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Simulation and Optimization of Artificial Neural Network Modeling for Prediction of Sorption Efficiency of Nanocellulose Fibers for Removal of Cd (II) Ions from Aqueous System

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Abstract

Simulation and optimization of an Artificial Neural Network (ANN) for modeling biosorption studies of cadmium removal using nanocellulose fibers (NCFs) was carried out. Experimental studies led to the standardization of the optimum conditions for the removal of cadmium ions i.e. biomass dosage (0.5 g), test volume (200 ml), metal concentration (25 mg/l), pH (6.5) and contact time (40 min). A Single layer ANN model was developed to simulate the process and to predict the sorption efficiency of Cd (II) ions using NCFs. Different NN architectures were tested by varying network topology, resulting in excellent agreement between experiment outputs and ANN outputs. The findings indicated that ANN provided reasonable predictive performance for training, cross validation and testing data sets (R^2 = 0.998, 0.995, 0.992). A sensitivity analysis was carried out to assess the influence of different independent parameters on the biosorption efficiency, and pH > biomass dosage > metal concentration > contact time > test volume were found to be the most significant factors. Simulations based on the developed ANN model can estimate the behavior of the biosorption phenomenon process under different experimental conditions.

Keywords: Artificial neural network, Biosorption, simulation and optimization, nanocellulose fibers, cadmium removal

Introduction

Heavy metals are of special concern due to their recalcitrant and persistency properties in nature. Cadmium containing wastewaters are common, as it is used in a number of industries, including electroplating, batteries manufacturing, mining, metal finishing and forging. The maximum level permitted in wastewater is 0.01 mg/l for cadmium. Cadmium may result in adverse effects such as cancer, cardiovascular disturbances and liver and kidney damage [1,2]. The toxicity and deleterious effects of cadmium has been very well documented. Methods like precipitation, oxidation/reduction, ion exchange, filtration and evaporation used for the purpose of removing cadmium, are extremely expensive, sometime inefficient and generate toxic sludge also. With the increase in environmental awareness and government environmental policies, there has been a push towards development of new environment friendly ways to clean metal-contaminated water. Biosorption is the most widely used and low-cost alternative technology for heavy metal removal [3,4]. Biosorption in environmental engineering is now an aesthetic attention and consideration for all nations, owing to its low initial cost, simplicity of design, ease of operation, insensitivity to toxic substances and complete removal of pollutants even from dilute solutions [5]. A

huge number of low-cost biosorbents based on natural materials or agro-industrial wastes have been used so far [6,7]. Current research shows the use of different nanomaterials (nanostructured catalytic membranes, nanosorbents, nanocatalysts, bioactive nanoparticles etc) in water treatment and purification [8-10]. Nanoparticles exhibit good adsorption efficiency especially, due to a higher surface area and greater number of active sites for interaction with metallic species [11,12]. The increasing interest in organic bio nanomaterials of plant origin and their unique properties has led to intensive research in the area of nanocellulosic materials [13,14]. Nanocellulose fibers (NCFs), with widths in the nanometer range, are nature-based materials with unique and potentially useful features [15-17].

The nature of the sorption process depends on the physical or chemical characteristics of the adsorbent systems and on the system conditions. The adsorption processes, irrespective of the adsorbate/adsorbent, are usually modelled using mechanistic or empirical based kinetic expressions. In addition, numerous empirical models have been employed to describe the biosorption equilibrium, namely the Langmuir, Freundlich, Brunauer-Emmett-Teller (BET), Sips, Dubinin-Radushkevich, Temkin and Toth models. Langmuir and Freundlich equations are the most popular and widely used models in a large number of studies. Nonetheless, in many cases, these empirical models fall short in representing the biosorption phenomena and its physical meaning [18]. In addition, predictive conclusions are difficult to draw from systems operating at different conditions. However, any attempt to make a relationship between the amount of solute uptake with all the operating variables, namely, metal concentration, biomass dosage, initial solution pH, volume of solution treated, and contact time, using the kinetic or mechanistic based models, will fail.

Neural networks are useful when a mathematical relationship is not available to describe a phenomenon to be modeled. If the property in question can be modeled by very complex and highly demanding computational techniques, neural networks provide an alternative approach to obtain accurate numerical values in a computationally less intensive fashion. Because of reliable, robust and salient characteristics in capturing the non-linear relationships of variables in complex systems, the application of ANN has been successfully employed in environmental engineering [19,20] and bioremediation [21,22].

In continuation of the work on biosorption of toxic metals using agricultural wastes [23-26], the present study deals with the optimization of ANN modeling for the biosorption of cadmium using nanocellulose fibers (NCFs) from water bodies. The study also includes an evaluation of the effects of various operational parameters, such as metal concentration, biosorbent dose, test volume, contact time and pH on the cadmium biosorption process, employing a batch experimental setup and ANN modeling.

Materials and methods

Extraction & preparation of NCFs

Native rice straw was collected from Dayalbagh agricultural farms, Agra, washed with distilled water several times, and dried in an oven at 80 °C for 24 h. They were chopped to an approximate length of 5 - 10 mm and finally crushed into small fibers. These fibers were soaked into sodium hydroxide solution (0.5 M) for 2 h and washed with distilled water. A bleaching treatment with a sodium chlorite solution (pH 4) for 1 h at 50 °C was carried out to remove the remained lignin and washed again with distilled water. The pre-treated pulp was hydrolyzed for 3 h at 70 °C and then washed with distilled water repeatedly. The acid treatment hydrolyzed the hemicelluloses and pectin by breaking down the polysaccharides to simple sugars and released NCFs. These fibers were ultra sonicated, dried and finally subjected for microscopic analysis.

Biosorption studies

Sorption studies using standard practices were carried out in batch experiments (triplicate) as a function of biomass dosage (0.1 - 1.0 g), contact time (10 - 60 min), volume of the test solution (100 - 300 ml), metal concentration (1 - 50 mg/l) and pH (2 - 8.5). A required amount of Cd (II) (Cadmium nitrate, AR grade) was taken in an Erlenmeyer flask and after pH adjustments, a known quantity of dried biosorbent was added and metal bearing suspensions were kept under magnetic stirring until equilibrium

conditions were reached. After shaking, the suspension was allowed to settle. The residual biomass sorbed with metal ion was filtered using Whatman 42 filter paper (Whatman International Ltd., Maidstone, England). Filtrate was collected and subjected to metal ion estimation using a Flame atomic absorption spectrometer. The percentage of metal uptake by the sorbent was computed using the equation: % Sorption = $(\frac{Co-Ce}{Co}) \times 100$, where Co and Ce were the initial and final concentration of metal ions in the solution.

Artificial neural network modeling

Neural Network Toolbox Neuro Solution 6.0 ® mathematical software was used to predict the sorption efficiency. The data gathered from batch experimental studies were divided into input matrix and output matrix. One hundred eighty experimental sets were used to develop the ANN model. As per the network topology, the neural network employed had five input matrix corresponding to the process variables, namely pH, metal concentration, biomass dosage, contact time, test volume and for output matrix corresponding to the biosorption efficiency of nanocellulose fibers for Cd (II) ions. Network topology had significant effects on the predictive results. The performance of neural networks as affected by several factors, such as selection of input variables, number of hidden layers, the number of neurons in the hidden layer and the type of the transfer function. The performance of the ANN models was measured in terms of mean squared error (MSE), mean absolute error (MAE) and correlation coefficient (R^2) between the predicted values of the ANN outputs and experimental outputs, which were calculated using Eqs. (1) - (3), respectively.

$$MSE = \frac{1}{Q} \sum_{i=1}^{Q} (y_{i,nn} - y_{i,expl})^2 \quad (1)$$

where Q is the number of data points, $y_{i,nn}$ is the network prediction, $y_{i,expl}$ is the experimental response and i is an index of the data.

$$MAE = \frac{1}{n} \sum_{i=1}^{n} \left| y_i^* - y_p^{(i)} \right| \quad (2)$$

$$R^2 = 1 - \frac{\sum_{i=1}^{n} (y_i^* - y_p^{(i)})^2}{\sum_{i=1}^{n} (y_i^* - \bar{y})^2} \quad (3)$$

where $\bar{y}$ is the average of y over the n samples, and y^*_i and $y^{(i)}_p$ are the i th desired and predicted value, respectively.

Back propagation neural network

The most popular ANNs are Multilayer Perceptron (MLP) back-propagation ANNs (BPANNs), belonging to the class of supervised learning techniques, because the methods consist of comparing responses of output units to desired responses via an iterative process in which an error term is calculated and used to readjust the weights in the network, in order to obtain network responses close to the desired responses. Considering the serious drawbacks of slow convergence and the inability to avoid local minima, BP with LMA is used to obtain a better performance. This technique is relatively faster but requires more memory. The LM update rule is shown in Eq. (4).

$$\Delta W = (J^T J + \mu I) - 1 \, J^T e \quad (4)$$

where, J is the Jacobean matrix of derivatives of each error to each weight, μ is a scalar, W is weight, T is target and e is an error vector. Levenberg-Marquardt algorithm is the fastest training algorithm for a network of moderate size, and is, therefore, used in the present study.

Sensitivity analysis

Sensitivity analysis is a method for extracting the cause and effect relationship between the inputs and outputs of a network. The basic idea is that each input channel to the network is offset slightly, and the corresponding change in the output(s) is reported. The input channels that produce low sensitivity values can be considered insignificant, and can most often be removed from the network. This will reduce the size of the network, which in turn reduces both the complexity and training time. Furthermore, this will likely also improve the network performance for the out-of-sample testing data. Sensitivity analysis was conducted to determine the degree of effectiveness of variables using Neuro Solution 6.0 software.

Results and discussions

Morphology of NCFs and sorption studies

Figure 1 shows the TEM micrograph of cellulose having long, curved elongated needles. Their morphology looks like rod-like micro fibrillated cellulose with high length and low diameter (40 - 80 nm). Sorption studies lead to the standardization of the optimum conditions as: metal concentration (25 mg/l), biomass dosage (0.5 g), contact time (40 min) and volume (200 ml) at pH 6.5 for maximum Cd (II) removal (90.21 %). The results indicate that the NCFs have considerable potential to be used as nano adsorbent for cadmium removal from water bodies. Studies, therefore, planned to predict the efficiency of NCFs for the removal of cadmium using ANN modeling. The effect of various experimental parameters was found to be as follows:

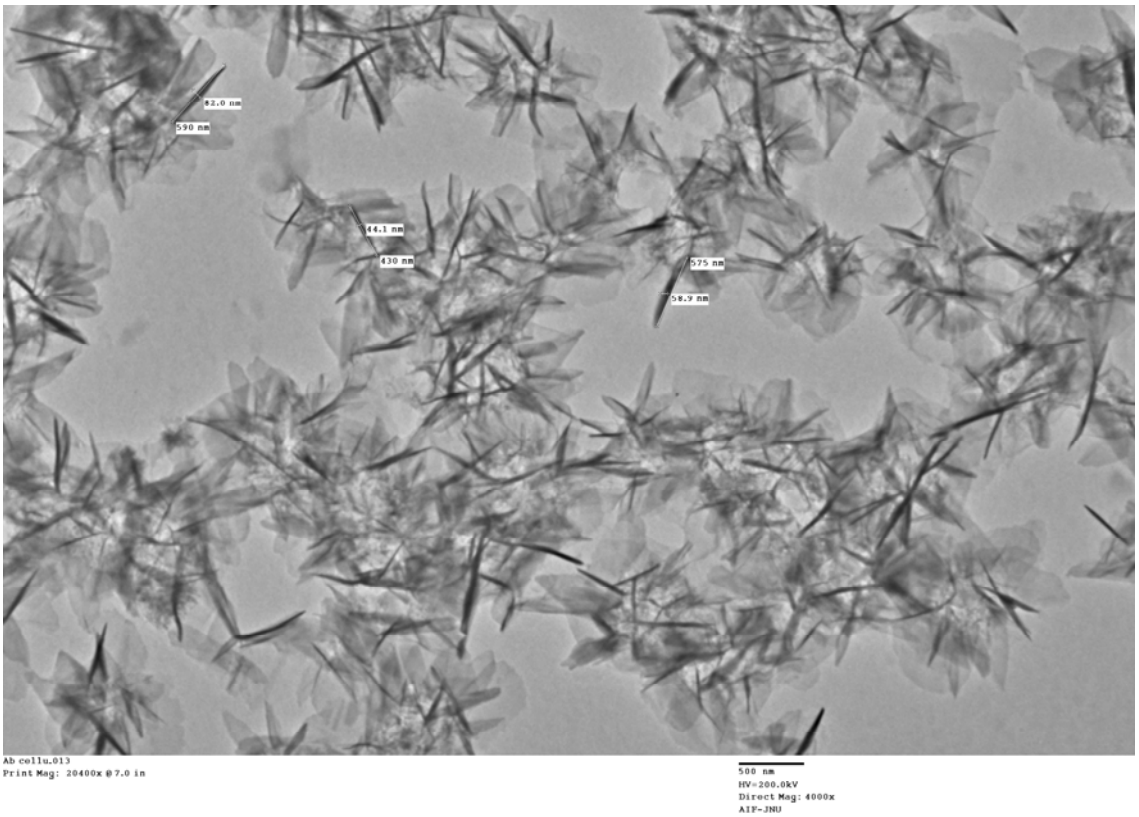

Figure 1 TEM micrograph of nanocellulose fibers (NCFs).

Effect of biomass dosage

NCF dosages used for the study varied from 0.1 - 1.0 g. The percentage of sorption increased with the increase of biosorbent dosage from 0.1 - 0.5 g. However, no significant increment in the sorption tendency was observed on further increasing the biosorbent dosage from 0.5 g onwards. This might be due to attainment of equilibrium between the adsorbate and adsorbent at the existing operating conditions, rendering the adsorbent incapable of further adsorption.

Effect of contact time

The effect of contact time on cadmium sorption on NCFs was studied for a duration of 10 - 60 min. The percentage of sorption of cadmium species gradually increased with time from 10 - 40 min, reaching the optimum value. Once equilibrium was attained, the percentage of sorption of cadmium species did not change with further increase of time.

Effect of metal concentration

Sorption behavior of Cd (II) on NCFs has been carried out in the range of cadmium concentration (1 - 50 mg/L). Sorption of Cd (II) increased with increasing concentration of the cadmium ion, reaching to an optimal level (25 mg/L), and then remained constant. The observation can be explained on the basis of the fact that at medium concentrations, the ratio of sorptive surface area to cadmium ions available is high, and there is a greater chance for cadmium removal. When cadmium ion concentrations are increased, binding sites become more quickly saturated as the amount of biosorbent concentration remain constant.

Effect of pH

The pH condition of the solution is an extremely important parameter in metal biosorption. Keeping the above views in mind, the effect of pH on the sorption of Cd (II) ion was studied in the pH range 2.5 to 8.5. The percentage of sorption of Cd (II) on nanocellulosic fibers increased as the pH of the solution increased from 2.5 to 6.5. No significant difference in sorption behavior was noticed with further increase in pH up to 7.5. The pH profile for Cd (II) sorption on seed powder shows that metal sorption is a function of pH, exhibiting maximum removal efficiency (90.21 %) at pH 6.5. Investigation into pH variation beyond 7.5 yielded an apparent increase in sorption up to pH 8.5, which might be due to precipitation carryover of Cd (II) starting at pH 7.5 onwards [27]. Cd (II) precipitation is indistinguishable from sorption phenomenon at pH 7.5 [28]. Experimental findings showed that sorption of cationic metallic species increases with rise in pH, attaining a plateau at around 6.5 to 7.5. At a relatively higher pH (above 4.5), the carboxylic groups are deprotonated and as such are negatively charged. These negatively charged carboxylate ligands are likely to attract the cationic metallic species [29]. NCFs-metal ion binding thus appears to be based on an ion exchange process between negatively charged OH^- and COO^- groups of nanocellulose fibers and metallic cation.

Simulation and optimization of the ANN model

The removal of Cd (II) ions using NCFs was calculated in the laboratory batch experiments as a function of biomass dosage, pH, contact time, volume of the solution and metal ion concentration in terms of percentage of sorption. Different ANN model architectures, based on the experimental data generated from the above batch experiments, was applied to train 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 network output is then compared with the experimental output, which results in an 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 experimental output for a given input vector. Different ANN architectures were tested by varying network topology as a function of number of neurons. The series of experiments resulted in the evaluation of performance based on 60 % data for training, 20 % data for testing and 20 % data for cross validation at 1000 Epoch with 0.7 momentums.

The performance of different network simulation was evaluated in terms of final mean square error (MSE) criteria. The final MSE in the group of five variables was determined for training and cross validation (**Figure 2**).

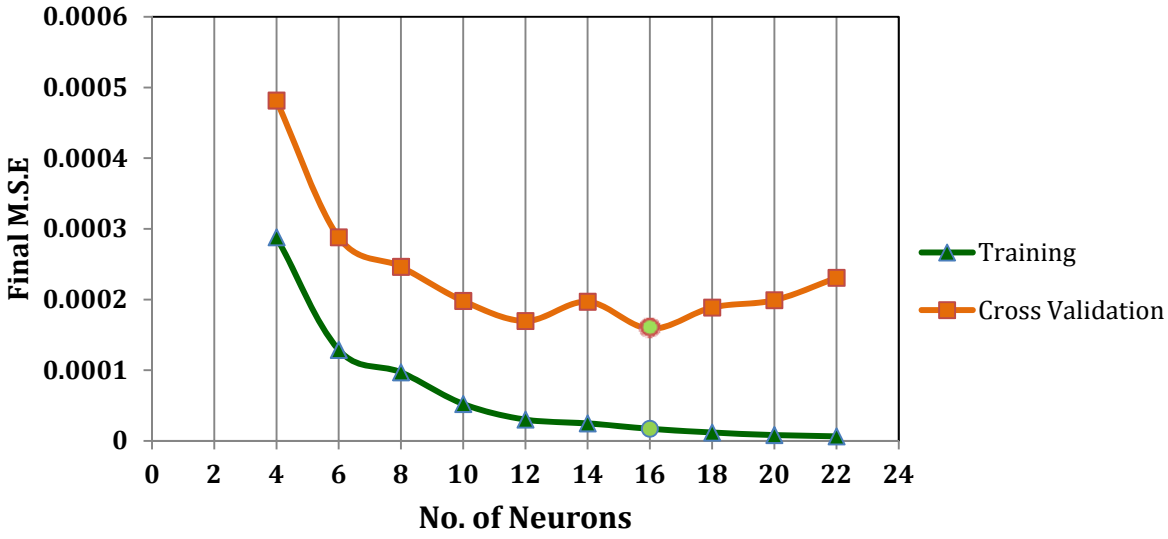

Figure 2 Final Mean Squared Error (MSE) as a function of number of neurons in hidden layer in ANN models.

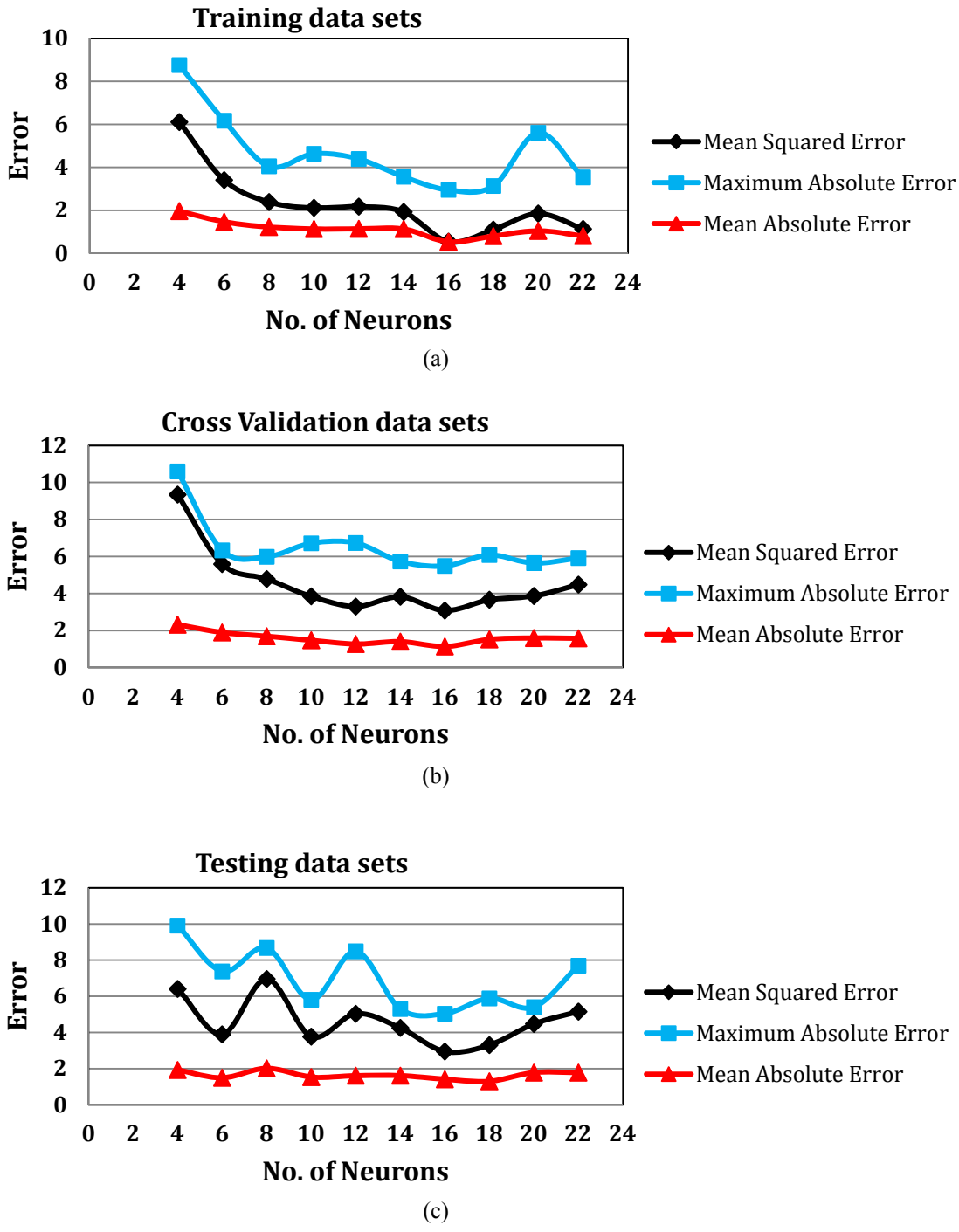

Figure 3 Mean squared error, maximum absolute error and mean absolute error during simulation of different ANN architectures for training (a), testing (b), and cross validation data sets (c).

Figure 3 shows the result obtained by testing different Neural Network simulations for training, testing and cross validation data sets in terms of mean squared error, maximum absolute error and mean absolute error.

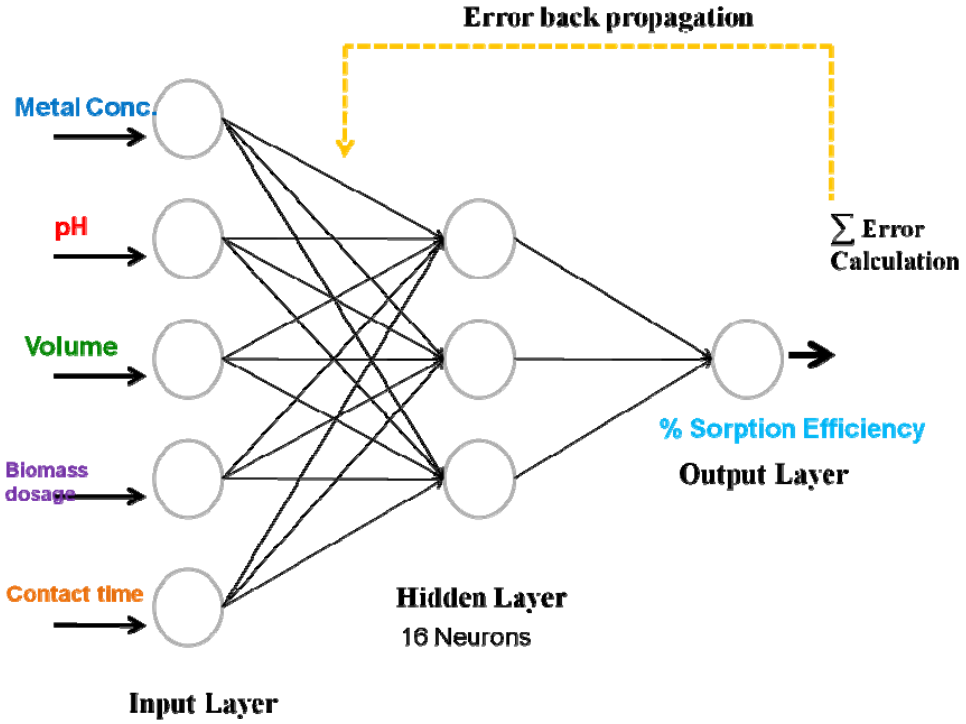

Figure 4 Single layer neural network models with back propagation for prediction of biosorption efficiency.

Figure 4 shows the optimum network structure including 16 hidden neurons, describing the dynamics of Cd (II) in effluent. The sigmoid axon was considered as a transfer function with 0.7 momentums. The Cd (II) ion concentrations were precisely predicted for the training data sets.

Testing and sensitivity analysis

The developed network model was examined for its ability to predict the response of input variables, when the experimental data did not form part of the training program. The network was finally tested for training, cross validation and testing data sets.

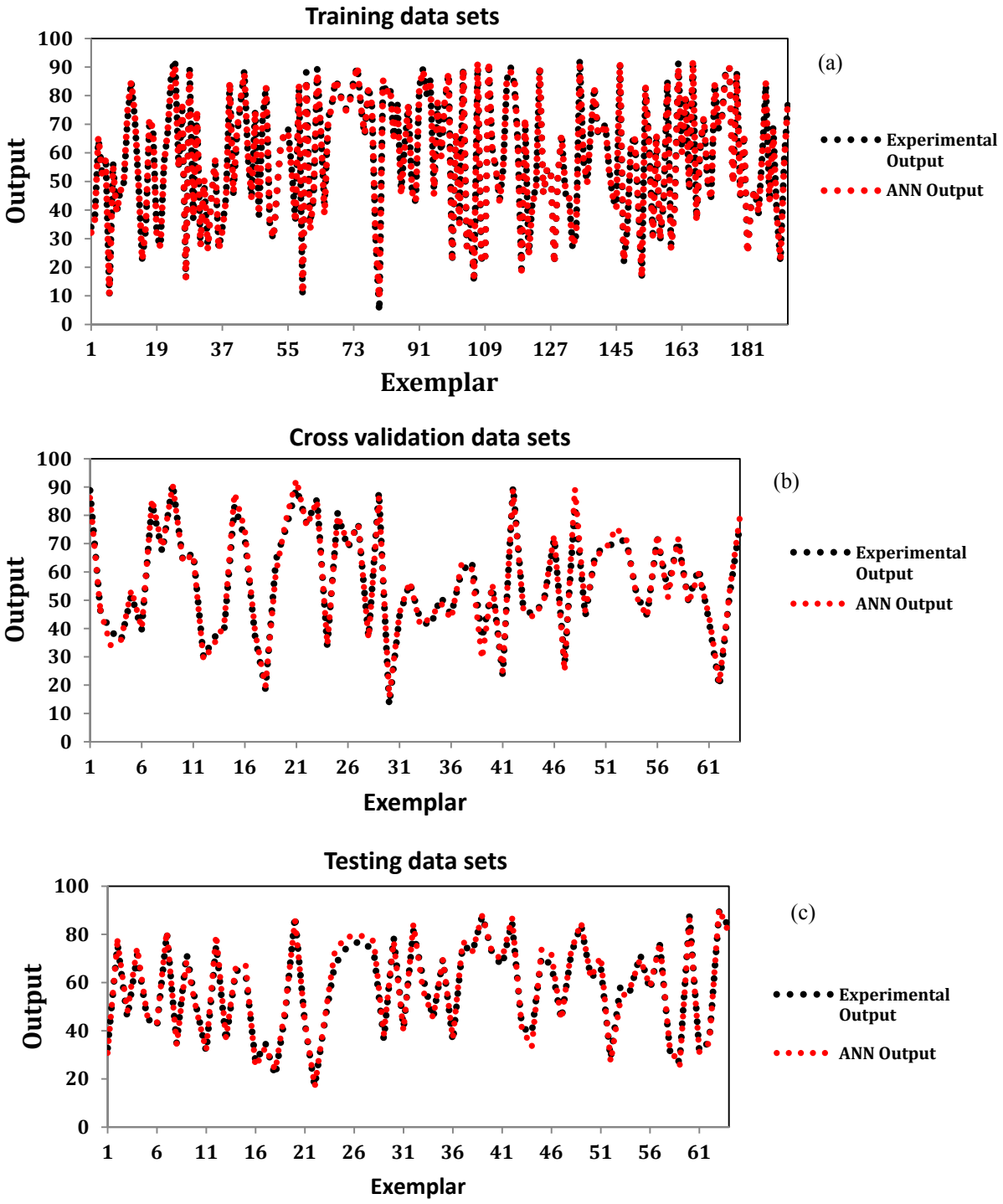

Figure 5 Comparison of experimental output and ANN output for training (a), testing (b), and cross validation data sets (c).

The comparison results of experimental outputs and ANN outputs are shown in **Figure 5**. During testing, linear correlation coefficients (R^2 = 0.998, 0.995 and 0.992) were obtained for the training, cross validation and testing data sets.

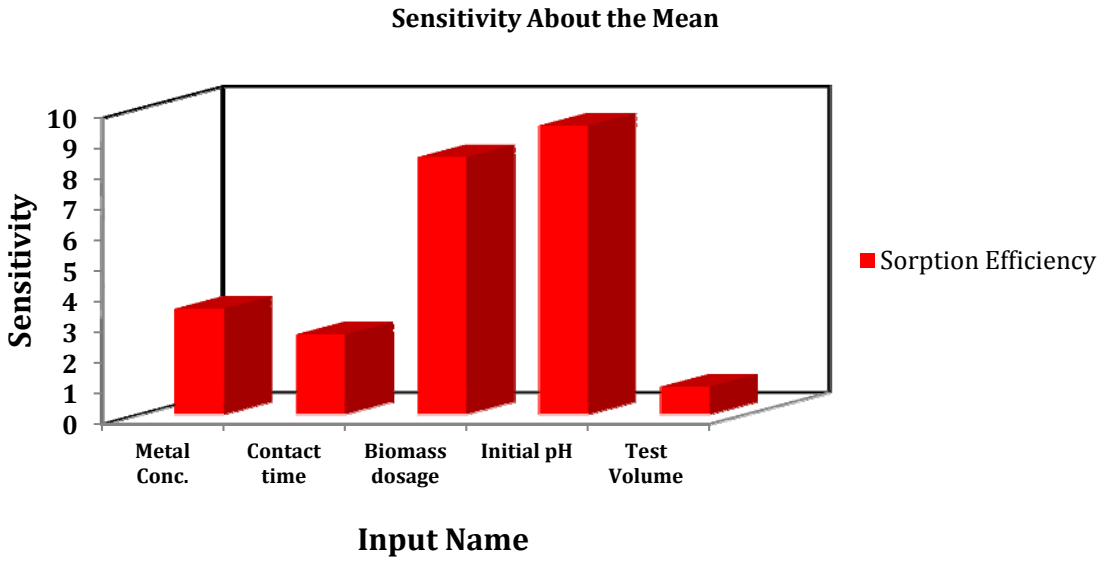

Figure 6 Sensitivity of the input variables correspond to sorption efficiency of NCFs.

A sensitivity analysis was conducted to determine the degree of effectiveness of the variables (**Figure 6**). Performance of the group of input vectors included biomass dosage, Cd (II) ion concentration, pH, contact time and volume. The degree of effectiveness of variables was found in the order of pH > biomass dosage > metal concentration > contact time > test volume. The perusal of experimental data and ANN outputs depicted that performance of the NN model is in good harmony with the experimental data.

Conclusions

Experimental results clearly show the high adsorption capacity of nanocellulose derived from rice straw for cadmium from waste water. Development of an artificial neural network model will certainly explain the real performance of the decontamination process with less need for experimentation, meaning less chemical consumption and time, with a better understanding of the mechanism of a real process. The developed ANN model could describe the behavior of the complex interaction process within the range of the experimental conditions adopted. The Levenberg-Marquardt algorithm (LMA) was found to be the best of the BP algorithms, with a minimum mean squared error (MSE) for training and cross validation of 1.72164×10^{-5} and 1.58602×10^{-4}, respectively.

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