ISSN : 0974 - 7451 Volume 7 Issue 6

Trade Science Inc.

Environmental Science
An Indian Journal

Current Research Paper

ESAIJ, 7(6), 2012 [205-209]

Removal of methylene blue using Azolla fern: Experimental and artificial neural network modeling

A.Alizadehdakhel*, R.Rakhshaee
Chemistry Department, Islamic Azad University, Rasht Branch, (IRAN)
E-mail: Alizadeh@iaurasht.ac.ir
Received: 4th March, 2012 ; Accepted: 4th April, 2012

ABSTRACT

An experimental and modeling investigation was carried out on removal of Methylene blue from a synthetic wastewater. Adsorption of the dye with Azolla fern was experimentally investigated in different operating conditions. Variable parameters were initial Methylene Blue concentration, Azolla doze, Azolla pre-treatment pH, contact time, adsorption pH and agitation rate. An artificial neural network with 6 neurons in input layer and one neuron in output layer was designed and trained to predict the removal efficiency of Methylene Blue at various conditions. Different number of neurons in the hidden layer, transfer functions and different training algorithms were examined and the optimum network was obtained by comparison of correlation coefficient and mean of square error. The experimental results showed that 8.5, 3, 150 min, 150 rpm, 1 g/lit are the optimum values for pH of pre-treatment, Adsorption pH, contact time, agitation rate and Azolla concentration, respectively. The investigation of modeling results showed that a network with 6, 15 and 1 neurons in input, hidden and output layers with Hyperbolic Tangent Sigmoid and linear transfer functions in hidden and output layers which is trained using Levenberg-Marquardt algorithm can predict the removal of Methylene blue with the best precision.

KEYWORDS

Azolla;
Adsorption;
Biotreatment;
Methylene blue;
Artificial neural network.

INTRODUCTION

The effluents from textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries are important sources of dye pollution. Many dyes and their break down products may be toxic for living organisms[1]. It is difficult to remove the dyes from the effluent, because dyes are not easily degradable and are generally not removed from wastewater by conventional wastewater systems[2]. Recently, biosorption methods are developed for removing dyes and other contaminants from water and wastewaters[3,4]. Azolla is a small aquatic fern. In fact, it is a symbiotic pair of Azolla filiculoides and a heterocystous blue-green alga Anabaena azollae. Azolla has been used as a fertilizer in botanical gardens because of nitrogen-fixing capability, therefore has been used for several decades as green manure in rice fields[5]. The non-living Azolla, has been shown to be able to effectively adsorb methylene blue and trivalent chromium, zinc (II) and nickel (II) from solutions and electroplating effluent and gold (III) from aqueous solution[6,7]. Artificial neural networks (ANNs) are powerful chemometric methods because of their high efficiency as predictors for non-linear systems. In fact many kinetic problems are intrinsically nonlinear[8]. Cinar et. al[9] modeled the performance of a submerged membrane bioreactor treating cheese whey wastewater using a cascade-forward back-propagation ANN consisting of 3-neurons hidden layer. Hamed et al.[10] modeled the effluent biochemical oxygen demand (BOD) and suspended solids (SS) concentration at a major wastewater treatment plant using two ANNs. Aguado et al.[11] utilized ANNs as a software sensor for inferring wastewater quality parameters such as effluent COD or total nitrogen concentrations.

In the present work, the optimum conditions for the process of Methylene Blue removal using Azolla were experimentally obtained. In addition, an artificial neural network was designed and trained to predict the removal efficiency.

MATERIALS AND METHODS

Fresh *Azolla* (as living biomass) was collected from the surface of the Anzali International Wetland in the north part of Iran. *Azolla* sample was prepared by washing with distilled water and air-drying in sunlight. Then it was sieved to particles with approximate size of 0.075 mm. *Azolla* samples were soaked in solutions with different pH to activate them and the optimum pre-treatment pH was determined. The adsorption experiments were carried out in a batch process using aqueous solution of Methylene Blue. Variables parameters were initial Methylene Blue concentration, Azolla doze, Azolla pre-treatment pH, contact time, adsorption pH and agitation rate. The Pharmacia Nova Model spectrophotometer was employed at a 663 nm wavelength to determine the percentage of Methylene Blue removal. In the next step, an artificial neural network with 6 neurons in input layer and one neuron in output layer was designed and trained to predict the removal efficiency of Methylene Blue at various conditions. Different number of neurons in the hidden layer, transfer functions and different training algorithms were examined and the optimum network was obtained by comparison of correlation coefficient and mean of square error. For each case, 70%, 15% and 15% of available experimental data was used as training, validation and test sets.

RESULTS

Experiments were carried out at different operating conditions and the optimum condition for removal of Methylene blue using Azolla fern was specified. The effect of pre-treatment pH on the removal efficiency is given in figure 1. The figure shows that increasing the pre-treatment pH from 2 to 8, significantly increases the removal efficiency. however, more increase in the pre-treatment pH has just negligible effects on the removal efficiency. Therefore, pH=8.5±0.1 was chosen as the pre-treatment pH.

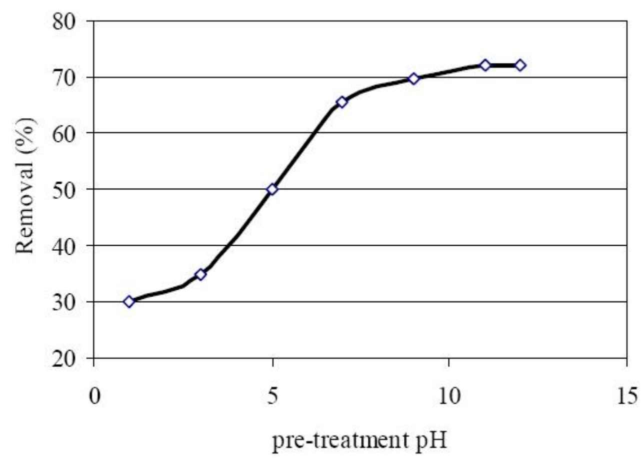

Figure 1 : Effect of pre-treatment pH

The effect of adsorption pH is given in Figure 2. According to this diagram, pH=3±0.5 was chosen as the optimum adsorption pH for the experiments. It should be mentioned that although the optimum values for pre-treatment and operating pH were obtained, the experiments were run at different conditions in order to consider the effect of probable interactions between variable parameters.

The effect of contact time is shown in Figure 3. According to this figure, 150min was determined as the optimum contact time to reach the maximum adsorption and equilibrium condition.

Experiments showed that agitation speed has a significant effect on the removal efficiency. Figure 4 illustrates that the removal efficiency increases by increasing the agitation rate and reaches to a maximum at a rotational speed of about 200rpm. Therefore, 200rpm was determined as the optimum agitation speed.

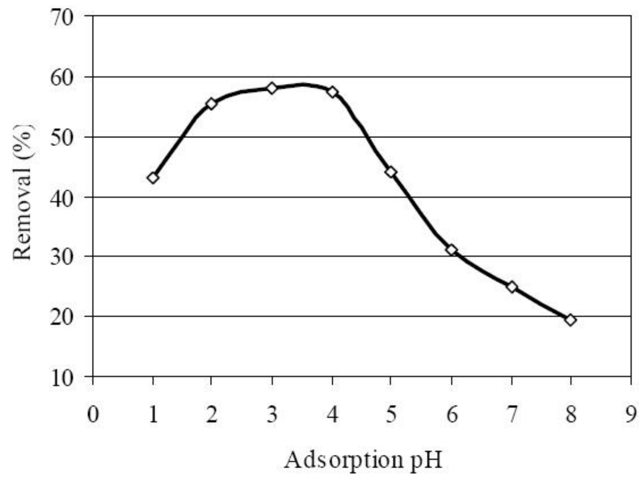

Figure 2 : Effect of adsorption pH

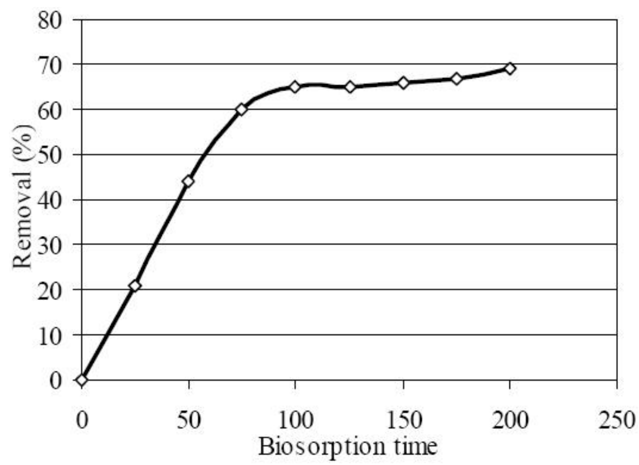

Figure 3 : Effect of contact time on removal of methylene blue

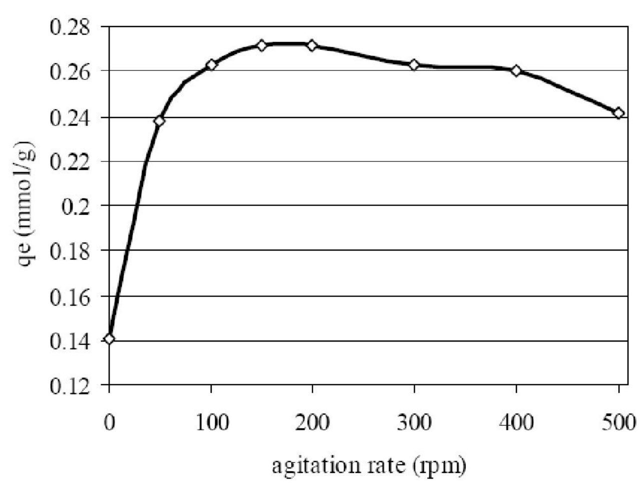

Figure 4 : The effect of agitation rate

Changes in the amount of equilibrium adsorption (mg Methylene Blue/g Azolla) versus Azolla doze (g/l) is drawn in figure 5. The figure reveals that by increasing the Azolla doze from 0.25 to 5 g/l, the amount of adsorbed dye per unit mass of adsorbent descends from 140 to 36 mg/g.

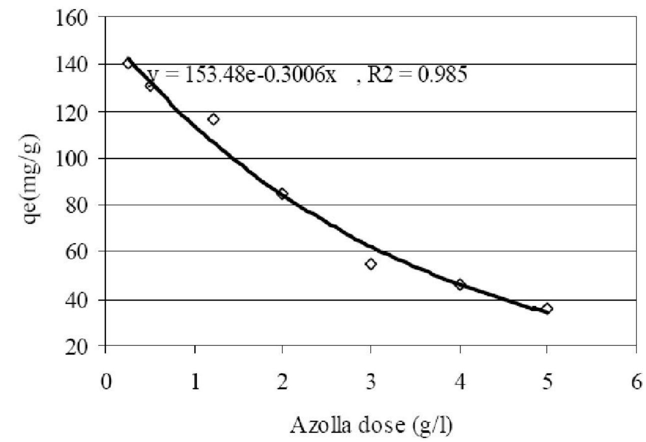

Figure 5 : Equilibrium amounts of adsorbed dye at various dozes of Azolla.

However, investigating the effect of Azolla doze on the percentage of removal (figure 6) showed that the removal percentage decreases by decreasing the Azolla doze. According to this diagram, by increasing the Azolla doze, from 0.2 to 1g/l, the percentage of dye removal increases from 45% and reach to a maximum of about 70%. Therefore, a concentration of 1 g Azolla/l was obtained as the optimum doze.

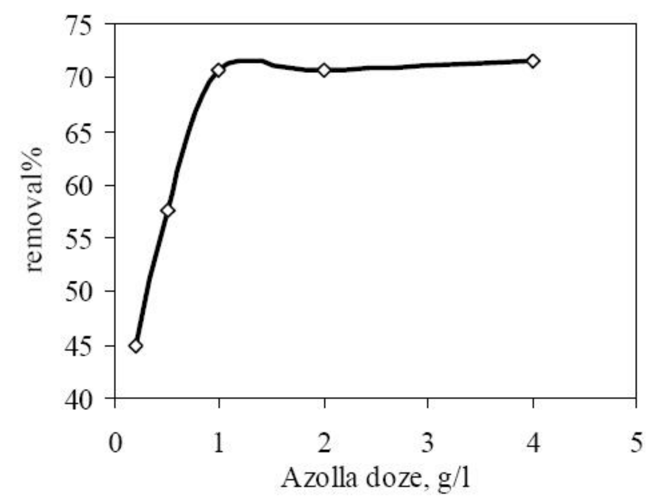

Figure 6 : Effect of Azolla adsorbent concentration on dye removal

An artificial neural network including six inputs (pretreatment pH, adsorption pH, agitation rate, Azolla doze, initial dye concentration and contact time) and one output (percentage of dye removal) was designed to pre-

Current Research Paper

dict the removal efficiency of Methylene Blue at different conditions. Three different transfer functions of the hidden layer were examined:

$$\textbf{Hyperbolic tangent sigmoid} = \frac{2}{(1+e^{-2x})} - 1 \qquad (1)$$

$$\textbf{Log-Sigmoid} = \frac{1}{1+e^{-x}} \qquad (2)$$

Linear=x (3)

Levenberg-Marquardt backpropagation algorithm was used to train the network. From the whole experimental data sets (225), 135 data sets were randomly chosen for training the network. Each data set includes 6 input and one output parameters. 45 numbers of data sets were used the validation set. The validation set is used to ensure that there is no overfitting in the final result. In the other word, training process is stopped when the mean of square errors for the validation set increases. The rest of data set (that are not used in the training process) constitutes the test set. The test set provides an independent measure of how well the network can be expected to perform on data not used to train it. Figure 7 shows the MSE changes of the training, validation and test sets during a training process. The figure shows that after 52 iterations, the errors of the validation set starts to increase, while the MSE of the training set is still descending. This shows that the network will overfit the data after 52 iterations. Therefore, the network with weights and biases that are obtained by 52 iterations is the best trained one. 3, 5, 10, 12, 15, 20 and 25 number of neurons in the hidden layer was examined and the resulted MSE and regression parameter were compared to find the optimum network. Because of random selection of the data sets and random initialization of the weights and biases, each

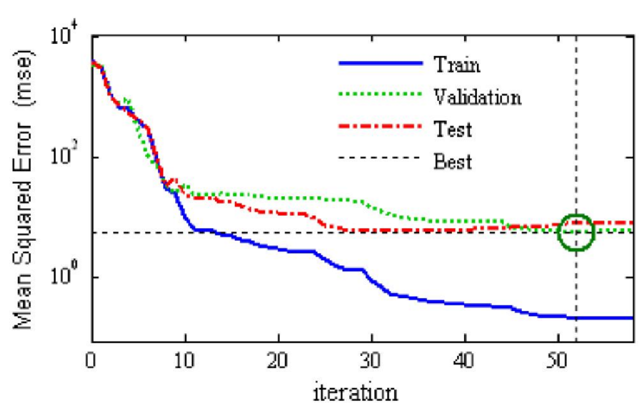

Figure 7 : The trend of MSE changes for training, validation and test sets

training process was repeated five times. The results showed that a network with 12 neurons in the hidden layer gives the least MSE.

In addition to the number of neurons in the hidden layer, different transfer functions for input and hidden layer were examined. The error values of training, validation and test sets obtained from a network with 12 neurons in the hidden layer and different transfer functions are given in TABLE 1. The numbers of this table are average values for five repetitions.

TABLE 1 : Performance of the network with different transfer functions

Transfer Function		Optimum No. of iteration	Mean of square error		
Hidden Layer	Output Layer		Training set	Validation set	Test set
purelin	purelin	2	148.4	198	211
purelin	logsig	6	322.8	374.3	412.8
purelin	tansig	4	125.6	143.5	125.6
tansig	purelin	21	0.925	15.35	9.04
tansig	logsig	14	223.29	268.12	340.37
tansig	tansig	17	3.49	19.08	26.5
logsig	purelin	17	1.95	17.6	21.2
logsig	logsig	23	237.4	398.2	188.3
logsig	tansig	12	2.45	14.1	32.3

The table shows that a network with Hyperbolic Tangent Sigmoid and linear transfer functions, respectively in the hidden and output layers has the best performance. A comparison between the measured amounts of dye removal and the predicted values using the best-trained network is shown in figure 8.

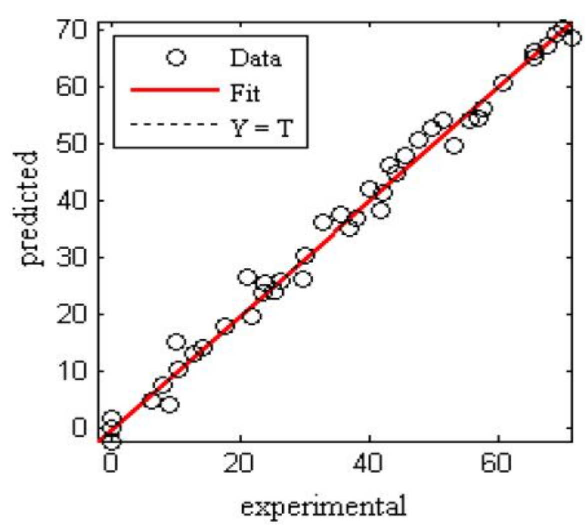

Figure 8 : Comparison between experimental and predicted results

The figure shows that the trained network is able to predict the removal of Methylene Blue at different unexpected conditions (test set) with a good precision. The best-fit line coincides the experiment=predicted line and the MSE for the test set was equal to 1.8.

CONCLUSION

Experiments at different conditions were carried out to investigate the removal of Methylene Blue using Azolla fern. Experimental results revealed that Azolla is a suitable bio-Adsorbent for removal of Methylene blue. It was observed that a removal efficiency of about 70% can be obtained using only one equilibrium stage at optimum conditions. An ANN was designed and trained to predict the removal process. Modeling results showed that the best-trained network can predict the experimental results with a MSE lower than two.

ACKNOWLEDGEMENT

The authors thank the Islamic Azad University-Rasht branch, for financial and other supports.

REFERENCES

[1] N.Kannan, M.M.Sundaram; Dyes Pigments, **51**, 25 **(2001)**.

[2] F.Kargi, S.Ozmihci; Enzyme Microbial.Technol., **35**, 267 **(2004)**.

[3] R.Han, Y.Wang, W.Yu, W.Zou, J.Shi, H.Liu; J.Hazard.Mater., **141**, 713 **(2007)**.

[4] T.Akar, S.Celik, S.T.Akar; Chem.Eng.J., **160**, 466 **(2010)**.

[5] G.A.Peters, J.C.Meeks; Ann.Rev.Plant Physiol.Plant Mol.Biol., **40**, 193 **(1998)**.

[6] M.Zhao, J.R.Duncan, R.P.Van Hille; Wat.Res., **33**, 1516 **(1999)**.

[7] A.P.M.Antunes, G.M.Watkins, J.R.Duncan; Biotechnol.Lett., **23**, 249 **(2001)**.

[8] M.Hasani, M.Moloudi; J.Hazard.Mater., **157**, 161 **(2008)**.

[9] O.Cinar, H.Hasar, C.Kinaci; J.Biotechnol., **123**, 204 **(2006)**.

[10] M.M.Hamed, M.G.Khalafallah, E.A.Hassanien; Environ.Modell.Softw., **19**, 919 **(2004)**.

[11] D.Aguado, A.Ferrer, A.Seco, J.Ferrer; Chemometr. Intell.Lab.Syst., **84**, 75 **(2006)**.