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APPLICATION OF ARTIFICIAL NEURAL NETWORK (ANN) FOR THE PREDICTION OF SIZE OF SILVER NANOPARTICLES PREPARED BY GREEN METHOD

PARVANEH SHABANZADEH[a*], NORAZAKSENU[a], KAMYAR SHAMELI[b,c], FUDZIAH ISMAIL[a], MARYAM MOHAGHEGHTABAR[d]

[a]*Department of Mathematics, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia*

[b]*Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia*

[c]*Materials and Energy Research Center, Meshkin-Dasht Road, Karaj 3177983634, Iran*

[d]*Department of Mathematics, Faculty of Science, University Gilan, 1914, Rasht, Iran*

The artificial neural network (ANN) models have the capacity to eliminate the need for expensive experimental investigation in various areas of manufacturing processes, including the casting methods. Determination of particle size is one of the critical parameters in nanotechnology.TheAg-NPs have attracted significant attention for chemical, physical and clinical applications due to their exceptional properties.The nano-silver crystals were prepared in the biopolymer mediated without any aggregation by using green chemical reduction method. The method has an advantage of size control which is essential in nano-metal synthesis. The resulting of silver nanoparticles (Ag-NPs) characterized by using of X–ray diffraction (XRD) and transmission electron microscopy (TEM) technique.XRD patterns confirmed that Ag-NPs crystallographic planes were face centered cubic (fcc) type. TEM results showed that mean diameters of Ag-NPs for four different amounts of variables were less than 40 nm. This method with comparison to other methods is green, high yield, speedy and easy to use.This paper presents an ANN model for the predictionsize of Ag-NPs by green method. Themodel accounts for the effect of NaOH volumes, temperature, stabilizer, and $AgNO_3$ concentration on the size of nanoparticle.The best model presented a trustworthy agreement in predicting experimental data. The characteristic parameters of the presented ANN models are fully reported in the paper.

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1. Introduction

The field of nanotechnology is one of the most active areas of research in recent materials science. Nanoparticles exhibit completely new or improved properties based on specific characteristics such as size, distribution and morphology. In addition, nanotechnology is a field that is burgeoning day by day, making an impact in all spheres of human life. Apparently, new applications of nanoparticles and nanomaterials are emerging rapidly [1–3]. There exist many preparation methods for the synthesis of metal nanoparticles, such as the green chemical reduction in aqueous medium with various biopolymer surfactants [4, 5], for instance in starch [6], chitosan

*Corresponding authors: parvaneh.shabanzade@gmail.com

[7], or in other natural polymer matrixes [8–10]. Ag-NPs have found wonderful applications in the field of high sensitivity of biomolecular detection and diagnostics [11], antimicrobials and therapeutics [12, 13], as well as catalysis [14] and micro-electronics [15]. However, there is still a need for economic, commercially viable as well environmentally green synthesis route to synthesize Ag-NPs. Having mentioned that, Ag-NPs can be successfully synthesized by using a green variety of biosynthesis methods, for example, plant extract [16], biopolymers [17], and irradiation process in the aqueous solution [18–21]. The green synthesis of Ag-NPs involves three main steps, which must be evaluated based on green chemistry perspectives, including selection of solvent medium, reducing agent and nontoxic substances for the Ag-NPs stability [6].

In recent years, the Artificial Neural Network (ANN) technique has been used for solving complex engineering problems in different application areas with a considerable reduction in computational time. The basic advantage of ANN is that it does not need any mathematical model since an ANN learns from examples and recognizes patterns in a series of input and output data without any prior assumptions about their nature and interrelations [22]. The ANN eliminates the limitations of the classical approaches by extracting the desired informatioin using the input data. Applying ANN to a system needs sufficient input and output data instead of a mathematical equation [23]. Selecting the optimum architecture of the network is one of the challenging steps in ANN modelling. The term 'architecture' mentions to the number of layers in the network and number of neurons in each layer. In recent years, ANN have been introduced in nanotechnology applications as techniques to model data showing non-linear relationships [24–28] and or estimation of particle size in variety nano particle samples [29]. Employing neural network models would lead to saving time and cost by predicting the results of the reactions so that the most promising conditions can then be verified [30, 31]. The objective of this paper is to develop an ANN model to predict the size of Ag-NPs, based experimental data.

2. Experimental Section

2.1. Materials

All chemicals and reagents in this work were of analytical grade and used as received without any purification. Materials used for the synthesis of Ag-NPs included silver nitrate (99.98%), was supplied by Merck (Germany), starch obtained from Hamburg Chemicals (Germany), and sodium hydroxide (99.0%) obtained from R & M Chemicals (USA). All aqueous solutions were prepared using double distilled water.

2.2 Synthesis of Ag-NPs by using Green Method

The aqueous solutions of $AgNO_3$ were taken in a flask and soluble starches were added to these solutions. These solutions were heated at 50, 60, 70 and 80 °C.The different volumes of aqueous solution of NaOH (1 M) were added to prepare various samples of Ag-NPs suspension. The suspension immediately turned to brawn, dark brown and black colour, that indicating the formation of Ag-NPs. The reactions were continued for 30 minutes. The obtained suspensions were centrifuged using a high centrifuge machine at 18,000 rpm and Ag-NPs powder was kept for further characterization.

2.3 Characterization Methods and Instruments

The synthesized Ag-NPs were characterized using transmission electron microscopy (TEM), and X-ray diffraction (XRD). TEM observations were conducted using a Hitachi H-7100 electron microscope while the particle size distribution were determined using the UTHSCSA Image Tool version 3.00 program. The structure of produced Ag-NPs has been studied using X-ray diffraction (XRD, Philips, X'pert, Cu Kα). PXRD patterns were recorded at a scan speed of 4°/min. After reactions the samples were centrifuged using a high-speed centrifuge machine (Avanti J25, Beckman).

2.4 Data Set

Table 1 show the experimental data used for ANN design. The experimental data were randomly divided into three sets (20, 5 and 5) which were used as training, validation and testing, respectively. The training data was applied to compute the network parameters while the validation data was applied to ensure robustness of the network parameters. If a network "learns too well" from the training data, the rules might not fit as well for the rest of the cases in the data. To avoid this "over fitting" phenomenon, the testing stage was used to control error; when it increased, the training stops [29]. For assessment the predictive ability of the generated model was used as the testing data set.

Table 1.The estimated results, obtained by the proposed ANN model.

No.	NaOH Volume (1M)	Temperature (°C)	Stabilizer (%w/w)	$AgNO_3$ Con. (M)	Mean Ag-NPs (nm) Actual	Mean Ag-NPs (nm) (Predict)
Training set						
1	4.5	80	1.00	1.00	38.52	38.56
2	2.5	70	1.25	0.75	26.83	26.83
3	4.5	50	1.00	1.00	31.21	30.02
4	8.5	60	1.00	1.00	17.65	17.39
5	6.5	70	1.25	0.75	11.34	11.22
6	6.5	70	1.25	1.25	13.92	14.10
7	4.5	60	1.00	0.50	36.24	37.13
8	4.5	60	1.00	1.00	25.18	25.15
9	2.5	50	1.25	1.25	18.41	18.01
10	2.5	70	1.25	1.25	22.17	22.19
11	6.5	50	0.75	1.25	30.27	32.48
12	4.5	60	0.75	1.00	24.81	24.90
13	4.5	60	1.50	1.00	28.54	29.80
14	4.5	60	1.00	1.50	34.57	34.90
15	2.5	50	0.75	1.25	27.36	27.36
16	2.5	70	0.75	1.25	24.7 7	23.52
17	6.5	50	1.25	0.75	13.03	13.65
18	2.5	50	1.25	0.75	23.17	24.11
19	4.5	70	1.00	1.00	30.30	31.09
20	2.5	60	1.00	1.00	41.58	38.26
Validation set						
21	4.5	60	0.50	1.00	29.52	29.52
22	6.5	60	1.00	1.00	22.38	22.81
23	0.5	60	1.00	1.00	35.94	37.34
24	2.5	70	0.75	0.75	24.18	24.75
25	4.5	40	1.00	1.00	31.33	31.77
Test set						
26	6.5	70	0.75	0.75	15.57	17.76
27	6.5	50	1.25	1.25	14.58	14.27
28	2.5	50	0.75	0.75	31.2	30.81
29	6.5	70	0.75	1.25	29.45	29.01
30	6.5	50	0.75	0.75	26.81	26.93

3. Results and discussion

3.1. Powder X-ray Diffraction

The powder X-ray diffraction (PXRD) patterns of the prepared samples at different variables indicate the formation of the Ag-NPs. As shown in Figure 1, all samples have similar diffraction profiles. The PXRD peaks at 2θ of 38.18°, 44.32°, 64.41°, 77.31° and 81.47° can be attributed to the 111, 200, 220, 311 and 222 crystallographic planes of face centered cubic (fcc) silver crystals, respectively (Ref. # 01-004-0783). For the all samples, the main crystalline phase was silver; no obvious impurities [4] were evident in the PXRD patterns. Moreover, no other peaks related to an impurity, indicating that the silver metal was relatively pure. The different volumes of NaOH between these four variables have been shown to accelerate the rate of reduction.

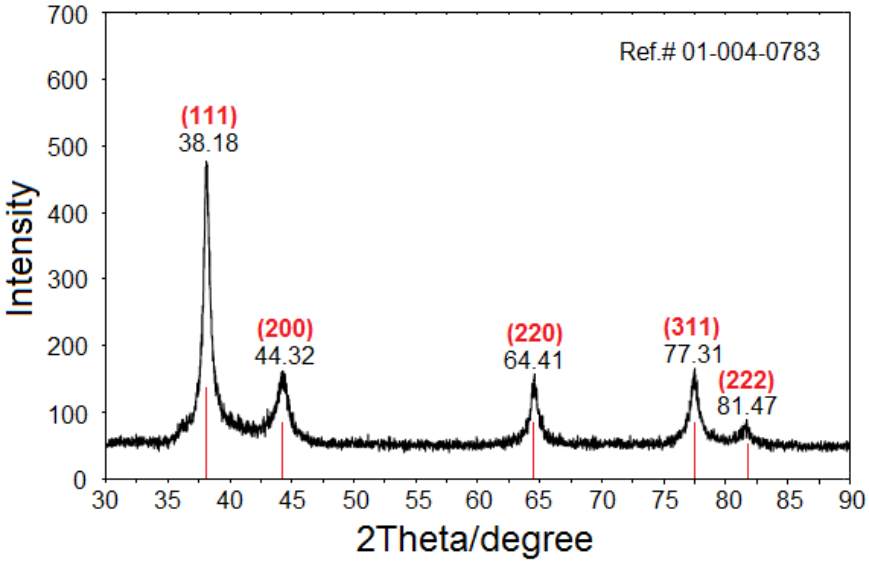

Fig. 1The PXRD patterns of Ag-NPs prepared.

3.2. Morphologies Study

The TEM results and image in Table 1 and Figure 2 demonstrate the formation of Ag-NPs at different variables. Figure 2 shows typical TEM image and the corresponding particle size distribution of the prepared Ag-NPs. According to training set results (Table 1) can be found that in lines 7, 8 and 14 with the changes in the $AgNO_3$ concentration from 0.50 to 1.00 M the mean diameters of Ag-NPs decreases from 36.24 to 25.18 nm but with the increase silver ions to 1.5 M, the mean particle size increase to 34.57 nm. Also, in the different percentage of stabilizer in the lines 8, and 12 the mean diameters of Ag-NPs change from 25.18 to 24.81 nm and with the decrease stabilizer percentage to 0.50 wt% (line 21) size of Ag-NPs increase to 29.52 nm. The TEM images and their corresponding particle size distributions of Ag-NPs at line 14 are shown in Figure 2. The total numbers of Ag-NPs counted for each TEM image was about 253.

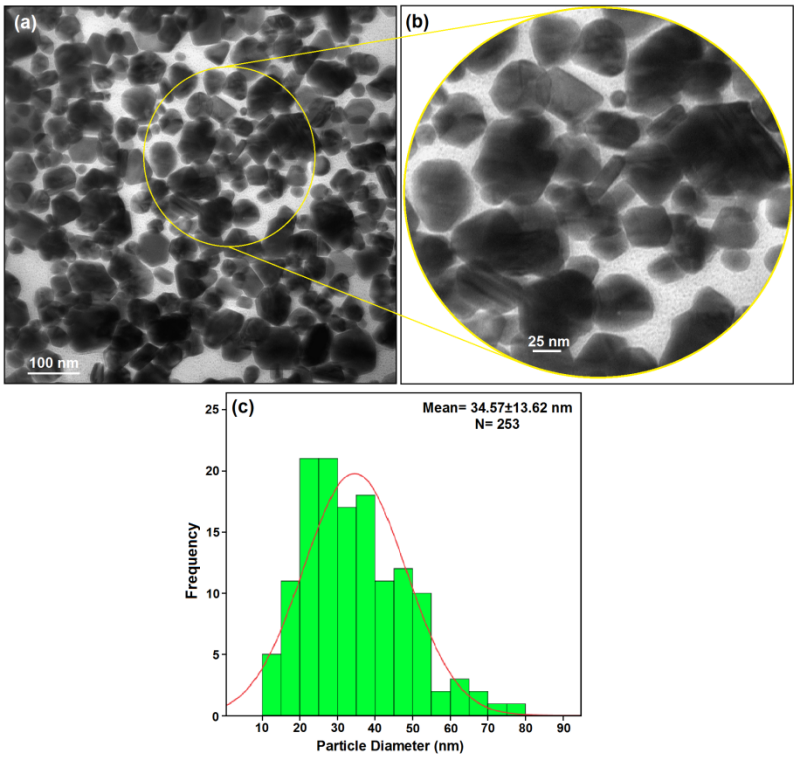

Fig. 2 TEM images of Ag-NPs and their particle size distribution (a–c).

3.3 ANN Modeling

The next step was the generation, optimization and training of theartificial neural network.ANNs are model systemsfor computation based on the linkage structure of biologicalneurons. Each logic processing unit in ANNs is a neuron whichtakes one or more inputs and generates an output based on theassociated weights (showing the importance) of inputs. Neuronsonly compute the weighted sum of all inputs and report it as an output. In most cases identical neurons are interconnected in at least three separate layers. The inputs of the system are taken in the input layer and the relationships between them are computed in a hidden layer (s), with the results reported through an output layer [32]. The experimental variables used as input for the ANN model include temperature, starch stabilizer, and $AgNO_3$ concentration. The output of the ANN model is size of nano particle. An important step in development of adjusting model was to split the experimental data into 3 main subsets: a training set (used to estimate the network model parameters), a validation set (used to check the generalization ability of the network) and test set (used to ability estimate the network model of new samples). Thus, in the study 20 sample were used to train the BP-ANN model, 5 samples were used to validate the optimized model and 5 sample were used in the model testing step.Two approachesare applied to prevent overtraining during training of the network. The maximum number of iterations is set to 1000. Also, 5 individual data records is taken out of the training process as testset and used to avoid overtraining. The training process stops when the correlation coefficient of the test dataset starts to decrease showing that the network is becoming overtrained prepared in random sequence in the experimental design and then examined. Different training parameters were cross-examined to optimize the network structure. Subsequent to training the ANN, the quality of training and the predictability of the models are validated using the correlation coefficient Rsquare (R^2) for training, test and validation data (Equation 1) [33-35].

$$R^2 = 1 - \frac{\sum_{i=1}^{r}(xp_i - xa_i)^2}{\sum_{i=1}^{r}(xa_i - x_m)^2} \quad (1)$$

where r is the number of points, x_{pi} is the predicted value obtained from the neural network model, x_{ai} is the actual value, and x_m is the average of the actual values. The best model will have the highest R^2 for all training, test and validation data [35]. Among the multiple developed ANN structures was selected a feed-forward with the error back-propagation learning rule. Feed-forward networks consist of a series of layers. The first layer has a connection from the network input. Each subsequent layer has a connection from the previous layer. The final layer produces the network's output [28]. Optimization process of ANN includes selection of the parameters related to each function known as the bias and weight values of the transfer-function of each neuron in order to maximize the regression (R^2) of an observing data set. The most popular transfer functions for a nonlinear relationship are the Linear, Hyperbolic Tangent Sigmoid [36] and Log-Sigmoid function. The first analysis regarded the optimal number of hidden neurons for the ANN model. The number of hidden neurons varied from 1to10.Number of neurons in hidden layer was attained by trial and error in accordance with trustworthy obtained results in training step. The key role in this section was played by network performance in relation with decrement in error and improvement in regression R^2 as close as possible to 1. Thetensing function was used to connect the input nodes with the hidden nodes and the sigmoidal function was applied to connect hidden nodes with output nodes. In this study, the network is trained by experimental data to the input layer and adopting the weights of each interconnection in such a way that the desired output could be obtained. In this paper, the single-layer architecture was selected for ANN that input neurons are attached to a layer of 10 hidden neurons, which are connected to the output neurons. Thesuggested network was trained with Levenberg–Marquardt back-propagation algorithm.In during all of the training patterns was used Random Learning cycle (epoch). It is important that weights are automatically updated in the training step in order to provide the best results and smallest error. The estimated results, obtained by the proposed BP-ANN are detailed in Table 1. During the training and validation steps, the main weight evaluation process occurs to provide more reliability and to check the network's capabilities. So whenthe architecture of the ANN model has been established, the model has been fit to the whole datasets to determine the optimal parameters. In Figure 3, is shown a diagram of neural network model with one hidden layer structure of proposed ANN. Table 2 shows the values of connection weights (parameters of the model) for the complete ANN model trained on the whole datasets. This information allows other researchers to compare present ANN models with their own experimental data.

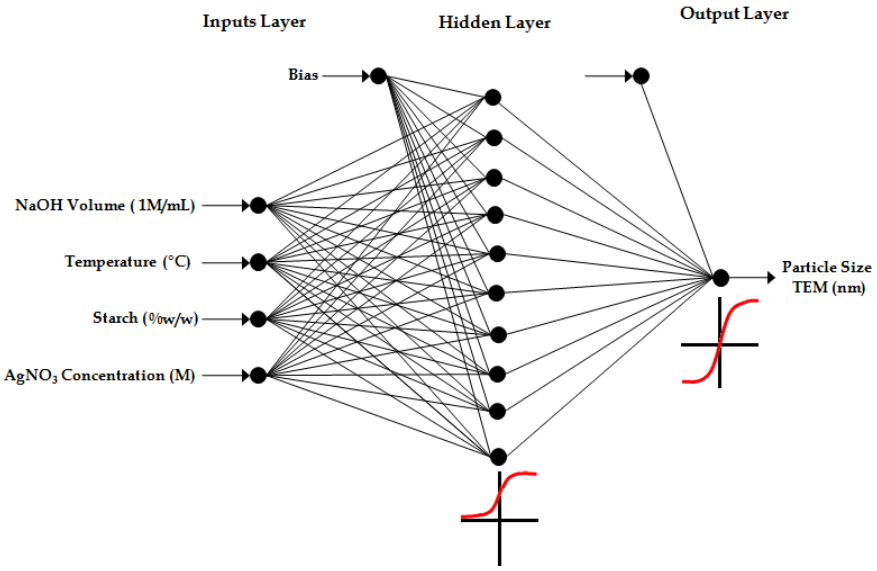

Fig. 3. Schematic diagram of neural network model.

Table 2 Values of connection weights (parameters of the model) for the complete ANN model

	Node 1	Node 2	Node 3	Node 4	Node 5	Node 6	Node 7	Node 8	Node 9	Node 10	Bias 2
Input 1	-2.8659	-0.73198	-5.0492	-1.1755	3.6382	5.9884	-0.5190	3.6328	1.4163	-1.4146	
Input 2	2.8377	-2.3975	0.01506	-0.6278	2.1662	-5.3394	0.0729	-1.8426	-3.5017	-4.2634	
Input 3	4.1182	-2.6249	-0.6899	-5.0749	-1.913	1.1576	6.7846	-2.9329	-3.6357	-1.683	
Input 4	-0.6572	-2.1902	1.117	-1.3122	-0.6247	-2.859	-.02954	-3.4565	-0.3725	2.2416	
Bias 1	4.3153	4.9606	3.044	-1.6098	1.3089	-0.5439	-3.2897	3.3914	4.1709	-4.7974	
Output	-1.4175	0.2138	1.2698	-1.1814	0.3037	0.9633	-2.963	0.4537	-0.7775	-0.9672	0.5825

The estimation performance is evaluated, on training, validation and testing data sets, by $R^2$and the resulting values are reported in Figure 4. Dataset is modeled by ANN and the best predictive model gave R^2 values of 0.9839, 0.9778 and 0.9787 for training data, validation dataand testdata, respectively, indicating a quality trainedmodel with appropriate predictive capability.

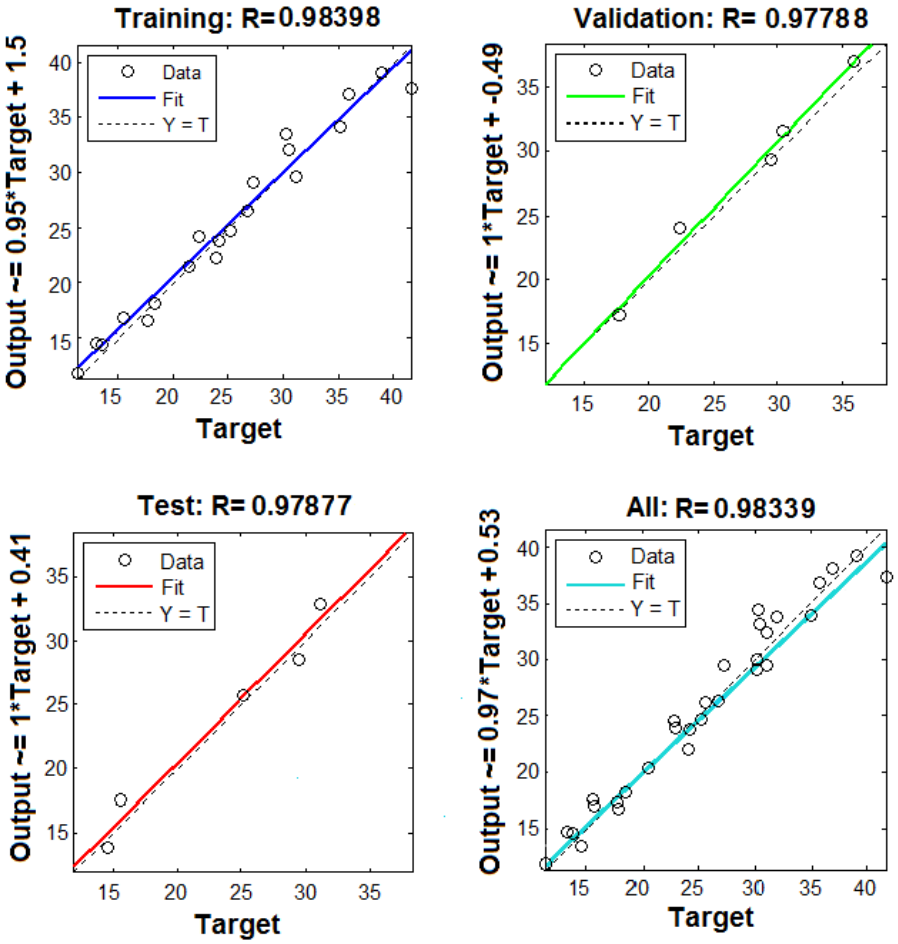

Fig. 4 The scatter plots of ANN model predicted versus actual values for training, validation, testing and all data sets.

4. Conclusion

A 4-input ANN model for predicting the size of Ag-NPs have been presented. The model accounts for the effect of volume of NaOH, temperature, starch as stabilizer, and $AgNO_3$ concentration on the size of NPs. The models have been trained on a set of data obtained by the present authors and tested with cross-validation. The model shows good performance agreement in predicting experimental data. The characteristic parameters of presented ANN model are reported in the paper, allowing the research community to compare model predictions with their own experimental data.

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