

# Mathematical and ANN Models of the Effect of Dosage on $\text{Cu}^{2+}$ Sorption Capacity of *Luffa Cylindrica*



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## Abstract

The biosorption of copper (II) ions onto *Luffa cylindrica* was investigated. *Luffa cylindrica*, a biomaterial with wide distribution particularly in the tropical world, is characterized with the surface area, chemical bonds, bulk density, pore size distribution, microstructures, composition, morphology and elemental composition which are determined. Biosorption studies were carried out with varying dosage and the experimental data obtained were fitted to Pseudo-Second order kinetic model. The regression value obtained from the various doses studies ranged from 0.991 to 0.999. A kinetic model was developed mathematically and as well 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 1.2754. Artificial neural network has the capability to predict the sorption capacity quite reasonably for the model.

## Keywords

Sorption Capacity; *Luffa Cylindrica*; Biosorption; Mathematical Modelling; Artificial Neural Network

## Introduction

Heavy metals are toxic, bio-accumulative and not biodegradable over time (Abdel-Ghani, Ahmad, El-Chaghaby and Lima, 2009). Copper metal contamination exists in aqueous waste streams from many industries such as electronic and electrical, metal plating, mining, manufacture of computer heat sinks, copper plumbing, as well as biostatic surface, as a component in ceramic glazing and glass colouring (Tumin, Chuah, Zawani and Abdul Rashid, 2008). Copper is commonly used in agricultural chemicals for mildew prevention, and as algicides in water treatment of industrial waters, a preservative for wood, leather, and fabrics. Workers, or those living near mines, smelters, metal fabrication and manufacturing plants, wood treatment plants, phosphate fertilizer

plants, and waste water plants may also experience excessive copper exposure (Jolley, O'Brien, and Morrison, 2003).

*Luffa cylindrica*, locally available and a summer season vegetable belonging to a sub-tropical plant, requires warm summer temperatures and long frost-free cultivation season when grown in temperate regions. It is an annual climbing which produces fruit containing fibrous vascular system. It is difficult to assign with accuracy the indigenous areas of *Luffa* species with a long history of cultivation in the tropical countries of Asia and Africa. Indo-Burma is reported to be the center of diversity for sponge gourd. The main commercial production countries are China, Korea, India, Japan and Central America (Bal et al., 2004).

The structure of *Luffa cylindrica*, is cellulose based (Rowell, James and Jeffrey, 2002; Mazali and Alves, 2005), and the surface of cellulose in contact with water is negatively charged. Copper compound used in this study will dissolve to give the cationic metal, which will undergo attraction on approaching the anionic *Luffa cylindrica* structure (Ho, Huang and Huang, 2002). On this basis, it is expected that a metal cation will have a strong sorption affinity for *Luffa cylindrica*.

However, no evidence is readily available that researches have addressed the mathematical modelling of the sorption of metal ions onto this biosorbent. Earlier reported mathematical models for the sorption of heavy metal ions onto some biosorbents included: surface-complexation, cation-exchange and triple-layer models (Gupta, Prasad, Singhal and Kumar, 2009).

An Artificial Neural Network is an adaptive (training phase), most often nonlinear system that learns to

perform a function from data. After the training phase the Artificial Neural Network parameters are fixed and the system is deployed to solve the problem at hand (the testing phase).

In engineering, neural networks serve two important functions: as pattern classifiers and as nonlinear adaptive filters. A neural network is a powerful data modelling tool able to capture and represent complex input/output relationships. The motivation for the development of neural network technology stemmed from the desire to develop an artificial system, like the human brain, with ability to learn from experience used when no exact mathematical relationship is available and when linear and nonlinear prediction problems have been solved. It is a computing tool made up of a number of simple but highly connected nodes (Baughman and Liu, 1995).

The objective of this study is to derive an empirical and artificial neural network models to predict sorption capacity of the *Luffa cylindrica* as a biosorbent for copper (II) ions.

## Materials and Methodology

### Preparation of *Luffa Cylindrica*

The seeds and sponges of *L. cylindrica* gathered into a clean plastic bag, have been 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 of particle sizes ranging from 0.3 to 0.6 mm, allowing for shorter diffusion path, which resulted in a higher rate of biosorption (Adeyinka, Liang and Tina, 2007). The ground seed and sponge were mixed at a ratio of 1:1.

### Preparation of Aqueous Solutions

Stock solution of copper was prepared with distilled water and copper (II) tetraoxosulphate (VI). The working solution was obtained by diluting the stock solutions with distilled water. The pH of the solution was adjusted to the pH of 7. 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 reproduced results (Marshall and Champagne, 1995).

### Biosorption Experiment

The biosorption studies on evaluation of the *Luffa cylindrica* mixture for removal of copper (II) ions from

aqueous solutions was carried-out in triplicate using the batch biosorption procedure (Basil et al., 2006; Lima et al., 2007).

### Characterization of *Luffa Cylindrica*

#### 1) 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) 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) (Jackson, Hunt and Doherty, 2004).

#### 3) 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.

#### 4) 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) (Coates, 2000).

#### 5) Determination of Bulk Density of *Luffa Cylindrica* Mixture

The method of Okaka and Potter (1979) was used to determine the bulk density.

## Results and Discussion

### Characterization of *Luffa Cylindrica*

TABLE 1 PHYSICAL PROPERTIES OF THE *LUFFA CYLINDRICA* BIOSORBENT

|   |                         |
|---|-------------------------|
| Specific surface area - BET (m <sup>2</sup> /g) | 0.28                    |
| Total Surface area (m <sup>2</sup> /g)          | 1.1895                  |
| Pore Diameter Range (µm)                        | 1051.309204 to 0.003577 |
| Bulk density (g/cm <sup>3</sup> )               | 0.34                    |

Table 1 shows the bulk density, surface area and pore diameter range for the biosorbent used in this study. The Specific surface area using the BET method is 0.28 m<sup>2</sup>/g and the Pore diameter range is between 1051.309204 to 0.003577 μm. The bulk density is 0.34 g/cm<sup>3</sup>. 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 in typical mesoporous materials (Hamoudi and Kaliaguine, 2003).

TABLE 2 ELEMENTAL COMPOSITION OF THE *LUFFA CYLINDRICA* BIOSORBENT

| Elements | Weight % | Atomic % |
|----------|----------|----------|
| C        | 79.33    | 86.91    |
| O        | 12.25    | 10.07    |
| P        | 00.95    | 00.40    |
| S        | 00.75    | 00.31    |
| Cl       | 01.58    | 00.59    |
| K        | 03.86    | 01.30    |
| Ca       | 01.29    | 00.42    |

Table 2 illustrates the elemental composition of *Luffa cylindrica* that was analysed by means of scanning electron microscopy (SEM). The *Luffa cylindrica* sample showed a very high percentage of carbon followed by oxygen and then potassium.

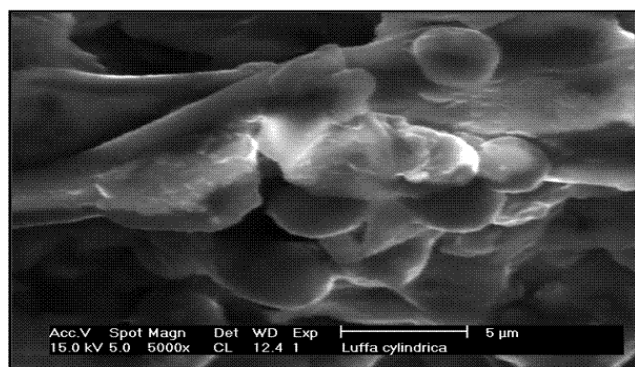


FIG. 1: SCANNING ELECTRON MICROSCOPY OF *LUFFA CYLINDRICA* BIOSORBENT: TRANSVERSAL VIEW OF THE MIXTURE OF SEED AND SPONGE 5000×

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 1 as observed shows the fibrous structure of *Luffa cylindrica* with some fissures and holes indicating the presence of macroporous structure. These should contribute to a little bit to the diffusion of the Cu (II) to the *Luffa cylindrica* biosorbent surface (Passos et al., 2006; Vagheti et al, 2003; Arenas et al., 2004; Passos et al.,

2008). The small number of macroporous structure is confirmed by the low specific surface area of the biosorbent (see Table 1). As the biosorbent material presented few numbers of macroporous structure, it adsorbed low amount of nitrogen, which led to a low BET surface area (Passos et al., 2006; Vagheti et al, 2003; Arenas et al., 2004; Passos et al., 2008). Therefore, the major contribution of the Cu (II) uptake can be attributed to micro- and mesoporous structures (Figure 1).

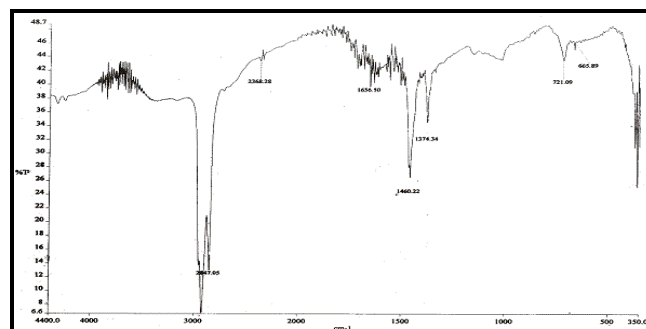


FIG. 2 FTIR SPECTRUM OF THE MIXTURE OF SEED AND SPONGE OF *L. CYLINDRICA* BIOSORBENT BEFORE BIOSORPTION

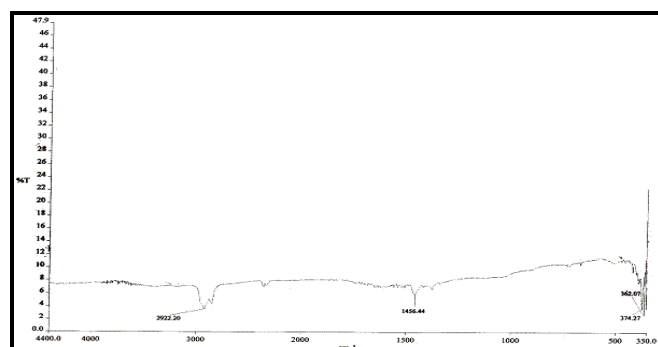


FIG. 3 FTIR SPECTRUM OF THE MIXTURE OF SEED AND SPONGE OF *L. CYLINDRICA* BIOSORBENT AFTER BIOSORPTION OF  $\text{Cu}^{2+}$  IONS

Figures 2 and 3 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 2. Functional groups found in the structure include carboxylic, alkynes or nitriles and amine groups (Pavia, Lampman, and Kriz, 1996).

The stretching vibrations of C-H stretch of -CHO group shifted from 2847.05 to 2922.20 cm<sup>-1</sup> after Cu<sup>2+</sup> ions biosorption. The assigned bands of the carboxylic, amine groups and alkynes or nitriles vibrations also shifted on biosorption, shown as Figure 3. The shift in the frequency showed that there was biosorption of

Cu<sup>2+</sup> ions on the *L. cylindrica* biosorbent and the carboxylic and amine groups were involved in the sorption of the Cu<sup>2+</sup> ions (Volesky, 2003).

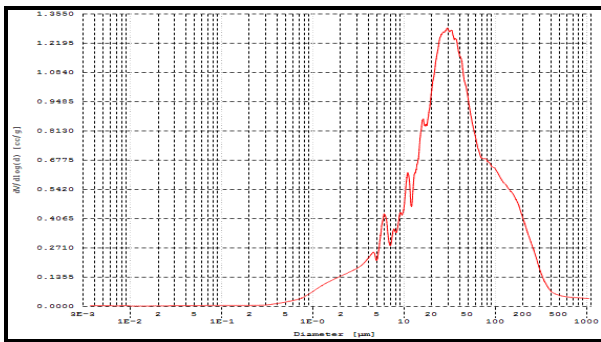


FIG. 4 A PLOT SHOWING THE PORE SIZE DISTRIBUTION OF THE BIOSORBENT *L. CYLINDRICA*

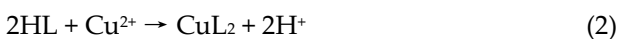
The pore size distribution of the *Luffa cylindrica* sample was obtained from Mercury intrusion method and shown in Figure 4. The distribution of average pore diameter curve presents a maximum with an average pore diameter of about 30 µm. The amount of pores seen in the *Luffa cylindrica* biosorbent decreases for average pore diameters ranging from 30 to 1000 µm. On the other hand, the amount of average pores ranging from 3.0 × 10<sup>-03</sup> to 30 µm is predominant. Therefore, this biosorbent can be considered mixtures of micro- and mesoporous materials (Passos et al., 2006; Vaghetti et al, 2003; Arenas et al., 2004; Passos et al., 2008).

**Mathematical Modelling**

*Luffa cylindrica* contains polar functional groups such as aldehydes, ketones, and acids that can be involved in chemical bonding and are responsible for the cation exchange capacity of the *Luffa cylindrica* (Intech, 2012; Ho and McKay, 2000). 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 (Naja, Murphy, and Volesky, 2009). Thus, the *Luffa cylindrica*-metal reaction may be represented in two ways:



and



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

In developing the mathematical model of this sorption process, some assumptions have been made (Ho and McKay, 2000).

The rate expression for the sorption described by

Eqs (1) and (2) is:

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

or

$$\frac{d(HL)_t}{dt} = k[HL_0 - HL_t]^2$$

where (L)<sub>t</sub> and (HL)<sub>t</sub> are the number of active sites occupied on the *Luffa cylindrica* at time t, (L)<sub>0</sub> and (HL)<sub>0</sub> are the number of equilibrium sites available on the *Luffa cylindrica* (Ho and McKay, 2000).

The kinetic rate equations can be rewritten as follows:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{3}$$

where k is the rate constant of sorption, (g/mg min), q<sub>e</sub> is the amount of divalent metal ion sorbed at equilibrium, (mg/g), q<sub>t</sub> is amount of divalent metal ion on the surface of the sorbent at anytime, t, (mg/g).

Separation of the variables in Eq. (3) gives:

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

while the integration of this for the boundary conditions t= 0 to t = t and q<sub>t</sub>= 0 to q<sub>t</sub>= q<sub>t</sub>, gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \tag{4}$$

this is the integrated rate law for a pseudo-second order reaction which can be rearranged to obtain:

$$q_t = \frac{t}{(1/kq_e^2 + t/q_e)} \tag{5}$$

$$h = kq_e^2 \tag{6}$$

Eq. (5) is substituted into Eq. (6), resulting in:

$$q_t = \frac{t}{(1/h + t/q_e)} \tag{7}$$

Although there are many factors influencing 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 which include *Luffa cylindrica* dose (Ho and McKay, 2000).

Figures 1 and 2 show typical sorption curves for effect

of *Luffa cylindrica* dose on the sorption kinetics of copper ions onto *Luffa cylindrica* at temperature of 25°C and initial ion concentration of 100 mg/l. The plotted experimental data (Figure 1) 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 it can be seen in Table 3

TABLE 3 THE EFFECT OF DOSAGE ON COPPER IONS BIOSORPTION DATA

| m (g) | r <sup>2</sup> | q <sub>e</sub> (mg/g) | k (g/mgmin) | h (mg/gmin) |
|-------|----------------|-----------------------|-------------|-------------|
| 0.2   | 0.992          | 26.1835               | 0.0047      | 3.2282      |
| 0.4   | 0.991          | 12.4329               | 0.0130      | 2.0150      |
| 0.6   | 0.996          | 8.0189                | 0.0249      | 1.6010      |
| 0.8   | 0.999          | 5.7322                | 0.0382      | 1.2551      |
| 1.0   | 0.995          | 5.0950                | 0.0390      | 1.0132      |

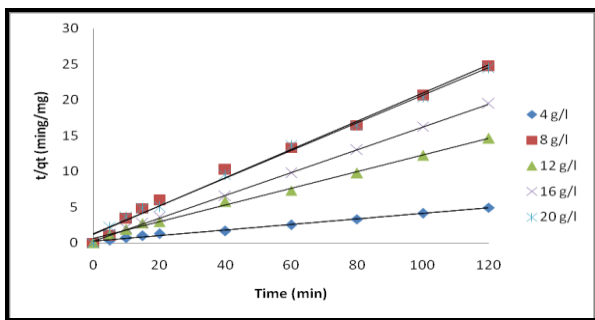


FIG. 5 THE SORBED CAPACITY VERSUS TIME FOR THE EFFECT OF VARIED DOSES ON THE SORPTION KINETICS OF COPPER ION ONTO LUFFA CYLINDRICA AT PH= 7.0

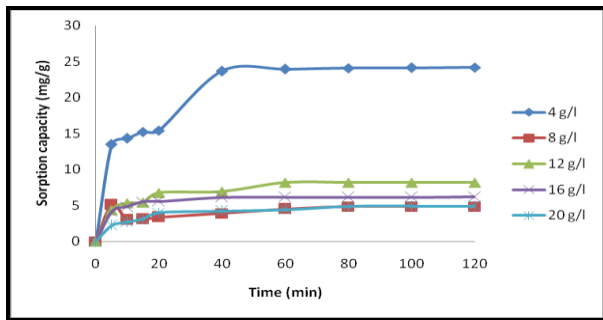


FIG. 6 THE SORBED CAPACITY AGAINST TIME FOR THE EFFECT OF VARIED DOSES ON THE SORPTION KINETICS OF COPPER ION ONTO LUFFA CYLINDRICA AT PH= 7.0

Figure 6 shows that for all the various dosages, the amount of the copper 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 before 20 minutes. The plots as seen in Figure 6 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 copper

ions studied was a function of *Luffa cylindrica* doses. The rate constant, k, the equilibrium sorption, q<sub>e</sub> and the initial sorption rate, h, of sorption at different *Luffa cylindrica* doses were calculated based on the intercept and slope of the straight line plots of t/q<sub>t</sub> versus t as shown in Figure 5. 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<sub>e</sub>, k and h against m (dosage) were regressed to obtain expressions with exponents for these values in terms of the m parameter.

$$\text{The expression, } x = Am^b \tag{8}$$

where x= q<sub>e</sub>, k or h

TABLE 4 EMPIRICAL PARAMETERS FOR PREDICTED Q<sub>E</sub>, K AND H

| A <sub>q</sub> | b <sub>q</sub> | r <sub>2</sub> | A <sub>k</sub> | b <sub>k</sub> | r <sub>2</sub> | A <sub>h</sub> | b <sub>h</sub> | r <sub>2</sub> |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 4.791          | 1.04           | 0.995          | 0.046          | 1.387          | 0.983          | 1.060          | 0.70           | 0.993          |

Table 4 shows the empirical parameters for predicted q<sub>e</sub>, k and h and their corresponding correlation coefficients.

By substitution of the values of A<sub>q</sub>, B<sub>q</sub>, A<sub>h</sub> and B<sub>h</sub> from Table 4 in Eq. (7), the rate law for a pseudo-second order reaction and the relationship among q<sub>t</sub>, m and t can be represented as:

$$q_t = \frac{t}{1/1.06m^{-0.70} + t/4.791m^{-1.04}} \tag{9}$$

This equation can then be used to derive the sorption amount of copper at any given dosage and the reaction time. The three-dimensional plot of the equation is shown in Fig. 7.

The equation representing a generalised predictive model for the amount of metal ion sorbed at any contact time and involved *L. cylindrica* dose, 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 the rise of 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 model has been derived for the sorption of a divalent metal ions onto *L. cylindrica*. The parameter which has the greatest influence on the kinetics of the sorption reaction was sorption equilibrium; while q<sub>e</sub> is a function of initial metal ion concentration, L.

*cyllindrica* dose and nature of solute, which is in agreement with previous research (Ho and McKay, 2000).

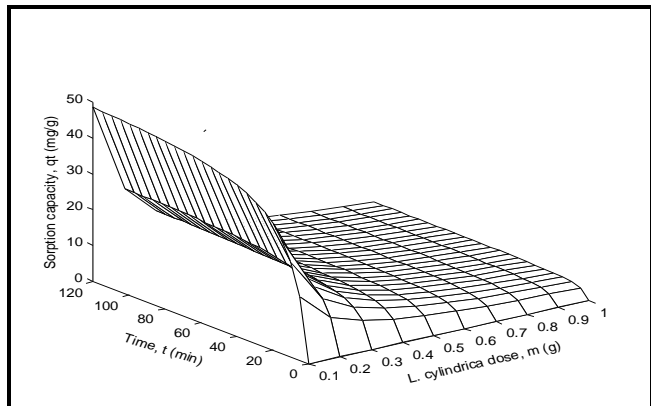


FIG. 7 EFFECT OF L. CYLLINDRICA DOSE ON COPPER SORPTION AT VARIOUS TIMES

**Artificial Neural Network Modelling**

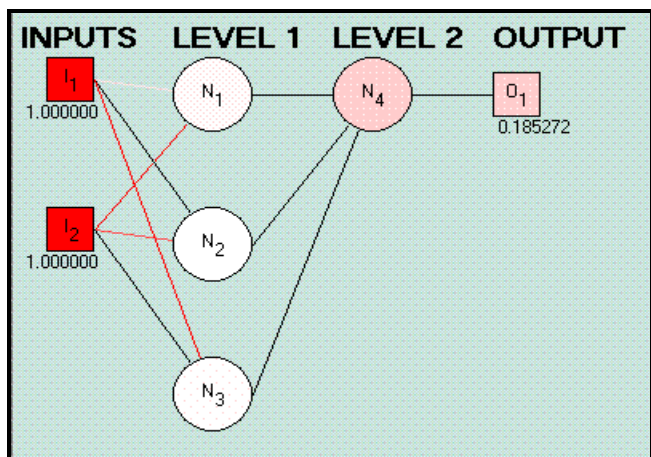


FIG. 8 MISO CU (2,3,1) 4 NEURONS, 2 LEVELS, 2 INPUTS, 1 OUTPUT. TRANSFER FUNCTION:FERMI(MIN=0.00, MAX=1.00, THLD=0.00, INC=1.00) LEARNING RATE 0.500

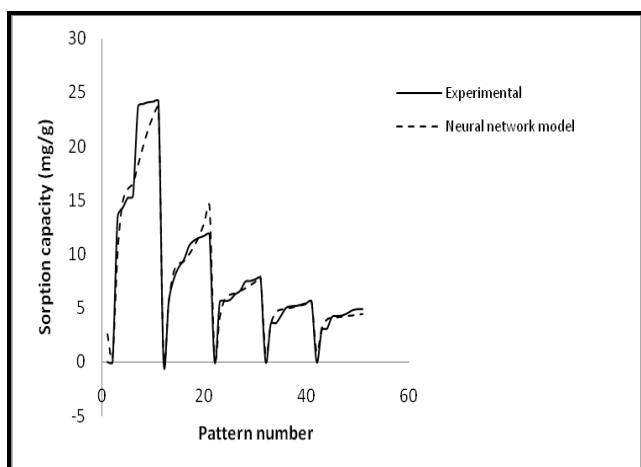


FIG. 9 ACCURACY OF PREDICTION OF SORPTION CAPACITY (MG/G) OF CU (II) IONS ONTO L. CYLLINDRICA FOR MISO CU NEURAL NETWORK MODEL

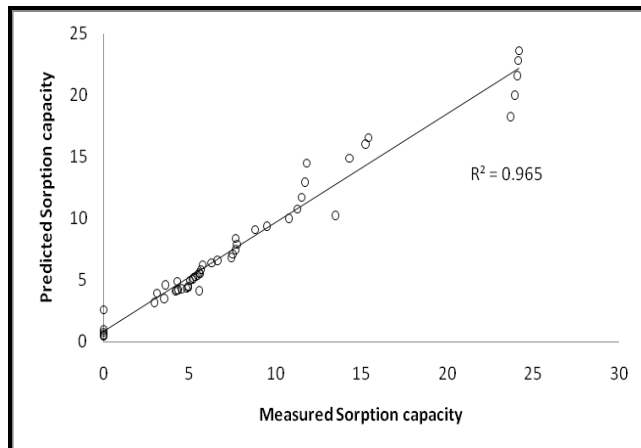


FIG. 10 SCATTER PLOT OF THE MEASURED SORPTION CAPACITY AND OF THE PREDICTED SORPTION CAPACITY DERIVED FROM A 4-NEURON MISO CU NEURAL NETWORK MODEL

Figure 8 shows the Artificial Neural Network architecture developed for the *Luffa cylindrica* dose and copper used in this study. The model had 4 neurons, 2 levels, 2 inputs, 1 output. A Feed forward back propagation Artificial Neural Network (ANN) was trained using the training data from the experimental results. Figure 9 shows the experimental and ANN predicted Sorption capacity for the neural network model developed for the effect of *Luffa cylindrica* dose on the biosorption of Cu(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 Figures 10. 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 0.965, which implied that the model succeeded in prediction of the sorption capacity

The root mean square error (RMSE) chosen as indicator of performance of the networks is calculated using the following formula (Goutam, Pankaj, Arnab and Neera, 2006; Khaing and Thinn, 2008):

$$RMSE = \sqrt{\frac{\sum(\text{Observed} - \text{Predicted})^2}{\text{number of Data}}}$$

Generally, the artificial neural network takes advantage over rapidity, accuracy and reliability 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 (Najafi, Ghobadian, Yusaf and Rahimi, 2007).

The root mean square error (RMSE) of the performance of ANN MISO model on the experimental data to predict Sorption capacity was 1.2754, which could be seen in Table 5. ANN was able to predict the sorption capacity quite reasonably for the model.

TABLE 5 THE RMSE VALUES FOR MISO CU NEURAL NETWORK MODEL

| Neural Network Model | RMSE   |
|----------------------|--------|
| MISO Cu              | 1.2754 |

## Conclusions

The *Luffa cylindrica* seeds and sponge mixture has been presented here as an desirable alternative biosorbent to Cu<sup>2+</sup> ions removal from aqueous solution. The mathematical and Artificial neural network models of the effect of dosage on Cu<sup>2+</sup> sorption capacity of *Luffa cylindrica* seeds and sponge mixture have been developed and validated. The equation derived represents a generalised predictive model for the amount of metal ion sorbed at any contact time and involved *L. cylindrica* dose and the ANN has the capability to predict the sorption capacity quite reasonably for the model.

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