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Application of Neural Network on the Loading of Copper onto Clinoptilolite

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***Abstract*—**The study investigated the implementation of the Neural Network (NN) techniques for prediction of the loading of Cu ions onto clinoptilolite. The experimental design using analysis of variance (ANOVA) was chosen for testing the adequacy of the Neural Network and for optimizing of the effective input parameters (pH, temperature and initial concentration). Feed forward, multi-layer perceptron (MLP) NN successfully tracked the non-linear behavior of the adsorption process versus the input parameters with mean squared error (MSE), correlation coefficient (R) and minimum squared error (MSRE) of 0.102, 0.998 and 0.004 respectively. The results showed that NN modeling techniques could effectively predict and simulate the highly complex system and non-linear process such as ion-exchange.

***Keywords*—**Clinoptilolite, loading, modeling, Neural network.

I. Introduction

HEAVY metals are common pollutants found in various mining and industrial discharges. As environmental regulations on heavy metals discharge are getting stricter and tighter, more efficient remediation methods for waste water are required [1], [2]. Ion-exchange process is one of the popular water treatments for water purification [3]. In order to improve the performance of ion-exchange process, optimization and analysis of the process should be accomplished. Modeling and simulation are tools to achieve the objectives. However modeling of a process covers a broad spectrum. At one extreme lie theoretical (or parametric) models based on fundamental knowledge of the process. These models are also called knowledge based models. At the other end lie empirical (or non-parametric) models which do not rely on the fundamental principles which governing the process. A large majority of modeling works on ion-exchange process are theoretical [4]. Most of these models are obviously derived from physical descriptions and understanding of ion-exchange process under the certain assumptions. These types of models are very useful for scale-up applications. However, as mentioned above, they are mathematically complex, computationally expensive and they ideally require a very detailed knowledge of the ion-exchange process. Due to complexity of the process, it is difficult to be modeled and simulated using conventional mathematical modeling. Neural Networks (NN) are now used in many areas of science and engineering and considered as promising tool because of their simplicity towards simulation, prediction and modeling [5]. The advantages of NN are that the mathematical description of the phenomena involved in the process is not required, less time for development than the traditional mathematical models and prediction ability with limited numbers of experiments [6]. Application of NN used to solve engineering processes has been reported in the literature [7]-[9]. However, few studies on applications of NN in physico-chemical wastewater treatment have been reported [10]-[12]. This paper presents the application of MLP Neural Network on the loading of Copper onto activated clinoptilolite. The NN modeling outputs were compared with the experimental data.

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II. Materials and Methods

A. Preparation of Clinoptilolite and Synthetic Solution

The clinoptilolite and synthetic solution used in this work were prepared as described by [13] and [14], respectively. The clinoptilolite was milled into powder with average particle sizes of approximately 75μm. The powder was then examined using an X-ray powder diffractometer (XRD), Phillips X'pert Model 0993 and X-ray fluorescence spectroscopy (XRF), Phillips Magix Pro to determine its composition and its elemental composition, respectively. The solution of copper was prepared by dissolving $CuSO_4.5H_2O$ in deionizer water at four different Cu^{2+} ion concentrations (100, 200, 300 and 500 mg/l). The experiments were conducted to determine the effects of pH (2, 3, 3.5 and 4) and temperature (30, 50, 70 and 90^oC) on the loading % of Cu^{2+} by the clinoptilolite. In each case, 10 g of the treated clinoptilolite was mixed with one litre of synthetic wastewater solution and held in closed polyethylene flask at 90^oC for 24 h. At the end of the treatment period, the ion-exchanger materials were then separated from solution sample by filtration. The sample solution of 40 ml was taken assayed using atomic adsorption spectroscopy (AAS), (Model Varian Spectra (20/20)) to determine the concentration of Cu^{2+} metals present in the solution. All the experimental analyses where conducted in triplicate and the results reported are the average deviation values of ± 0.002. The loading efficiency (%) was calculated as follows:

$$\text{Loading } \% = (C_o - C_f)\, x100/C_o \quad (1)$$

where C_o and C_f are the initial and final ions concentrations of the solution, respectively.

B. Definition of the Neural Network Model

Neural network is known for their ability of learning, simulation and prediction of data. The multilayer feed-forward

network is a parallel interconnected structure consisting of input layer and includes independent variables, number of hidden layers and output layer [15]. In this work, a three-layered neural network with tangent sigmoid transfer function (*tansig*) at hidden layer and a linear transfer function (*purelin*) at output layer was used. The network consists of a large number of simple processing elements (neurons). These elements are commonly organized in layers and process data in the feed forward direction, i.e from the network input to its output. Neurons are connected by weighted links which can be adapted during network training. The role of each single neuron is to sum the incoming signals, transform them according to its transfer function and either delivers the result to subsequent layers for further processing [16]. The experimental data were processed using Matlab V4.0 for NN and Design expect (6.0.6) mathematical software, for experimental design matrix and data analysis. A training set of ninety experimental data sets was selected to develop the NN model and was divided into input matrix [p] and target matrix [t]. The input variables were pH, temperature and initial concentration. The corresponding Cu (II) loading efficiency (%) was used as a target. The experimental data were randomly divided into three subsets of training, validation and testing for developing NN model.

III. Results and Discussion

A. Neural Network Model

Five important aspects that must be determined in design procedure of NN are as follows [19]: (a) Data distribution in three subsets (training, validation and testing); (b) Selection of back propagation training algorithm and transfer function; (c) Selection of NN structure; (d) Selection of initial weights and (e) Testing the NN generalization.

1. Data Distribution in Three Subsets (Training, Validation and Testing)

The data sets were used to feed the optimized network in order to train, test and validate the model. During training, the output matrix is computed by a forward pass in which the input matrix is computed by a forward pass in which the input matrix is propagated forward through the network to compute the output value of each unit. The output matrix is then compared with the desired matrix which results into error, appropriate adjustment were made for each of the weights of the network. A regression analysis of the network response between NN outputs and the corresponding target was performed. Taking into account the non-linear dependence of the data, linear regression shows a good agreement between NN outputs predicted data and the corresponding targets (experimental values). The best fit was correlation coefficient (R^2) 0.999 and MSE 0.000365. This agrees well with the correlation coefficient reported in the literature [5], [15] and [16].

2. Selection of Backpropagation Training Algorithm and Transfer Function

Due to the convergence speed and the performance of network to find better solution, the Levenbert-Marquardt (LMA) training method was selected in this work as a proper training algorithm in agreement with the literature [17]. Different transfer functions were examined in each layer, separately and with respect to the mean squared error (MSE) of testing data, the proper transfer functions were chosen. MSE is calculated as follows:

$$MSE = \frac{\sum_{N} (SP_{cal} - SP_{\exp})^2}{N} \quad (2)$$

where subscripts c_{al} and C_{exp} denote calculated and experimental values of scaled outputs (SP), respectively. N is the number of validation and training data. The most widely used criteria including MSE are 0.016, 0.150 and 0.434 for training, validation and testing data respectively; MSRE are 0.004, 0.001 and 0.010 for training, validation and testing data respectively and R is 0.998 for all.

$$R = \frac{\sum_{N} \left(SP_{cal} - SP_{cal,Ave}\right)\left(SP_{\exp} - SP_{\exp,Ave}\right)}{\sqrt{\sum_{N} \left(SP_{cal} - SP_{cal,Ave}\right)} \sqrt{\sum_{N} \left(SP_{\exp} - SP_{\exp,Ave}\right)}} \quad (3)$$

3. Selection of NN Structure

NN structure has significant effects on the predicted results [17]. The optimal number of hidden layers and the optimal number of neurons in each layer are case dependent and there is no straightforward method for determination of them. The literature revealed that use of more than one hidden layer provided greater flexibility and enables the approximation of complex functions with fewer neurons [17]. Reference [18] found out that adding a second hidden layer improves the network prediction capability significantly without having any detrimental effects on the generalization of the testing data set. The optimal architecture of the NN model and its parameter variation were determined based on the minimum value of the MSE of the training and predicted set. In this work, the optimal NN structure was 3-11-1 with a MSE value of 0.000365 as found by Kabuba and Mulaba [4].

4. Initial Weights

The wrong choice of initial weights can lead to the local minimum values and therefore bad performance of the networks. In order to prevent these phenomena, 25 runs were performed using different random values of initial weights and the best training network was selected.

5. Testing the NN Generalization

The experimental design using analysis of variance (ANOVA) was chosen for testing the adequacy of the NN and for optimizing of the effective parameters. In Figs. 1-3 the generalization of NN is shown using 3D diagrams by plotting the predicted loading efficiency versus input variables.

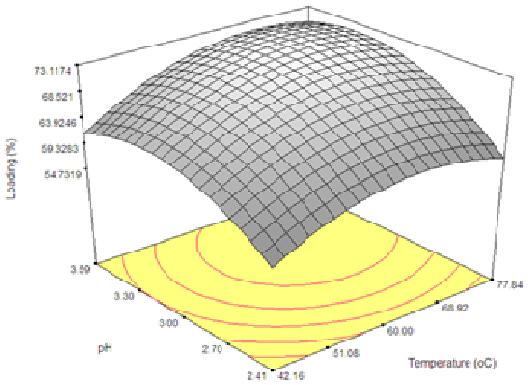

Fig. 1 Generalization performances of optimal NN, effect of Temperature and pH

The mechanism of ion-exchange of Cu^{2+} onto the clinoptilolite surface reflects the nature of physicochemical interaction of the metal ions in the solution and the active sites of the clinoptilolite. There is a need to investigate the effect of pH and temperature on the Cu^{2+} ion loading from the solution by clinoptilolite. As one can see in Fig. 1, effect of temperature and pH on the loading % was carried out as per the selected model with selected range of temperature (42.16–77.84°C) and pH (2.41-3.59) to investigate their combined effect on the system. The result in Fig. 1 shows that the loading was highest at pH 3.59 which correspond to the temperature of 42.16°C. Fig. 2 shows the mutual effect of concentration and temperature, loading was carried out as per the selected model with selected range of concentration and temperature to investigate their combined effect on the system. As seen in Fig. 2, the effect of temperature and initial concentration on the loading of Cu^{2+} ion from the solution by clinoptilolite was carried out as per selected model with selected range of temperature (42.16-77.84°C) and initial concentration (0.84-2.26 mg/L) to investigate their combined effect on the system. Fig. 3 illustrates the effect of pH and initial concentration, combined effect of pH and initial concentration has been analyzed from the Box-Benklen model as show in Figs. 1-3. It has been estimated that as concentration increases from 0.84 to 2.26 mg/l, keeping temperature constant, loading % decrease. Increasing in temperature is expected to increase the movement of cations, since at higher temperature electrostatic interaction becomes weaker with causes the ions to becomes smaller and promote the loading of the ions onto the surface of the clinoptilolite. It can be observed that loading of Cu^{2+} ions increases with increase in temperature at different initial concentration. At the lower initial concentration of 084 mg/L, the loading % is 70.0001. Reference [19] reported that adsorption sites take up available metal more quickly at low concentrations. However, at high concentration, metals need to diffuse to the clinoptilolite surface by intraparticle diffusion and greatly hydrolyzed ion will diffuse at a slower rate because of the saturation of the active site available on the clinoptilolite for interaction with metal ions. It can be concluded that the loading efficiency decreases with increasing metal concentration in aqueous solutions. Based on developed NN model, the optimization of process variables was carried out in order to establish the optimal conditions that ensure the maximal loading efficiency.

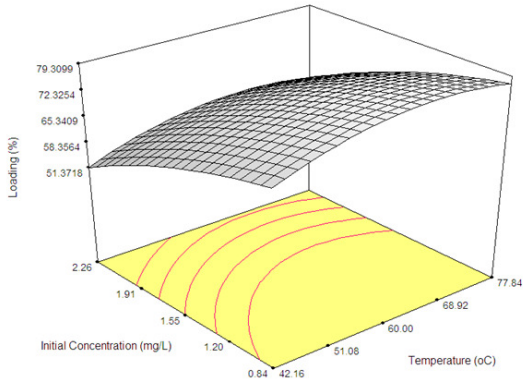

Fig. 2 Generalization performances of optimal NN, effect of Temperature and Concentration

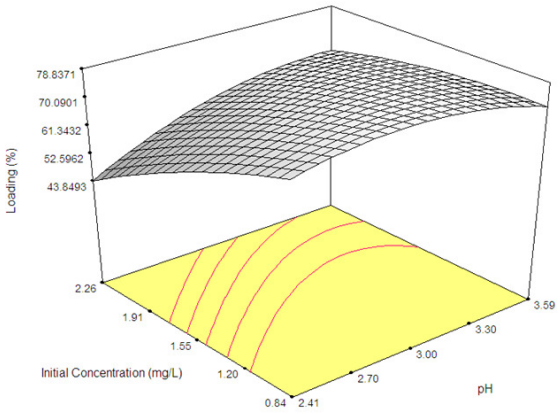

Fig. 3 Generalization performances of optimal NN, effect of pH and initial Concentration

IV. Conclusion

NN modeling was employed for prediction of the loading of Cu (II) onto clinoptilolite. A (3-11-1) feed forward NN model with a tangent sigmoid transfer function (*tansig*) at hidden layer with 11 neurons and a linear transfer function (*purelin*) at out layer was proposed to predict the efficiency of copper loading. The developed NN model showed a good prediction of the experimental data with a satisfactory result. NN predicted results are very close to the experimental results with R^2 = 0.997 and MSE = 0.000365. Analysis of the response surface showed that the experimental variables have significant effect on the loading %. NN successfully tracked the nonlinear behavior of removal versus pH, temperature, concentration with MSE, R and MSRE of 0.102, 0.998 and 0.004, respectively. Training of the NN was accomplished through the BP algorithm in MLP. NN modeling technique

was found to have favorable features such as efficiency, generalization and simplicity, which make it an attractive choice for modeling of highly complex system and non-linear process, such as ion loading on exchangers.

REFERENCES

[1] R.E. Clement,G.A. Eiceman, C.J. Koester, "Environmental analysis". J. Anal. Chem. 1995,vol.67,pp.221-255.

[2] E. Muzenda, J. Kabuba,F. Ntuli, M. Mollagee and A.F. Mulaba-Bafubiandi, "Cu (II) Removal from Synthetic Waste Water by Ion Exchange Process", Proceedings of the WCECS, vol. II, 2011, Oct. 19-21, San Francisco, USA.

[3] A. Amankwah,J. Kabuba , A.F. Mulaba-Bafubiandi, "*Modeling of Ion exchange process using time delayed Neural Networks*". Proceedings of the ICMET, 2011, vol. 1, pp. 447-451.

[4] J. Kabuba, A.F. Mulaba-Bafubiandi, "*Modeling of Co-Cu elution from clinoptilolite using Neural Network*", World Academy of Science, Engineering and Technology, 2012, vol. 68, pp. 1222-1225.

[5] E.S. Elmolla, M. Chaudhuri, M.M. Eltoukhy,"*The use of artificial neural network (ANN) for modeling of COD removal from antibiotic aqueous solution by the Fenton process*", *J. Haz. Mat*., 2010, vol 179: 127-134.

[6] V.K. Pareek, M.P. Brungs, A.A. Adesina, R. Sharma. "*Artificial neural network modeling of a multiphase photodegradation system*", *J. Photochem. Photobiol. A: Chem.,* 2002, vol. 149, pp. 139-146.

[7] M. Cote M, B.P.A. Grandjean, P. Lessard, J. Thibault, "*Dynamic modeling of activated sludge process: improving prediction using neural networks*", *water Res*., 1995, vol. 29, pp. 995-1004.

[8] I. Machon, H. Lopez, J. Rodriguez-Iglesias, E. Maranan, I. Vazquez, " Simulation of a coke wastewater nitrification process using a feed-forward neuronal net" , Environ. Model Softw., 2007, vol. 22, pp.1382-1387.

[9] A. Aleboyeb, M.B. Kasiri, M.E. Olya, H. Aleboyeh, " Prediction of azo dye decolorization by UV/H_2O_2 usingartificial neural networks", Dyes Pigments, 2008, vol. 77, pp. 288-294.

[10] N. Prakash, S.A. Manikandan, L. Govindarajan, V. Vijayagopal. "Prediction of biosorption efficiency for the removal of copper (II) using artificial neural networks", J. of Hazardous Materials, 2008, pp.1268-1275.

[11] N. Daneshvar, A.R. Kahataee, N. Djafarzadeh, "*The use of artificial neural networks (ANN) for modeling of decolorization of textile dye solution containing C.I. basic Yellow 28 by electrocoagulation process*", J. of Hazardous Materials, 2006, vol. B 137, pp. 1788-1795.

[12] A. Amankwah, J. Kabuba, "Comparison of Neural Networks and Kalman Filter for the modeling of Ion Exchange Process", Life Sci J., 2013, vol. 10, pp. 1012-1015.

[13] S.A. Abdulkareen, E. Muzenda, A.S. Afolabi, J. Kabuba, " Treatment of clinoptilolite as an Adsorbent for the Removal of copper Ion from Synthetic Wastewater solution", Arab. J. Sci. Eng., 2013, vol. 38, pp. 2263-2272.

[14] B.B. Mamba, D.W. Nyembe and A.F. Mulaba-Bafubiandi, "The effect of conditioning with NaCl, KCl and HCl on the performance of natural clinoptilolite's removal efficiency of Cu^{2+} and Co^{2+} Synthetic solution", Water SA., 2009, vol. 36, pp. 437-444.

[15] E. Oguz,A. Tortum, B. Keskinler. "Determination of the apparent rate constants of the degradation of humic substances by ozonation and modeling of the removal of humic substances from the aqueous solutions with neural network", J. of Hazardous Materials, 2008, vol. 157, pp. 455-463.

[16] F.L. Toma, S. Guessasma, D. Klein, G. Montavon, G. Bertrand,C. Coddet,"Neural computation to predict TiO_2photocatalytic efficiency for nitrogen oxides removal. J. Photochem. Photobiol. A; Chem.2004, vol. 165, pp. 91-96.

[17] D.R. Baughman and Y.A. Liu, "Neural Networks in Bioprocessing and Chemical Engineering". Academic Press, San Diego, California, USA, 1995.

[18] M. Sadrzadeh, T. Mohammadi, J. Ivakpour, N. Kasiri, "Separation of lead ions from wastewater using electrodialysis: Comparing mathematical and neural network modeling", Chemical Engineering Journal, 2008, vol. 144, pp. 431-441.

[19] M. Horsfall, A.I. Spiff, "Effects of metals ion concentration on the biosorption of Pb^{2+} and Cd^{2+} from aqueous solution by Caladium bicolor (Wild Cocoyan)", Afr. J. Biotechnol. 2005, vol. 4, pp. 191-196.