+Modelling the Sorption of Zn$^{2+}$ Ions onto *Luffa cylindrica*

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Citation

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Abstract: Biosorption experiment for Zn (II) was investigated in this study using the plant material *Luffa cylindrica*. The applicability of some selected kinetic models was tested. Characterization like the surface area, chemical bonds, bulk density, Pore size distribution, microstructures, composition, morphology and elemental composition were determined. The coefficient of determination ($R^2$) of all the models studied were mostly greater than 0.9. In most cases these coefficients were found to be close to one. This indicates that all the kinetic models adequately describe the experimental data of the biosorption of Zn (II) ions. Kinetic models were developed mathematically, and also, Artificial Neural Network (ANN) was applied to develop a Multiple Input Single Output (MISO) back propagation neural network model which was validated. The RMSE value was found to be 0.5912 and 1.6267 for MISO Zn-1 and MISO Zn-2 respectively. Artificial neural network was able to predict the sorption capacity quite reasonably for the model.

Keywords: Artificial Neural Network, Kinetic Model, *Luffa cylindrica*, Biosorption, Waste Water

1. Introduction

Environmental pollution due to the discharge of heavy metals from various industries, including metal plating, mining, painting and agricultural sources such as fertilizers and fungicidal sprays are causing significant concern because of their toxicity and threat to human life, especially when tolerance levels are exceeded [1].

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 [2].

Zinc is often found in effluents discharged from industries involved in acid mine drainage, galvanizing plants, natural ores and municipal waste water treatment plants and is not biodegradable and travels through the food chain via bioaccumulation. Therefore, there is significant interest regarding zinc removal from waste waters since its toxicity for humans is 100-500 mg/day. World health organization (WHO) recommended the maximum acceptable concentration of zinc in drinking water as 5 mg/L [3].

Activated carbon is the most employed adsorbent for heavy metal removal from aqueous solution and have been well documented in the literature [4-5]. However, the extensive use of activated carbon for metal removal from industrial effluents is expensive [6], limiting its large application for wastewater treatment. Therefore, there is a growing interest in finding new alternative low-cost adsorbents for metal removal from aqueous solution, such as: the residuals of agricultural products [7-8].

Biosorption is an attractive technology which involves sorption of dissolved substances by a biomaterial [9].

Very low cost and environmentally friendly plant materials are now used 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 [10]. The structure of *Luffa cylindrica* for example, is cellulose based [11-12], and the surface of cellulose in contact with water is negatively charged. Metal compounds used in this study will dissolve to give the cationic metal and this will undergo attraction on approaching the anionic *Luffa cylindrica* structure [13].

However, few 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 [1].

Artificial Neural Network (ANN) modelling is a non-linear statistical technique used to solve problems that conventional statistical methods cannot solve. Apart from that, application of ANN in modelling is about 20 times faster than numerical integration of a differential equations system [14]. Therefore the application of ANN in various branches of science and process technology by researchers is becoming popular and hence its usage in this study.

The purpose of this work is to develop empirical models for the effect of Luffa cylindrica dosage and the initial ion concentration on the uptake of Zinc (II) ions from aqueous solution.

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 [15]. The ground seed and sponge were mixed at a ratio of 1:1.

2.2. Preparation of Aqueous Solutions

Stock solution of Zinc was prepared with distilled water and Zinc (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 [16].

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 2400 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 Zinc (II) ions from aqueous solutions was carried-out in triplicate using the batch biosorption procedure [7-8].

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-Ic 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) [17].

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) [18].

2.9. Determination of Bulk Density of Luffa cylindrica Mixture

The method of Okaka and Potter [19] was used in determining the bulk density.

3. Results and Discussion

<table>
<thead>
<tr>
<th>Table 1. Physical properties of the Luffa cylindrica biosorbent.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area - BET (m²/g)</td>
</tr>
<tr>
<td>Total Surface area (m²/g)</td>
</tr>
<tr>
<td>Pore Diameter Range (µm)</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
</tr>
</tbody>
</table>

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 [20].
Figure 1. SEM Scan and plot showing elemental composition of Luffa cylindrica.

Figure 1 gave 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.

Figure 2. Scanning electron microscopy of Luffa cylindrica biosorbent: A transversal view of the mixture of seed and sponge 1000×.

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 when observed show 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 Zn (II) ions to the Luffa cylindrica biosorbent surface [21-24]. 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 [21-24]. Therefore the major contribution of the Zn (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 Zn$^{2+}$ ions.
Figures 3 a - b 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 3 a - b. Functional groups found in the structure include carboxylic, alkynes or nitriles and amine groups [25].

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 Zn²⁺ 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 Zn²⁺ ions on the L. cylindrica biosorbent and the carboxylic and amine groups were involved in the sorption of the Zn²⁺ ions [10].

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 x 10⁻³ to 30 µm is predominant. Therefore, this biosorbent can be considered mixtures of micro- and mesoporous materials [21-24].

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**Table 2a.** Kinetic models and parameters of initial ion concentration for Zn (II) ions using L. cylindrica as biosorbent.

<table>
<thead>
<tr>
<th>Kinetic parameters</th>
<th>Concentration (mol/dm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first order</td>
<td></td>
</tr>
<tr>
<td>qₑ (mg/g)</td>
<td>25.0 50.0 100.0 200.0</td>
</tr>
<tr>
<td>k_f (min⁻¹)</td>
<td>1.1161 2.3641 4.8582 9.8589</td>
</tr>
<tr>
<td>R²</td>
<td>0.9981 0.9997 0.9999 0.9999</td>
</tr>
<tr>
<td>Pseudo-Second order</td>
<td></td>
</tr>
<tr>
<td>qₑ (mg/g)</td>
<td>1.1217 2.3698 4.8609 9.8615</td>
</tr>
<tr>
<td>k_f (g/mg/min)</td>
<td>7.6376 7.4646 15.285 15.296</td>
</tr>
<tr>
<td>R²</td>
<td>0.9985 0.9998 0.9999 0.9999</td>
</tr>
</tbody>
</table>

**Table 2b.** Kinetic models and parameters of Dosage for Zn (II) ions using L. cylindrica as biosorbent.

<table>
<thead>
<tr>
<th>Kinetic parameters</th>
<th>Dosage (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first order</td>
<td>0.2 0.4 0.6 0.8 1.0</td>
</tr>
<tr>
<td>qₑ (mg/g)</td>
<td>24.32 12.29 8.105 6.083 4.867</td>
</tr>
<tr>
<td>k_f (min⁻¹)</td>
<td>1.230 1.016 1.199 1.303 0.973</td>
</tr>
<tr>
<td>R²</td>
<td>0.999 0.999 0.999 0.999 0.999</td>
</tr>
<tr>
<td>Pseudo-Second order</td>
<td></td>
</tr>
</tbody>
</table>
A selected set of kinetic reaction models [26-30] were used to fit the experimental data and the correlation coefficients were as high as the rate law for a pseudo-second order (Table 2a and 2b). The sorption of metal ion onto Luffa cylindrica could be a pseudo-second order process.

These results reinforce the need of using a statistical error function to better evaluate the adsorption models, as previously reported [24], [31].

Additionally, it was verified that the \( q_e \) values found in the pseudo-second-order for both Table 2a and 2b 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 Zn (II) removal by the L. cylindrica biosorbent.

When analyzing the values of the kinetic parameters depicted on Tables 2a and 2b, it should be mentioned that the \( k_r \) values strongly depend on the initial concentration, since its units is g mg\(^{-1}\) min\(^{-1}\). Table 2a show that the kinetic results fitted very well to all the kinetic models studied. Table 2b show that the kinetic results fitted very well to all the kinetic models studied with \( R^2 \) values of 0.999 except for 0.2 g Luffa cylindrica dose which had 0.997 for the Elovich kinetic model.

### 3.1. Derivation of Empirical Model for Zn\(^{2+}\) Ions Sorbed by Luffa cylindrica

*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* [32]. 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 [33]. Thus, the *Luffa cylindrica*-metal reaction may be represented in two ways:

\[
2L^+ + \text{Zn}^{2+} \rightarrow \text{ZnL}_2
\]  
(1a)

and

\[
2\text{HL} + \text{Zn}^{2+} \rightarrow \text{ZnL}_2 + 2\text{H}^+ 
\]  
(1b)

where \( \text{L} \) and \( \text{HL} \) 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 [32].

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

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

or

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

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* [32].

The kinetic rate equations can be rewritten as follows:

\[
\frac{dq_e}{dt} = k(q_e - q_t)^2 
\]  
(2)

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

Separating the variables in Eq. (2) gives:

\[
\frac{dq_e}{(q_e - q_t)^2} = kdt
\]

integrating this for the boundary conditions \( t= 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = q_e \), gives:

\[
\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt 
\]  
(3)
Eq. (3) can be rearranged to obtain:

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

$$h = kq_e^2$$  \hspace{1cm} (5)

Substituting Eq. (5) into Eq. (4), gives:

$$q_t = \frac{t}{\left(\frac{1}{h} + \frac{t}{q_e}\right)}$$  \hspace{1cm} (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, Luffa cylindrica dose and nature of solute [32].

### 3.2. Effect of Initial Metal Ions Concentration and Nature of Solute

The sorption capacity data obtained when Zn$^{2+}$ and their initial concentrations were varied at temperature of 25°C and Luffa cylindrica dose of 20g/l are as shown in Figures 5a and 5b. Figure 5a shows typical data for the zinc (II) ions plotted so that the constants initial sorption rate and equilibrium sorption capacity in Eq. (6) can be derived. These constants are given in Table 3. The agreement between the sets of data reflects the extremely high correlation coefficients obtained and shown in Table 3. Figure 5b shows typical sorption curves for effect of initial metal ion concentrations on the sorption kinetics of of zinc ions onto Luffa cylindrica. In other words, the data showed good compliance with the proposed pseudo-second order equation. It was shown in the data that the initial metal ion concentrations influenced the contact time necessary to reach equilibrium and that the sorption capacity increased for the higher initial metal ion concentrations (Table 3).

![Figure 5a](image_url)

**Figure 5a.** The sorbed capacity against time for the effect of varied initial ion concentration on the sorption kinetics of Zinc ion onto Luffa cylindrica at pH= 5.0.

**Figure 5b.** The sorbed capacity against time for the effect of varied initial ion concentration on the sorption kinetics of Zinc ion onto Luffa cylindrica at pH= 5.0.

<table>
<thead>
<tr>
<th>M$^{2+}$</th>
<th>$C_0$ (mg/l)</th>
<th>$r^2$</th>
<th>$q_e$ (mg/g)</th>
<th>$k$ (g/mgmin)</th>
<th>$h$ (mg/mgmin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>25</td>
<td>0.999</td>
<td>1.1406</td>
<td>1.3902</td>
<td>1.8088</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1.000</td>
<td>2.3822</td>
<td>2.0605</td>
<td>11.6935</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.000</td>
<td>4.8671</td>
<td>4.1497</td>
<td>98.3001</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.000</td>
<td>9.8649</td>
<td>5.3538</td>
<td>521.0116</td>
</tr>
</tbody>
</table>

The value of the initial sorption rates, $h$, was determined by using the values of the intercept of the straight lines plotted in Figure 5a. The initial sorption rate increases with an increase in the initial metal concentrations for the zinc (II) ions studied. While $h$ varies from 1.8088 to 521.0116 mg/g min, the $C_0$ varies from 10 to 100 mg/l for zinc(II) ions, the values of rate constant, $k$, was found to increase from 1.3902 to 5.3538 g/ mg min, for an increase in the initial zinc concentration from 25 to 200 mg/l.

The corresponding linear plots of the values of $q_e$, $k$ and $h$ against $C_0$ were regressed to obtain expressions for these values in terms of the initial metal ion concentration with high correlation coefficients (Table 4). Therefore it is further considered that $q_e$, $k$ and $h$ can be expressed as a function of $C_0$ for zinc as follows:

$$q_e = \frac{C_0}{Aq_0 + Bq_e}$$  \hspace{1cm} (7)

$$k = \frac{C_0}{Aq_0 + B_k}$$  \hspace{1cm} (8)

$$h = \frac{C_0}{Aq_0 + B_h}$$  \hspace{1cm} (9)

Substituting the Eqs (7), (8) and (9) into Eq. (6), the rate law for a pseudo-second order and the relationship of $q_e$, $C_0$ and $t$ can be represented as follows:

$$q_t = \frac{t}{\frac{1}{\frac{C_0}{Aq_0 + B_q} + \frac{t}{C_0}} + \frac{t}{\frac{C_0}{Aq_0 + B_q}}}$$  \hspace{1cm} (10)
when Eq. (10) is rearranged it becomes

\[ q_t = \frac{C_0 t}{A_h C_0 + B_h + (A_q C_0 + B_q)t} \] (11)

Substituting the values of the empirical parameters \( A_h, B_h, A_q \) and \( B_q \) from Table 4 into Eq. (11), the rate law for a pseudo-second order and the relationship of \( q_t, C_0 \) and \( t \) can be represented as follows:

\[ q_t = \frac{C_0 t}{-0.00766C_0 + 1.9153 + (-0.00414C_0 + 21.089)t} \] (12)

The Equation (12) represents the generalised predictive model for the zinc ion sorbed at any contact time and initial metal ion concentration within the given range. These equations can then be used to derive the amount of metal sorbed at any given ion concentration and the reaction time.

![Figure 6](image)

**Figure 6.** Effect of initial concentration on zinc sorption at various reaction times.

Table 4. Empirical parameters for predicted \( q_e \), \( k \) and \( h \) from \( C_0 \).

<table>
<thead>
<tr>
<th>( M^{2+} )</th>
<th>( A_h )</th>
<th>( B_h )</th>
<th>( r^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>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>-0.0041</td>
<td>21.089</td>
<td>0.9999</td>
<td>0.1039</td>
<td>15.844</td>
<td>0.9776</td>
<td>-0.008</td>
<td>1.915</td>
<td>0.9960</td>
</tr>
</tbody>
</table>

3.3. Effect of *Luffa cylindrica* Dose and Nature of Solute

Table 5. The effect of dosage on metal ions biosorption data.

<table>
<thead>
<tr>
<th>( M^{2+} )</th>
<th>( m ) (g)</th>
<th>( r^2 )</th>
<th>( q_t ) (mg/g)</th>
<th>( k ) (g/mg.min)</th>
<th>( h ) (mg/g.min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.2</td>
<td>1.000</td>
<td>24.3924</td>
<td>0.4205</td>
<td>250.2186</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.999</td>
<td>12.3217</td>
<td>1.1412</td>
<td>173.2589</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>1.000</td>
<td>8.1220</td>
<td>2.0598</td>
<td>135.8782</td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>1.000</td>
<td>6.0932</td>
<td>3.0570</td>
<td>113.4967</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>1.000</td>
<td>4.8765</td>
<td>4.2307</td>
<td>100.6064</td>
</tr>
</tbody>
</table>

Figures 6 shows the three-dimensional plot of Equation (12) it indicate that the Zn (II) ions sorbed at any contact time is higher for a greater initial metal ion concentration. This is obvious for higher \( C_0 \) values, as a more efficient utilisation of the sorptive capacities of the sorbent is expected due to a higher concentration gradient pressure [32].

The plotted experimental data (Figure 7a) 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 5.

![Figure 7](image)

**Figure 7.** Typical sorption curves for effect of *Luffa cylindrica* dose on the sorption kinetics of zinc, nickel, copper and lead ions onto *Luffa cylindrica* at temperature of 25°C and initial ion concentration of 100 mg/l. The plots as seen in Figure 7a also showed that sorption capacity increased for lower *Luffa cylindrica* dosages at any specific time. There were effects on the contact time required to reach saturation due to the variation in *Luffa cylindrica* doses. It was found that the equilibrium sorption of metal ions studied was a function of *Luffa cylindrica* doses. The rate constant, \( k \), the equilibrium sorption, \( q_e \) and the initial sorption rate, \( h \), of sorption at different *Luffa cylindrica* doses were calculated from the intercept and slope of the straight line plots of \( t/q_t \) versus \( t \). The initial sorption rate decreased with an increase in the *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.

Figure 7a. The sorbed capacity against time for the effect of varied doses on the sorption kinetics of Zinc ion onto Luffa cylindrica at pH= 5.0.

Figure 7b. The sorbed capacity against time for the effect of varied doses on the sorption kinetics of Zinc ion onto Luffa cylindrica at pH= 5.0.

The expression

$$x = Am^b$$

Where $x = q_e$, $k$ or $h$.

Table 6. Empirical parameters for predicted $q_e$, $k$ and $h$

<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>Zn</td>
<td>4.879</td>
<td>-1.00</td>
<td>0.999</td>
<td>4.238</td>
<td>1.433</td>
<td>0.999</td>
<td>100.9</td>
<td>-0.57</td>
<td>0.998</td>
</tr>
</tbody>
</table>

Table 6 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 6 in Eq. (13), the rate law for a pseudo-second order reaction and the relationship between $q_e$, $m$ and $t$ can be represented as:

$$q_t = \frac{t}{1/100.9m^{0.57} + t/4.879m^{1.0}}$$

Figure 8. Effect of L. cylindrica dose on zinc sorption at various times.

This equation can then be used to derive the sorption amount zinc (II) ions at any given dosage and the reaction time. The three-dimensional plot of the Equation (14) is shown in Figure 8.

The Equation represent a generalised predictive model for the amount of zinc (II) ions sorbed at any contact time and involved $L$. cylindrica dose. It indicates that the zinc (II) ions 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.

Kinetic models have been derived for the sorption of zinc (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 initial metal ion concentration, $L$. cylindrica dose and nature of solute and this is in agreement with previous research [32].

3.4. Artificial Neural Network Model Development

Different categories of software can be used to do mathematical modeling [34]. Pythia is a program for the development and design of Neural Networks. Pythia features Backpropagation Networks and train neural networks on any Windows machine [35].

In this study, 2 models of back-propagation feed forward network were developed in Pythia environment. The models are MISO Zn-1 and MISO Zn-2.

3.5. Selection of Input and Output Variables

The most important task in developing a Neural Network model is to select the most significant variables as estimator inputs. In this process of biosorption of Zinc (II) ions onto $L$. cylindrica, there are a lot of variables that can affect the efficiency of system.

Therefore, in order to simplify the model structure, input variables that gave dominant impact to the process outputs were selected while the others were neglected. The independent experimental variables selected are Contact time, initial metal ion concentration and biosorbert dosage. The
output was sorption capacity.

The signal moves from the input layer towards the output layer as shown in Figures 9a and b, and in this process each neuron uploads all the neurons of the successive layers, transferring a portion of the signal that has been accumulated. The portion of signal transferred is regulated by a transfer function [36].

A feed-forward back-propagating ANN structure as illustrated in Figures 9a and b was used to develop yield prediction models. Data move through the layers in one direction, from the input through the hidden to the output layers, without loops as opposed to feedback networks.

![Figure 9a. Layers and connections of a feed-forward back propagating artificial neural network (MISO-1).](image)

![Figure 9b. Layers and connections of a feed-forward back propagating artificial neural network (MISO-2).](image)

**3.6. Developing Yield Prediction Models with BPNN**

In the present work, the input variables to the feed forward back propagation neural network (BPNN) were as follows: the amount of *L. cylindrica* (g) and initial ion concentration of Zn (II) ions (mg/l). The sorption capacity was chosen as the experimental response or output variable. The sigmoidal transfer function was used as a transfer function in the hidden and output layers. This is the most widely used transfer function. The training function was Fermi (Min=0.00, Max=1.00, Thld=0.00, Inc=1.00) and the learning rate was 0.500. The several data points generated were used to develop the ANN model [37].

BPNN modelling for initial ion concentration and nature of solute

![Figure 10a. MISO Zn-1 (2,3,3,1) 7 neurons, 3 levels, 2 inputs, 1 output. Transfer function: Fermi (Min=0.00, Max=1.00, Thld=0.00, Inc=1.00) Learning rate 0.500.](image)
Figure 10b. Accuracy of prediction of Sorption capacity (mg/g) of Zn (II) ions onto L. cylindrica for MISO Zn-1 neural network model.

Figure 10c. Scatter plot of the measured sorption capacity and of the predicted sorption capacity derived from a 7-neuron MISO Zn-1 neural network model.

Figure 10a show the Artificial Neural Network architecture developed for the initial ion concentration. For MISO Zn-1 model the number of neurons was 7.

A Feed forward back propagation Artificial Neural Network (ANN) was trained using the training data from the experimental results. Figure 10b show the experimental and ANN predicted Sorption capacity for MISO Zn-1 neural network model developed for the effect of Initial ion concentration on the biosorption of Zn(II) ions onto Luffa cylindrica as biosorbent. The accuracy of the prediction of the trained ANN was then compared with the actual measured values. It was observed that ANN gave near accurate prediction for Sorption capacity values.

To have a more precise investigation into the various models, a regression analysis of outputs and desired targets was performed as shown in Figure 10c. There was a high correlation between the predicted values by the ANN model and the measured values resulted from experimental data. The correlation coefficient was 0.973 for MISO Zn-1 model, which implied that this model succeeded in the prediction of the sorption capacity.

3.7. BPNN Modelling for Luffa cylindrica Dose and Nature of Solute

Figure 11a show the Artificial Neural Network architecture developed for the Luffa cylindrica dose and Zn (II) ions used for this study. For the MISO Zn-2 model the maximum number of neurons was 12.

Figure 11b. Accuracy of prediction of Sorption capacity (mg/g) of Zn (II) ions onto L. cylindrica for MISO Zn-2 neural network model.

Figure 11c. Scatter plot of the measured sorption capacity and of the predicted sorption capacity derived from a 12-neuron MISO Zn-2 neural network model.

A Feed forward back propagation Artificial Neural Network (ANN) was trained using the training data from the experimental results. Figure 11c shows the experimental and ANN predicted Sorption capacity for MISO Zn-2 model developed for the effect of Luffa cylindrica dose on the biosorption of Zn(II) ions. The accuracy of the prediction of the trained ANN was then compared with the actual measured values. It was observed that ANN gave near
accurate prediction for sorption capacity values.

To have a more precise investigation into the various models, a regression analysis of outputs and desired targets was performed as shown in Figure 11c. There was a high correlation between the predicted values by the ANN model and the measured values resulted from experimental data. The correlation coefficient was 0.950 for MISO Zn-2, which implies that the models succeeded in prediction of the sorption capacity.

Table 7. The RMSE values for MISO neural network models.

<table>
<thead>
<tr>
<th>Neural Network model</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>MISO Zn-1</td>
<td>0.5912</td>
</tr>
<tr>
<td>MISO Zn-2</td>
<td>1.6267</td>
</tr>
</tbody>
</table>

The root mean square error (RMSE) is chosen as indicator of performance of the networks. The Root Mean Squared error (RMSE) is calculated using the following formula [38-39]:

\[
RMSE = \sqrt{\frac{1}{n} \sum \left( \text{Observed} - \text{Predicted} \right)^2}
\]  

(15)

Generally, the artificial neural network offers the advantage of being fast, accurate and reliable in the prediction or approximation affairs, especially when numerical and mathematical methods fail. There is also a significant simplicity in using ANN due to its power to deal with multivariate and complicated problems [40].

The root mean square error (RMSE) of the performance of ANN MISO model on the experimental data for predicting sorption capacity is 0.5912 and 1.6267 for MISO Zn-1 and MISO Zn-2 models respectively as can be seen in Table 7. ANN was able to predict the sorption capacity quite reasonably for all models.

4. Conclusion

A kinetic study was carried out and the experimental data fitted into Pseudo-first order, Pseudo-second order, Intraparticle diffusion and Avrami models. This was done using the nonlinear regression method to obtain the kinetic parameters.

Kinetic models have been developed and fitted for the sorption of the divalent metal ions onto L. cylindrica on the effect of Luffa cylindrica dose and the initial ion concentration. The results showed sorption for Zn (II) ions onto L. cylindrica during agitation by suspended shaking; the process can be described by all kinetic models but 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.

In this study two ANN models were developed, which were all MISO networks. BPNN models were able to predict the sorption capacity quite reasonably for the effect of initial ion concentration and Luffa cylindrica dose for the biosorption process.

References


