Comparison between Neural Network Technique and Mathematical Modelling for Ion-Exchange Process

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***Abstract*—The ion-exchange process is one of the methods employed for the removal of heavy metals from industrial wastewaters. This process is complex and non-linear involving many factors influencing the chemical process of the removal which are not well understood. To improve the efficiency of the ion-exchange process, analysis and optimization of the process should be accomplished. Simulation and modelling are tools to achieve the objectives. Mathematical model was developed to compare to the Neural Network techniques and for optimizing of the effective input parameters including pH, temperature and initial concentration. Feed Forward Neural Network successfully tracked the non-linear behavior of the ion-exchange process. The predictability of the network was statistically assessed 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 Feed Forward Neural Network modelling techniques could effectively predict and simulate the highly complex system and non-linear process such as the ion-exchange using activated zeolite.**

Keywords: Feedforward neural network, heavy metals, ion-exchange, mathematical modelling.

I. Introduction

SINCE the beginning of the last century, the application of Neural Network (NN) techniques, specially Feed Forward Neural Networks with Back Propagation has been considered as a promising tool because of their simplicity towards simulation, prediction and modelling [1]-[7]. This technique present some advantages compared to the traditional mathematical models to predict the degree of non-linearity and their ability to learn complex relationships without requiring the knowledge of model structure [1]-[6]. The ion-exchange process has been widely employed for the removal of heavy metals from industrial wastewaters [8]-[12]. This process is complex non-linear and involves many factors influencing the loading mechanisms from the pregnant solutions, the subsequent step being the elution. In order to improve the performance of this process, optimization and analysis of the process should be accomplished; modelling and simulation are tools to achieve the objectives. Modelling of a process covers a broad spectrum, firstly theoretical models based on fundamental knowledge of the process and secondly empirical models which do not rely on the fundamental principles governing the process. A large number of ion-exchange models are theoretical, obviously derived from physical descriptions and understanding of the process under the certain assumptions. They are mathematically complex, computationally expensive and they ideally require a very detailed knowledge of the process. There is a need to find an alternative means for predicting process performance and thus the interest in applying Neural Network techniques. In this study, NN is developed for modelling ion-exchange process for the removal of copper from industrial wastewater using activated zeolite based on the mass exchange between industrial wastewater and activated zeolite for differential bed height. In order to compare the predictability of neural network technique and mathematical model, the results of each parameter are compared with experimental data at the same conditions.

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II. Theory

A. Neural Network

A Neural network (NN) is an information processing paradigm that is inspired by the way a biological nervous system learns and process information [13]. The power of the feed-forward neural network comes from the parallel processing of the information from the data. [14]. Feed-forward neural networks can be applied to a wide range of industrial wastewater treatment problems because of the high degree of accuracy, data-driven self-adaptive methods in that there are few a priori assumptions about the models for ion-exchange process.

B. Development of a Neural Network Model

Neural network Toolbox 5.1 in MATLAB 7.4 (R 2007a) mathematical software package was used for the prediction of the copper removal efficiency. To find the network having the best performance, seven networks involving 4-10 hidden neurons were trained and tested while ten Back Propagation training algorithm and transfer functions were applied to each. The approach to the comparison of the networks was to evaluate an error function using data which were independent on those used for training. Seven networks were also trained and tested separately each by minimization of an appropriate error function defined with

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respect to data set. During training and testing set the error decreased. However, when the network began to overfit the data, the error began to rise on the testing set. The training set was stopped when the testing error increased for a specified number of iterations, and the weights and biases at the minimum of the testing error were returned. Generalization error was obtained and evaluated to assess the network for validating set. Each selected network was run on the validating set. The best network received inputs including pH, temperature and initial concentration and predicted the removal efficiency as output. In order to evaluate the results, the regression coefficient mean square error and predicted values were statistically compared with experimental data. The configuration of the network giving the smallest mean squared error was (3-10-1) with a tangent sigmoid transfer function (*tansig*) at hidden layer with 10 neurons and a linear transfer function (*purelin*) at out layer. To improve the generalization of the selected network, the network with a structure 3-10-1 presented in Fig. 1 was run on experimental data and regression coefficient as well as regression line between predicted values from the neural network. The experimental data were obtained to assess the network predictability.

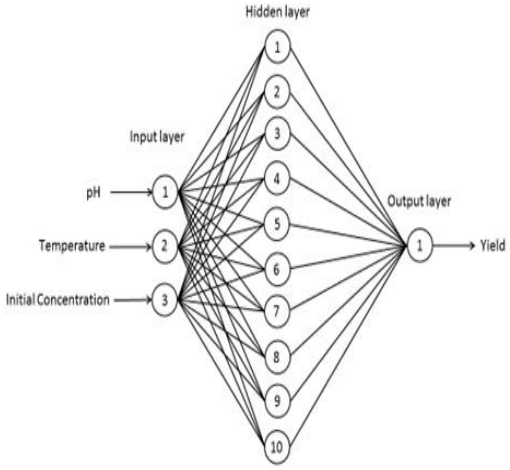

Fig. 1. Schematic diagram of the neural network structure

C. Mathematical Modelling

The mathematical model ion-exchange process was formulated using the process based on the mass balance (mass exchange between industrial wastewater and activated zeolite) for differential bed height.

$$u_o \frac{\partial c(x,t)}{\partial x} + (1-\varepsilon)\rho s \frac{\partial q(x,t)}{\partial t} + \varepsilon \frac{\partial c(x,t)}{\partial t} = \varepsilon D_{eff} \frac{\partial^2 c(x,t)}{\partial x^2(x,t)} \quad (1)$$

Equation (1) can be solved analytically or numerically, but simplifying assumptions are necessary [15]. If the main mass transfer resistance is assumed to be on the liquid side, i.e. the residence of mass transfer from the industrial wastewater to the activated zeolite determines the rate, then $\frac{\partial q(x,t)}{\partial t}$ can be described using (2).

$$(1-\varepsilon)\rho s \frac{\partial q}{\partial t} = \beta a (C - C_e) \quad (2)$$

In this paper, expression $\left(\frac{\partial q}{\partial t}\right)$ can be approximated from sorption kinetics equations. If we assume that the sorption kinetics is determined by chemical adsorption, then as it was proved by [16], changes in sorbent particle can be described by (3).

$$\frac{dq}{dt} = k_2 (q^* - q)^2 \quad (3)$$

where: q is the adsorption (mg/g d.m), q^* is the equilibrium adsorption (mg/g d.m) and k_2 is the coefficient in pseudo second-order equation (g/mg min). On the other hand, if we assume that the sorption kinetics is determined by physical adsorption, then the expression $\left(\frac{\partial q}{\partial t}\right)$ has the form:

$$\frac{dq}{dt} = k_1 (q^* - q) \quad (4)$$

where: k_1 is the coefficient in pseudo first-order equation (1/min). For two points in the column at different distances from the input, concentrations of ions both in industrial wastewater and activated zeolite are different, and changes of the concentration are delayed in time. This is the reason why (5) is proposed:

$\xi = \{u_o t - x \text{ for } u_o t \geq x;\ 0 \text{ for } u_o < x\}$ (5)

This substitution has been used by [17] in the analysis of multi-component adsorption. Every process could be considered from the Lagrange's point of view. The adsorption process can be followed from Lagrange's point of view if the variable in form (5) is assumed i.e., electrostatic interaction becomes weaker. From (5) the following transformation is valid

$$\frac{\partial c(x,t)}{\partial x} = -\frac{dC(\xi)}{d\xi} \quad (6)$$

$$\frac{\partial C(x,t)}{\partial t} = u_o \frac{dC(\xi)}{d\xi} \quad (7)$$

$$\frac{\partial^2 C(x,t)}{\partial x^2} = \frac{d^2 C(\xi)}{d\xi^2} \quad (8)$$

The assumption of the new variable (5) offers a possibility of transforming (1) to the form of the ordinary second-order differential equation of one variable. Upon substitution of (2), (7) and (8); (1) takes the following form:

$$\frac{\varepsilon D_{eff}}{u_o (1-\varepsilon)} \frac{d^2 C}{d\xi^2} + \frac{dC}{d\xi} = \rho s \frac{dq}{d\xi} \quad (9)$$

An analytical or numerical solution of (9) is possible provided that the expression of component $\rho s \frac{dq}{d\xi}$ is known.

Assuming that at every site of the column, sorption kinetics can be described by (3) or (4), we can find relation $q = f(\xi)$ after a relevant modification of the variable.

$$\frac{\partial q}{\partial t} = k_2 (q^* - q)^2 = u_o \frac{dq}{d\xi} \quad (10)$$

After separation of variables and integration of (10) within the range $[\xi_o, \xi]$ and $[q(\xi_o), q(\xi)]$ we will have the form:

$$q(\xi) = \frac{q^* \alpha \xi}{1 + \alpha \xi} \text{ for } u_o t \geq x \text{ and } q(\xi) = 0 \text{ for } u_o t < x \quad (11)$$

where: $\alpha = \frac{q^* k_2}{u_o}$ (12)

Similar transformation can be done for (5) or for another

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form which described the sorption kinetics. The derivative $\frac{dq}{d\xi}$ can be calculated from (13) and (14). It has the following form:

$$\frac{dq}{d\xi} = \frac{q^* \alpha}{(1+\alpha\xi)^2} \quad (13)$$

Equations (8) and (10) can be used to identify the adsorption column. The identification will consist of calculation of the coefficients k, q and D_{eff} by solving (8) with the use of input-output data measured in the column in definite time intervals (e.g. to time of breakthrough and above). Integration of (8) in the range from ξ_o to ξ gives the following result:

$$\frac{\varepsilon D_{eff}}{u_o(1-\varepsilon)} \int_{\xi_o}^{\xi} \frac{d^2C}{d\xi^2} d\xi + \int_{\xi_o}^{\xi} \frac{dC}{d\xi} d\xi = \rho s \int_{\xi_o}^{\xi} \frac{dq}{d\xi} d\xi \quad (14)$$

After relevant transformations we get:

$$\frac{\varepsilon D_{eff}}{u_o(1-\varepsilon)} \left(\frac{dC}{d\xi}(\xi) - \frac{dC}{d\xi}(\xi_o) \right) + C - C_o = \rho s q^* \left(\frac{\alpha\xi}{1+\alpha\xi} - \frac{\alpha\xi_o}{1+\alpha\xi_o} \right) \quad (15)$$

The first term in the bracket in (15) can be approximated in the following way:

$$\frac{dC}{d\xi}(\xi) = \rho s \frac{dq}{d\xi}(\xi) \quad (16)$$

For this purpose (13) should be used.

$$\frac{dC}{d\xi}(\xi) = \frac{q^* \alpha \rho s}{(1+\alpha\xi)^2} \quad (17)$$

Taking into account (10) and (12), the final equation takes the following form:

$$C = C_o + \rho s q^* \left(\frac{\alpha\xi}{1+\alpha\xi} - \frac{\alpha\xi_o}{1+\xi_0} \right) - \frac{\varepsilon D_{eff} q^* \alpha \rho s}{u_o(1-\varepsilon)} \left(\frac{1}{(1+\alpha\xi)^2} - \frac{1}{(1+\alpha\xi_o)^2} \right) \quad (18)$$

For $u_o t \geq x$

$C = 0$ for $u_o t < x$

Equations (18) and (10) enable calculation of the concentration distribution along the column in both the industrial wastewater, and the activated zeolite, depending on time and distance from the inlet. A similar analysis can be carried out for multi-component mixture. In such a case, each component will have individual coefficients q*, k and D_{eff} [17]. Mathematical model values and experimental data are depicted in Figs. 2-4. It should be noted that, although experimental values and mathematical model curves do not completely coincide with each other (significant deviations are observed in some cases), they properly described the trend of the behavior. Obviously, it can be said that mathematical model is of great important because:

- It satisfies experimental data to a moderately sufficient degree of correlation coefficient;
- it can be used for different scales;
- it can be easily used to calculate copper removal at different operational conditions;
- it can be used to scale up.

III. Results and Discussion

A. Comparing the Mathematical Model and Neural Network

Mathematical Model, NN modeling predictions and experimental data were juxtaposed in Figs. 2-4.

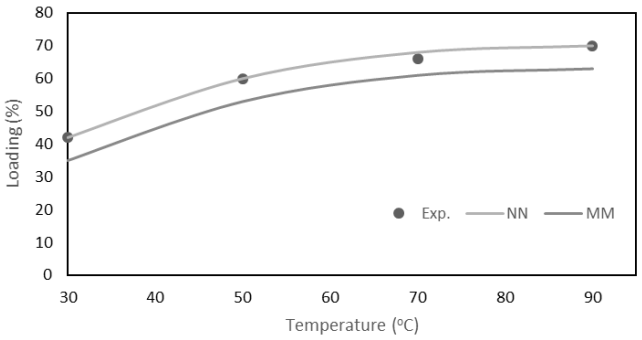

Fig. 2. Comparing mathematical model, NN and experimental data: effect of Temperature on the removal

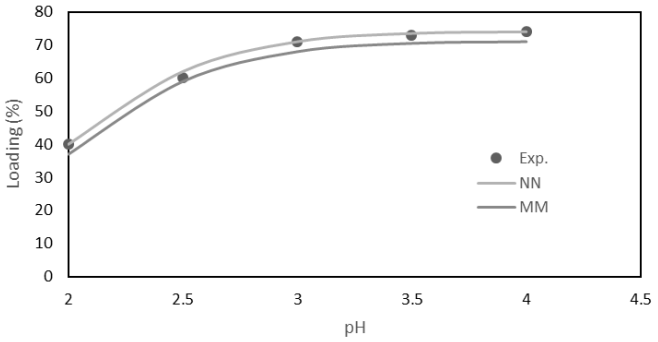

Fig. 3. Comparing mathematical model, NN and experimental data: effect of pH on the removal

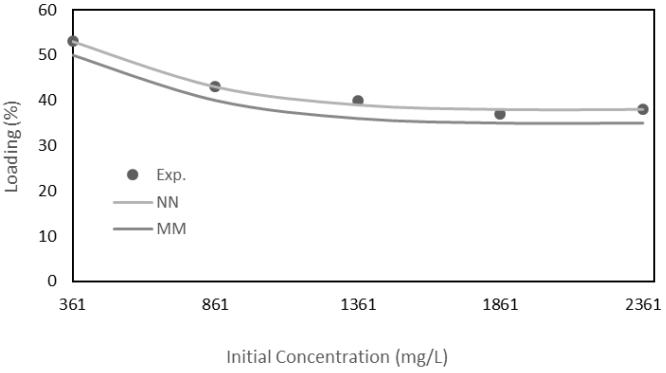

Fig. 4. Comparing mathematical model, NN and experimental data: effect of Initial Concentration on the removal

As can be seen from Figs. 2-4, the NN can predict copper removal at various operational conditions much better than the mathematical model. The better performance of the NN model was confirmed by comparing the MSE, RMSE and MSRE of two models in Tables I.

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TABLE I
COMPARISON BETWEEN MATHEMATICAL MODELING AND NN

Error	NN	Mathematical Model
MSE	0.9697	0.768
RMSE	0.9520	0.658
MSRE	0.9527	0.665

Excellent agreement between NN results and experimental data indicates the capacity of NN to model the complicated process. Figs. 2-4 confirm that mathematical model tends to describe the nonlinear behavior of the ion-exchange process in almost a linear manner. According to Figs. 2-4, increasing pH, concentration and temperature increase the value of the removal. It is obvious due to the fact that increasing temperature and concentration decreases the solution resistance, while increasing pH increases the driving force. From Figs. 2-4, it is found that the differences between the removal value regarding medium and high levels of parameters are negligible compared to those regarding low and medium levels, i.e. at higher values of parameters, almost constant values of removal are achieved.

B. Confirmation experiments

To support the optimized data given by numerical modeling under optimized conditions, the confirmatory experiments were conducted with the parameters as suggested by the model, and the removal was found to be 80%. The effect of pH, temperature and initial concentration were studied to support the results, and the data is in accordance with the results obtained from optimized conditions.

IV. CONCLUSION ON THE LOADING

Mathematical model and NN modeling were employed for predicted of the ion-exchange process in aqueous solution in terms of Cu (II) removal. A feed forward NN model structure 3-10-1 with a tangent sigmoid transfer function (*tansig*) at the hidden layer with 10 neurons and a linear transfer function (*purelin*) at the out layer was proposed to predict the loading efficiency of copper. The developed NN model showed a good prediction of the experimental data with a satisfactory result. NN successfully tracked the complex and nonlinear behavior for the process of the removal efficiency versus pH, temperature, initial concentration with MSE, R and MSRE of 0.102, 0.999 and 0.004, respectively. The Neural Network modeling technique was found to have many favorable features such as efficiency, generalization and simplicity, which make it an attractive choice for modeling of highly complex systems and non-linear processes, such as the ion-exchange process.

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