibrium sorption capacity per unit mass of the adsorbent decreased considerably with increase in sorbent dose for both metal ions as shown in figure 7. This may be due to a decrease in the total sorption surface area available to the metal ions, possibly caused by the aggregation/agglomeration of sorption sites, as a result the sorption capacity of the adsorbent is not fully utilised [34]. Conversely, a higher adsorbent dose may also provide more active sorption sites, so that sorption sites remain unsaturated, leading to their full utilization as reported by Barka et al., [17].

Figure 1. FTIR spectra of bambara groundnut husk before sorption.

Figure 2. FTIR spectra of bambara groundnut husk after sorption.

Figure 3. A&B: Scanning electron microscopy (SEM) image of bambara groundnut husk (A) before and (B) after sorption.
3.6. Equilibrium Isotherm Modeling

Equilibrium adsorption isotherms are used to show the relationship between adsorbate concentration in solution and the amount on the adsorbent at equilibrium [35]. These parameters often provide fundamental information on the sorption mechanism, surface properties and the affinity of adsorbents, which helps to determine the applicability of sorption as a unit operation [9]. Therefore, it is important to establish the most suitable correlation of equilibrium curves in order to optimize the conditions for designing adsorption systems. The most frequently used isotherms, the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich models, were therefore used to analyse the data (Table 1).

3.6.1. The Langmuir Isotherm

This model describes monolayer adsorption onto the surface of an adsorbent with a finite number of identical adsorption sites and no interaction between sites. The model is expressed as [36]:

$$\frac{C_e}{q_e} = \frac{1}{q_L} + \frac{C_e}{q_L K_L}$$  \hspace{1cm} (3)

Where $q_L$ (mg/g) is the monolayer adsorption capacity of the adsorbent, and $K_L$ (L/mg) is the adsorption constant, which reflects the affinity between the adsorbent and adsorbate. $q_L$ and $K_L$ were determined from the slope and intercept of the plots of $C_e/q_e$ versus $C_e$. An essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor ($R_L$), defined as:

$$R_L = \frac{1}{1 + K_L C_0}$$  \hspace{1cm} (4)

Adsorption is said to be favourable if $0 < R_L < 1$ and unfavourable if $R_L > 1$. Table 1 shows high correlation coefficients ($r^2$) of 0.997 for Cd(II) and 0.910 for Pb(II), indicating that the adsorption followed the Langmuir isotherm closely. A favourable adsorption process was, also indicated by the $R_L$ values, that ranged between 0.5578-0.2478 for Cd(II) and 0.2770-0.0822 for Pb(II) at all concentrations studied as shown in table 2.

3.6.2. The Freundlich Isotherm

This model describes monolayer adsorption onto the surface of an adsorbent with a finite number of identical adsorption sites and no interaction between sites. The model is expressed as [36]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$  \hspace{1cm} (5)

Where $q_L$ (mg/g) is the monolayer adsorption capacity of the adsorbent, and $K_F$ (L/mg) is the adsorption constant, which reflects the affinity between the adsorbent and adsorbate. $q_L$ and $K_F$ were determined from the slope and intercept of the plots of $C_e/q_e$ versus $C_e$. An essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor ($R_L$), defined as:

$$R_L = \frac{1}{1 + K_F C_0}$$  \hspace{1cm} (4)

Adsorption is said to be favourable if $0 < R_L < 1$ and unfavourable if $R_L > 1$. Table 1 shows high correlation coefficients ($r^2$) of 0.997 for Cd(II) and 0.910 for Pb(II), indicating that the adsorption followed the Langmuir isotherm closely. A favourable adsorption process was, also indicated by the $R_L$ values, that ranged between 0.5578-0.2478 for Cd(II) and 0.2770-0.0822 for Pb(II) at all concentrations studied as shown in table 2.
3.6.3. The Temkin Isotherm
This model is based on the assumption that the free energy of adsorption is a function of the surface coverage; it is expressed as [39]:

$$q_e = B \ln A + B \ln C_e$$ \hspace{1cm} (6)

Where $$B = RT/b$$ (mg/g) is the isotherm constant related to the heat of adsorption, and $$A$$ (L/g) is the equilibrium binding constant corresponding to the maximum binding energy, $$R$$ is the gas constant and $$T$$ (K) is absolute temperature. The constants $$A$$ and $$B$$ as shown in Table 1 were determined from the plot of $$q_e$$ versus $$\ln C_e$$. The $$r^2$$ values obtained (Table 1) for both metal ions showed a poor fit for the data compared to the Langmuir and Freundlich models.

3.6.4. The Dubinin–Radushkevich Isotherm
This model does not assume a homogeneous surface or a constant adsorption potential and is expressed as [40]:

$$\ln q_e = \ln q_m - \beta e^2$$ \hspace{1cm} (7)

Where $$q_m$$ (mg/g) is the theoretical saturation capacity, $$\beta$$ (mol$$^2$/J$$^2$$) is a coefficient related to the mean free energy of adsorption, and $$e$$ is the Polanyi expressed as:

$$e = RT \ln(1 + 1/C_e)$$ \hspace{1cm} (8)

The constants $$q_m$$ and $$\beta$$ were calculated from the intercept and slope of $$\ln q_e$$ versus $$e^2$$. The isotherm provided a poor fit to the experimental data, as indicated by the $$r^2$$ values shown in Table 1. Furthermore, the low values of the apparent energy $$E$$ (kJ/mol) of all the metal ions as shown in Table 2 were below 8 kJ/mol, suggesting that the adsorption was largely due to physisorption mechanism. This is similar to the results from previous studies [9, 17, 41].

Therefore, the adsorption of Cd(II) and Pb(II) ions onto bambara groundnut husk conformed best to the adsorption isotherm models in the order Langmuir > Freundlich > Temkin > Dubinin–Radushkevich isotherm. The differences in the adsorbed amounts deduced from the four models are simply a result of the different equations for analysing the experimental data. Similar results have been reported by many researchers [9, 17, 42, 43].

Table 1. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm parameters for the sorption of Cd(II) and Pb(II) ions onto bambara groundnut husk (BGH).

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Bambara groundnut husk (BGH)</th>
<th>Cd (II)</th>
<th>Pb (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir model</td>
<td>$$q_e$$ (mg/g)</td>
<td>6.944</td>
<td>13.51</td>
</tr>
<tr>
<td></td>
<td>$$A$$ (L/mg)</td>
<td>0.123</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>$$B$$</td>
<td>0.997</td>
<td>0.910</td>
</tr>
<tr>
<td></td>
<td>$$R^2$$</td>
<td>0.247</td>
<td>0.082</td>
</tr>
<tr>
<td>Freundlich model</td>
<td>$$K_F$$ (L/g)</td>
<td>0.389</td>
<td>0.538</td>
</tr>
<tr>
<td></td>
<td>$$1/n$$</td>
<td>0.616</td>
<td>0.201</td>
</tr>
<tr>
<td></td>
<td>$$N$$</td>
<td>1.623</td>
<td>4.975</td>
</tr>
<tr>
<td></td>
<td>$$R^2$$</td>
<td>0.979</td>
<td>0.800</td>
</tr>
<tr>
<td>Temkin model</td>
<td>$$q_m$$ (mg/g)</td>
<td>5.954</td>
<td>11.156</td>
</tr>
<tr>
<td></td>
<td>$$B$$ (mol$$^2$/J$$^2$$)</td>
<td>1 x 10$$^4$$</td>
<td>2 x 10$$^5$$</td>
</tr>
<tr>
<td></td>
<td>$$E$$ (kJ/mol)</td>
<td>0.529</td>
<td>0.4553</td>
</tr>
<tr>
<td></td>
<td>$$r^2$$</td>
<td>0.994</td>
<td>0.792</td>
</tr>
</tbody>
</table>

Table 2. Values for the separation factor ($$R_s$$) of BGH at different initial metal ion concentrations of Cd(II) and Pb(II).

<table>
<thead>
<tr>
<th>Initial conc.(mg/l)</th>
<th>BGH $$R_s$$ values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd (II)</td>
</tr>
<tr>
<td>52.5</td>
<td>0.5578</td>
</tr>
<tr>
<td>61.5</td>
<td>0.5185</td>
</tr>
<tr>
<td>122.0</td>
<td>0.3514</td>
</tr>
<tr>
<td>179.0</td>
<td>0.2701</td>
</tr>
<tr>
<td>201.0</td>
<td>0.2478</td>
</tr>
</tbody>
</table>

3.7. Effect of Contact Time
The effect of contact time on the adsorption of Cd(II) and Pb(II) ions onto bambara groundnut husk is shown in Fig. 8. An initial increase in percentage removal with increased contact time from 5-60 minutes was observed, and adsorption became fairly stable over time. Equilibrium removal was achieved around 60 min for Cd(II) and 80 min for Pb(II), after which further increases in contact time did not result in significant adsorption. Maximum adsorption was achieved at 120 min for both metal ions, and this time was used in all experiments to ensure maximum removal. The faster removal rate with Cd(II) than with Pb(II) may be due to the smaller ionic radius of Cd(II) (0.72 Å) than Pb(II) (0.80 Å), which makes for easier, more rapid diffusion to the surface of the adsorbent. The rapid adsorption during the initial stages might be due to the presence of abundant active sites on the surface of bambara groundnut husk, which become saturated with time. Initially, sorption is controlled mainly by diffusion from the bulk to the surface of the adsorbent, whereas, later, sorption is probably an attachment-controlled process due to the presence of fewer active sites [9, 44].

3.8. Kinetic Modeling
The kinetic mechanism controlling adsorption was investigated with pseudo-first order, pseudo-second order, and intraparticle diffusion rate equations. The kinetic parameters are shown in Table 3.

3.8.1 The Pseudo-First Order or Lagergern Equation
This is based on the assumption that the rate of adsorption site occupation is proportional to the number of unoccupied sites [39]. The linear form of the Lagergren equation is given as:

$$\log(q_e - qt) = \log q_e - (K_t \cdot t)/2.303$$ \hspace{1cm} (9)

Where $$K_t$$ (min$$^{-1}$$) is the rate constant and $$qt$$ and $$q_e$$ are the
amounts of metal ion adsorbed at time t (min) and equilibrium respectively. The constant $K_i$ and $q_{cal}$ (calculated sorption capacity) as presented in table 3 were obtained from the slope and intercept of the plot of log ($q_e - q_t$) versus $t$. The model presented a good fit to the kinetic data on $r^2$ values obtained for the two metal ions as shown in table 3. However, the values of the calculated sorption capacity ($q_{cal}$) were lower than those of experimental sorption capacity ($q_{exp}$) obtained, indicating a disagreement as also reported by Das and Mondel [31] and Dawodu and Okpomie [9].

### 3.8.2. The Pseudo-second Order Kinetic Model

The model is based on the assumption that chemisorption is the rate determining step, provided a good fit to the experimental data as can be seen from the very high linear regression ($R^2$) values (table 3). Several studies have also reported high regression ($R^2$) values for this model [3, 31, 45]. The values of $q_{cal}$ for pseudo-second order were almost equivalent to the experimental values ($q_{exp}$) obtained, confirming it as the model that best described the kinetic mechanism of the removal of Cd(II) and (Pb) ions from wastewater in this study. This has also been reported in several studies [9, 17, 31, 35].

### 3.8.3. Intra-Particle Diffusion

This is the sole rate-determining step if the plot is linear and passes through the origin. The presence of the intercept ($I$), as shown in table 3 means the plots did not pass through the origin. This deviation from the origin is due to the difference in the rate of mass transfer in the initial and final stages of the adsorption process [45]. The good regression of both metal ions (close to 1) showed the existence of intraparticle diffusion mechanism in the sorption of Cd(II) and Pb(II) ions onto BGH. Moreover, occurrence of the intercept $C$ shows the existence of a boundary layer effect, indicating a surface phenomenon such as mass transfer or liquid film diffusion during the sorption process. Dawodu and Okpomie, [9] reported a similar observation on simultaneous adsorption of Ni(II) and Mn(II) ions from aqueous solution onto a Nigerian kaolinite clay.

### Table 3. Kinetic Parameters for the Adsorption of Cd(II) and Pb(II) onto Bambara groundnut husk and Sorghum husk.

<table>
<thead>
<tr>
<th>Models</th>
<th>Bambara groundnut husk (BGH)</th>
<th>Sorghum husk (SH)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd (II)</td>
<td>Pb(II)</td>
</tr>
<tr>
<td>$q_{exp}$ (mg/g)</td>
<td>7.5</td>
<td>8.0</td>
</tr>
<tr>
<td>Pseudo-first order</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_{cal}$ (mg/g)</td>
<td>2.974</td>
<td>4.481</td>
</tr>
<tr>
<td>$K_i$ (min$^{-1}$)</td>
<td>0.025</td>
<td>0.013</td>
</tr>
<tr>
<td>$R^2$</td>
<td>7.100</td>
<td>9.400</td>
</tr>
<tr>
<td>Pseudo-second order</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_{cal}$ (mg/g)</td>
<td>7.752</td>
<td>9.522</td>
</tr>
<tr>
<td>$K_i$ (g/mg·min$^{-1}$)</td>
<td>0.023</td>
<td>0.011</td>
</tr>
<tr>
<td>$h$ (mg/g/min)</td>
<td>1.399</td>
<td>0.996</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.992</td>
<td>0.952</td>
</tr>
<tr>
<td>Intraparticle diffusion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_d$ (mg/g min$^{-1}$)</td>
<td>0.327</td>
<td>0.449</td>
</tr>
<tr>
<td>$C$</td>
<td>4.251</td>
<td>3.382</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.959</td>
<td>0.945</td>
</tr>
</tbody>
</table>

Where $q_{exp}$ (mg/g) is the experimental adsorption capacity and $q_{cal}$ (mg/g) is the calculated sorption capacity.

### 4. Conclusion

This study has demonstrated favourable properties of bambara groundnut husk for the bioremediation of Pb(II) and Cd(II) ions from wastewater through batch adsorption studies. The adsorption of lead and cadmium ions in this study was highly dependent on experimental parameters such as contact time, initial metal concentration, pH, adsorbent dosage and particle sizes. Following the isotherm modeling of the experimental data, Langmuir isotherm model provided the best fit to the experimental data of the adsorption of Cd(II) and Pb(II) ions compared to the other isotherm models tested. The D-R isotherm model suggested that the process was mainly due to physisorption mechanism based on the low values of the apparent energy (<8kJ/mol) of adsorption. While pseudo-second order model provided the best fit to the experimental data after kinetic modeling, implying that the adsorption process followed a second order rate mechanism. It could therefore be inferred from this study that bambara groundnut husk is a potential low-cost, efficient, ecofriendly and active adsorbent that could be harnessed for the bioremediation of wastewater and industrial effluent contaminated with heavy metal ions.

### References


