Biosorption of Cd$^{2+}$, Ni$^{2+}$ and Pb$^{2+}$ by the shell of *pentaclethra macrophylla*: equilibrium isotherm studies

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**ABSTRACT**

Pretreatment of the seed shell of Pentaclethra macrophylla Benth was carried out using 0.3 mol of thioglycollic acid. Biosorption analysis was conducted using different variations in the initial metal ion concentrations (100, 80, 60, 40, 20, and 10) mg/l at pH of neutral point, room temperature, contact time of 1 hr using 1 gram of the 250 mesh size of both the untreated and treated Pentaclethra macrophylla seed shells. Biosorption capacity of Pentaclethra macrophylla seed shell was observed to be high with increasing higher concentrations of the metal ions in both treated and untreated Pentaclethra macrophylla seed shells though maximum concentrations of Cd$^{2+}$ and Pb$^{2+}$ sorbed were observed by untreated Pentaclethra macrophylla seed shell while Ni$^{2+}$ was highly sorbed by the treated Pentaclethra macrophylla seed shell. Data gotten via study gave good fit for different sorption isotherms such as Freundlich, Temkin and Dubinin-Radushkevich (D-RIM). Multilayer biosorption with non-uniform distribution over the heterogeneous surface was observed and the biosorption of the metal ions onto untreated and treated Pentaclethra macrophylla seed shells was spontaneous and was consistent with the pattern of physical adsorption.

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**I. Introduction**

The quest for safer method in remediating industrial wastewater contaminated with toxic heavy metals has made biosorption (unconventional method) to come into play. According to Volesky (1990),...
biosorption is a process by which metals in solution adhere to the surface of a biomass through physico-chemical interactions and ion-exchange adsorption (Gad and White, 1993). Nowadays, environmental biotechnology uses this process to reduce the concentrations of these trace metals in industrial wastewaters to permissible level. In biosorption process, the metal ions in solution will be moved to the cell wall of the biomass due to the presence of their opposite charges and adsorb through various means until equilibrium is achieved. Level of attractions of these ions determines their distributions. Biosorption is a feasible process that is highly advantageous (Wilde and Benemann, 1993; Schiewer and Volesky 1995; Kratochvil and Volesky, 1998a; USEPA, 2000; Biowise, 2003; Aboulroos et al., 2006). Despite the quite extensive literature available on metal biosorption by different biosorbents, little attention seems to have been given to the study of multiple-metal biosorption by the Pentaclethra macrophylla seed shell. The present study aims to confirm the biosorption of the Pentaclethra macrophylla seed shell as a cost effective metal biosorbent for Cd2+, Ni2+ and Pb2+ removal and equally explain the adsorption equilibrium through different adsorption isotherms and kinetic models.

II. Materials and Methods

Pentaclethra macrophylla was obtained from Umuahia main Market, Abia State and processed to get the shell. The shell was ground into tiny particle size using manual grinder and sieved through a test-sieve shaker after washing with deionized water and drying in oven at 50 °C for 12hrs to get 250 μm mesh size. It was then activated by soaking in 2% (v/v) dilute nitric acid solution for 24 hours, filtered, rinsed severally with de-ionized water and allowed to dry in the oven at 105 °C for about 6 hours. Hence labeled unmodified sample. About 15 g portion of the activated sample was modified using mercarptoacetic acid by soaking the sample into 1000 cm³ of 0.3 mol mercarptoacetic acid for 2hrs at 25 °C, filtered, rinsed with de-ionized water and finally dried at 50 °C for 12 hence, labeled modified sample.

Preparation of adsorbate solutions (metal ion solutions): Chemicals used in the experiment were analytical grade reagents. CdCl₂, NiSO₄.6H₂O and Pb(NO₃)₂ salts were used as the source of Cd²⁺, Ni²⁺ and Pb²⁺ and all the solutions were made in deionized water. The solutions of Cd²⁺, Ni²⁺ and Pb²⁺ were prepared from a stock solution containing 1000 mg/l of Cd²⁺, Ni²⁺ and Pb²⁺ respectively. This was done by dissolving one gram (1 g) of each salt in 1000 cm³ of deionized water and made up to the mark of the volumetric flask. Each of these solutions represented the metal ion solution (wastewater) of 1000 mg/l concentration. From the stock solutions of 1000 mg/l, various aliquots (5, 4, 3, 2, 1 and 0.5) cm³ were pipetted into beakers and made up to the mark of 50 ml volume with deionized water to give a range of concentrations between 100 and 10 mg/ml (i.e., 100, 80, 60, 40, 20and 10) mg/l. The initial concentration of metal ion solutions used for the biosorption study on investigating the effects of time was 100 mg/l (prepared as an aliquot from the stock of 1000 mg/l of the various metal ions). The concentrations of 80, 60, 40, 20 and 10 mg/l (prepared from stock by serial dilution) as initial concentrations were used to investigate the effect of variation in the initial concentrations of metal ions on biosorption.

Biosorption experiment: Equilibrium biosorption experiment was performed under the following experimental conditions of initial metal ion concentrations (100, 80, 60, 40, 20, and 10) mg/l.

Effect of initial metal ion concentration on the biosorption of Cd²⁺, Ni²⁺ and Pb²⁺: Equilibrium biosorption of Cd²⁺, Ni²⁺ and Pb²⁺ onto the Pentaclethra macrophylla seed shell was carried out using 50 cm³ of various concentrations (100, 80, 60, 40, 20, and 10 mg/l) at constant metal ion-substrate contact period of 1 hour, at a temperature of 25 °C and pH of 7.5. 1 gram (250 μm size) of the shell was put into the 50 cm³ of each of the metal ion solutions of specified (varied) concentrations and the mixture shaken intermittently with a rotating shaker for 1 hour. The solution mixtures were filtered rapidly into separate sample bottles using Whatman 42 filter paper. Filtrates were analyzed for residual metals using Atomic Absorption Spectrophotometer (Buck model 200A). The equilibrium (final) concentration of each metal ion was determined using Atomic Absorption Spectrophotometer (Buck model 200A). The described procedure for the parameter was carried out (repeated) for the biosorption of Cd²⁺, Ni²⁺ and
Pb\(^{2+}\) onto unmodified and modified *Pentaclethra macrophylla* seed shell. The amounts of Cd\(^{2+}\), Ni\(^{2+}\) and Pb\(^{2+}\) adsorbed by the adsorbents during the series of batch investigations were determined using a simplified mass balance equation as expressed by *(Bhatti et al., 2007)*,

\[
Q_e = C_o - C_e
\]  

(01)

Where, \(Q_e\) = amount adsorbed (mg/g) by the adsorbents at equilibrium or metal ion concentration on adsorbent at equilibrium, \(C_e\) = metal ion concentration (mg/l) (final concentration) in the solution (of the filtrate) at equilibrium while \(C_o\) = initial metal ion concentration (mg/l) in solution used.

### III. Results and Discussion

**Effect of concentration of heavy metal on biosorption**

The data for the amount of Cd\(^{2+}\), Ni\(^{2+}\) and Pb\(^{2+}\) adsorbed by the shell of *Pentaclethra macrophylla* seed from aqueous solutions containing various concentrations of the metals at a temperature of 298 K are presented in Table 01 and equally in Figure 01.

**Table 01. Heavy metal ions adsorbed by unmodified and modified Pentaclethra macrophylla seed shell from aqueous solution, containing various concentrations of the metals temperature of 298K**

<table>
<thead>
<tr>
<th>Concentrations (mg/l)</th>
<th>Unmodified (OBS)</th>
<th>Modified (OBS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd(^{2+}) (mg/g)</td>
<td>Ni(^{2+}) (mg/g)</td>
</tr>
<tr>
<td>10</td>
<td>8.327±0.123</td>
<td>8.520±0.044</td>
</tr>
<tr>
<td>20</td>
<td>13.345±1.787</td>
<td>17.418±0.125</td>
</tr>
<tr>
<td>40</td>
<td>39.386±0.296</td>
<td>39.999±0.999</td>
</tr>
<tr>
<td>60</td>
<td>59.419±0.073</td>
<td>59.999±0.310</td>
</tr>
<tr>
<td>80</td>
<td>79.375±0.729</td>
<td>77.403±0.076</td>
</tr>
<tr>
<td>100</td>
<td>99.449±0.603</td>
<td>96.935±0.424</td>
</tr>
</tbody>
</table>
Figure 01. Equilibrium biosorption capacities of Cd(II), Ni(II) and Pb(II) ions onto unmodified and modified Pentaclethra macrophylla seed shell for the effect of initial metal ion concentration variation.

It was observed that the biosorption capacity of Pentaclethra macrophylla seed shell increases with increase in the concentration of metal ion in solution indicating that at higher concentrations of the metals, adsorption is enhanced by competitive diffusion (Table 01). The maximum concentrations of Cd\(^{2+}\) and Pb\(^{2+}\) adsorbed by unmodified Pentaclethra macrophylla seed shell Table 01, also revealed that (Cd\(^{2+}\) = 99.45 mg/g; Pb\(^{2+}\) = 99.31 mg/g) were slightly higher than those biosorbed by modified one (Cd\(^{2+}\) = 98.35; Pb\(^{2+}\) = 94.72 mg/g) indicating that modification reduces the biosorption capacity of the shell for Pb\(^{2+}\) and Cd\(^{2+}\). Concentrations of Ni\(^{2+}\) biosorbed by unmodified shell (96.94 mg/l) was lower than the concentration biosorbed by modified one (99.07 mg/g) indicating that modification of Pentaclethra macrophylla seed shell increases its biosorption capacity for Ni\(^{2+}\).

From the results presented in Table 01, it is evident that the extent of biosorption of Cd\(^{2+}\), Ni\(^{2+}\) and Pb\(^{2+}\) by unmodified and modified Pentaclethra macrophylla seed shell increases with increase in concentration. The relationship between the degree of surface coverage and concentration of biosorbent at constant temperature is often treated in terms of adsorption isotherms. Data obtained from the study were fitted into different adsorption isotherms and from the results obtained, the best isotherms that described the biosorption characteristics of Cd\(^{2+}\), Ni\(^{2+}\) and Pb\(^{2+}\) onto Pentaclethra macrophylla seed shell are Freundlich and Temkin adsorption isotherms. The expression establishing the Freundlich adsorption isotherm can be written as follows (Foo and Hameed, 2010):

\[
q_e = \frac{1}{K_F C_e^n} 
\]  

(02)

Where, \(q_e\) is the amount of adsorbate in the adsorbent at equilibrium (mg/g), \(K_F\) is the Freundlich adsorption constant (mg/g) (dm\(^3\)/g)\(^n\) related to the adsorption capacity and \(C_e\) is the equilibrium concentration of the adsorbate (mg/l). Simplification and linearizing equation 02 yielded equation 03,
From equation 03, the Freundlich isotherm plot is fitted by plotting values of log \( q_e \) against log \( C_e \) and the slope of the plot should be equal to the reciprocal of \( n \) while the intercept should be equal to KF. Figure 02 and 03 show the Freundlich adsorption isotherms for the biosorption of Cd\(^{2+}\), Ni\(^{2+}\) and Pb\(^{2+}\) by \textit{Pentaclethra macrophylla} seed shell before and after modification respectively.

![Figure 02](image1.png)

**Figure 02.** Plot for Freundlich isotherm model for the biosorption Cd(II), Ni(II) and Pb(II) ions onto unmodified \textit{Pentaclethra macrophylla} seed shell.

![Figure 03](image2.png)

**Figure 03.** Plot for Freundlich isotherm model for the biosorption Cd(II), Ni(II) and Pb(II) ions onto modified \textit{Pentaclethra macrophylla} seed shell.

Values of Freundlich adsorption parameters deduced from the plots are presented in Table 02. From the results obtained, it can be seen that values of \( R^2 \) approached unity in all cases indicating the application of Freundlich adsorption model for the biosorption of Cd\(^{2+}\), Ni\(^{2+}\) and Pb\(^{2+}\) by unmodified and modified...
Pentaclethra macrophylla seed shell. The suitability of the Freundlich isotherm to the adsorption of the studied ions also implies that there is multilayer adsorption with non-uniform distribution over the heterogeneous surface (Adamson and Gast, 1997). According to Haghseresht and Lu, the value of 1/n is an index for measuring the adsorption intensity (Haghseresht and Lu, 1998). Generally, when the value of 1/n is in the range, 0 to 1, is a measure of the adsorption intensity or surface heterogeneity. The surface becomes more heterogeneous as the value of n tend towards 0 (Foo and Hameed, 2012). On the other hand, 1/n value less than unity suggest chemisorption mechanism whereas 1/n value above unity point toward co-operative adsorption. Therefore, the adsorption of Cd$^{2+}$, Ni$^{2+}$ and Pb$^{2+}$ supports the mechanism of physical adsorption since values of 1/n are approximately unity (Table 02).

It has been found that the Freundlich adsorption constant ($K_F$) is related to the free energy of adsorption according to the following equation (Mittal et al., 2007),

$$\Delta G_{ads}^0 = -2303RT \log K_F$$  \hspace{1cm} (04)

Where, R is the universal gas constant and T is the temperature. Values of calculated from equation 4 are also presented in Table 02. From the results obtained, it can be seen that the free energies values are negatively less than the threshold value needed for the mechanism of chemisorption. Therefore the adsorption of Cd$^{2+}$, Ni$^{2+}$ and Pb$^{2+}$ unto unmodified and modified Pentaclethra macrophylla seed shell is spontaneous and is consistent with the mechanism of physical adsorption.

Table 02. Freundlich parameters for the biosorption of Cd$^{2+}$, Ni$^{2+}$ and Pb$^{2+}$ by unmodified and modified Pentaclethra macrophylla seed shell (Pmss)

<table>
<thead>
<tr>
<th>System</th>
<th>Ions</th>
<th>Slope</th>
<th>Intercept</th>
<th>1/n</th>
<th>$\Delta G^0$ (J/mol)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pmss</td>
<td>Cd(UM)</td>
<td>1.132</td>
<td>-0.2562</td>
<td>0.88</td>
<td>-1486.4</td>
<td>0.9872</td>
</tr>
<tr>
<td></td>
<td>Ni(UM)</td>
<td>1.0676</td>
<td>-0.1342</td>
<td>0.94</td>
<td>-778.57</td>
<td>0.9984</td>
</tr>
<tr>
<td></td>
<td>Pb(UM)</td>
<td>1.0016</td>
<td>-0.0067</td>
<td>1</td>
<td>-38.87</td>
<td>1</td>
</tr>
<tr>
<td>Pmss</td>
<td>Cd(M)</td>
<td>1.073</td>
<td>-0.138</td>
<td>0.93</td>
<td>-800.62</td>
<td>0.9986</td>
</tr>
<tr>
<td></td>
<td>Ni(M)</td>
<td>1.0727</td>
<td>-0.1411</td>
<td>0.93</td>
<td>-818.6</td>
<td>0.9994</td>
</tr>
<tr>
<td></td>
<td>Pb(M)</td>
<td>1.0727</td>
<td>-0.1411</td>
<td>0.93</td>
<td>-818.6</td>
<td>0.9994</td>
</tr>
</tbody>
</table>

The biosorption of Cd$^{2+}$, Ni$^{2+}$ and Pb$^{2+}$ unto modified and unmodified Pentaclethra macrophylla seed shell was also found to obeyed the Temkin adsorption model, which can be written as follows (Foo and Hameed, 2012),

$$q_e = \frac{RT}{b_T} \ln A_r \cdot C_e$$  \hspace{1cm} (05)

Where, $q_e$ is the amount of adsorbate in the adsorbent at equilibrium, R is the gas constant, T is the temperature, $b_T$ is the Temkin isotherm constant, $A_r$ is the Temkin isotherm equilibrium binding constant and $C_e$ is the equilibrium concentration. Equation 05 can be simplified to a linear form as follows,

$$q_e = \frac{RT}{b_T} \ln A_r + \frac{RT}{b_T} \ln C_e$$ \hspace{1cm} (0 6)

From equation 06, a plot of $q_e$ versus $\ln C_e$ should be linear with slope and intercept equal to and $\ln A_r$ respectively. Figure 04 shows the Temkin isotherm for the adsorption of Cd$^{2+}$, Ni$^{2+}$ and Pb$^{2+}$ by unmodified and modified Pentaclethra macrophylla seed shells respectively.
R² values (Table 03) shown below calculated from the plots were very close to unity indicating the application of the Temkin isotherm for the adsorption of Cd²⁺, Ni²⁺ and Pb²⁺ by the shells. Bₜ values were positive and relatively low indicating the attractive behavior of the biosorbent. Generally, the higher the value of bₜ, the higher the degree of interaction between the adsorbate and the adsorbent. The present data strongly point toward a relatively weak interaction, which also supports the mechanism of physical adsorption. The Temkin equilibrium constant can be used to estimate the free energy of adsorption of the heavy metal ions using the following equation,

\[
\Delta G_{ads}^0 = -2.303RT \log A_r
\]  

(07)

Values of ΔG_{ads}^0 calculated from equation 07 are also recorded in Table 03. From the results obtained, the free energies are negatively less than the threshold value expected for the mechanism of chemical adsorption, which also confirms that, the adsorption of Cd²⁺, Pb²⁺ and Ni²⁺ onto unmodified and modified Pentaclethra macrophylla seed shells is consistent with mechanism of physical adsorption.

Figure 04. Variation of qₑ with log Cₑ for the adsorption of Cd²⁺, Ni²⁺ and Pb²⁺ by unmodified and modified Pentaclethra macrophylla seed shells.
Table 03. Temkin parameters for the adsorption of Cd$^{2+}$, Ni$^{2+}$ and Pb$^{2+}$ by unmodified and unmodified *Pentaclethra macrophylla* seed shells

<table>
<thead>
<tr>
<th>System</th>
<th>Ions</th>
<th>Slope</th>
<th>Intercept</th>
<th>lnA$_r$</th>
<th>A$_r$</th>
<th>b$_T$</th>
<th>$\Delta G^0$ (J/mol)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pmss</td>
<td>Cd(UM)</td>
<td>90.456</td>
<td>-94.610</td>
<td>-1.046</td>
<td>0.351</td>
<td>27.8494</td>
<td>-2634.8</td>
<td>0.9101</td>
</tr>
<tr>
<td></td>
<td>Ni(UM)</td>
<td>86.596</td>
<td>-88.281</td>
<td>-1.019</td>
<td>0.361</td>
<td>29.0907</td>
<td>-2568.2</td>
<td>0.9259</td>
</tr>
<tr>
<td></td>
<td>Pb(UM)</td>
<td>86.798</td>
<td>-87.462</td>
<td>-1.008</td>
<td>0.365</td>
<td>29.0230</td>
<td>-2538.4</td>
<td>0.9149</td>
</tr>
<tr>
<td>Pmss</td>
<td>Cd(M)</td>
<td>87.729</td>
<td>-89.480</td>
<td>-1.020</td>
<td>0.361</td>
<td>28.7150</td>
<td>-2569.4</td>
<td>0.9233</td>
</tr>
<tr>
<td></td>
<td>Ni(M)</td>
<td>81.382</td>
<td>-82.357</td>
<td>-1.012</td>
<td>0.363</td>
<td>30.9545</td>
<td>-2549.3</td>
<td>0.9058</td>
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<tr>
<td></td>
<td>Pb(M)</td>
<td>81.382</td>
<td>-82.357</td>
<td>-1.012</td>
<td>0.363</td>
<td>30.9545</td>
<td>-2549.3</td>
<td>0.9056</td>
</tr>
</tbody>
</table>

Distinction between physical and chemical adsorption can be confirmed through the Dubinin-Radushkevich (D-RIM) adsorption isotherm, which can be expressed according to equation (Noor, 2009),

$$\ln q_e = \ln Q_{max} - a\sigma^2$$  \hspace{1cm} (08)

Where, $Q_{max}$ is the maximum surface coverage and $\sigma$ is the Polanyi potential and can be estimated from the following equation,

$$\sigma = \frac{RT\ln\left(1 + \frac{1}{Ce}\right)}{2}$$  \hspace{1cm} (09)

Where, $R$ is the gas constant (8.31 J mol$^{-1}$K$^{-1}$) and $T$ is the temperature (K). From equation 08, a plot of $\ln q_e$ versus $\sigma^2$ should give a straight line with slope equals to a constant, ‘a’. This constant, ‘a’ can be defined as half the square of the reciprocal of the mean adsorption energy (i.e. $a = \frac{1}{2}\left(1/E\right)^2$. It has been found that E value less than 8 kJ/mol supports the mechanism of physical adsorption but E values greater than 8 kJ/mol are consistent with the mechanism of chemisorption. Fig. 05 shows D-RIM isotherm for the adsorption of Cd$^{2+}$, Ni$^{2+}$ and Pb$^{2+}$ by unmodified and modified *Pentaclethra macrophylla* seed shells. $R^2$ values for the plots (Table 04) were very close to unity while the value of E (707 J/mol) was constant (Table 04) for all the systems indicating that the mechanism of physical adsorption is more likely.

![Figure 05. Dubinin-Radushkevich isotherm for the adsorption of Cd$^{2+}$, Ni$^{2+}$ and Pb$^{2+}$ by unmodified and modified *Pentaclethra macrophylla* seed shells](image-url)
Table 04. Dubinin-Radushkevich parameters for the adsorption of Cd$^{2+}$, Ni$^{2+}$ and Pb$^{2+}$ by unmodified and modified Pentaclethra macrophylla seed shells (Pmss)

<table>
<thead>
<tr>
<th>System</th>
<th>Ions</th>
<th>Slope</th>
<th>Intercept</th>
<th>E (J/mol)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pmss</td>
<td>Cd(M)</td>
<td>0.0001</td>
<td>4.3855</td>
<td>7.07E+01</td>
<td>0.8705</td>
</tr>
<tr>
<td></td>
<td>Ni(M)</td>
<td>0.0001</td>
<td>4.3782</td>
<td>7.07E+01</td>
<td>0.8672</td>
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<tr>
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<td>Pb(M)</td>
<td>0.0001</td>
<td>4.3679</td>
<td>7.07E+01</td>
<td>0.8939</td>
</tr>
<tr>
<td>Pmss</td>
<td>Cd(UM)</td>
<td>0.0001</td>
<td>4.4292</td>
<td>7.07E+01</td>
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<td>Ni(UM)</td>
<td>0.0001</td>
<td>4.4016</td>
<td>7.07E+01</td>
<td>0.9512</td>
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<tr>
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<td>Pb(UM)</td>
<td>0.0001</td>
<td>4.3761</td>
<td>7.07E+01</td>
<td>0.8705</td>
</tr>
</tbody>
</table>

IV. Conclusion

Biosorption process is a general acceptable method hence, highly advantageous. This research examined the effect of both untreated and treated Pentaclethra macrophylla seed shells on biosorption of metal ion using concentrations of the initial metal ion as the important experimental condition. From every indication as observed, untreated Pentaclethra macrophylla seed shell had proven better, and could be used effectively in the treatment of metal bearing effluents.

Acknowledgement

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VI. Reference

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