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ARTIFICIAL NEURAL NETWORK FOR MODELING OF CU(II) BIO-SORPTION FROM SIMULATED WASTEWATER BY FUNGAL BIOMASS

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Abstract: A three-layer artificial neural network model was developed to predict the removal efficiency of Cu(II) ions from simulated wastewater by fungal biomass based on 85 batch experiments. The effect of different parameters such as contact time between adsorbate and adsorbent (10-180 min), initial pH of the solution (3-7), initial metal concentration (50-250 mg/L), adsorbent dosage (0.05-2 g/100 mL), agitation speed (0-250 rpm) and temperature (10-60 ºC) were studied. The best values of these parameters that achieved the maximum removal efficiency (=95 %) of Cu(II) were 90 min, 6, 50 mg/L, 2 g/100 mL, 200 rpm and 20 ºC, respectively.The present model was able to predict adsorption efficiency with a tangent sigmoid transfer function (tansig) at hidden layer with 8 neurons and a linear transfer function (purelin) at output layer. The linear regression between the network outputs and the corresponding targets were proven to be satisfactory with a correlation coefficient of greater than 0.99778 for used six model variables. The sensitivity analysis based on the artificial neural network indicated that the initial pH of the solution with a relative importance of 22.1% appeared to be the most influential parameter in the Cu(II) removal, followed by dosage (19.5%), agitation speed (18.2%), temperature (14.1%), time (13.3%), and concentration (12.8%).

Keywords: *Neural network; Adsorption; fungal biomass; Modeling; Copper.*

نمذجة الشبكة العصبية الأصطناعية لأزاله أيون النحاس من مياه الصرف الصحي باستخدام الكتلة الحيوية الفطرية

الخلاصة: تم استخدام نموذج الشبكه العصبية الأصطناعية يثلاث طبقات للنمذجة والتنبؤ بكفاءة الازاله لأيون النحاس من المياه الثقيله الملوثه باستخدام ماده ممتزه الكتله الحيويه الفطريه. تم استخدام (٨٥) فحصاً عملياً كقاعدة بيانات لتشكيل نموذج الشبكه العصبيه الأصطناعيه لتخمين عدة متغيرات مختلفه مثل زمن التماس بين المادة المزاله والممتزة (١٠-١٨٠) دقيقه ، الدالة الحامضية (٣-٧) ،التركيز الأبتدائي للمعدن (٥٠-٢٥٠ ملغم/لتر) ، كميه المادة الممتزة (.٠٥-٢ غم/١٠٠ مل) ، سرعه الأهتزاز (٠-٢٥٠ دوره/دقيقه) ، ودرجه الحرارة (١٠ -٦٠ م). ان افضل قيم لهذه المتغيرات والتي تم من خلالها الحصول على كفاءه ازالة لأيون النحاس هي (٩٥%) هي ٩٠ دقيقه، ٥٠ ملغم /لتر ،٢ غم/١٠٠ لتر ،٢٠٠ دوره/دقيقه و ٢٠م على التوالي .تم استخدام الشبكه العصبيه الأصطناعيه الهيكليه المعماريه والتي تتكون من ٨ نواة وداله خطية .الأنحدار الخطي بين المتغير الخارج والمتغيرات الست الداخله يساوي ٩٩٧٧٨ . النتائج المستحصله من تحليل الحساسيه للشبكه العصبيه الأصطناعيه بينت ان الداله الحامضيه من اكثر العوامل اهميه في التاثير على كفاءة الأزاله لأيون النحاس (٢٢,١%) تم يتبعها كميه الماده الممتزه ، سرعه الأهتزاز ، درجه الحراره ، زمن التماس ، واخيرا التركيز الأبتدائي للمعدن .

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1. Introduction

The production of inorganic wastes in mining- and metal-related industries has always been an important concern. These wastes are often high in heavy metals, constituting a major threat to human populations, aquatic species, plants, ecosystems, and groundwater quality because of their biological non-degradability and stability in the environment [1–3]. Among these metallic pollutants, Cu(II), an extremely toxic heavy metal causes a potential risk because it is incorporated into the food chain, mainly by plant uptake [4].

Many surface chemistry practices for wastewater treatment such as precipitation, adsorption, membrane processes, ionic exchange, floatation, and others [5, 6] have been studied. However, because of inherent limitation of such techniques as less competent, perceptive operating settings, and production of sludge, they further require costly disposal [7], whereas, adsorption is by far the most versatile and widely used method, and activated carbon is the furthermost commonly used adsorbent [8]. Conversely, the use of activated carbon is expensive, so there has been considerable interest in the use of other efficient sorbent materials, particularly bio-sorbents [9]. In recent years, agricultural by products have been widely considered for metal sorption studies including peat, banana pith, pine bark, peanut, shells, hazelnut shell, rice husk, wood, sawdust, wool, soybean and cottonseed hulls, orange peel, leaves and compost [10-14].

Modeling of adsorption process is a topic of interest for the prediction of the metal partitioning between the aqueous solution and the solid surface, and its subsequent application to the design of adsorption treatment units, as well as for the evaluation of the fate and transport of these metals in natural environments such as surface water, groundwater…etc [15]. Adsorption isotherm models such as Langmuir, Freundlich and others are used frequently for description the equilibrium relationship between the adsorbate concentration on the adsorbent particles and the adsorbate concentration in the fluid phase at a given temperature [16]. Hence, there is a need to use a more representative model that can identify the non-equilibrium/ equilibrium adsorption process for different values of temperature. This model can potentially be integrated into large-scale advection-dispersion equation describing the dissolved contaminant transport in the surface water or groundwater. Accordingly, artificial neural networks (ANNs) have drawn great attention as an alternative approach in the determination of complex relationship between operating parameters. The ANN is an information processing tool that is capable of establishing an input–output relationship. This done by extracting controlling features from a database presented to the network. It is based on predictive models which are powerful in terms of learning the nonlinear relationships to understand and solve and thereby achieving ability to predict accurately [17-20]. However, the significance of the present study is characterization the non-equilibrium/equilibrium non-isotherm copper removal from aqueous solutions using fungal biomass by ANN model in comparison with batch experimental results for different operational conditions.

2. Materials and Methods

2.1 Materials

The spent fungal biomass was collected from agricultural land of Diyala province / Iraq. It was washed extensively with water; sun dried and crushed into powder with average particle size of approximately 1mm [21].

Copper was selected as a representative of heavy metal contaminants. To simulate copper contamination in the water, $CuSO_4 \cdot 5H_2O$ solution (manufactured by Germany) was prepared and added to the specimen to obtain the representative concentration. For example, to prepare a water sample with copper concentration of 50 mg/L, 0.196 g of $CuSO_4.5H_2O$ dissolves in 1000 mL of distilled water.

2.2 Batch Experiments

Series of batch adsorption tests were conducted to determine the effect of contact time, initial pH, initial concentration of Cu(II) ions, adsorbent dosage, and operating temperature on adsorption performance of fungal biomass used as adsorbent materials. Therefore, various adsorbent dosages of 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5, 0.6, 1, 1.2, 1.4, 1.5, 1.6, 1.8, 1.9 and 2 g were introduced into 250 mL flasks with 100 mL solution containing 50 mg/L of Cu(II) ions. The flasks were then placed in an orbital shaker (Edmund Buhler SM25, German) and agitated up to a total contact time of 180 min at a fixed agitation speed of 200 rpm. Samples were taken at predetermined time intervals (10, 15, 20, 30, 50, 60, 80, 90, 100, 120, 150 and 180 min) and then separated by filtration. Cu(II) ion concentration in the samples were analyzed by atomic absorption spectrophotometer (AAS) (Norwalk, Connecticut (USA)).

Batch tests were carried out in a pH range of 3–7 to determine the effect of initial pH on adsorption because the precipitation of copper is occurred at pH greater than (7.1-7.3) [22]. The pH of the aqueous solution was adjusted by adding 0.1 M HNO_3 or 0.1 M NaOH as required. Effects of various operating temperatures ranging from 10 to 60 ºC were also investigated in batch studies. Temperature adjustments were conducted in the same orbital shaker. Percentage of Cu(II) ions removal being the output parameter of the ANN model was considered as a measure of adsorption efficiency of fungal biomass. The efficiency of adsorption (R, %) was calculated as follows:

$$R = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (1)$$

where C_o and C_e are the initial and the equilibrium Cu(II) concentrations of the copper solution, respectively.

2.3. Definition of the ANN Model

Artificial neural network is inspired by the working principle of natural networks of biological neurons. The basic processing element of a neural network is called a neuron or node. The neuron impulse or the output of a node is calculated as weighted sum of the input signals from the proceeding neuron, altered by the transfer function. The learning capability

of a neuron is accomplished by adjusting the weights in conformity to chosen learning algorithm. The process is iterative for artificial neural network. The basic ANN architecture consists of three types of layers input, hidden and output layers. Number of neurons in input and output layer depends upon the number of input and output parameters respectively. The selection of the number of neuron in a hidden layer is an important decision however there is no definite formula [17].

3. Results and Discussion

3.1. Developing and Optimization of the ANN Model

ANN model with Levenberg–Marquardt back propagation (LMA) training algorithm for correlating the removal efficiency of copper ions from aqueous solution by adsorption method was developed. This algorithm was calculated using Matlab program version 7.9 (R2009b). Topology of an artificial neural network is determined by number of its layers, number of nodes in each layer and the nature of the transfer functions. Optimization of ANN topology is probably the most important step in development of the model which can be achieved by dividing the original experimental data into training, validation and test subsets. Therefore 51, 17 and 17 samples were used for the training, validation and test subsets, respectively. The experimental data was loaded into the workspace at random for each subset.

The training data is the biggest set and is used by neural network to learn pattern presented in the data by updating the network weights. The testing data is used to evaluate the quality of the network. The final check on the performance and generalization ability of the trained network is made using validation data. Tangent sigmoid transfer function (tansig) at hidden layer and a linear transfer function (purelin) at output layer were used in the present study. The input variables to the feed forward neural network were as follows: contact time (min), initial pH, dosage of fungal biomass (g/100 mL), copper concentration (mg/L), agitation speed (rpm) and temperature (ºC). In addition, the removal efficiency (%) was chosen as the experimental response or output variable.

The optimal architecture of the ANN model and its parameter variation were determined based on the minimum value of the mean square error (MSE) of the training and prediction set. In optimization of the network, two neurons were used in the hidden layer as an initial guess. With an increase in the number of neurons, the network gave several local minimum values and different MSE values were obtained for the training set. With 8 hidden neurons, the MSE reached its minimum value of 0.000174. Hence, the neural network containing 8 hidden neurons was chosen as the best case.

The training was stopped after 17 epochs for the LMA because the differences between training error and validation error started to increase. Figure 1 illustrates training, validation and test mean square errors for the LMA. Finally, the optimal ANN structure for prediction of copper ions removal from aqueous solution by adsorption method was 6:8:1 as shown in Figure 2. The best regression for training, validation and testing for the Levenberg-Marquardt algorithm was set in Figure 3. It can be seen that the correlation coefficient for training, validation, testing and all data was 0.99٨٥٣, 0.99431, 0.99859 and 0.99738 respectively.

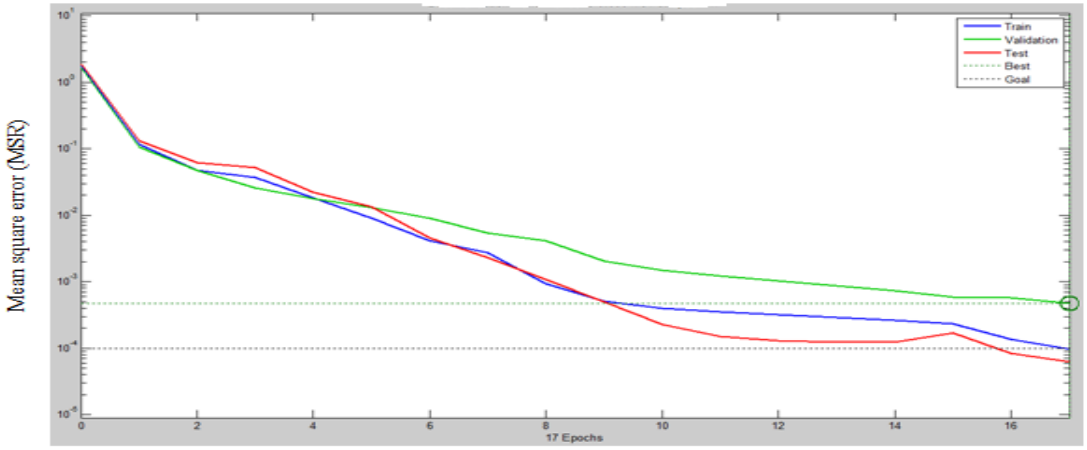

Figure 1. Training, validation and test mean square errors for the Levenberg–Marquardt algorithm.

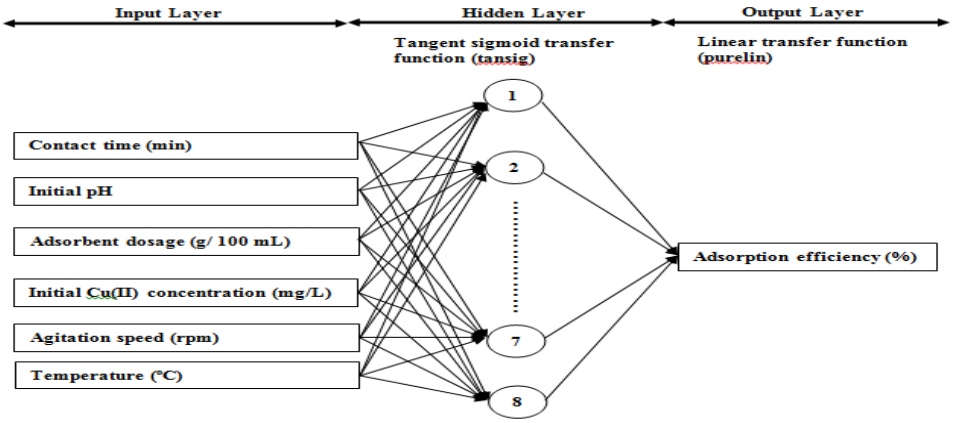

Figure 2. The optimal architecture of ANN.

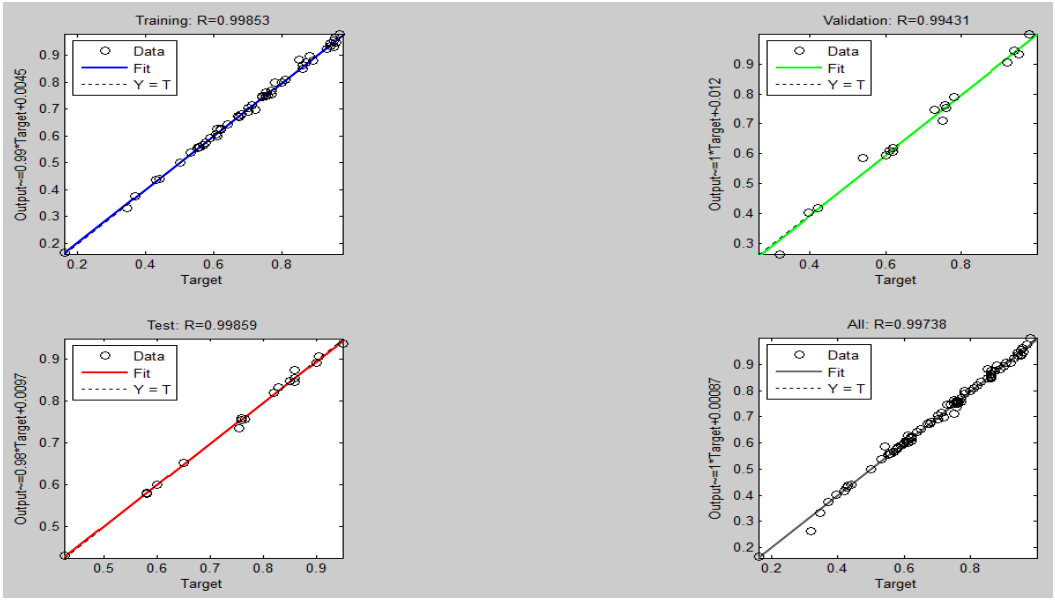

Figure 3. Training, validation and testing regression for the Levenberg-Marquardt algorithm

3.2. Effect of Contact Time and Initial pH of Solution

The data obtained from the sorption of Cu(II) on the fungal biomass showed that a contact time of 90 min was sufficient to achieve equilibrium and the sorption did not change significantly with further increase in contact time as shown in Figure 4. It is clear that the removal efficiency was increased rapidly in the beginning and, then, remained constant with time until it reached equilibrium time. This may be due to the presence of large number of adsorbent sites available for the adsorption. As the remaining vacant surfaces decreasing, the adsorption rate slowed down due to formation of repulsive forces between the metals on the solid surfaces and in the liquid phase [23, 24].

According to Figure 4, the increase in the metal removal as the pH increases (3 to 6) can be explained on the basis of a decrease in competition between proton and metal species on the surface sites, and the decrease in the positive surface charge, which results in a lower columbic repulsion of the sorbing metal [25]. However, further increase in pH values (more than 6) would cause a decreasing in removal efficiency. This may be attributed to the formation of soluble hydroxy complexes which are precipitated from the solution making true sorption studies impossible [26]. However, pH 6 was found as the optimal initial pH for further batch experiments investigating the effects of other operational parameters on the efficiency of Cu(II) ions removal. The agreement between the ANN model predictions and the experimental data as a function of initial pH is shown in Figure 4.

3.3. Effect of Fungal Biomass Dosage

Experimental results (Figure 5) generally showed that as the adsorbent mass increased from 0.05 to 2 g, the percentage of Cu(II) ions removed also increased from 16 to 95 % for a fixed initial metal concentration of 50 mg/L. This can be attributed to the fact that the number of adsorption sites or surface area increases with the weight of adsorbent, resulting in a higher percent metal removal at a high dosage [27]. Figure 5 shows a comparison between the ANN model predictions and the experimental data as a function of adsorbent dosage. It can be seen that the ANN model satisfactorily predicts the trend of the experimental data.

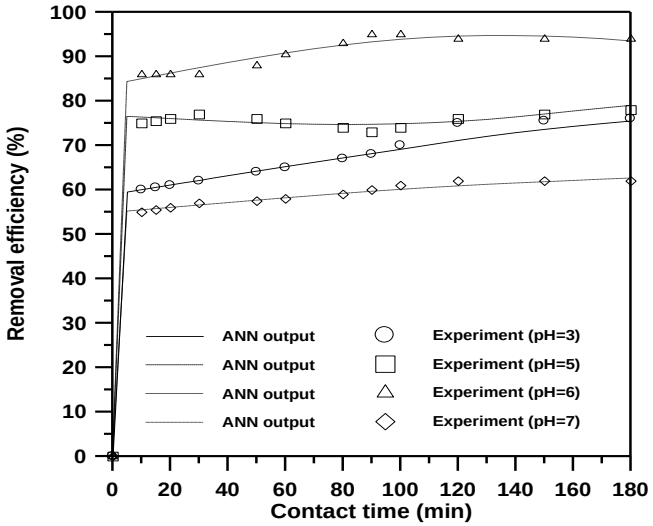

Figure 4. Comparsion between ANN outputs and experimental data as a function of initial pH (Co = 50 mg/L, fungal biomass = 2 g/ 100 mL, agitation speed = 200 rpm and temperature = 20 ºC)

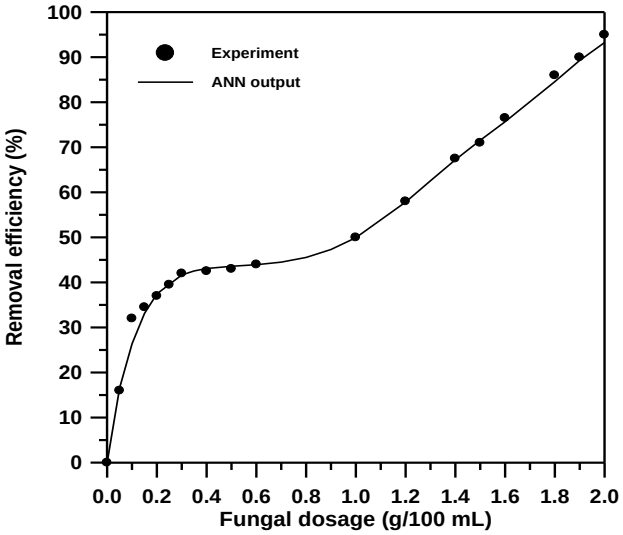

Figure 5. Comparison between ANN outputs and experimental data as a function of adsorbent dosage (initial pH = 6, Co = 50 mg/L, contact time = 90 min, agitation speed = 200 rpm and temperature = 20 ºC)

3.4. Effect of Initial Copper Concentration

Figure 6 explains that the removal efficiency of Cu(II) decreased from 95 to 80 % with increasing the initial concentration from 50 to 250 mg/L. This may be attributed to the lack of sufficient surface area to accommodate much more metal available in the solution. At lower concentrations, all Cu(II) ions present in solution could interact with the binding sites and thus the removal efficiency was higher compared with high concentrations. As a result, the treatment yield can be increased by diluting the wastewaters containing high metal ion concentrations [28]. It can be seen from this figure that the ANN model shows a good performance on prediction of the experimental data.

3.5. Effect of Agitation Speed

Figure 7 shows that about 53 % of the Cu(II) was removed before shaking (agitation speed = zero). There was an increase in contaminants uptake as the agitation speed was increased from zero to 250 rpm at which about 95 % of contaminant had been removed. This can be attributed to improving the diffusion of ions towards the surface of the reactive media and, consequently, proper contact between ions in the solution and binding sites can be achieved [29]. It is clear that the ANN model presents a good prediction for the experimental data.

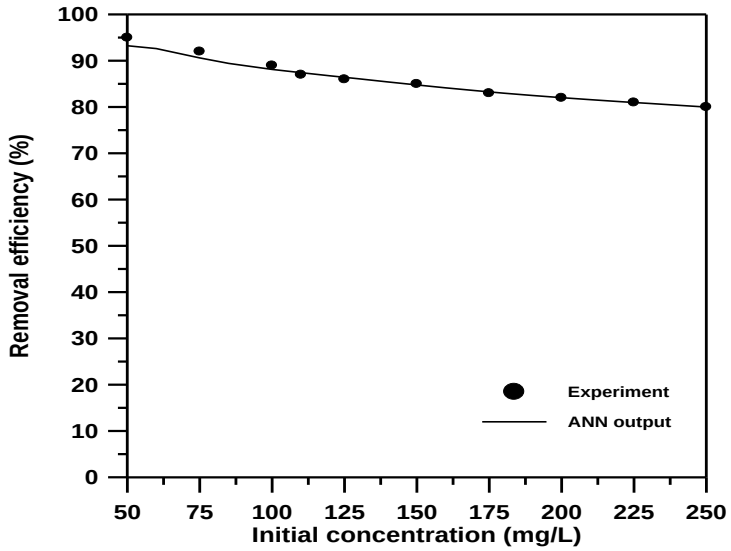

Figure 6. Comparsion between ANN outputs and experimental data as a function of initial copper concentration (initial pH = 6, fungal biomass dosage = 2 g/ 100 mL, contact time = 90 min, agitation speed = 200 rpm and temperature = 20 ºC)

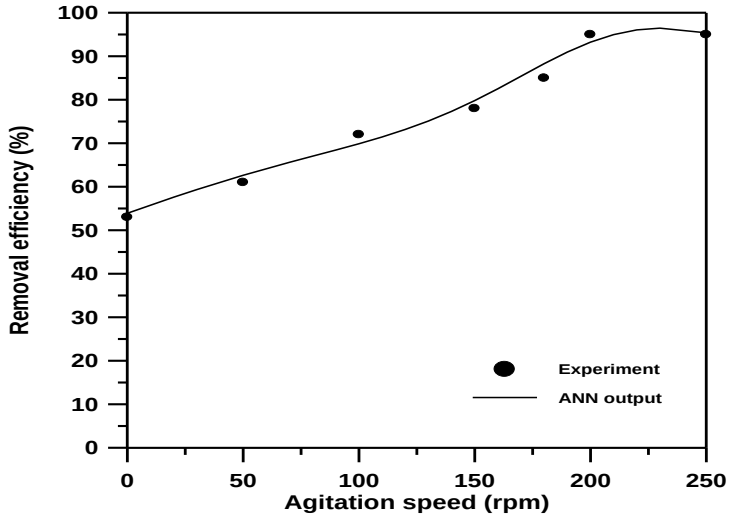

Figure 7. Comparsion between ANN outputs and experimental data as a function of agitation speed (initial pH = 6, Co = 50 mg/L, fungal biomass dosage = 2 g/ 100 mL, contact time = 90 min and temperature = 20 ºC)

3.6. Effect of Temperature

Experimental results showed that adsorption of Cu(II) ions onto fungal biomass was fairly dependent on the temperature (Figure 8). The adsorption of Cu(II) onto fungal biomass increased from 54 to 98 %, when the temperature was increased from 10 to 60 ºC. This may be due to increase the diffusion rate of the contaminant ions across the external boundary layer and the internal pores of the adsorbent particles. However, taking into account the cost of energy consumed in heating and the magnitude of such an increase in the adsorption of Cu(II) ions at high temperatures, an operating temperature of 20 ºC was found to be sufficient for batch experiments. It can be seen from Figure 8 that there is a good agreement between predictions of the ANN model and the experimental data.

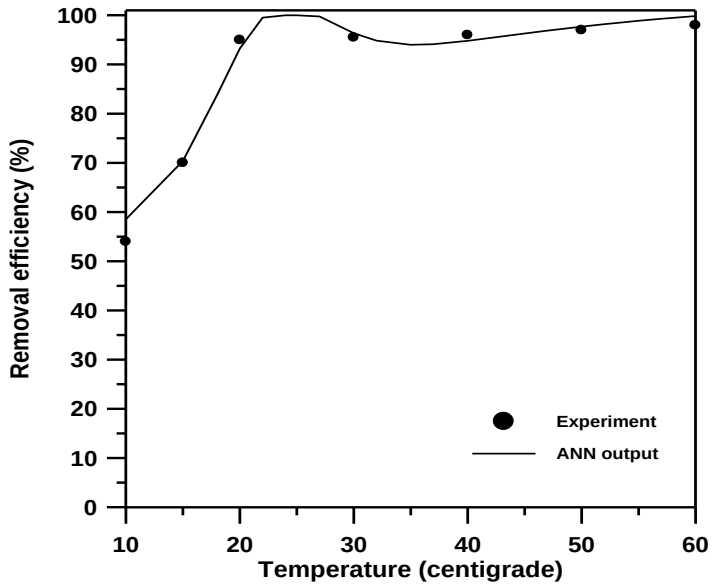

Figure 8. Comparsion between ANN outputs and experimental data as a function of temperature (initial pH = 6, Co = 50 mg/L, fungal biomass dosage = 2 g/ 100 mL, contact time = 90 min and agitation speed = 200 rpm)

3.7. Fourier Transform Infrared Analysis

FTIR spectral analysis is important to identify the characteristic functional groups on the surface of the adsorbent, which are responsible for adsorption of metal ions [30]. The IR spectrum of fungal biomass was recorded to obtain the information regarding the stretching and bending vibrations of the functional groups which are involved in the adsorption of the adsorbate molecules. The IR spectra of fungal biomass before and after Cu(II) adsorption are shown in Figure 9. The IR spectral analysis of fungal biomass powder indicated broad adsorption band at 3423.28 cm^{-1}, representing –OH and -NH stretching, 2925.21$cm^{-1}$and 2854.16 cm^{-1} represented –CH stretching. The absorption band at 1742.68 cm^{-1} could be attributed to C=O group of carboxylic acid and a sorption band at 1417.14 cm^{-1} representing carboxylate group. Further at 1180.53 cm^{-1} indicating –OH group of sugars and 1076.53 cm^{-1} and 1031.88 cm^{-1} are representing amide C-N stretching and –P=O stretching respectively. In all the FTIR spectroscopic analysis of the biomass, dead powder of fungal biomass after adsorption of heavy metal ions revealed that the shift of 32 to 40 for the peaks at 3423.23, 1742.68 and 1180.53 cm^{-1}. It clearly indicated that the carboxylic acid and hydroxylic groups are the main functional groups for complexation of metal ions.

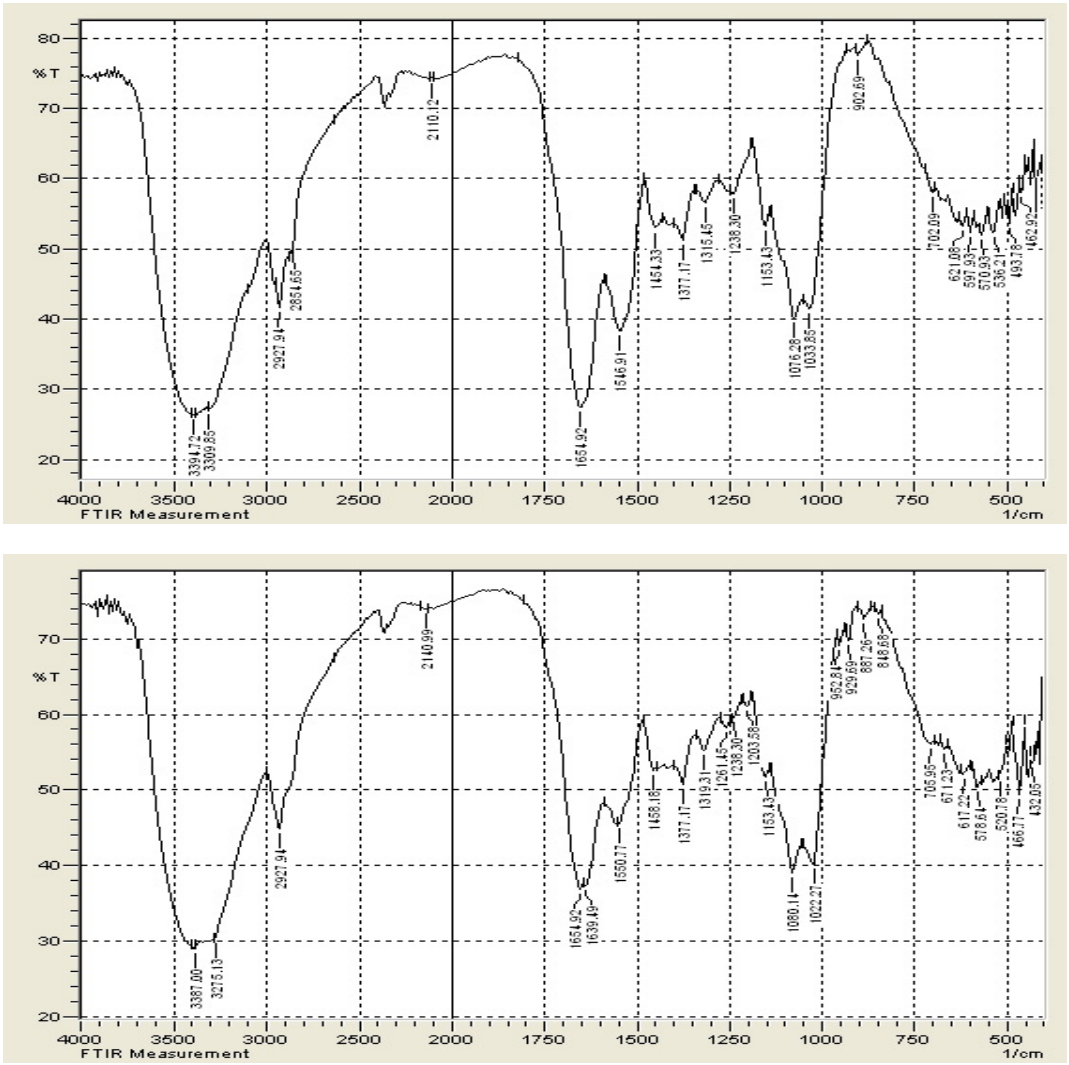

Figure 9. IR spectrum of fungal biomass powder (a) before loaded Cu(II) and (b) after loaded Cu(II).

3.8. Sensitivity Analysis

In order to assess the relative importance of the input variables, the sensitivity analysis was conducted based on the neural net weight matrix and Garson equation. Garson (1991) proposed an equation based on the partitioning of connection weights as follows [31]:

$$I_j = \frac{\sum_{m=1}^{m=Nh}\left(\left(\frac{|W_{jm}^{ih}|}{\sum_{k=1}^{Ni}|W_{km}^{ih}|}\right)\times|W_{mn}^{ho}|\right)}{\sum_{k=1}^{k=Ni}\left\{\sum_{m=1}^{m=Nh}\left(\frac{|W_{km}^{ih}|}{\sum_{k=1}^{Ni}|W_{km}^{ih}|}\right)\times|W_{mn}^{ho}|\right\}} \qquad (2)$$

where I_j is the relative importance of the j^{th} input variable on the output variable, *Ni* and *Nh* are the numbers of input and hidden neurons, respectively, *Ws* are connection weights, the superscripts *i*, *h* and *o* refer to input, hidden and output layers, respectively, and subscripts *k*, *m* and *n* refer to input, hidden and output neurons, respectively.

The initial pH of the solution with a relative importance of 22.1 % appeared to be the most influential parameter in the adsorption process of fungal biomass for Cu(II) removal (Figure 10), followed by adsorbent dosage (19.5 %), agitation speed (18.2 %), temperature (14.1 %), contact time (13.3 %), and Cu(II) concentration (12.8 %). However, many researchers proved that the influential variable and effect of each variable depended upon the experimental ranges adopted in the fitting model [32].

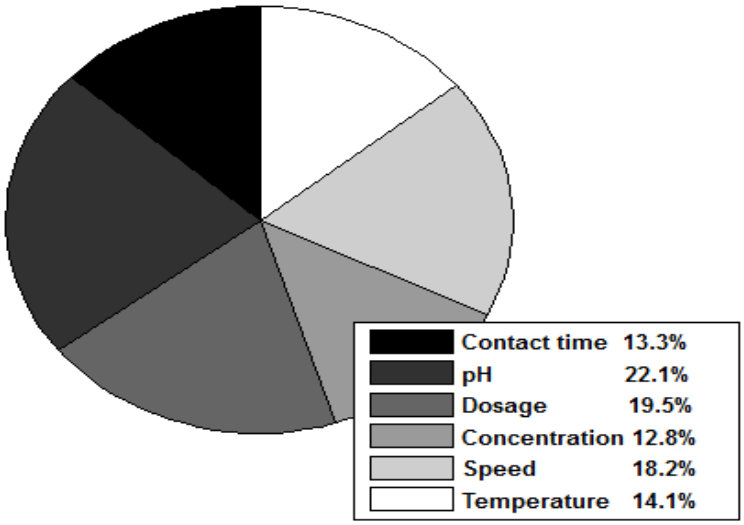

Figure 10.Piechart for Sensitivity analysis using artificial neural network

4. Conclusion

Batch adsorption experiments for removal of Cu(II) ions from aqueous solutions showed that best operating conditions were determined to be an initial pH of 6, an adsorbent dosage of 2 g/ 100 mL, an initial Cu(II) concentration of 50 mg/L, an agitation speed of 200 rpm and temperature of 20 ºC. A contact time of 90 min was found to be sufficient to achieve equilibrium. Experimental findings proved that the removal of Cu(II) ions could be effectively improved up to about 95 % by using fungal biomass as low-cost adsorbent.

A three layer ANN with a tangent sigmoid transfer function (tansig) at the hidden layer and a linear transfer function (purelin) at the output layer were proposed to predict the efficiency of Cu(II) ions removal. The optimal neuron number for the LMA was determined to be 8 hidden neurons with MSE of 0.000174. The proposed ANN model showed a precise and an effective prediction of the experimental data with a high correlation coefficient of greater than 0.99 for six operating variables. This model can be integrated with advection dispersion equation for description the non-equilibrium / equilibrium non-isotherm solute transport through field applications. The initial pH of the solution with a relative importance of 22.1% appeared to be the most influential parameter in the adsorption process by artificial neural network.

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