ANN Modeling for Cadmium Biosorption from Potable Water Using a Packed-Bed Column Process

Dariush Jafari, Seyed Ali Jafari

Abstract—The recommended limit for cadmium concentration in potable water is less than 0.005 mg/L. A continuous biosorption process using indigenous red seaweed, *Gracilaria corticata*, was performed to remove cadmium from the potable water. The process was conducted under fixed conditions and the breakthrough curves were achieved for three consecutive sorption-desorption cycles. A modeling based on Artificial Neural Network (ANN) was employed to fit the experimental breakthrough data. In addition, a simplified semi empirical model, Thomas, was employed for this purpose. It was found that ANN well described the experimental data ($R^2>0.99$) while the Thomas prediction were a bit less successful with $R^2>0.97$. The adjusted design parameters using the nonlinear form of Thomas model was in a good agreement with the experimentally obtained ones. The results approve the capability of ANN to predict the cadmium concentration in potable water.

Keywords—ANN, biosorption, cadmium, packed-bed, potable water.

I. INTRODUCTION

HEAVY metals are very toxic elements that accumulate through the food chain and affects the human health. Cadmium is one of the big three toxic metals that can readily enter to the surface waters. The recommended limit for this metal in potable water is less than 0.005 mg/L [1].

Biosorption is a unique technique for heavy metal removal from aqueous solutions that includes many advantages over the traditional physicochemical methods. Numerous biomaterials have been studied for heavy metal biosorption purposes. Among them, seaweeds are very less costly and available in high amounts in coastal cities like Bushehr, Iran. In addition, it has been proved that they have high ability in heavy metal biosorption. Therefore, this makes the process more economical.

Separation based on adsorption-desorption cycles are widely used in various scales. Packed-bed column is usually preferred due to its effectiveness and high sorption capacity with very low effluent concentrations [2], [3].

A reliable modeling can help to calculate some characteristics or design parameters as well as to predict the breakthrough curve behavior for scale up purposes and performance comparison. Several factors including axial dispersion, sorption kinetics, mass transfer, and intraparticle

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diffusion resistances should be considered to have a reliable and perfect model for a packed-bed column process. Solving such a complex model needs a series of non-linear partial differential equations [4].

The simplified semi empirical models are known as alternative methods to fulfill this purpose. Thomas model is one of them has frequently been employed by several researchers for describing the experimental breakthrough curve data [1], [2], [5]. This model suggests some simplifications that are usually not validated in reality. Therefore, the precision is not high enough to trust the results. However, this is good for achieving some design parameters based on experimental data [4].

Most of the equations which were used in these modeling studies are not applicable for a wide range of conditions in various processes, because they are only appropriate for a certain set of conditions and they could be used under some assumptions. Therefore the significance of techniques which are directly based on experimental data and their development to predict the result of processes seems to be obvious. Among these techniques, Artificial Neural Network (ANN) is an excellent tool to predict the results of processes using experimental data. Similar studies have proved this fact [6]-[8]. The neural network based models are recently used to describe the column data. It has been employed by several researchers [9]-[11].

In the present study, a continuous-flow packed-bed column with indigenous red seaweed, *Gracilaria corticata*, was employed for continuously removing cadmium contaminations from potable water. The breakthrough curves were plotted for three consecutive sorption-desorption cycles under fixed flow rate, influent concentration, and bed height. ANN approach was employed to describe the breakthrough curves. The semi empirical Thomas model was also employed to obtain some design parameters as well as to compare by ANN fitting.

II. MATERIALS AND METHODS

A. Biosorbent Preparation

The red seaweed, *Gracilaria corticata*, was harvested from Bushehr coastal waters, Iran. It was washed several times with tap water to removal salts and sands. Dried biomass in size between 0.5 to 0.7 mm was employed in the column.

B. Column

A glass column with an internal diameter of 2.5 cm and 20 cm height was used and a 3 cm height of glass beads (1 mm in diameter) was placed at the top and the bottom of the bed in order to pack the biomass as well as provide a uniform inlet

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flow of the solution into the column. An upward flow was pumped through the column and sampling was done at the column outlet.

C. Experiments

The feed solution was prepared by dissolving the required amount of cadmium salt in tap water to achieve 50 mg/l cadmium concentration. The pH was initially adjusted to 6 by 0.1 M NaOH or 0.1 M HNO_3. The experiments were performed at room temperature, 29-30 °C. Feed solution was pumped upward through the column at a fixed flow rate of 35 ml/min using a peristaltic pump. The bed height of 12.2 cm was placed in the column by 13 g of biomass. Sampling was done regularly from the column effluent and analyzed for cadmium residual concentration using a flameless atomic absorption spectrophotometer (PG instruments, AA500).

The bed regeneration was performed using $CaCl_2$ solution acidified to pH 3 by 1 M HCl.

D. Modeling

1. Thomas Model

The breakthrough curves obtained in the present experiments need to be examined quantitatively. The Thomas model is the most widely employed model that is usually used to fit the experimental breakthrough curve data [12]. This model has the linear and non-linear forms as (1) and (2), respectively [13]:

$$\ln(\frac{C_i}{C} - 1) = \frac{K_{Th}MQ}{F} - K_{Th}C_i t \qquad (1)$$

$$\frac{C}{C_i} = \frac{1}{1 + \exp[(K_{Th}/F)(QM - C_i tF)]} \qquad (2)$$

where C and C_i are the effluent and influent cadmium concentrations (mg/l), respectively, F is the volumetric feed flow rate (ml/min), M is the mass of biomass used in bed (g), t is process time (min), K_{Th} is Thomas rate constant (l/mg min), and Q is the maximum biosorption capacity (mg/g). This is a key parameter that is required in design. The model parameters were achieved using both the linear and non-linear equations and the results were compared together. The unknown parameters in (1), K_{Th} and Q, are achieved from the slope and intercept of plot of $\ln(C_i/C - 1)$ versus time, respectively.

The model precision was assessed using R^2, standard squared error (SSE), mean squared error (MSE), and root mean squared error (RMSE) as follows:

$$SSE = \sum_{i=1}^{n} (Y_{Model,i} - Y_{Exp,i})^2 \qquad (3)$$

$$MSE = \sum_{i=1}^{n} (Y_{Model,i} - Y_{Exp,i})^2 / n \qquad (4)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n} (Y_{Model,i} - Y_{Exp,i})^2}{n}} \qquad (5)$$

where Y_{Exp} and Y_{Model} are the experimental and predicted C/C_i by model, respectively and n is number of points.

2. ANN Modeling

Neural networks (NNs) which are inspired by biological systems are computer algorithms comprised of elements called neurons. They are applied for information processing purposes. Actually, they are neurocomputers which possess parallel distributed processors [14]. Neurons are the main elements of neural networks which are connected to the networks by a set of connections, called assigned weights. The performance of a network is strongly dependent on weights values. The neurons are organized in input, output, and the hidden layers. A neural network performs the modeling affair in a way that receives the input, sums them with their weights and adds a bias to the result of summation, then sends the results as an argument to the transfer function.

There are several types of neural networks, where multi-layer perception (MLP) is the most common one [15]. The MLP network has one input layer, one output layer, and usually one hidden layer. The number of input and output variables of the network depends on the type of process [16]. As mentioned in majority of cases a network with one hidden layer leads to satisfactory results. Therefore, the number of hidden layer is considered one in this paper. Each neuron in a layer is usually connected to the neurons of the latter one.

The network training is done by assigning a pattern to the input pattern, after that the results of activation level calculation are propagated forward toward the output layer. Calculation units sum the inputs and utilize a function to calculate the output. Finally the output of the network is achieved in the output layer. The improvement of network convergence is done by the addition of a constant term by the bias units of the input and hidden layers to the weighted sum. When the network outputs are compared to the target values, the errors of hidden units are determined, and then their weights are manipulated to minimize the error. This procedure is shown in Fig. 1. Generally it can be claimed that the reduction of global error is the consequent of weight and bias adjustment using training algorithms.
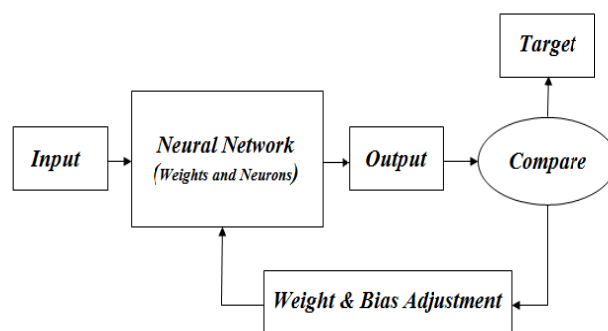

Fig. 1 Schematics of ANN model and weight and bias adjustment

The neuron k can be expressed mathematically using (6) and (7):

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$$u_k = \sum_{j=1}^{m} w_{kj} x_j \qquad (6)$$

$$y_k = \varphi(u_k + b_k) \qquad (7)$$

where x_j is the input signal, w_{kj} is the neuron's weight, u_k is the linear combiner output due to input signals, b_k is its bias, φ is the activation function, and y_k is the output signal of neuron.

MLP neural network is used in the current study, where it is trained by the Levenberg Marquardt (LM) algorithm. The transfer functions of hidden and output layers are linear. The current training algorithm has provided the lowest error value; consequently, the optimal number of hidden layer neurons has been achieved. The operating parameter is the process time, so the input layer of the network has 1 neuron. The output is the ratio of input cadmium concentration in to output cadmium concentration, which results in one neuron in the output layer. The number of hidden layer neurons is achieved by the training of several networks with different number of hidden layer neurons and the comparison between the results of

predictions for the desired output. The number of hidden layer's neurons for cycles 1, 2, and 3 are 9, 15, and 9, respectively. The adequacy criterion for the optimized number of neurons is determined by the calculation of MSE between the network output and the training data.

III. RESULTS AND DISCUSSIONS

Plotting the effluent metal concentration versus time gives a sigmoid shape profile, which is called breakthrough curve. It is used to characterize the performance of a packed-bed column. The Cd^{2+} biosorption process was stopped when the effluent cadmium concentration reached the influent one (Figs. 2 and 3). It is where the biosorbent is saturated and it is essential to be regenerated for reuse in several cycles due to economic reasons [17]. The regenerant gradually destructs the surface ligands and decreases number of accessible biding sites for metal ions. This causes to reduce the column performance, maximum biosorption capacity (Table I), and decline the slope of breakthrough curve (Figs. 2 and 3) as the cycles progressed.

TABLE I
COMPARISON OF LINEAR AND NONLINEAR THOMAS MODEL WITH ANN FOR FITTING THE BREAK THROUGH CURVES FOR THREE CONSECUTIVE CYCLES

Model	Cycle No.	Q_{exp} (mg/g)	Q_{model} (mg/g)	K_{Th} (l/mg min)	R^2	SSE	MSE	RMSE
Linear Thomas	1	23.53	0.135	0.00059	0.478	-	-	-
	2	21.96	0.131	0.00057	0.586	-	-	-
	3	20.80	0.134	0.00047	0.796	-	-	-
Nonlinear Thomas	1	23.53	22.44	0.00073	0.996	0.025	0.0008	0.0288
	2	21.96	20.01	0.00058	0.990	0.078	0.0025	0.0502
	3	20.80	18.94	0.00042	0.979	0.103	0.0034	0.0588
ANN	1	-	-	-	0.999	6.94×10^{-6}	2.24×10^{-7}	0.0005
	2	-	-	-	0.994	6.93×10^{-6}	2.17×10^{-7}	0.0004
	3	-	-	-	0.996	6.94×10^{-6}	2.31×10^{-7}	0.0005

The low values of correlation coefficient, R^2, as well as non-consistency between the experimental and predicted Q values reported in Table I for linear Thomas model, imply that it was not successful at all to achieve reliable parameters for describing the experimental data. It could be due to the asymmetry profile of the experimental breakthrough curves. The Thomas model simply ignores axial dispersion and also is useful for fitting symmetry curves [13], [18].
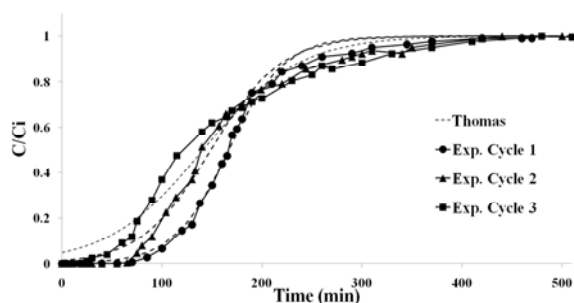

Fig. 2 The breakthrough curves for three consecutive cycles by nonlinear Thomas model

As an alternative method, the model directly fitted to the

experimental data using a nonlinear least-squares fitting by Excel software. It can be seen from Table I that the R^2, SSE, MSE, and RMSE are significantly good for nonlinear Thomas model. Furthermore, the predicted Q values are in good agreement with the experimental ones. The dashed lines in Fig. 2 illustrate data fitting by Thomas model for three cycles.

As can be seen in Fig. 2, there are over predictions in the leading and trailing edges of the curves.

The input variables of NNs significantly affect their efficiency, since they reflect the physical principles of the studied system. The input data have been normalized between zero and one prior to training step. The input variable in this study is the process time. The structure of an ANN network comprises of three layers, including: input, hidden, and the output. There is one node in input layer corresponded to one input operating variable. The inputs are directly sent from the input nodes to the hidden layer (considered one) by the weights, where the main data processing is performed there by the calculation of inputs weighted summation. The output layer has one node since there is only one output variable, the ratio of input cadmium concentration in to output cadmium concentration. It is worth noting that a set of initial values are assigned to weights which are corrected during the training

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through the comparison between experimental data and the model results. The minimization of errors is done as the result of their back propagation.

70%, 80%, and 80% of all of cycles 1, 2, and 3 experimental data are randomly selected for the training and the rest were used for the network testing. The hidden layer neuron number is determined through the minimization of difference between the validation set of data and the results of network calculations. LM algorithm presented more accurate results during the training compared to scaled conjugate gradient, gradient descent with momentum, adaptive learning rate back-propagation, and resilient back-propagation. Therefore, the current network was trained using LM algorithm. After the training the network was tested by the new set of data which were not used during the training. Fig. 3 represents the graphical comparison between the experimental data and the results of ANN modeling. The dashed lines depicted in Fig. 3 shows the data prediction by ANN model.
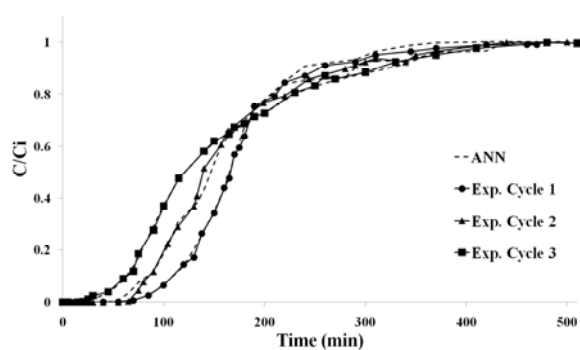

Fig. 3 The breakthrough curves for three consecutive cycles by ANN modelling

The value of correlation coefficient was 0.999, which denotes that the model output follows the target properly. It can be said that there is an excellent agreement between the data produced by the experimental data and the results of ANN modeling.

The values of SSE, MSE, RMSE, and R^2 are reported in Table I.

The high value of R^2 and the reported errors show that the output variations are shown well by the target. The results of modeling approved the fact that ANN is an appropriate tool to predict the ratio of input cadmium concentration in to output cadmium concentration.

Figs. 4 (a)-(c) show the evaluation of network error in training, validation, and testing as a function of learning epochs. The MSE became constant after 7, 1, and 7 epochs in cycles 1, 2, and 3, respectively, which denotes the network convergence. Therefore the acceptable error was achieved these number of epochs.
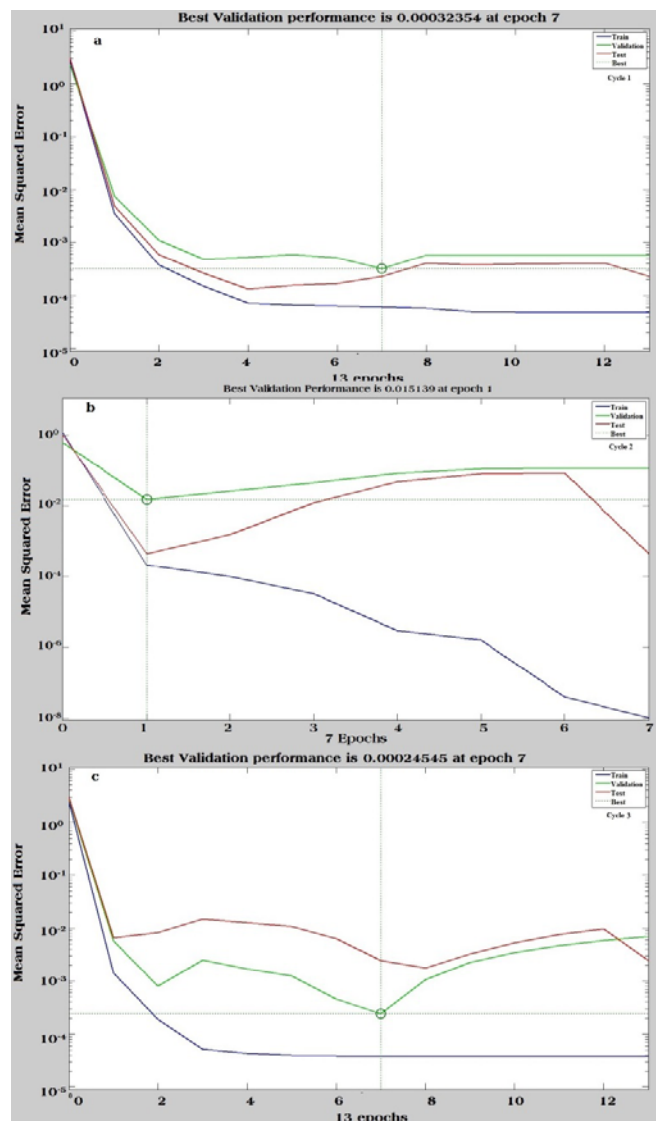

Fig. 4 Evolution of MSE values of training, validation, and test errors during ANN training for cycles 1 (a), 2 (b), and 3 (c)

IV. CONCLUSION

A reliable modeling can be useful for characterizing the breakthrough curve. It can be also applied for design parameter adjustment or prediction the system behavior. A semi empirical model, Thomas, and a neural network based modeling, ANN, were employed to describe the breakthrough data obtained by cadmium biosorption from potable water using a packed-bed column. It was found that, the precision of parameters obtained by the linear form of Thomas model was not good enough to describe the experimental data. However, fitting the nonlinear form of Thomas directly to the experimental data achieved more precise results. The ANN modeling results suggest a reliable method for predicting the breakthrough data. The high values of correlation of coefficient, R^2, revealed that this approach well fitted the experimental data and can be applicable for prediction of cadmium removal from potable water.

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