Modelling the Effect of Dosage on the Biosorption of Ni$^{2+}$ Ions onto *Luffa Cylindrica*

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Citation

Abstract
Nickel metal contamination exists in industrial processes that use nickel catalysts, such as coal gasification, petroleum refining, and hydrogenation of fats and oils. Therefore, a systematic study on the removal of nickel from wastewater is of considerable significance from an environmental point of view. *Luffa cylindrica*, a plant material with wide distribution particularly in the tropical world, was characterized as the surface area, chemical bonds, bulk density, pore size distribution, microstructures, composition, morphology and elemental composition were determined. Biosorption studies were carried out with the dosage varied and the experimental data obtained were fitted to some selected kinetic models. Non-linear regression method was used and the regressed data obtained for the various doses studies ranged from 0.948 to unity. A kinetic model was developed. This empirical model for predicting the sorption capacity for Ni$^{2+}$ ions sorbed by *Luffa cylindrica* was derived from the rate constant, equilibrium sorption capacity and the initial sorption rate.

1. Introduction

Biosorption is an attractive technology which involves sorption of dissolved substances by a biomaterial. It is a potential technique for the removal of heavy metals from solutions and recovery of precious metals [1]. It is a metabolism independent process and thus can be performed by both living and dead cells [2].

The species with the most toxicological relevance found in the industrial effluents are the heavy metals. These species are bio-accumulative and not biodegradable over time [3]. Water contaminated with metal ions can cause several health problems. Heavy metal ions such as cadmium, zinc, nickel, chromium, copper and lead can bio-accumulate to be toxic compounds through the food chain [4].

Nickel is toxic and relatively widespread in the environment. It is used in a wide variety of industries such as plating and cadmium–nickel battery, phosphate fertilizers, mining, pigments, stabilizers and alloys, and find its way to the aquatic environment through wastewater discharge [5].

Activated carbon is the most employed adsorbent for heavy metal removal from aqueous solution and have been well documented in the literature [6-7]. However, the extensive use of activated carbon for metal removal from industrial effluents is expensive [8], limiting its large application for wastewater treatment. Therefore, there is a growing interest in finding alternative low-cost adsorbents for metal removal from aqueous solution, such as: the residuals of agricultural products [9-10].

The utility of these very low cost and environmentally friendly plant materials as biosorbents for the removal of divalent cations from aqueous solutions as the cellulose,
hemicelluloses, pectin and lignin present in the cell wall are the most important sorption sites [11]. The structure of Luffa cylindrica for example, is cellulose based [12-13], and the surface of cellulose in contact with water is negatively charged. Nickel compound used in this study will dissolve in this study will dissolve to give the cationic metal and this will undergo attraction on approaching the anionic Luffa cylindrica structure [14]. On this basis, it is expected that a metal cation will have a strong sorption affinity for Luffa cylindrica.

However, some researchers have addressed the mathematical modelling of the sorption of metal ions onto these biosorbents. Earlier reported mathematical models for the sorption of heavy metal ions included: surface-complexation, cation-exchange and triple-layer models [15].

The purpose of this study is to develop an empirical model for describing the effect of dosage on equilibrium sorption of nickel (II) ions on Luffa cylindrica.

2. Materials and Methods

2.1. Preparation of Luffa cylindrica

The seeds and sponges of L. cylindrica were gathered into a clean plastic bag. They were dried in the oven at 105°C for 24 hours and afterwards ground with a grinding mill. The ground seeds and sponges were sieved and were of particle size 0.3 to 0.6mm. This was to allow for shorter diffusion path, resulting in a higher rate of biosorption [16]. The ground seed and sponge were mixed at a ratio of 1:1.

2.2. Preparation of Aqueous Solutions

Stock solution of Nickel was prepared with distilled water and Nickel (II) tetraoxosulphate (VI). All working solutions were obtained by diluting the stock solutions with distilled water. The pH of the solutions was adjusted to their respective optimum pH. The concentration of metal ions in solutions was analyzed by Atomic Absorption Spectrophotometer. A duplicate was analyzed for every sample to track experimental error and show capability of reproducing results [17].

2.3. Determination of Optimum pH

A gramme of L. cylindrica seeds and sponge mixture were put into 250ml conical flasks containing 50 ml of the aqueous solutions each adjusted to pH 2, 3, 4, 5, 6, 7, 8, 9 and 10 for each metal ions studied. They were agitated for 2h at 25°C. The biosorbents were removed from the aqueous solutions after biosorption using the centrifuge at 24000 rate per minute (rpm) for 10 minutes. The final concentrations of the metal ions remaining were determined using Atomic Absorption Spectrophotometer (AAS).

2.4. Biosorption Experiment

The biosorption studies for evaluation of the Luffa cylindrica mixture for removal of Nickel (II) ions from aqueous solutions was carried-out in triplicate using the batch biosorption procedure [9-10].

The method of least squares was used to predict the kinetic model by linear regression method. A trial and error was used for nonlinear regression to minimize or maximize the objective function using the solver add-in function, Microsoft Excel, Microsoft Corporation.

2.5. Determination of Surface Area

The Autosorb-1c was used for the determination of the surface area of the ground Luffa cylindrica mixture under study.

2.6. Determination of Pore Size Distribution

The PoreMaster PM-60 was used to test the ground Luffa cylindrica mixture sample. The instrument determines both Pore volume and Pore diameter of a solid or powder by forced intrusion of a non-wetting liquid (mercury) [18].

2.7. Determination of the Microstructures, Composition, Morphology and Elemental Composition of the Luffa cylindrica Mixture

The microstructures, composition, and morphology of the Luffa cylindrica mixture were analysed by means of scanning electron microscopy (SEM). A Philips scanning electron microscope (ESEM XL30) equipped with energy dispersive X-ray spectrometer (EDX) was used to analyse the various elemental composition found in the Luffa cylindrica mixture.

2.8. Determination of Chemical Bonds in Luffa cylindrica Mixture

Fourier transform infrared spectroscopy (FTIR) of the adsorbent was done by using an FTIR spectrometer (Model FTIR 2000, Shimadzu, Kyoto, Japan) [19].

2.9. Determination of Bulk Density of Luffa cylindrica Mixture

The method of Okaka and Potter [20] was used in determining the bulk density.

3. Results and Discussion

<table>
<thead>
<tr>
<th>Specific surface area - BET (m²/g)</th>
<th>0.28</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Surface area (m²/g)</td>
<td>1.1895</td>
</tr>
<tr>
<td>Pore Diameter Range (µm)</td>
<td>1051.309204 to 0.003577</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Table 1. Physical properties of the Luffa cylindrica biosorbent.

Table 1 show the bulk density, surface area and pore diameter range for the biosorbent used for this study. The Specific surface area using the BET method was 0.28m²/g and the Pore diameter range was between 1051.309204 to 0.003577µm. The bulk density was 0.34g/cm³. As observed, the surface area for the seed and sponge mixture of L. cylindrica is relatively low, with pore diameter values in agreement with those found for typical mesoporous materials [21].
Figure 1 gives the elemental composition of *Luffa cylindrica* that was analysed by means of scanning electron microscopy (SEM). The *Luffa cylindrica* showed it contained a very high percentage of carbon at 79.33% followed by oxygen, potassium, calcium, chlorine, phosphorus and sulphur with weight % values of 12.25, 3.86, 1.58, 1.29, 0.95 and 0.75 respectively.

Scanning electron microscopy (SEM) of the *Luffa cylindrica* biosorbent was taken in order to verify the presence of macropores in the structure of the fiber. In the micrographs presented, Figure 2 shows the fibrous structure of *Luffa cylindrica*, with some fissures and holes, which indicate the presence macroporous structure. These, should contribute a little bit to the diffusion of the Ni (II) ions to the *Luffa cylindrica* biosorbent surface [22-25]. The small number of macroporous structure is confirmed by the low specific surface area of the biosorbent (see Table 1). As the biosorbent material presents few numbers of macroporous structure, it adsorbed low amount of nitrogen, which led to a low BET surface area [22-25]. Therefore the major contribution of the Ni (II) ions uptake can be attributed to micro- and mesoporous structures (see Figure 2).
Figure 3a. FTIR spectrum of the mixture of seed and sponge of L. cylindrica biosorbent before biosorption.

Figure 3b. FTIR spectrum of the mixture of seed and sponge of L. cylindrica biosorbent after biosorption of Ni$^{2+}$ ions.
Figures 3a and 3b show the FTIR spectral. The functional groups on the binding sites were identified by FTIR spectral comparison of the free biomass with a view to understanding the surface binding mechanisms. The significant bands obtained are shown in Figure 3a and 3b. Functional groups found in the structure include carboxylic, alkynes or nitriles and amine groups [26]. The stretching vibrations of C-H stretch of -CHO group shifted from 2847.05 to 2922.20, 2852.58, 2852.46 and 2852.43 cm$^{-1}$ after Ni$^{2+}$ ions biosorption. The assigned bands of the carboxylic, amine groups and alkynes or nitriles vibrations also shifted on biosorption. The shift in the frequency showed that there was biosorption of Ni$^{2+}$ ions on the L. cylindrica biosorbent and the carboxylic and amine groups were involved in the sorption of the Ni$^{2+}$ ions [11].

![Figure 4](image-url)  
*Figure 4. A plot showing the pore size distribution of the biosorbent - L. cylindrical.*

### Table 2: Kinetic models and parameters for Ni (II) ions using L. cylindrica as biosorbent.

<table>
<thead>
<tr>
<th>Kinetic parameters</th>
<th>Dosage</th>
<th>R$^2$</th>
<th>1.000</th>
<th>1.000</th>
<th>1.000</th>
<th>1.000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first order</td>
<td>0.3g</td>
<td>0.5g</td>
<td>0.7g</td>
<td>0.9g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_e$ (mg/g)</td>
<td>12.88</td>
<td>7.859</td>
<td>5.673</td>
<td>4.446</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{f}$ (min$^{-1}$)</td>
<td>0.194</td>
<td>0.165</td>
<td>0.148</td>
<td>0.136</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R$^2$</td>
<td>0.981</td>
<td>0.983</td>
<td>0.983</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pseudo-Second order</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_e$ (mg/g)</td>
<td>13.27</td>
<td>8.126</td>
<td>5.883</td>
<td>4.622</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{s}$ (g/mg/min)</td>
<td>0.030</td>
<td>0.040</td>
<td>0.048</td>
<td>0.054</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intra-particle diffusion</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_{d}$ (mg/g min$^{-1}$)</td>
<td>0.284</td>
<td>0.184</td>
<td>0.148</td>
<td>0.125</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>10.04</td>
<td>5.780</td>
<td>3.990</td>
<td>3.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R$^2$</td>
<td>0.965</td>
<td>0.957</td>
<td>0.952</td>
<td>0.948</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Avrami</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_e$ (mg/g)</td>
<td>12.88</td>
<td>7.859</td>
<td>5.673</td>
<td>4.446</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_{a}$ (min$^{-1}$)</td>
<td>0.029</td>
<td>0.024</td>
<td>0.022</td>
<td>0.020</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R$^2$</td>
<td>0.984</td>
<td>0.983</td>
<td>0.983</td>
<td>0.983</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The pore size distribution of the *Luffa cylindrica* sample was obtained by Mercury intrusion method, and it is shown in Figure 4. The distribution of average pore diameter curve presents a maximum with an average pore diameter of about 30 µm. The amount of pores seen in the *Luffa cylindrica* biosorbent; decreases for average pore diameters ranging from 30 to 1000 µm. On the other hand, the amount of average pores ranging from $3.0 \times 10^3$ to 30 µm is predominant. Therefore, this biosorbent can be considered as mixtures of micro- and mesoporous materials [22-25].

Some selected set of kinetic reaction models [27-31] were used to fit the experimental data but the correlation coefficients were not as high as the rate law for a pseudo-second order (Table 2). The $q_e$ values found in the pseudo-second-order for Table 2 were in good agreement with the experimental $q_e$ values. These results indicate that the pseudo-second-order kinetic model should be taken into account for explaining the biosorption process of Ni (II) ions removal by the *L. cylindrica* biosorbent.

When analyzing the values of the kinetic parameters depicted on Table 2, it should be mentioned that the $k_v$ values strongly depend on the initial concentration, since its units is gmg$^{-1}$ min$^{-1}$. Table 2 shows that the kinetic results obtained fitted very well to the pseudo-second-order kinetic model for the nickel (II) ions studied with $R^2$ values of unity for the various dosages under consideration. The sorption of Ni (II) ions onto *Luffa cylindrica* could be a pseudo-second order process.

### 3.1. Derivation of Empirical Model

*Luffa cylindrica* contains polar functional groups such as aldehydes, ketones, and acids. These groups can be involved in chemical bonding and are responsible for the cation exchange capacity of the *Luffa cylindrica* [28]. It appears reasonable that in many cases ion exchange rather than sorption to free sites is the relevant overall-mechanism for the binding of metal ions in biosorption. Since the overall charge of the biomass particle has to be neutral, any binding of one cation must be accompanied by either a stoichiometric release of other cations or by the binding of anions [32]. Thus, the *Luffa cylindrica*-metal reaction may be represented in two ways:

$$2L^+ + Ni^{2+} \rightarrow NiL_2$$  \hspace{1cm} (1a)

and

$$2HL + Ni^{2+} \rightarrow NiL_2 + 2H^+$$  \hspace{1cm} (1b)

where L and HL are polar sites on the *Luffa cylindrica* surface.

In developing the mathematical description of this sorption process, certain assumptions were made:

a. The process may be pseudo-second order and the rate limiting step may be chemical sorption or chemisorption;

b. There is a monolayer of metal ion on the surface of *Luffa cylindrica*;

c. The energy of sorption for each ion is the same and independent of surface coverage;

d. The sorption occurs only on localised sites and involves no interactions between sorbed ions;

e. The rate of sorption is almost negligible in comparison with the initial rate of sorption.

The rate of pseudo-second order reaction may be dependent on the amount of divalent metal ion on the surface of *Luffa cylindrica* and the amount of divalent metal ion sorbed at equilibrium. The sorption equilibrium, $q_e$, is a function of, for example, the initial metal ion concentration, the *Luffa cylindrica* dose and the nature of solute-sorbent interaction [28].

The rate expression for the sorption described by Eqs (1a) and (1b) is:

$$\frac{d(L)_0}{dt} = k[(L)_0 - (L)_t]^2$$

or

$$\frac{d(HL)_0}{dt} = k[(HL)_0 - (HL)_t]^2$$

where (L)$_0$ and (HL)$_0$ are the number of active sites occupied on the *Luffa cylindrica* at time $t$, (L)$_t$ and (HL)$_t$ are the number of equilibrium sites available on the *Luffa cylindrica* [28].

The kinetic rate equations can be rewritten as follows:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2$$  \hspace{1cm} (2)

where $k$ is the rate constant of sorption, (g/mg min), $q_t$ is the amount of divalent metal ion sorbed at equilibrium, (mg/g), $q_e$ is amount of divalent metal ion on the surface of the sorbent at anytime, $t$, (mg/g).

Separating the variables in Eq. (2) gives:

$$\frac{dq_t}{(q_e - q_t)^2} = kdt$$

integrating this for the boundary conditions $t=0$ to $t=t$ and $q_t = 0$ to $q_e = q_e$ gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt$$  \hspace{1cm} (3)

this is the integrated rate law for a pseudo-second order reaction.

Eq. (3) can be rearranged to obtain:

$$q_t = \frac{t}{[1/kq_e^2 + t/q_e]}$$  \hspace{1cm} (4)

$$h = kq_e^2$$  \hspace{1cm} (5)
Substituting Eq. (5) into Eq. (4), gives:

\[ q_t = \frac{t}{\left(1/h + t/q_e\right)} \]  

(6)

Although there are many factors which will influence sorption, contact time, pH, temperature, sorbent concentration, nature of the solute and its concentration, a kinetic model is concerned only with the effect of observable parameters on the overall rate. These include initial metal ion concentration, temperature, \textit{Luffa cylindrica} dose and nature of solute [28].

3.2. Effect of \textit{Luffa cylindrica} Dose and Nature of Solute

Figures 5 and 6 show typical sorption curves for effect of \textit{Luffa cylindrica} dose on the sorption kinetics of zinc, nickel, copper and lead ions onto \textit{Luffa cylindrica} at temperature of 25°C and initial ion concentration of 100 mg/l. The plotted experimental data (Figure 5) also gave a good fit with the pseudo-second order equation and the regression coefficients for the linear plots were very close to 1.00 as can be seen in Table 3.

### Table 3. The effect of dosage on metal ions biosorption data.

<table>
<thead>
<tr>
<th>Dosage (g)</th>
<th>( r^2 )</th>
<th>( q_e ) (mg/g)</th>
<th>( k ) (g/mgmin)</th>
<th>( h ) (mg/gmin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>1.000</td>
<td>13.2687</td>
<td>0.0371</td>
<td>6.4899</td>
</tr>
<tr>
<td>0.5</td>
<td>1.000</td>
<td>8.1256</td>
<td>0.0487</td>
<td>3.1907</td>
</tr>
<tr>
<td>0.7</td>
<td>1.000</td>
<td>5.8826</td>
<td>0.0582</td>
<td>1.9987</td>
</tr>
<tr>
<td>0.9</td>
<td>1.000</td>
<td>4.6216</td>
<td>0.0666</td>
<td>1.4093</td>
</tr>
</tbody>
</table>

Figure 6 show that for all the various doses, the amount of the divalent metal ions sorbed increases rapidly with time in the beginning and very slowly towards the end of the reaction. Furthermore, a large fraction of the total amount of metal was removed within a short time that is before 20 minutes. The plot as seen in Figure 6 also showed that sorption capacity increased for lower \textit{Luffa cylindrica} dosages at any specific time. There were effects on the contact time required to reach saturation due to the variation in \textit{Luffa cylindrica} dosages. It was found that the equilibrium sorption of metal ions studied was a function of \textit{Luffa cylindrica} doses. The rate constant, \( k \), the equilibrium sorption, \( q_e \) and the initial sorption rate, \( h \), of sorption at different \textit{Luffa cylindrica} doses were calculated from the intercept and slope of the straight line plots of \( t/q_e \) versus \( t \). The initial sorption rate decreased with an increase in the \textit{Luffa cylindrica} dose from 0.2 -1.0 g. The corresponding linear plots of the values of \( q_e \), \( k \) and \( h \) against \( m \) (dosage) were regressed to obtain expressions with exponents for these values in terms of the \( m \) parameters for all the metal ions studied.

The expression

\[ x = Am^h \]  

(7)

Where \( x = q_e, k \) or \( h \)

<table>
<thead>
<tr>
<th>( M^{2+} )</th>
<th>( A_q )</th>
<th>( b_q )</th>
<th>( r^2 )</th>
<th>( A_h )</th>
<th>( b_h )</th>
<th>( r^2 )</th>
<th>( A_k )</th>
<th>( b_k )</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>4.177</td>
<td>- 0.96</td>
<td>1.000</td>
<td>0.0704</td>
<td>0.5331</td>
<td>1.000</td>
<td>1.2174</td>
<td>- 1.39</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Table 4 shows the empirical parameters for predicted \( q_e \), \( k \) and \( h \) and their corresponding correlation coefficients. Substituting the values of \( A_q, B_q, A_h \) and \( B_h \) from Table 4 in Eq. (6), the rate law for a pseudo-second order reaction and the relationship between \( q_e, m \) and \( t \) can be represented as:

\[ q_t = \frac{t}{1/1.2174m^{-1.39} + t/4.177m^{-0.96}} \]  

(8)
These equations can then be used to derive the sorption amount of nickel at any given dosage and the reaction time. The three-dimensional plot of the Equation (8) is shown in Figure 7.

The Equation represent a generalised predictive model for the amount of metal ion sorbed at any contact time and involved L. cylindrica dose. It indicates that the metal sorbed at any contact time is higher as the L. cylindrica dose is decreased. This is due to the fact that increasing the L. cylindrica dose increases the surface area for sorption and hence the rate of metal sorption is increased when the initial metal ion concentration is constant.

A kinetic model has been derived for the sorption of the nickel (II) ions onto L. cylindrica. The parameter which has the greatest influence on the kinetics of the sorption reaction was sorption equilibrium; q_e is a function of L. cylindrica dose and nature of solute and this is in agreement with previous research [28].

4. Conclusion

A kinetic study was carried out and the experimental data fitted into Pseudo-first order, Pseudo-second order, Intra-particle diffusion and Avrami models using the non-linear regression method to obtain the kinetic parameters.

A kinetic model has been developed and fitted for the sorption of the divalent nickel ions onto L. cylindrica. The results showed sorption for Ni (II) ions onto L. cylindrica during agitation by suspended shaking; the process can be described by all kinetic models with pseudo-second order having the R^2 value of unity for all the doses studied. The experimental data fits the pseudo-second order model based on the assumption that the rate limiting step may be chemical sorption involving ion exchange between sorbent and sorbate. The parameter which has the influence on the kinetics of the sorption reaction was the sorption equilibrium capacity, q_e, a function of initial metal ion concentration, Luffa cylindrica dose and the nature of solute ion.

References


