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Prediction of Pb (II) and Cu (II) Ions Biosorption by *Annona muricata L.* Seeds Using Artificial Neural Network (ANN) Approach

Zulfi Abdullah, Melia Innes Kurniawan, Rahmiana Zein, Hermansyah Aziz and Edison Munaf*

Laboratory of Environmental Analytical Chemistry, Faculty of Matematics and Natural Sciences, Andalas University, Padang 25163, Indonesia

ABSTRACT

A model of biosorption based on a three-layers structure of Artificial Neural Network (ANN) was developed to predict the efficiency of removing Pb(II) and Cu(II) ions from aqueous solutions using *Annona muricata L.* seed. Data obtained from the experimental conditions was applied using the back propagation learning algorithm with one input layer contains two neurons, one hidden layer which contains nine neurons, 15 neurons biased and one output layer contains one neuron (2-9-1 structure) to predict the artificial neural network approach of the biosorption process. Experimental data set used as the input training data on ANN. For each set of experimental data, the model will issue 100 data ANN prediction, where 5% to 10% were cross-validated with experimental data. Linear regression between the network outputs and the corresponding targets proved satisfactory with the minimum mean squared error (MSE) approximately 0.0012 and average correlation coefficient of about 0.9985 to seven sets of experimental data. Modified Freundlich and Langmuir models is also made of the 100 ANN's output data (called Langmuir-ANN and Freundlich-ANN) and displayed along with experimental data.

Keywords: Artificial Neural Network, Back propagation, Adsorption isotherm, *Annona muricata* L. seed, Toxic metals

Corresponding author

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INTRODUCTION

Heavy metal ions, such as Pb(II) and Cu(II) were highly toxic pollutant in developed countries for their significant impact on the environment and human health. There were numerous methods currently employed to remove these ions from aqueous environment such as reverse osmosis, electro-dialysis, ultra-filtration, ion-exchange, chemical precipitation and phyto-remediation [1-4].

Recently, the removal of toxic metal ions from wastewater has direct contribution to the biosorption, based on metal binding capacities of various biological materials. For example Zein R *et al* studied removal of Pb(II), Cd(II) and Co(II) from aqueous solution using *Garcinia mangostana L.* fruit shell [5]. The major advantages of biosorption over conventional treatment methods were low cost, high efficiency, no additional nutrient requirement, regenerated of biosorbent and possibility of metal recovery. The mechanism of biosorption was complex, mainly ion exchange, chelation and adsorption by physical forces [3].

The applications of ANNs have been successfully conducted in various parts of environmental engineering field, such as estimation of lead concentration ingrasses [6], prediction of the bulking phenomenon in wastewater treatment plants [7], prediction of membrane fouling during nano filtration of ground and surface water [8], and predicting single droplet collection efficiency of counter current spray towers [9].

In this study, a three-layer ANN model was made to predict the Pb(II) and Cu(II) removal efficiency by *Annona muricata L.* seeds. The ANN model was calculated based on the experimental data obtained by the previous experiment [10].

On the basis of batch adsorption experiments, we proposed outputs obtained from the ANN modeling were compared with the experimental data, and advantages and further developments were discussed.

MATERIALS AND METHODS

Preparation of Solutions

The biosorption experiments were conducted by using stock standard solution (1000 mg/L) of $Pb(NO_3)_2$ and $Cu(NO_3)_2$ in 0.5M HNO_3. These solutions were purchased from E. Merck (Germany). Working standard solutions were prepared just before used by the appropriate dilution of the stock solutions. 0.1 mol/L HNO_3 and NaOH were used for pH adjustment.

Annona muricata L. seeds preparation and characterization

Annona muricata L. seeds were used as a biosorbent for sorption of Pb(II) and Cu(II) from an aqueous solution. The chemical composition of *Annona muricata L.* seeds were palmitic, stearic, oleic and linoleic Acid [6]. The seeds were washed with deionized water, air-

dried for 3 days and ground using crusher (Fritsch, Germany). Then the powder was dried in an oven (Memmert, Germany) at 60°C for 40 h and finally ground using mortal grinder (Fritsch, Germany). The powder was activated by soaking 20 g biomass in excess of 80 mL HNO_3 0.01 M for 2 h, followed by washing thoroughly with deionized water and then air-dried. The resulting pale brown powder can be stored for a long time.

The dry powder was treated with 25 mL Pb(II) or Cu(II) 10 mg/L, shaked for 1.5 h with 100 rpm and then was filtered. The filtrate (colorless, has no smell and pH about 6) was measured with atomic absorption spectrometric (VARIAN SPECTRAA240) to determine the total amount of Pb(II) or Cu(II) presence in the filtrate. There were several parameters to be treated to get the optimal adsorption of heavy metal ions with biomass.

The amount of adsorbed metal ions per gram of the biomass (biosorption capacity, Q) was obtained using the following equation:

$$Q = \frac{(Co - Ce)V}{m} \quad (1)$$

Where Co and Ce were initial and equilibrium metal ions concentration in solutions (mg/L), respectively; V was volume of the solution (L); m was the amount of biomass (g). Detail of experimental data (10) calculated for the artificial neural network.

RESULTS AND DISCUSSION

The Biosorption Behaviour by Using Artificial Neural Network (ANN) Model

The biosorption Neural Network Tool that created from Delphi 7.0 software was used to predict the adsorption efficiency. The ANN models were applied in this study using the back propagation learning algorithm (back propagation) with one input layer contains one neurons, one hidden layer which contains nine neurons, 15 neurons biased and one output layer contains one neuron (2-9-1 structure). At each hidden layer is used tangent sigmoid transfer function and at the output layer used a linear transfer function. Experimental data used as the input training data on ANN. For each set of experimental data, the model will issues 100 ata ANN prediction by 5% to 10% were cross-validated with experimental data. For each data validation, through a linear regression between the network outputs and the corresponding targets, look for a minimum value of the means quared error (MSE) and correlation coefficient. Modified Freundlich and Langmuir models is also made of the 100 ANN's output data (called Langmuir-ANN and Freundlich-ANN) and displayed along with the original Langmuir and Freundlich models derived from experimental data as shown in Figure 1.

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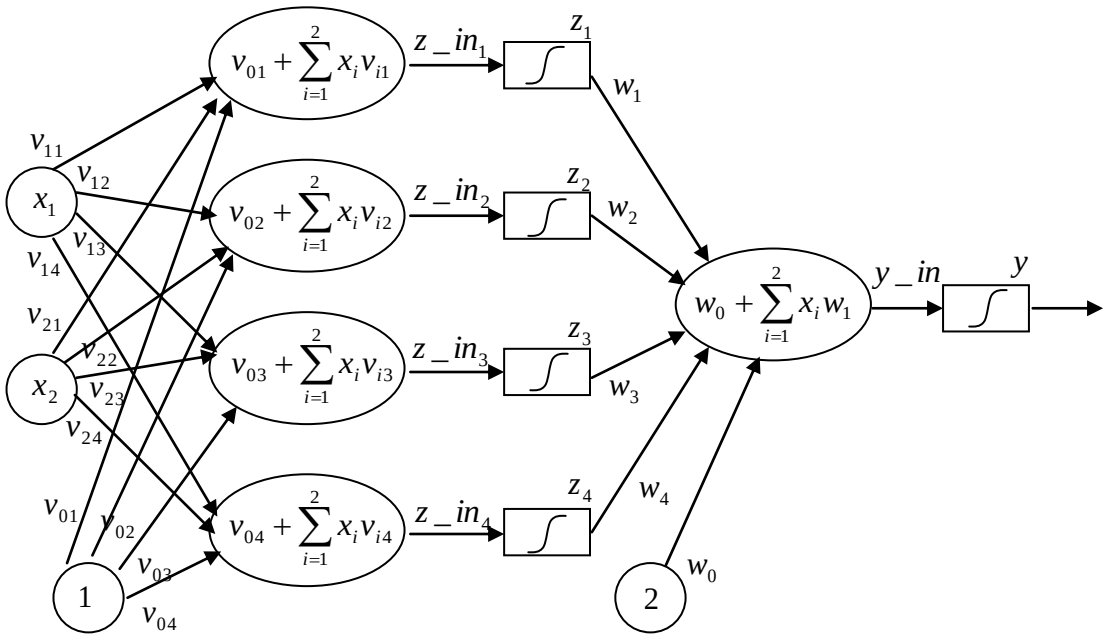

Figure 1: AnANN model for backpropagation algorithm

Optimization of the modeling structure of ANN

The optimal architecture of the ANN model and its parameter variation were determined based on the minimum value of the Mean Squared Error (MSE) of the training and prediction set (equation 2) :

$$MSE = \frac{1}{N}\sum_{p=1}^{N}(t_p - o_p)^2 \qquad (2)$$

where N is number of data, P is index number of data, t_p is target value (expected value) for the p^{th} data and o_p is output of the p^{th} data

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. Figure 2: illustrates the dependence between the neuron number at hidden layer as the best BP algorithm. Figure 2depicts that the MSE reached its minimum value of 0.0011 at 9 hidden neurons and 15 biases. Hence, the neural network containing 9 hidden neurons and 15 biases (MSE 0.0011) was chosen as the best condition.

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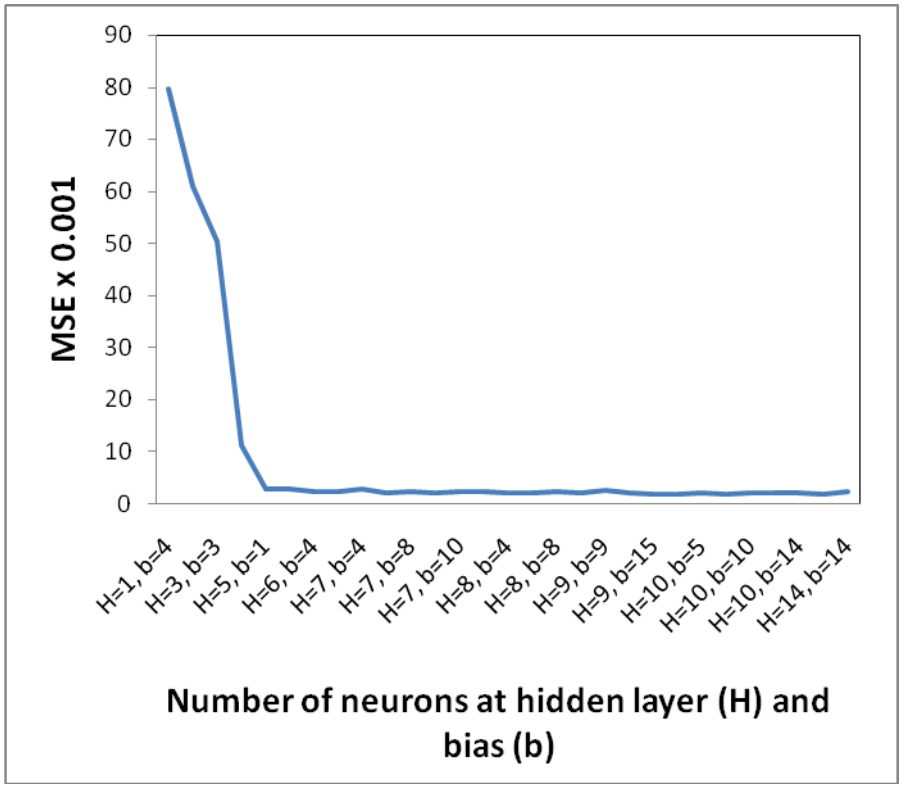

Figure 2: Dependence between MSE and number of neurons at hidden layer and bias for back propagation algorithm

A regression analysis of the network response between ANN outputs and the corresponding targets was performed. The performance control of ANN outputs was evaluated by estimating the correlation coefficient (R^2) which is defined as [11]:

$$R^2 = \frac{\sum_{p=1}^{N}(t_p - t_{mean})^2 - \sum_{p=1}^{N}(t_p - o_p)^2}{\sum_{p=1}^{N}(t_p - t_{mean})^2} \qquad (3)$$

where $R^2$is the correlation coefficient, N is the number of thepatterns, p is the index number for pattern, t_p is the target value for the pth pattern, t_{mean} is the mean target value, $o_p$is the out put of the pth pattern which is produced by the ANN model. Taking into account the non-linear dependence of the data, linear regression shows a good agreement between ANN outputs (predicted data) and the corresponding targets (experimental data), the value of correlation coefficient, R^2, is 0.9985.

Comparison of experimental data and artificial neural network

The pH of solution had a significant impact on the removal of heavy metals, since it determined the surface charge of the adsorbent (has carboxylate, phosphate and amino group) and its degree of ionization. Figure 3 showed the maximum biosorption of Pb(II) occurred at pH 3.0. The amount of adsorbed heavy metal ions of that pH was found to be 0.3995 mg/g for

prepared biomass. There was a decrease in biosorption capacity (Q) with an increase pH from 3.0 to 7.0. The uptake of Cu(II) increased from 0.1985 mg/g to 0.4249 mg/g when the pH increased from 2.0 to 4.0 and then decreased to 0.4113 mg/g at pH = 5.0. When pH was further increased up to 5.0 until 7.0 for Pb(II) and Cu(II) respectively, the percentage adsorption was decreased. This was due those divalent cations might react with OH^- ion to give some precipitation and thereby decreased the free metal ions available in the solution. Heavy metal cations seemed to be mostly unsorbed at low pH values (pH = 1.0 – 2.0). Increased acid concentration, metal ions in solution entered into competition with H^+ for the sorption sites.

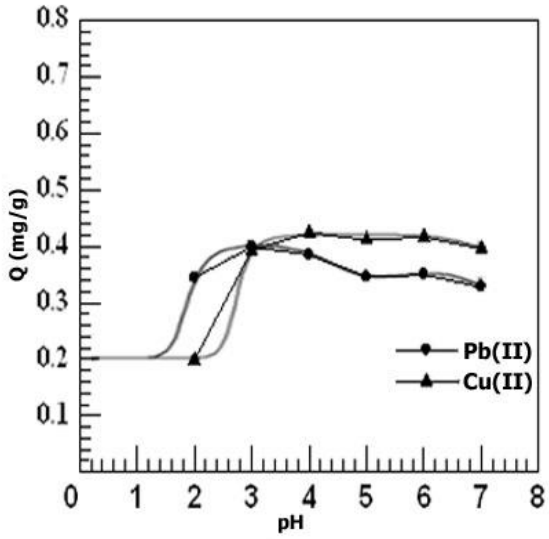

Figure 3. Effect of pH on Pb(II) and Cu(II) biosorption by *Annona muricata L.* seed; 25 mL metal solution; concentration = 10 mg/L; mass of sorbent = 0.5 g; contact time = 90 min; stirring speed = 100 rpm.The agreement between the ANN model predictions and the experimental data:R^2 value is 0,9975.

Based on the calculation data using the prediction of ANN methods, the experimental data quiet similar with the data aobained using the ANN model predictions with R^2 is 0,9975. From this plot it can be seen that obtained results from the proposed ANN model are in good agreement with the experimental data.

Based on our calculating data using ANN method, the data obtained from the experimental results such as effect of contact time, amount of biomass, strigien effect and initial concentration for the sorption behaviour of Cu(II) and Pb(II) is similar wtith the data obained through the modelling of ANN simulation with correlation is 0.9995.

Prediction of adsorption isotherm using ANN modeling

An adsorption isotherm describes the relationship between the amount of adsorbate uptaken by the adsorbent and the adsorbate concentration remaining in solution. This isotherm was derived from equilibrium constant of the interaction of adsorbate with adsorbent. In the

present study, the equilibrium data for Pb(II) and Cu(II) adsorption on *Annona muricata L.* seed were evaluated by the Langmuir and Freundlich models.

The Langmuir isotherm was based on assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecule on the adsorbent surface, the energy of adsorption constant and there was no transmigration of adsorbate in the plane of the surface. The results is shown in Figure 4. The Langmuir model was described by the following equation:

$$Qe = \frac{K_L.Qm.Ce}{1+K_L.Ce} \quad (4)$$

A linier expression for the Langmuir isotherm could be written as:

$$\frac{Ce}{Qe} = \frac{1}{Qm.K_L} + \frac{Ce}{Qm} \quad (5)$$

Where Qm was the maximum metal uptake corresponding to the saturation capacity (mg/g), K_L was energy of adsorption (L/mg), Qe was the amount of metal adsorbed on the biomass (mg/g) and Ce was equilibrium metal concentration in solution (mg/L). In contrast, the Freundlich isotherm (Figure 5) could be used for non-ideal adsorption that involves heterogeneous.

The general Freundlich equation was given as:

$$Qe = K_f.Ce^{1/n} \quad (6)$$

The linear form of this model was:

$$Ln\ Qe = Ln\ K_f + \left(\frac{1}{n}\right).\text{Ln Ce} \quad (7)$$

Where n was adsorption affinity and K_f was Freundlich constant (as a measure of the degree or strength of adsorption). As the Freundlich isotherm equation was exponential, it could only be reasonable applied in the low to intermediate concentration ranges.

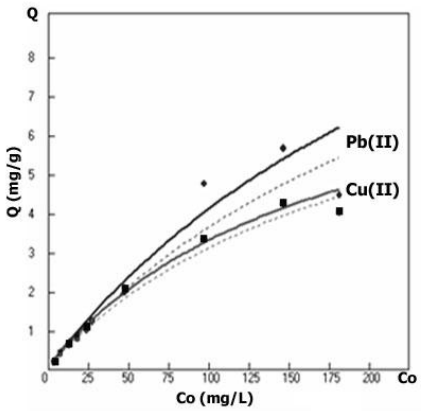

Figure 4. Solid line are Langmuir-ANN model, based on ANN output and dot line are original Langmuir model, based on experimental data

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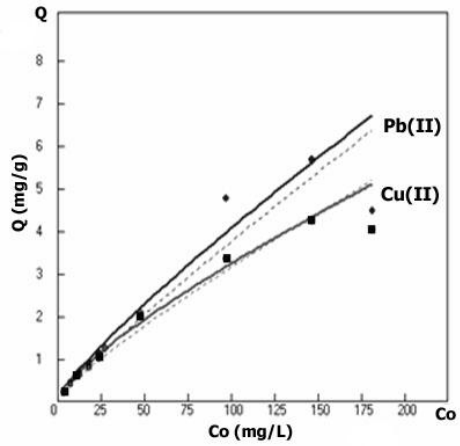

Figure 5. Solid line are Freundlich-ANN model, based on ANN output and dot line are original Freundlich model, based on experimental data.

Based on the slope of linear functions from Figure 4 and 5, the theoretical values of Qm for Pb(II) and Cu(II) ions were 6.8306 and 5.5463 mg/g, respectively. However, those experimental values were 5.585 and 4.1685 mg/g, as shown in Figure 4 and 5, respetively.

These studies indicated that the capacity biosorption of Pb(II) and Cu(II) ions by *Annona muricata L.* seed were affected by pH solution, contact time, stirring speed, initial metal ion concentration and biomass dosage. The optimum pH for adsorption of Pb(II) and Cu(II) ions were found to be at pH 3.0 and 4.0, respectively. The uptake of Pb(II) and Cu(II) ions increased with increasing contact time and equilibrium were attained in 45 and 60 minutes of contact, respectively. The influence of the stirring speed on the biosorption showed that an optimum value was obtained at 150 and 100 rpm for removal of Pb(II) and Cu(II), respectively. The biosorption capacity decreased as the dosage of biomass increased.

The equilibrium data fitted well to the Freundlich isotherm. However, Langmuir isotherm may be used to predict the theoretical values of Qm for Pb(II) and Cu(II) ions, those were 6.8306 and 5.5463 mg/g, respectively. The experimental values of Qm for Pb(II) and Cu(II) ions were 5.585 and 4.1685 mg/g, respectively. The biosorption of binary solution showed that adsorption capacity of the leading ion onto *Annona muricata L.* seed relatively did not influenced by another ion.

CONCLUSION

On the basis of batch adsorption experiments, an important objective was to obtain an ANN model that could make reliable prediction on the percentage of Pb(II) and Cu(II) ions removal. A threelayer ANN with a tangent sigmoid transfer function (*tansig*) at hidden layer and a linear transfer function (*purelin*) at output layer were proposed to predict the efficiency of Pb(II) ions removal.

The optimal neuron number for the Back Propagation algorithm was determined to be hidden neurons with MSE of 0.0012. The proposed ANN model showed a precise and an

effective prediction of the experimental data with a satisfactory average correlation coefficient of about 0.9985 for seven operating set variables. To conclude, a simulation based on the ANN model can provide a further contribution to develop a better understanding of the dynamic behaviour of process where still some phenomena cannot be explained in all detail

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