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# ANN Approach for Modeling of Zinc oxide Nanoparticle Using Sensitivity Analysis

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**ABSTRACT**: An Artificial Neural Network (ANN) representation was developed to anticipate the biosorption proficiency of Zinc oxide nanoparticle deep-seated on activated silica using *Emblica officinalis* (ZNO-NPs-AS-*Eo*) for the confiscation of total As (III) from aqueous solution based on 95 data sets obtained in a laboratory batch study. Experimental parameters affecting the biosorption succession such as initial concentration, dosage, pH, contact time and agitation were intended. A contact time of 120 min was drivable to bring about equilibrium. The utmost adsorption capacity of (ZNO-NPs-AS-*Eo*) in AS (III) removal was found to be 2.96 g/L. The sensitivity analysis confirmed that MSE values decreased as the number of variables used in the ANN model increased. The qualified increase in the performance due to inclusions of $V_2$, adsorbent dosage and $V_5$, agitation speed is larger than the contribution of other variables. The projected ANN model provided pragmatic experimental data with a reasonable correlation coefficient of 0.999 for two operating variables like adsorbent dosage and agitation speed.

**KEYWORDS**: Agitation, Back propagation, Concentration, Contact time, Dosage, Neurons, pH, Zinc oxide.

## I. INTRODUCTION

In waste water treatment various technologies are available such as chemical precipitation, ion exchange, electrochemical precipitation, solvent extraction, membrane separation, concentration, evaporation, reverse osmosis, emulsion per traction and adsorption (Naiya et al. 2009) [1]. Among these technologies adsorption is a user friendly technique for the removal of heavy metals. This process includes the selective transfer of solute components in the liquid phase onto the surface or onto the bulk of solid adsorbent materials. In last two decades artificial neural network (ANN) models have been extensively studied in different fields of engineering, finance with a basic objective of achieving human like performance. The neural networks are powerful tools to identify underlying highly complex relationships from input– output data (Plippman 1987) [2]. ANN derived from the biological counterparts and based on the concept that a highly interconnected system of simple processing elements known as nodes or neurons, enables to learn highly complex nonlinear interrelationships existing between input and output variables of the data-set. In ANN model of system feed-forward architecture namely multilayer perception (MLP) is most commonly used. This network consists of at least three layers namely input layer, one or several hidden layers and output layer. Each layer consists of a number of elementary processing units known as neurons. Each neuron in the input is connected to its hidden layer through weights. Also there is connection between hidden and output layers. When an input is introduced to the neural network the synaptic weights between the neurons are simulated and these signals propagate through layers and the output result is formed. The main objective is to form the output by the network in such a way that it should be close to the expected output. The weights between the layers and the neurons are modified in such a way that next time the same input will provide an output that are closer to the expected output. Various algorithms are available for the training of the neural networks. Feed-forward back propagation (BP) algorithm is the most versatile and robust technique which provides the most efficient learning procedure for MLP networks. This algorithm is especially capable of solving predictive problems (Haykin 1999 and Barnard et al. 1992) [3], [4]. Researchers pointed out that increasing the number of hidden layers enables a trade-off between smoothness and closeness-of-fit. The greater number of hidden layers improves the closeness- of-fit while a smaller number of hidden layers improve the smoothness or extrapolation capability of the ANN. Single hidden layer with arbitrarily large quantity of neurons is capable of modeling accurately (White 1990) [5]. It is also observed that two hidden layer networks are better than the single hidden layer network for specific problem (Walczak 1995) [6]. Single hidden layer can solve most of the problems for more input variables and

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outputs. Recently researchers have successfully modeled a three layer feed forward BP network to predict the removal of Cu(II) from industrial leachate by pumice and Zn(II) from hazelnut shell (Bansal et al. 1993 and Tamura et al. 1997) [7], [8]. The present paper deals with a development of a more general and system-independent neural network based on MLP having a single hidden layer trained with BP and Levenberg-Marquardt (LM) algorithms for the prediction of the percentage removal of As (III) from aqueous solution using five different variables under different operating conditions using two different transfer functions in a single hidden layer. Preceding studies with established technical approaches are reported for the amputation of arsenic using Zirconium(IV) monophosphonic acid resin, Polyamide composite nano filtration membranes and Fe(II) loaded and Fe(III)loaded apricot stone-based ACs, used as a biomaterial for the removal of As(V) and As(III) , As(V) - at a pH of 3.0-7.0, 3-10 using column and membrane studies [9-11] and other sources of adsorption. Recently, the use of neural networks has gained popularity for modeling biological wastewater treatment processes. The details of the adsorption study of these adsorbents are reported in our earlier publications and the relevant experimental data are taken for this ANN analysis (Gnanasangeetha 2014) [12].

## II. MATERIALS AND METHODS

### A. Adsorbent preparation and characterisation

Aqueous leaf extract of *Emblica officinalis* was stirred for 30 min to that 1g of Zinc acetate dihydrate was added under vigorous stirring. After 1hr stirring 10 g of activated silica was introduced into the above solution followed by the addition of aqueous NaOH resulted in a white aqueous solution at pH 12. This was then sited in a magnetic stirrer for 2hr. The activated silica supported ZnO nanoparticle were then filtered and washed with double distilled water. The synthesized ZnO-NPs-AS-*Eo* was maintained at 60ºC for 12 hrs. ZnO-NPs-AS-*Eo* structure was primed by green synthesis method. A mortar was used to homogeneously ground ZnO-NPs- AS-*Eo*. The proposed sorbent were stored in air at room temperature. The X-Ray powder diffraction pattern of the as- synthesized sample was recorded on an X-ray diffractometer (XRD, PW 3040/60 Philips X'Pert) using Cu (Kα) radiation (λ =1.5416 A˚) operating at 40 kv and 30 mA with 2θ ranging from 10- 90˚.The external morphology of the sample were characterized by scanning electron microscope (SEM) (LEO 1530FEGSEM).

### B. Batch adsorption studies

The equilibrium sorption capacity of the sorbent at the corresponding equilibrium conditions was calculated using a mass balance equation as in Eq. (1).

$$Qe = \frac{Ci - Ce}{M} xV \qquad \text{———} \qquad (1)$$

where $Q_e$ is the amount of the metal uptake by the bioadsorbent (mg/g) in the equilibrium; $C_i$ is initial metal ion concentration in solution (mg/L); $C_e$ is the equilibrium metal ion concentration in solution (mg/L); V is volume of the medium (L); and M is the amount of the bioadsorbent used in the reaction mixture (g). The percent removal (%) of As (III) was calculated using the following equation:

$$Removal\ \% = \frac{Co - Ce}{Co} x100 \qquad \text{———} \qquad (2)$$

Where $C_0$ and $C_e$ are the initial and final equilibrium As(III) concentration.

Batch adsorption experiments were conducted in 250 mL glass-stoppered, Erlenmeyer flasks with 20 mL As (III) solution of desired concentration and pH. A weighed amount of adsorbent was added to the solution. The flasks were agitated at a constant speed of 250 rpm until reaching equilibrium. The influence of pH (1.0 , 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0), adsorbent dose (0.5, 1, 1.5. 2, 2.5, 3, 3.5, 4, 4.5 5, 5.5, 6, 6.5,7,7.5,8 g), contact time (10, 20, 30,40, 50, 60, 70, 80, 90,100,110,120,130 min) and initial As(III) concentration (0.005,0.075,0.01,0.02,0.03, 0.04 ,0.05, 0.06, 0.07 ,0.08, 0.09, 0.1N) were evaluated during the present study. Each test lasted for nearly 2 h after which the adsorbent was

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separated from the solution by centrifugation at 400 rpm for 20 min. The residual As (III) concentration in the adsorbent was then characterized using ED-AX and XRD.

**C. ANN Structure and its Optimization Procedure**

Neural networks can map a set of input patterns onto a corresponding set of output patterns after a series of past process data from a given system have been acquired. Moreover, neural network has a distinctive ability to learn nonlinear functional relationships without the requirement for structural knowledge of the process to be modeled. Among the various ANN models, the one of our interest was the feed forward back propagation network (Turan et al. 2011 and Imandi et al. 2008) [13], [14]. The feed forward back propagation neural network consisting of forward five neurons corresponding to the five process variables (initial metal ion concentration, pH, time, dosage and agitation) were used in the input layer, twenty in the hidden layer and one in the output layer of the network. The number of neurons per layer should be high enough to allow the network to reproduce the behavior of the system. However, too large of a neuron number can cause data over fitting a situation that can be encountered when correlating experimental data. This is due to the fact that the large number of parameters to be adjusted when using too many neurons might induce the network to memorize the data used in the training while losing one of its more functional characteristics generalization (Lee et al. 2002, Zhao et al. 1997, Pal et al. 2009 and Hornik 1991) [15], [16], [17], [18]. Once the neural network was created it was trained to accurately model the given phenomenon by using the experimental data in MATLAB. The mean square error (MSE) was used as the error function and defined as:

$$MSE = \sum \frac{(y' - y)^2}{n} \qquad (3)$$

where **y** is the measured values, **ý** the corresponding predicted values and n is the number of samples. Sensitivity tests were conducted to ascertain the relative significance of each of the independent parameters (input neurons) on the removal efficiency (output) in the ANN model. In the sensitivity analysis, each input neuron was in turn eliminated from the model and its influence on prediction of removal efficiency (Qe) was evaluated in terms of correlation coefficient ($R^2$), and mean square error (MSE).

## III. RESULTS AND DISCUSSION

**A. ANN model for LM algorithm**

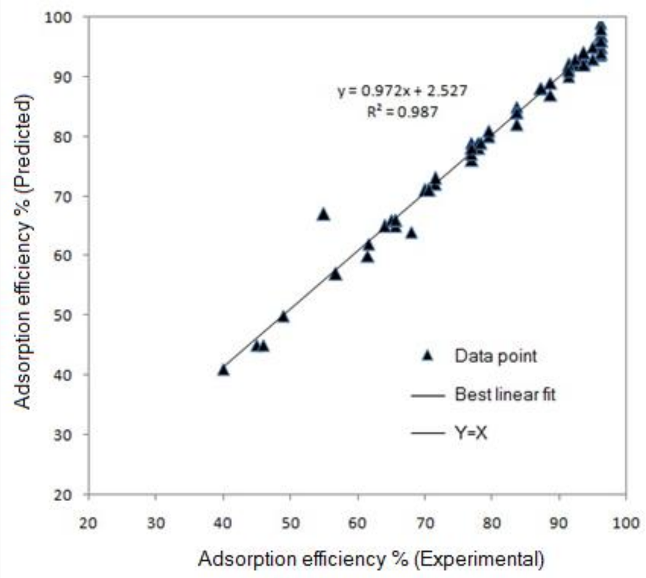


Figure 1 ANN outputs plotted versus the corresponding experimental targets for the Levenberg-Marquardt algorithm

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Artificial neural network (ANN) models have been used with basic objective underlying highly complex relationships from input–output data of achieving human like performance with accuracy. The main objective is to form the output by the network in such a way that it should be close to the expected output. In the present study, an ANN based model was developed for predicting the As (III) removal efficiency of (ZNO-NPs-AS-*Eo*). The present paper deals with a development of a more general and system-independent neural network based on MLP having a single hidden layer trained with BP and Levenberg-Marquardt (LM) algorithms for the prediction of the percentage removal of As (III) from aqueous solution using five different variables under different operating conditions using two different transfer functions in a single hidden layer. The input layer had five neurons as pH, adsorbent dosage, initial concentration, agitation and contact time while the output layer had the As (III) removal efficiency as the only neuron. In order to determine the optimum number of hidden nodes, a series of topologies was used, in which the number of nodes were varied from 2 to 20. Each topology was repeated three times to avoid random correlation due to random initialization of the weights. The Mean square error (MSE) was used as the error function to measure the performance of the network according to the above equation (3). The MSE was minimum just about 10 neurons. Therefore, the number of neurons in the hidden layer was selected as 10. A regression analysis of the network response between ANN outputs and the corresponding targets performed shows a good agreement between ANN outputs (predicted data) and the corresponding targets (experimental data). The best linear fit was indicated in the Figure 1 with a good correlation coefficient of 0.987.

**B. Sensitivity Analysis**

**Table 1 Recital appraisal of grouping of input variables for LMA with 10 neurons in the hidden layer for sensitivity analysis**

| S.No. | CN | MSE | $R^2$ | IN | Gradient | BLE |
|---|---|---|---|---|---|---|
| **1.** | **$V_1$** | **9.06** | **0.917** | **47** | **$1.00 \times 10^{-5}$** | **0.83x +16** |
| 2. | $V_2$ | 203.26 | 0.322 | 7 | $2.68 \times 10^{-3}$ | 0.35x +53 |
| 3. | $V_3$ | 110.48 | 0.449 | 7 | $8.48 \times 10^{-3}$ | 0.21x +69 |
| 4. | $V_4$ | 229.17 | 0.66 | 10 | $1.26 \times 10^{-4}$ | 0.43x+44 |
| 5. | $V_5$ | 32.37 | 0.887 | 8 | $7.43 \times 10^{-3}$ | 0.77x +20 |
| 6. | $V_1+V_2$ | 8.38 | 0.995 | 56 | $3.89 \times 10^{-3}$ | 0.99x+1 |
| 7. | $V_1+V_3$ | 71.66 | 4.530 | 11 | $9.34 \times 10^{3}$ | 0.36x+61 |
| 8. | $V_1+V_4$ | 42.63 | 0.915 | 09 | $7.49 \times 10^{3}$ | 0.98x +2.5 |
| 9. | $V_1+V_5$ | 25.52 | 0.872 | 11 | $1.26 \times 10^{3}$ | 0.76x +21 |
| 10. | V 2+$V_3$ | 35.40 | 0.873 | 16 | $5.23 \times 10^{3}$ | 0.75x +22 |
| 11. | $V_2+V_4$ | 51.27 | 0.903 | 17 | $1.35 \times 10^{4}$ | 0.81x +16 |
| **12.** | **$V_2+V_5$** | **5.4** | **0.999** | **100** | **$7.31 \times 10^{4}$** | **1x** |
| 13. | $V_3+V_4$ | 123.4 | 0.738 | 12 | $5.32 \times 10^{3}$ | 0.57 x+37 |

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|---|---|---|---|---|---|---|
| 14. | $V_3+V_5$ | 94.12 | 0.620 | 13 | $3.53x\ 10^3$ | 0.35x+57 |
| 15. | $V_4+V_5$ | 12.04 | 0.974 | 23 | $5.52x\ 10^3$ | 0.94x+5 |
| 16. | $V_1+V_2+V_3$ | 43.67 | 0.782 | 13 | $1.93x\ 10^3$ | 0.6x+35 |
| **17.** | **$V_1+V_2+V_4$** | **5.71** | **0.985** | **27** | **$2.3x\ 10^3$** | **0.97x+2.7** |
| 18. | $V_1+V_2+V_5$ | 8.82 | 0.963 | 14 | $3.68x\ 10^3$ | 0.9x+8.3 |
| 19. | $V_1+V_3+V_4$ | 33.96 | 0.899 | 64 | $1.68x\ 10^3$ | 0.81x+17 |
| 20. | $V_1+V_3+V_5$ | 53.19 | 0.739 | 12 | $7.84x\ 10^3$ | 0.49x+45 |
| 21. | $V_1+V_4+V_5$ | 11.54 | 0.967 | 20 | $6.97x\ 10^3$ | 0.93x+6 |
| 22. | $V_2+V_3+V_4$ | 27.94 | 0.94 | 23 | $5.06x\ 10^3$ | 0.88x+9.9 |
| 23. | $V_2+V_3+V_5$ | 21.95 | 0.91 | 33 | $2.08x\ 10^3$ | 0.8x+16 |
| 24. | $V_2+V_4+V_5$ | 34.32 | 0.922 | 14 | $2.83x\ 10^3$ | 0.85x+14 |
| 25. | $V_3+V_4+V_5$ | 31.43 | 0.932 | 26 | $1.38x\ 10^3$ | 0.86x+11 |
| 26. | $V_1+V_2+V_3+V_4$ | 19.03 | 0.941 | 15 | $1.27x\ 10^3$ | 0.88x+11 |
| 27. | $V_1+V_2+V_3+V_5$ | 25.68 | 0.895 | 14 | $1.66x\ 10^3$ | 0.79x+19 |
| **28.** | **$V_1+V_2+V_4+V_5$** | **6.94** | **0.98** | **17** | **$1.01x\ 10^3$** | **96x+3.5** |
| 29. | $V_1+V_3+V_4+V_5$ | 25.5 | 0.92 | 18 | $2.54x\ 10^3$ | 0.87x+11 |
| 30. | $V_2+V_3+V_4+V_5$ | 2.54 | 0.94 | 30 | $1.89x\ 10^3$ | 0.9x+8.9 |
| 31. | $V\ 1+V_2+V_3+V_4+V_5$ | 18.55 | 0.94 | 21 | $1.43x\ 10^3$ | 0.89x+9.9 |

**CN-combination; MSE-mean squared error; $R^2$-correlation coefficient; IN-iteration; BLE- best linear equation; $V_1$-concentration; $V_2$-adsorbent dosage; $V_3$-contact time; $V_4$-pH; $V_5$-agitation speed.**

In this cram a sensitivity analysis was accomplished to establish the extent of effectiveness of a variable using the projected ANN model. In the analysis recital assessment of various possible combinations of variables were investigated. Therefore performance of the groups of one, two, three, four, and five variables were tested by the optimal ANN structure using the LMA with 10 hidden neurons. The groups of input vectors were defined in this form $V_1$, initial As (III) ions concentration; $V_2$, adsorbent dosage; $V_3$, contact time; $V_4$, initial pH and $V_5$, agitation speed. Results of the performance evaluation of 31 combinations are summarized in Table 1. Findings of the sensitivity analysis showed that $V_1$, initial As (III) ions concentration was found to be the most effective parameter, among those considered in the group of one variable. As shown in Table 1, the MSE value significantly decreased from 71.86 to 5.4 when $V_2$ + $V_5$ (dosage & agitation) was used in combination with subsequent group of two variables. The minimum MSE in the group of three variables was determined to be 5.71 using the combination of $V_1$ + $V_2$ +$V_4$ (As (III) ions concentration ,adsorbent dosage and pH ) with a further contribution of $V_5$ (agitation speed) the MSE decreased up to 6.94 from 25.5 which is the minimum value of the group of four variables. The MSE value significantly deceased 25.5 to 18.55 when $V_3$ (contact time) was used in combination with other variables in the subsequent group of five variables with reasonable correlation coefficient of 0.94. On the basis of the performance evaluation of combinations of input

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variables best group performances according to number of parameters are listed in Table 1. The respective MSE values as given in Table 1 show that MSE values decrease as the number of variables in the group increases. Furthermore it can also be concluded that the relative increase in the performance due to inclusions of $V_2$, adsorbent dosage and $V_5$, agitation speed is larger than the contribution of other variables. Single hidden layer with arbitrarily 10 neurons is capable of modeling accurately. A single hidden layer solved the problems for 5 input variables and 1 output. This is in agreement with the work reported for adsorption of Lanaset Red G dye on walnut husk (Celekli et al. 2011) [19]. These results confirm that the developed ANN model reproduces the adsorption in this system within experimental ranges adopted in the fitting model with best linear correlation of 0.999.

## IV. CONCLUSION

The (ZNO-NPs-AS-*Eo*) used as a low-cost adsorbent showed good adsorption performance for removal of As (III) ions from aqueous solutions. Batch adsorption experiments showed that optimal operating initial concentration of 0.06N, pH of 5, an adsorbent dosage of 4.5 g and agitation speed of 250 rpm and contact time of 120 min was found to be sufficient to achieve equilibrium. The optimal neuron number for the LMA was determined to be 10 hidden neurons with MSE of 5.4 with a tangent sigmoid transfer function (tansig) at hidden layer and a linear transfer function (purelin) at output layer. The proposed ANN model showed a precise and an effective prediction of the experimental data with a satisfactory correlation coefficient of 0.999 for two operating variables like $V_2$, adsorbent dosage and $V_5$, agitation speed. The maximum adsorption capacity of the (ZNO-NPs-AS-*Eo*) in As (III) removal was found to be 2.96 g/L. The relative increase in the performance is due to inclusions of $V_2$, adsorbent dosage and V5, agitation speed. The sensitivity theoretical analysis confirmed that this system was in good agreement with experimental pseudo second order kinetics.

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