ANN MODELING ON PREDICTIONS OF BIOSORPTION EFFICIENCY OF ZEA MAYS FOR THE REMOVAL OF Cr (III) AND Cr (VI) FROM WASTE WATER

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ABSTRACT

Various low cost sorbents have been used for removal of toxic metals from aqueous solution for the treatment of Cr (III) and Cr (VI) containing waste water using agricultural wastes. Artificial Neural Network (ANN) was applied to sorption batch studies to develop and validate a model that can predict Cr (III) and Cr (VI) removal efficiency. Earlier investigations correlated the experimental data with available models or some modified empirical equations but these results were unable to predict the values of parameters from a single equation. ANN is effective in modeling and simulation of highly non linear multivariable relationships. A well designed network can converge even on multiple numbers of variables at a time without any complex modeling and empirical calculations. The prediction of removal of Cr (III) and Cr (VI) from waste water has been made using variables of metal concentration, biomass dosage, contact time and initial volume. Different types of the ANN architecture have been tested by varying the neuron number of entrance and the hidden layers, resulting into an excellent agreement between the experimental data and the predicted values. The data of one hundred eighty laboratory experimental sets were used for structuring single layer ANN model. Series of experiments resulted into the performance evaluation based on considering 20 % data for testing and 20 % data for cross validation at 3000 Epoch with 0.70 momentums. The Levenberg–Marquardt algorithm (LMA) was applied giving a minimum mean squared error (MSE) for training and cross validation.

Keywords: **Artificial Neural Network; Biosorption; Zea mays; Cr (III) and Cr (VI) removal**

INTRODUCTION

The pollution, because of the heavy metal presence, is an ambient problem of world wide interest. The heavy metals such as Cr (III) and Cr (VI) are, among others, the common pollutants found in the industrial effluents. Even in low concentrations, these metals are toxic for diverse organism including human beings. Conventional techniques used for the removal of heavy metals from waste water include filtration, precipitation, flocculation, ion exchange resins and reverse osmosis [1]. However, these methods are not economically viable if sophisticated instrumentation is utilized [2]. The advantage of biosorption is that it uses biomass and industrial plant waste which are cheap and abundant [3]. Broad range of biosorbents can collect most of the metal ions from the solution and a certain

concentration of a specific metal could be achieved either during the sorption uptake by manipulating the properties of a biosorbent, or upon desorption during the regeneration cycle of these biosorbent. The mechanism of biosorption is highly complex and is difficult to model and simulate using conventional mathematical modeling. This is mainly due to interaction of more number of sorption process variables, and hence the resulting relationships are highly non linear [4].

To achieve an optimum management for any control measure, the concept of modeling for an efficient operation and design should be developed. A high quality representative model can provide a favorable solution to the process control. It is likely to explain the real process performance developing a continuous control strategy for such type of technologies. Because of reliable, robust and salient characteristics in capturing the non-linear relationships of variables in complex systems, application of Artificial Neural Network (ANN) has been successfully employed in environmental engineering [5-7]. ANN is known for their superior ability to learn and classify data. The inspiration of Neural Network came from studies on the structure as function of the brain and nerve systems as well as the mechanism of learning and responding. The objective of the network is to compute output values from input values by some internal calculations [8]. Basic component of the neural network is the neuron also called "node". The inputs are represented by x_1, x_2… x_n and the output by y_k [Fig.1]. There can be many input signals to a node. The node manipulates these inputs to give a single output signal [9]. The values w_{1j}, w_{2j}…w_{nj} are weight factors associated with the inputs to the node. Weights are adaptive coefficients within the network that determine the intensity of input signal. Every input (x_1, x_2… x_n) is multiplied by its corresponding weight factor (w_{1j}, w_{2j}…w_{nj}) and the nodes use summation of these weighted inputs ($w_{1j}.x_1$, $w_{2j}.x_2$….$w_{nj}.x_n$) to perform further calculation.

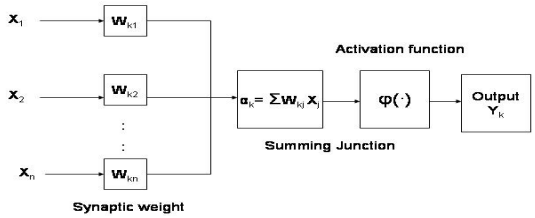


Figure 1

There are two broad classifications of Neural Network structures (external and internal). External structure describes the overall macro arrangement of connections between inputs, outputs and hidden layers that compose the output. The several general external arrangements are single input and single output (SISO), multiple outputs and single output (MISO), multiple inputs and multiple outputs (MIMO). Internal structure refers to the actual connections between individual nodes both within and between layers. The relative position of the origin to the end point of the connection defines the network internal structure. The different types of networks [10] based on their incremental complexity are feed forward network, recurrent network, stochastic network, modular network etc.

In continuation of our work on biosorption of toxic metals using agriculture from waste water [11-13], this paper suggests a single layer ANN model based on back propagation (BP) algorithm to predict the removal efficiency of Zea mays cob powder (ZMCP) for Cr (III) and Cr (VI) ions. Pursuing benchmark comparisons of BP algorithms, a study was conducted to determine the optimal network structure. The output obtained from the ANN modeling was compared with the experimental data. The present piece of work predicts the sorption efficiency for the metal ions from waste water using ZMCP in the range of metal concentrations with which lab experiments have not been conducted.

Experimental

Biosorbent preparation

Cobs of Zea mays were collected in June 2007. They were washed repeatedly with

water to remove dust and soluble impurities, dried at 65^{o}C for 24 h, crushed and finally sieved through 105, 210 and 420 µm mesh of copper sieves. No other chemical or physical treatments were used prior to the sorption experiments.

Biosorption studies

Sorption studies using standard practices were carried out in batch experiments (triplicate) as a function of biomass dosage (1.0-4.0g), contact time (10-60 min), volume of the test solution (100-300 ml), Cr (III) and Cr (VI) concentration (1-50 mg/l), particle size (105-420 µm) and pH (2.5-8.5). The details of methodology have been described in our earlier publications [11-13]. Percent metal uptake by the sorbent was computed using the equation: % Sorption = Co-Ce/Co · 100, where Co and Ce were the initial and final concentration of metal ions in the solution.

ANN Structure

Network structure has significant effects on the predictive results. As per the network topology the Neural Network employed has four input nodes corresponding to the process variables namely metal concentration, biomass dosage, contact time, initial volume and for output nodes corresponding to the sorption efficiency of Cr (III) and Cr (VI). However, the optimal number of hidden layers and the optimal number of nodes in each layer are case dependent and there is no straight forward method for the determination of them. Neural Network Toolbox Neuro Solution 5 ® mathematical software was used to predict the sorption efficiency. One hundred eighty experimental sets were used to develop the ANN model. A single layer ANN with sigmoid axon transfer function was used for input and output layers. The data gathered from batch experiments were divided into input matrix and desired matrix. The single layer sigmoid network represents functional relationship between inputs and output, provided sigmoid layer has enough neurons.

Back propagation training algorithm

The back propagation algorithm is a generalization of the least mean square algorithm modifies network weights to minimize the mean square error between the desired and actual outputs of the network. Back propagation uses supervised learning in which the network is trained using data for which inputs as well as desired outputs are frozen as can be used to compute output values for new input samples. Start with randomly selected weights while MSE is unsatisfactory and computational bounds are not exceeded, do for each input pattern. First the input is propagated through the ANN to the output. After this the error e_k on a single output neuron k can be calculated as:

$$e_k = d_k - y_k$$

Where y_k is the calculated output and d_k is the desired output of neuron k. This error value is used to calculate a δ_k value, which is again used for adjusting the weights .The δ_k value is calculated by:

$$\delta_k = e_k\, g'(y_k)$$

Where g' is derived activation function.

When the δ_k value is calculated, we can calculate the δ_j values for proceeding layers. The δ_j values of the previous layer are calculated from the δ_k values of this layer by the following equation:

$$\delta j = \eta g'(y_j) \sum_{k=0}^{K} \delta_k W_j k$$

Where K is the number of neurons in this and η is the learning rate parameter, which determines how much the weight should be adjusted. The more advanced gradient descent algorithms does not use a learning rate, but a set of more advanced parameters that makes a more qualified guess to how much the weight should be adjusted. Using these δ values, the δw values that the weight should be adjusted by, can be calculated by:

$$\delta w_{jk} = \delta_j\, y_k$$

The δw_{jk} value is used to adjust the weight $w_{jk,}$ by $w_{jk} = w_{jk} + \delta w_{jk}$ and the back propagation algorithm moves on to the next input and adjusts the weight according to the output. This process goes on until a certain stop criteria is reached. The stop criteria are typically determined by measuring the mean square error of the training data while training with the data, when this mean square error reaches a certain limit, the training is stopped. More advanced stopping criteria involving both training and testing data are also used. Levenberg-Marquardt algorithm is fastest training algorithm for network of moderate size, therefore, used in the present study [14].

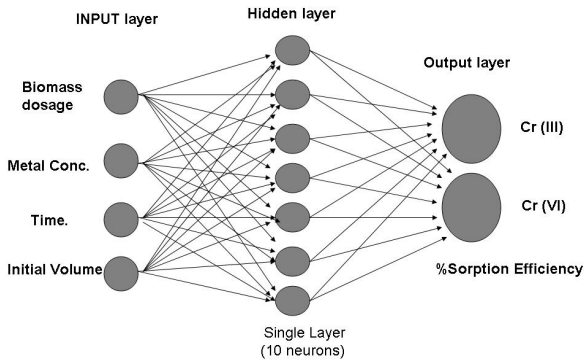


Figure 2

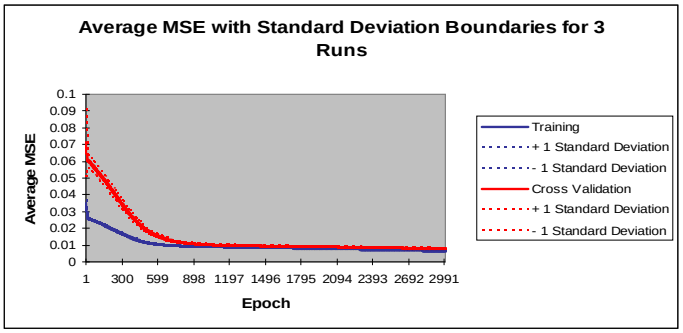
Results and discussions

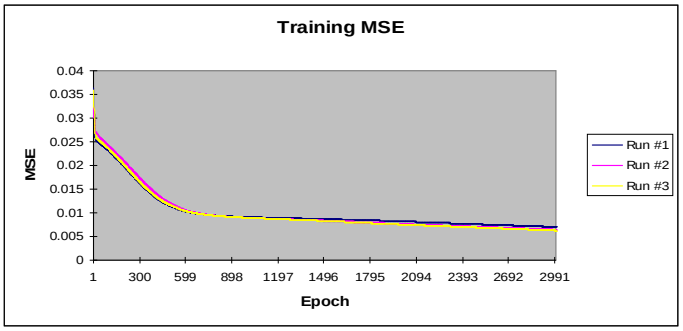
Sorption Studies

Sorption studies led to the standardization of the optimum conditions as: metal concentration (10 mg/l and 25 mg/l), biomass dosage (2.0 gm), contact time (40 min) and volume (200 ml) at pH 6.5 and 2.5 for maximum removal of Cr (III) (89.16 %) and Cr (VI) (62.28 %). The effect of various experimental parameters was studied and compared with performance of ANN model.

Selection and Optimization of the ANN Architecture

The removal of Cr (III) and Cr (VI) ion using ZMCP was calculated in the laboratory batch experiments as a function of biomass dosage, contact time, volume of the solution and metal ion concentration in terms of percentage sorption. As biosorption influenced by number of process variables which holds complex non-linear relationship among them so as to affect the sorption process, any simple feed forward network may not be sufficient to handle the prediction efficiency [10]. ANN model based on single layer recurrent back propagation algorithm for the experimental data, generated from the above batch experiments was applied to train the Neural Network. During training, the output vector is computed by a forward pass in which the input is propagated forward through the network to compute the output value of each unit. The output vector is then compared with the desired vector which resulted into error signal for each output unit. In order to minimize the error, appropriate adjustments were made for each of the weights of the network. After several such iterations, the network was trained to give the desired output for a given input vector. The single layer network structure included ten hidden neurons, describing the dynamics of Cr (III) and Cr (VI) in effluent (Fig. 2). The sigmoid axon was considered transfer function with 0.7 momentums. The performance of network simulation was evaluated in terms of mean square error (MSE) criterion. The MSE for the training and cross validation data sets were found at the ninth place of decimal. The developed network model was examined for its ability to predict the response of experimental data not forming the part of the training program.





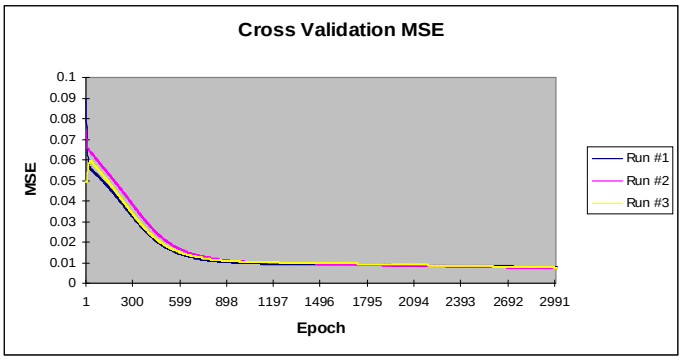
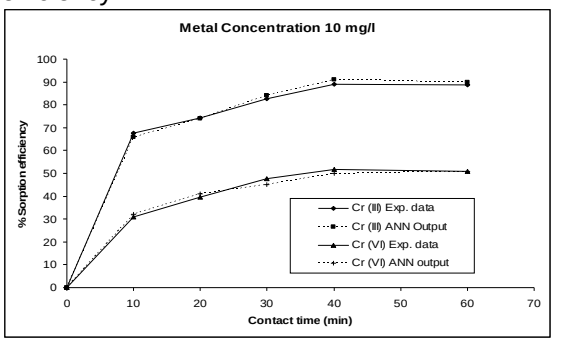


Fig. 3 shows the result obtained by the Neural Network simulation for both the training and cross validation data sets. The Cr (III) and Cr (VI) ion concentrations were precisely predicted for the training data sets.

Sensitivity analysis

A sensitivity analysis was conducted to determine the degree of effectiveness of variables. Performance of the group of input vectors included biomass dosage, Cr (III) and Cr (VI) ion concentration, contact time and volume. Series of experiment resulted into the evaluation of performance based on 60 % data for training, 20 % data for testing and 20 % data for cross validation at 3000 Epoch with 0.70000 momentums. The minimum MSE in the group of four variables was determined for training and cross validation are 0.006237719 and 0.007242542 respectively.

Effect of metal concentration and sorption efficiency



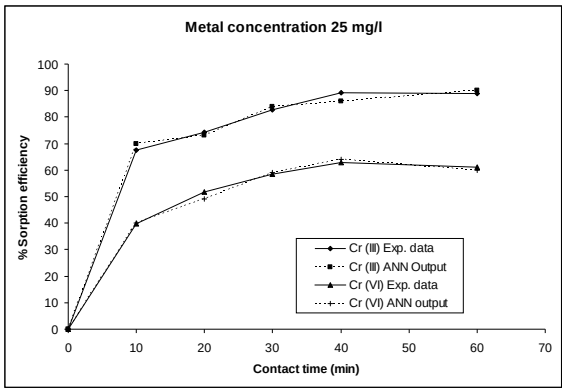


Fig. 4 represents the effect of metal concentration on the sorption behavior of Cr (III) and Cr (VI) ions on ZMCP in the range of metal concentration (1–50 mg/l). Sorption of Cr (III) and Cr (VI) ions on ZMCP increased with increasing concentration of the metal ion reaching to an optimal level (Cr (III) 10 mg/l, Cr (VI) 25 mg/l). Later, an increase in concentration decreased the percentage binding. These observations can be explained by the fact that at medium concentrations, the ratio of sorptive surface area to metal ions available is high and thus, there is a greater chance for metal removal. When metal ion concentrations are increased, binding sites become more quickly saturated as the amount of biomass concentration remained constant [15]. The comparison of experimental data and ANN outputs for Cr (III) and Cr (VI) ions concentrations shows that the ANN model performed well for prediction of the experimental data.

Effect of biomass dosage and sorption efficiency

Percent sorption increased with the increase of biomass dosage from 0.5 to 4.0 g. However, no significant increment in the sorption tendency was observed on further increasing the biomass dosage from 2.0 g onwards. This might be due to attainment of equilibrium between sorbate and sorbent at the existing operating conditions rendering sorbent incapable of further sorption. The amount of biomass (2.0 g) used in present case seems to be quite reasonable, as practically similar sorption efficiencies for the same set of metals were reported with relatively higher biomass dosages from 6.0 to 10.0 g of different biosorbents like Okra wastes [16] and Nile rosa [17]. A perusal of experimental data and ANN outputs as a function of biomass dosages (Fig. 5) depicted performance of the model in good harmony with the experimental data.

Effect of Initial volume and sorption efficiency

The effect of volume on the percent sorption of Cr (III) and Cr (VI) on ZMCP was observed under similar experimental conditions in different set of volumes (100–300 ml). Maximum sorption was obtained in the volume (200 ml) of the test solution. It shows that the ratio of sorption surface of the ZMCP to total Cr (III) and Cr (VI) ions availability is optimum, exhibiting maximum percentage removal of Cr (III) (89.16 %) and Cr (VI) (62.28 %). ANN model showed performance in resemblance with experimental data (Fig. 6).

Effect of contact time and sorption efficiency

The effect of contact time on Cr (III) and Cr (VI) sorption on ZMCP was studied for duration of 10–60 minutes. The percent sorption of metal ion gradually increased with time from 10 to 30 minutes, finally reaching the optimum value at 40 minutes. Once equilibrium was attained, the percentage sorption of Cr (III) and Cr (VI) ion did not change with further increase of time. On comparison basis, sorption

efficiency of the present process is much better than earlier reported contact time ranging from 60 to 120 minutes for same metals shown by other agricultural byproducts such as Rice husk [18]. ANN model prediction was found in match with experimental data.

Effect of pH and sorption efficiency

The effect of pH on the sorption of Cr (III) and Cr (VI) was studied in the pH range 2.5 to 8.5.The percentage sorption of Cr (III) on ZMCP increases as the pH of the solution increased from 2.5 to 6.5.The pH profile for Cr (III) on ZMCP shows that metal sorption is a function of pH, exhibiting maximum removal pH 6.5. Anionic metallic species Cr (VI) showed high sorption tendency in acidic pH 2.5. Further increase in pH from 2.5 to higher range resulted into a sharp decreasing trend of sorption. ANN model predictions were made at optimum pH 6.5 for Cr (III) and pH 2.5 for Cr (VI).

Conclusions

The present piece of work demonstrates the successful removal of Cr (III) and Cr (VI) ions from the aqueous solutions using ZMCP with maximum removal efficiency Cr (III) (89.16 %) and Cr (VI) (62.28 %). The single layer ANN modeling technique was applied to optimize this process. The Levenberg–Marquardt algorithm (LMA) was found best of BP algorithms with a minimum mean squared error (MSE) for training and cross validation as 0.006237719 and 0.007242542 respectively. Thus a simple back propagation of the recurrent network using the momentum training algorithm is proved meaningful supplement for the conventional and complicated mathematical models in the prediction of bioprocess. Introduction of knowledge-based systems is efficient for scientific research of unstudied dependence among different by natural variables (physical, chemical, biological) for solving tasks of inferential measurement and process optimization without requiring a big amount of precise experimental data.

Acknowledgements

The authors gratefully acknowledge Prof. V.G. Das, Director and Prof. L.D. Khemani, Head, Department of Chemistry, Dayalbagh Educational Institute, Dayalbagh, Agra. Dr. Sandeep Paul, Technical College, Dayalbagh Educational Institute is also acknowledged for fruitful scientific discussions.

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