Usefulness of *Telfairia occidentalis* Waste for the Adsorption of Toxic Heavy Metals from Simulated Effluent

F. U. Okwunodulu¹, S. A. Odoemelam²

¹,² Department of Chemistry, Michael Okpara University of Agriculture Umudike, Nigeria

**Abstract:** Exploitation of unmodified and thioglycolic acid modified waste as a low-cost adsorbent for the adsorption of Cd²⁺, Ni²⁺ and Pb²⁺ from simulated aqueous solutions was investigated. The results clearly demonstrate the effect of particle size and contact time as important experimental parameters on the adsorption process in batch experiments. The maximum evaluated particle size concentration and time concentration for Cd²⁺, Ni²⁺ and Pb²⁺ uptake onto unmodified and modified *Telfairia occidentalis* waste biomass were 99.68 mg/g Cd²⁺, 99.99 mg/g Ni²⁺, 99.75 mg/g Pb²⁺ at 250 µm for the unmodified and 98.88 mg/g Ni²⁺ at 250µm and 98.52 mg/g Pb²⁺ at 125 µm for the modified waste. 99.99 mg/g Ni²⁺ and 99.89 mg/g Pb²⁺ at 10 minutes for the unmodified waste and 99.45 mg/g Cd²⁺ at 60 minutes, 99.73 mg/g Ni²⁺ at 90 minutes, 88.80 mg/g Cd²⁺ at 90 minutes for the modified. The kinetic of metal ions adsorption on *Telfairia occidentalis* waste biomass has also been studied by fitting the data in Lagergren’s first-order, Ho-Mckay’s pseudo-second-order kinetics hypothesis and Elovich adsorption model. It was observed that the removal of metal ions over the waste biomass showed a better fit with the pseudo-second-order process and Elovich adsorption model than the pseudo-first-order.

**Keywords:** Adsorption kinetics, contact time, heavy metal ions, particle size, *Telfairia occidentalis* coat.

1. **Introduction**

The mobilization of heavy metals in the environment through industrial activities is of serious concern because of the toxicity of these metals to the environment [1]. However, some metals such as cadmium, nickel and lead are markedly very toxic, even at very low concentrations [2]. Thus their removal is vital from the standpoint of environmental pollution control [3 – 4]. Several physico-chemical processes for the removal and recovery of heavy metals from effluents exist out of which the adsorption is one of the most effective as the important aspect of adsorption process is easy regenerability and cost effective [5].

Adsorption principle and techniques have proven successful in the treatment of metal contaminated effluents from industries and other sources. Aksu and co-workers [6-15] have made substantial contributions in this area. According to literature *Telfairia occidentalis* waste has been a good adsorbent in heavy metal removal from industrial wastewaters [16]. This waste is generated during the processing of the *Telfairia occidentalis*. It has been reported that this waste serves as livestock meal but its digestibility is considered poor due to its anti-nutritional factors [17]. The proximate composition of *Telfairia occidentalis* coat has been given [18] and as a result of this composition, it has been classified as a lignocellulosic material, hence the interest in finding out its feasibility of adsorbing toxic metals from solutions. In this present study, *Telfairia occidentalis* coat has been utilized as an adsorbent for the removal of Cd²⁺, Ni²⁺ and Pb²⁺ from simulated aqueous solutions. During this study, the effect of particle size and period of contact have been observed on the adsorption of the metal ions over the *Telfairia occidentalis* coat. The kinetics of adsorption has been studied to determine the efficiency of the adsorption process.

2. **Materials and Method**

All reagents used were analytical grade, purchased and used without further purification. The waste biomass was gotten by removing the coat of the *Telfairia occidentalis* which was obtained from Umuahia main Market, Abia State. The coat was crushed in a mill, washed with deionized water and over dried at 50°C for 12hrs. This was sieved to obtain different sizes (125, 250, 375, 600, 625, 850) µm and activated with 2% (v/v) nitric acid overnight, washed with deionized water and finally oven-dried at 105°C for 6hrs. The activated samples represented the unmodified sample. About 5 g portion of the activated 250 µm particle size of the sample were taken from the bulk of the activated sample and modified [19] by soaking the sample into 1000 cm³ of 0.3M thioglycolic acid at 25 °C for 24hrs. The mixture was filtered, washed with de-ionized water and then with methanol. It was finally washed with de-ionized water and dried at 50 °C. The thiolated sample represented the modified samples for the experiment.

3. **Experimental Procedure**

Stock solution of 1000 mg/l of Cd²⁺, Ni²⁺ and Pb²⁺ as a synthetic wastewater, was prepared by dissolving 1 g of each salt in 1000cm³ of de-ionized water and made up to the mark of the volumetric flask. Each of these solutions represented the metal ion solution of 1000 mg/l concentration. From the stock solutions of 1000 mg/l, 5cm³ of each of the solution was pipetted into beakers and made up to the mark of 50ml volume with deionized water to give a concentration of 100 mg/l which was used for the adsorption process. The adsorption studies were conducted using a batch technique at 25 °C and pH of 7.5. 1g of the various sizes (125, 250, 375, 600, 625, 850) µm of both unmodified and modified samples were put into a 250cm³ conical flasks containing 50 cm³ i.e. (5 ml aliquot of 1000 mg/l stock solutions + 45 cm³ de-ionized water) portion of the test solutions and allowed to stand for 1 hr with
intermittently shake. The solutions were filtered and the filtrates were analyzed for residual metals using atomic absorption spectrophotometer (Buck model 200 A). For the time effect, 50 cm³ of each of the metal ion solutions of 100 mg/l were placed into various flasks containing 1 g (250 µm) size of the sample. The flasks were agitated for various time intervals of 10, 30, 60, 90 and 120 minutes, after which the mixtures were filtered and the filtrates were analyzed for residual metal using AAS (Buck model 200 A). Triplicate analysis were made and the amounts of Cd²⁺, Ni²⁺ and Pb²⁺ adsorbed during the series of batch investigations were determined using a simplified mass balance (Qe = C₀ – Cₑ), where Qₑ = amount adsorbed (mg/g) by the adsorbents at equilibrium or metal ion concentration on adsorbent at equilibrium, C₀ = metal ion concentration (mg/l) (final concentration) in the solution (of the filtrate) at equilibrium while Cₑ = initial metal ion concentration (mg/l) in solution used.

4. Results and Discussion

Table 1: Amount of heavy metal ions adsorbed by various sizes of Telfairia occidentalis waste from aqueous solution at 298 K

<table>
<thead>
<tr>
<th>Particle size(µm)</th>
<th>Unmodified Telfairia occidentalis coat</th>
<th>Modified Telfairia occidentalis coat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd²⁺ (mg/g)</td>
<td>Ni²⁺ (mg/g)</td>
</tr>
<tr>
<td>125</td>
<td>99.589±0.017</td>
<td>99.999±0.018</td>
</tr>
<tr>
<td>250</td>
<td>99.675±0.018</td>
<td>99.999±0.018</td>
</tr>
<tr>
<td>375</td>
<td>99.670±0.016</td>
<td>99.999±0.018</td>
</tr>
<tr>
<td>600</td>
<td>99.655±0.010</td>
<td>99.999±0.018</td>
</tr>
<tr>
<td>625</td>
<td>99.660±0.012</td>
<td>99.872±0.034</td>
</tr>
<tr>
<td>850</td>
<td>99.589±0.017</td>
<td>99.860±0.039</td>
</tr>
</tbody>
</table>

Table 1 shows concentrations of Cd²⁺, Ni²⁺ and Pb²⁺ adsorbed by various sizes of unmodified and modified Telfairia occidentalis waste from aqueous solutions. The data generally revealed that the adsorption capacity of the Telfairia occidentalis waste increases with decrease in particle size indicating that the adsorption of Cd²⁺, Ni²⁺ and Pb²⁺ by Telfairia occidentalis waste increases with increase in the surface area of contact. The breaking of larger particles tend to open tiny cracks and channels on the particle size surface of the material resulting in more accessibility to better diffusion, owing to the smaller particle size [20]. Slight difference was observed between the adsorption capacities of unmodified and modified samples of Telfairia occidentalis waste. Modification was found to decrease the adsorption capacity of the adsorbent and equally showed irregular pattern of adsorption unlike in the unmodified sample [Fig 1]. Adsorption capacity of the unmodified adsorbent was best for Ni²⁺ followed by Pb²⁺ and least for Cd²⁺ while Ni²⁺ followed by Cd²⁺ and least for Pb²⁺ was the order of adsorption for the modified adsorbent. Maximum concentrations were given as follows: 99.99 Ni²⁺, 99.75 Pb²⁺ and 99.68 Cd²⁺ mg/g for the unmodified sample, 98.88 Ni²⁺, 98.78 Cd²⁺ and 98.52 Pb²⁺ for the modified waste sample. Therefore the different particle sizes have different removal abilities as 250 µm showed highest removal ability for metal ions than other particle sizes.

5. Time Dependency

Table 2: Concentrations of Cd²⁺, Ni²⁺ and Pb²⁺ adsorbed by Telfairia occidentalis waste from aqueous solutions at various temperatures.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Unmodified Telfairia occidentalis coat</th>
<th>Modified Telfairia occidentalis coat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd²⁺ (mg/g)</td>
<td>Ni²⁺ (mg/g)</td>
</tr>
<tr>
<td>303</td>
<td>99.986±0.018</td>
<td>99.999±0.023</td>
</tr>
<tr>
<td>323</td>
<td>99.962±0.006</td>
<td>99.979±0.023</td>
</tr>
<tr>
<td>343</td>
<td>99.953±0.003</td>
<td>99.972±0.020</td>
</tr>
<tr>
<td>363</td>
<td>99.931±0.001</td>
<td>99.869±0.026</td>
</tr>
<tr>
<td>383</td>
<td>99.902±0.020</td>
<td>99.821±0.048</td>
</tr>
</tbody>
</table>

Table 2 shows the variation of the concentrations of Cd²⁺, Ni²⁺ and Pb²⁺ adsorbed by Telfairia occidentalis waste from aqueous solutions at various time intervals. Unlike the modified waste sample that showed longer time with irregular pattern of adsorption of the metal ions, adsorption of the metal ions by the unmodified waste samples was found to increase at a shorter time (10 min). Maximum concentrations were given as 99.99 Cd²⁺, 99.99 Ni²⁺ and
99.89 Pb\(^{2+}\) mg/g. Irregular adsorption with modified waste sample indicated that modification had effects on the adsorption capacity of this adsorbent.

6. Kinetic Studies

Pseudo-first-order, pseudo-second-order and Elovich adsorption model were used to describe the adsorption of the on-going process. The pseudo-first-order model did not give any correlation with the data hence plot is not shown. The pseudo-second-order model as developed by [21] was plotted using equation below. A pseudo-second-order adsorption rate equation can be expressed as follows,

\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{1}
\]

where \(k_2\) is the rate constant of pseudo-second-order adsorption (gmg\(^{-1}\)min\(^{-1}\)), \(q_e\) and \(q_t\) are the adsorption capacity at equilibrium and at time, \(t\), respectively. Introducing boundary conditions to equation 1, i.e. \(t = 0\) to \(t\) and \(q_e = 0\) to \(q_t = q_e\), integrated form of equation 1 was obtained (equation 2) and upon simplification, equations 3 and 4 were obtained.

\[
\frac{1}{(q_e - q_t)} = \frac{1}{q_t} + k_2t \tag{2}
\]

\[
\frac{1}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}(t) \tag{3}
\]

\[
\frac{1}{q_t} = \frac{1}{h} + \frac{1}{q_e}(t) \tag{4}
\]

The implication of equation 4 is that a plot of \(1/q_t\) versus \(t\) should be linear with slope and intercept equal to \(q_e\) and \(1/h\) (\(h = k_2q_e^2\)) respectively. Fig. 2 shows pseudo-second-order kinetic plots for the adsorption of Cd\(^{2+}\), Ni\(^{2+}\) and Pb\(^{2+}\) by unmodified and modified *Telfairia occidentalis* wastes respectively. Adsorption parameters obtained from the plots are presented in Table 3.

From the results obtained, it can be seen that values of \(R^2\) are very close to unity indicating the application of a pseudo-second-order model to the adsorption of Cd\(^{2+}\), Ni\(^{2+}\) and Pb\(^{2+}\) by unmodified and modified *Telfairia occidentalis* wastes. It is also evident from the results that values of \(k_2\) calculated from the plots are relatively low. It was also observed that \(h\) and \(k_2\) values for the adsorption of Ni\(^{2+}\) and Pb\(^{2+}\) by modified *Telfairia occidentalis* adsorbent were higher than those obtained from the unmodified adsorbent. The reverse was however observed for the adsorption of Cd\(^{2+}\) by *Telfairia occidentalis* waste. According to Sharma and Goya (2009), a pseudo-first and second-order kinetics cannot reveal the mechanism of adsorption therefore, a model of Elovich was also used to test for the adsorption mechanism of the studied adsorbates. Elovich adsorption model can be expressed as follows (Chien and Clayton, 1980, Sparks, 1986):

\[
\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{5}
\]

where \(\alpha\) is the initial adsorption rate (mgg\(^{-1}\)min\(^{-1}\)) and \(\beta\) is the desorption constant (gmg\(^{-1}\)) during any one experiment. Chien and Clayton (1980) had proposed that \(q_t\) should be linear with \(\ln(t)\) and if the boundary conditions are applied (i.e. \(t = 0\) and \(q_t = q_e\) at \(t = 0\)), the Elovich equation becomes,

\[
q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln(t) \tag{6}
\]

The implication of equation 6 is that a plot of \(q_t\) versus \(\ln(t)\) should be linear with slope and intercept equal to \(1/\beta\) and \(1/\beta \ln(\alpha \beta)\) respectively. Fig. 4 shows Elovich plots for the adsorption of Cd\(^{2+}\), Ni\(^{2+}\) and Pb\(^{2+}\) by unmodified and modified *Telfairia occidentalis* waste. Values of Elovich constants deduced from the plots are presented in Table 4. From the results obtained, it can be seen that the adsorption of the heavy metal ions by *Telfairia occidentalis* waste fitted the Elovich adsorption model excellently.

### Table 3: Pseudo-second-order adsorption parameters for the adsorption of Cd\(^{2+}\), Ni\(^{2+}\) and Pb\(^{2+}\) by unmodified and modified *Telfairia occidentalis* waste

<table>
<thead>
<tr>
<th>System</th>
<th>Ions</th>
<th>(q_e)</th>
<th>(h)</th>
<th>(k_2)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(UM)</td>
<td>0.01</td>
<td>-4.00E-15</td>
<td>-2.50E+11</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Ni(UM)</td>
<td>0.0109</td>
<td>-0.0303</td>
<td>-3.30E+01</td>
<td>3.92E-03</td>
<td>0.9945</td>
</tr>
<tr>
<td>Pb(UM)</td>
<td>0.01</td>
<td>-0.0001</td>
<td>-1.00E+04</td>
<td>-1.00E+00</td>
<td>1</td>
</tr>
<tr>
<td>Cd(M)</td>
<td>0.0101</td>
<td>-0.0004</td>
<td>-2.50E+03</td>
<td>-2.55E-01</td>
<td>1</td>
</tr>
<tr>
<td>Ni(M)</td>
<td>0.01</td>
<td>0.0003</td>
<td>3.33E+00</td>
<td>3.33E-02</td>
<td>1</td>
</tr>
<tr>
<td>Pb(M)</td>
<td>0.0112</td>
<td>0.0074</td>
<td>1.35E+02</td>
<td>1.70E-02</td>
<td>0.9998</td>
</tr>
</tbody>
</table>

#### Footnotes:


7. Conclusion

*Telfairia occidentalis* coat as a cheap natural waste has been proven as a good adsorbent for toxic heavy metals removal in wastewater especially when unmodified at 250 μm, pH of 7.5, temperature of 25 °C, concentration of 100 mg/l and period of 30 minutes contact. Almost 100% heavy metals removal was achieved. Kinetically, Elovich adsorption model gave better fit for the data than pseudo-first and pseudo-second order models. Hence, there is need to investigate the probable changes of adsorption efficiency in conditions of encountering the various metals in actual wastewaters using *Telfairia occidentalis* coat.

8. Future Scope

The impact of this study to the society involves the use of low cost adsorbents in maintaining pollution free environment since it involves waste management and detoxification of toxic pollutants. Moreover this study gives an insight for the upcoming researchers to adopt this method in different areas such as in agricultural research i.e. a situation where this adsorbent will be mixed with fertilizers before application in order to minimize its leaching to the environment.

References


**Table 4:** Elovich parameters for the adsorption of Cd\(^{2+}\), Ni\(^{2+}\) and Pb\(^{2+}\) by unmodified and modified *Telfairia occidentalis* waste

<table>
<thead>
<tr>
<th>System</th>
<th>Metal ion</th>
<th>Slope Intercept (I)</th>
<th>β</th>
<th>lnβ</th>
<th>α</th>
<th>R(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T.o</td>
<td>Cd(UM)</td>
<td>-100.14</td>
<td>-39.5257</td>
<td>-3954.94</td>
<td>0</td>
<td>0.9066</td>
</tr>
<tr>
<td></td>
<td>Ni(UM)</td>
<td>-100.14</td>
<td>-17.6367</td>
<td>-1766.14</td>
<td>0</td>
<td>0.8047</td>
</tr>
<tr>
<td></td>
<td>Pb(UM)</td>
<td>-100.14</td>
<td>-18.7617</td>
<td>-1876.17</td>
<td>0</td>
<td>0.947</td>
</tr>
<tr>
<td></td>
<td>Cd(M)</td>
<td>0.1045</td>
<td>98.915</td>
<td>9.5694</td>
<td>0</td>
<td>0.5493</td>
</tr>
<tr>
<td></td>
<td>Ni(M)</td>
<td>0.0299</td>
<td>99.57</td>
<td>33.4448</td>
<td>0</td>
<td>0.7729</td>
</tr>
<tr>
<td></td>
<td>Pb(M)</td>
<td>1.742</td>
<td>80.22</td>
<td>0.5741</td>
<td>0</td>
<td>0.9064</td>
</tr>
</tbody>
</table>
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Author Profile

F. U. Okwunodulu did B.Sc. in Pure Chemistry from University
of Nigeria Nsukka, did M.Sc. and Ph.D in Environmental
Chemistry from Michael Okpara University of Agriculture
Umudike, Nigeria. Currently he is an academic staff of Michael
Okpara University of Agriculture Umudike, Nigeria