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A MODELING STUDY BY ARTIFICIAL NEURAL NETWORK ON PROCESS PARAMETER OPTIMIZATION FOR SILVER NANOPARTICLE PRODUCTION

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ABSTRACT

Artificial neural network (ANN) is the most accepted method for non-parametric modelling and process optimization of chemical engineering. The paper focuses on using ANN to analyse the yield production rate of silver nanoparticles (AgNPs). The study examines the effect of $AgNO_3$ concentration, stirring time and tri-sodium citrate concentration on the production of AgNPs yield. The yield of AgNPs was modelled and optimized as a function of three independent variables. Furthermore, assessment of the model through the coefficient of determination (R^2 = 0.9778) and mean square error (MSE) showed that the optimized production conditions were found at 1mM $AgNO_3$ concentration,15 min of stirring time and 1% tri-sodium citrate. Optimal and maximal AgNPs production were 20.62 (Area*) of yield experimentally, which was calculated using area under the curve from UV-vis analysis in the wave length range of 350 nm to 420 nm. Meanwhile, under the same conditions, the ANN predicted value is 19.84 (Area*) of AgNPs yield with 3.95% error. Besides that, the ANN model was employed to construct an output surface plot to reveal the impact of input variable as well as figure out the interaction effect and clear representation of optimized condition. Synthesized AgNPs at optimized condition (absorbance 0.93AU at 420 nm wavelength) were then characterized using Field Emission Scanning Electron Microscopy (FESEM) and UV-vis analysis.

Keywords: silver nanoparticles, coefficient of determination, mean square error, ANN and FESEM.

INTRODUCTION

In the modern active research area, nanotechnology has gained importance and popularity all over the world. Research on nanoparticle has increased recently due to size, shape, and high surface area, optical, physical and chemical properties, which opened up various applications of nanoparticle. Silver nanoparticles (AgNPs) is one of the most used nanoparticles due to its size dependent property, which reveals wide range of applications such as biological product development, and cancer drug delivery system. It is also used to combat cancer and antimicrobial activity, and used in water purification [1].

However, research on synthesis and characterizations of AgNPs has increased extensively due to their potential applications from electronic devices to biological effects. Different sized and shaped AgNPs has different plasmon resonance band with different suspension coloured synthesis of high yield spherical Ag NPs that has become important from the beginning. Besides that, industrial manufacturers need an optimized condition of current approaches to increase the profitability of production and confirming a sufficient supply of AgNPs. Thereby, high yield nanoparticles synthesis and their size study have become a fundamental focus of demanding research. In the last two decades, different mathematical tools were used to develop a model and optimize the production conditions, such as artificial neural network (ANN) and evolutionary computing. Artificial neural network (ANN) is a powerful method for modeling and simulating the various processes in real applications [2] and they possess the ability to approximate any real value of continuous function to any preferred degree of accuracy [3]. The ANN model has wide applicability predictive tools in an extensive range of disciplines, including engineering, owing to their ability of employing learning algorithms and separate input-output relationships for complex, nonlinear system [4].

Furthermore, neural network designs generally composed of three steps, configuration: how the layer are organized and connected, learning: how the information is stored, and generalization: how the network generate reasonable outputs for inputs not found in the training [5]. In addition, ANN is a hugely interconnected network structure containing many simple processing parts and those parts are capable to execute parallel computation for data processing. The fundamental processing part of ANN simulates the basic functions of biological neurons [6].

Besides that, there have been many publications done for optimization based on varying the magnitude of different independent parameters for AgNPs synthesis to gain better stability, high yield and remove aggregation of AgNPs bulk production, for instance, stirring time that has an effect on surface plasma resonance (SPR) [7].

However, in this study, the analysis of artificial neural network (ANN) model to determine the optimum condition of three significant parameters for AgNPs production was done. To the best of our knowledge, so far

no published method has been reported in literature on developing the artificial neural network (ANN) model for improving the yield of AgNPs production process. Ultra violet visible spectroscopy (UV-vis) and Field Emission Scanning Electron Microscopy (FESEM) were used to characterize the silver nanoparticle.

EXPERIMENTAL DESIGN

In this study, the AgNPs yield (380 nm to 450 nm) is considered as the response parameter, such as $AgNO_3$ concentration, stirring time, whereas the reducing agent (tri-sodium citrate) concentration was selected as AgNPs production variable.

Silver nanoparticle production predictive modeling and optimization using ANN

In a typical experiment, 20 mL of 0.001M $AgNO_3$ was kept at 90°C for 5 minutes on a hot plate. After 5 minutes, 2.5 mL of 1% tri-sodium citrate was added drop-by-drop. Once the reduction process begins, the colour changed and the solution turned into pale yellow, the solution was then placed on to a magnetic stirrer for 15 minutes. 'Yield' is represented by the estimated area under the spectral curve from 350 to 420 nm wavelength (Figure-1), which represented the quantitative presence of AgNPs with approximate sizes of 5-50 nm [8, 9].

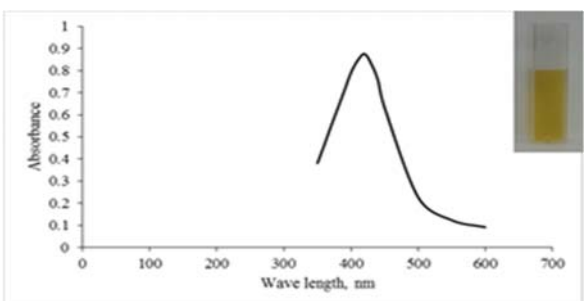

Figure-1. UV-vis spectra of AgNPs at optimized condition. Inert: visual pale yellow colour of AgNPs solution.

Predictive modeling and optimization using ANN

ANN is a mathematical model that loosely approximates the biological neural network function. A multilayer perception (MLP) is a commonly used feed-forward ANN consisting of three or more layers of neurons, where the first layer represents the independent variable. Each of the neuron of first layer connected with one or more layers of hidden neurons that represent nonlinear activation functions and all of these neurons are connected to the final level of output neuron through the learning algorithm. However, this study used ANN to build a predictive model with three input parameters with AgNPs yield (Area*) as the response parameter and experimental design were presented in Table-1. ANN was developed in MATLAB (Version 2015b). To determine the optimal network topology, the best number of hidden neurons was determined by heuristic trial and error. Each network was trained until mean square error (MSE), average correlation coefficient (R) and average determination coefficient (DC) were higher than 0.9 and lower than 0.01 respectively. The ANN predictions were then used to generate a 3D output surface. The response was calculated using UV-vis analysis in the wavelength range of 350 to 420 nm. After determination of the optimized conditions, further characterization was tested for silver NPs, where a freeze dried sample was used for FESEM.

Characterization of silver nanoparticle

After obtaining the optimized conditions from statistical analysis, silver nanoparticles were found to have unique optical properties as they are extraordinarily efficient at absorbing and scattering light. Spherical silver nanoparticles have Surface Plasmon Resonance (SPR), at the wavelength of 300 nm to 600 nm in a Multiskan™ GO Microplate Spectrophotometer. FESEM (JEOL JSM 6700F), was used to characterize the morphological shape and size of silver nanoparticles.

Table-1. Experimental design for ANN using three independent variables combination and AgNPs yield as experimental response along with ANN predicted value.

TSC	Time	$AgNO_3$	ANN experimental	ANN predicted
0.5	10	0.5	7.07088	7.095933
1.5	10	0.5	12.1892	12.19246
0.5	20	0.5	11.22029	11.21236
1.5	20	0.5	9.900494	9.918625
0.5	10	1.5	20.6941	20.38611
1.5	10	1.5	11.17222	11.17315
0.5	20	1.5	29.65991	27.09
1.5	20	1.5	13.60886	13.64301
0.5	15	1	20.13978	20.11168

1.5	15	1	13.43712	13.44699
1	10	1	16.1538	16.15207
1	20	1	18.39006	16.34809
1	15	0.5	9.449257	9.448177
1	15	1.5	14.3159	12.70211
1	15	1	19.83665	19.83725
1	15	1	19.83665	20.62133
1	15	1	19.83665	20.22929
ANN testing set: bold and italic ANN validation set: bold				

RESULT AND DISCUSSIONS

In order to determine, an optimal ANN architecture and suitable topology, which is highly important for a successful application, several ANN architectures and topologies were tested for the estimation and prediction of silver nanoparticle yield (Area*) production. Table-2 summarized the top eleven ANN model based on learning algorithms and the number of hidden neurons.

The effect of learning algorithm and transfer function

Training a neural network model is critically important to select one model from the set of allowed models that maximizes the silver nanoparticle (AgNPs) production yield. This study tested different algorithms available in input-output and curve fitting functions in Matlab. In order to accept the model, the neural network fitting function evaluated the performance using mean square error (MSE) and regression analysis, and all accepted model with MSE < 0.01 and R < 0.85 have shown that Levenberg-Marquadt-Backpropagation (LMBP) algorithm was the most suitable algorithm for the prediction of AgNPs yield production.

In order to apply the LMBP learning algorithm, this algorithm requires more memory but less time, and training automatically stops when generalization stops improving, as indicated by an increase in the MSE of validation sample. During training, a set of input is presented to a network provide in Table-1, where weight was randomly assigned, each neuron in the hidden and output layer first calculated the weighted sum of its inputs and passed the result through a transfer function to produce a predicted data set that corresponds to the input data set. The result is compared to the expected value and error to adjust the connection weight according to the learning weight. This procedure is repeated until the predetermined MSE is reached.

In the present work, hidden neurons with a two-layer feed-forward network with sigmoid tangent (Tanh) and linear output neuron function was present. The best model was obtained at 3-7-1 and 3-30-1 topology.

Table-2. The effect of different ANN architecture topology on R^2 and MSE in the estimation of AgNPs production obtain during training, testing and validation of ANN model (The top eleven ANN model based on learning algorithm and the number of hidden neurons).

ANN structure (input-hidden-output layer)	Learning algorithm	Connection type	Training Set		Validation set		Testing set	
			MSE	R^2	MSE	R^2	MSE	R^2
3-3-1	LMBP	MFF	0.017722	0.49593599	0.015596	0.997955	0.057408	0.967815
3-5-1	LMBP	MFF	1.10E-20	1	0.017343	0.806461	0.015891	0.31234
3-7-1	LMBP	MFF	3.81E-05	0.99954885	0.00622	0.954411	0.098604	0.956602
3-10-1	LMBP	MFF	3.15E-03	0.96857618	0.025211	0.998666	0.068138	0.930408
3-14-1	LMBP	MFF	2.13E-17	1	0.050535	0.994727	0.072125	0.92068
3-17-1	LMBP	MFF	4.47E-07	0.99999515	0.050497	0.864464	0.002749	0.998845
3-20-1	LMBP	MFF	4.48E-05	0.99915224	0.059938	0.94588	0.04134	0.641162
3-24-1	LMBP	MFF	0.002484	0.98193238	0.174578	0.999267	0.054828	0.968498
3-27-1	LMBP	MFF	3.81E-05	0.99925353	0.036644	0.997864	0.035418	0.934672
3-30-1	LMBP	MFF	3.83E-07	0.99999412	0.003147	0.959321	0.077122	0.971386
3-35-1	LMBP	MFF	3.81E-05	0.99949645	0.074697	0.986896	0.347016	0.937982

Optimal number of hidden neurons

Optimal number of hidden neuron selection is highly important and the selection needs to be carefully done, depending on the type and complexity of the task, which is usually done by trial and error. The increase of hidden neurons up to a certain amount presents a better learning performance, whereas too little hidden neurons limit the ability of model performance and too many allows much freedom for the weight to be adjusted, which create noise in database that is used for training [5]. This study presents the effect of hidden neuron numbers in terms of checking goodness of fit. On the basis of statistical analysis presented in Table-2, the MSE for validation is minimum at neuron 7 and neuron 30, and the coefficient of determination (R^2) values are also high for all three training, testing and validation set data for both models. Then, both topology 3-7-1 and 3-30-1 were chosen for further analysis.

Figure-2 presents the comparison between experimental productions of AgNPs yield and predicted values using both topology 3-7-1 and 3-30-1. The R^2 value was 0.9778 of model 3-30-1 presenting the better fit of experimental data than the 3-7-1 topology R^2 value which was 0.8803. The 3-30-1 topology were chosen as the best model for AgNPs production due to better prediction capability.

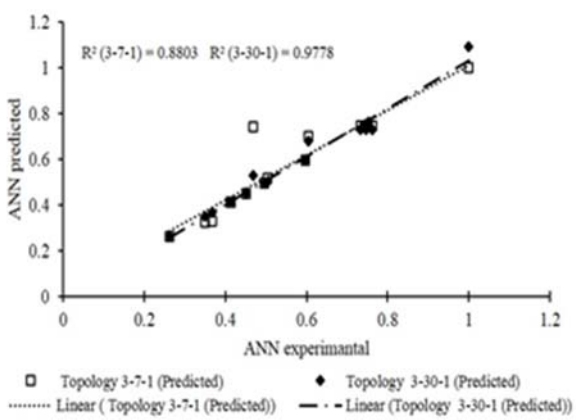

Figure-2. Correlation plot between ANN actual and predicted value.

Artificial neural network analysis for silver nanoparticle production

In this study, the best ANN model was found to have two-layer feed-forward network with sigmoid tangent (Tanh) hidden neuron function and linear output neuron function. The model has 30 hidden neurons. In this model, the learning process completed at MSE $=3.83^{-07}$ and $R^2 = 1$. Similarly, for the testing data set MSE = 0.077122 and $R^2 = 0.97$, and for validation data set MSE = 0.003147 and $R^2 = 0.96$. Comparison of experimental and predicted data value in training, testing and validation data sets, proved that the capability of the ANN model prediction for known data sets, along with derived model from ANN can be used to satisfactorily describe the relationship between input and output of AgNPs production.

Furthermore, numerical optimization searches the design space using the developed model. Desirability is simply a mathematical model to find optimum goal. Using ANN model matrices of AgNPs production parameter and output obtained from ANN, it is possible to visualize the comparative relation between each combination of run to produce a 3D surface plot. The third variable were constant for each plot at its middle value (1mM $AgNO_3$ and 15 min of stirring time) to generate a 3D surface plot, as presented in Figure-3 and Figure-4. U-shaped 3D response surface curve in Figure-3 suggested that there were optimized conditions of $AgNO_3$ concentration effect on Ag NPs yield and the stirring time effect on yield production is almost constant. Similarly, in Figure-4 when the stirring time increased, the yield increased and TSC concentration effect on yield production is almost constant. Hence, it can be seen from the 3D plot, the numerical optimization finds a point that maximizes the production. This work objective is to maximize the AgNPs production. Optimal and maximal AgNPs production was 20.62 of yield, experimentally at 1mM $AgNO_3$ concentration, 15 min of stirring time and 1% tri-sodium citrate, which was calculated using the area under the curve from UV-vis analysis in the wave length range of 350 to 420 nm. Whereas the ANN predicted value is 19.84 of AgNPs yield with 3.95% error at optimum condition.

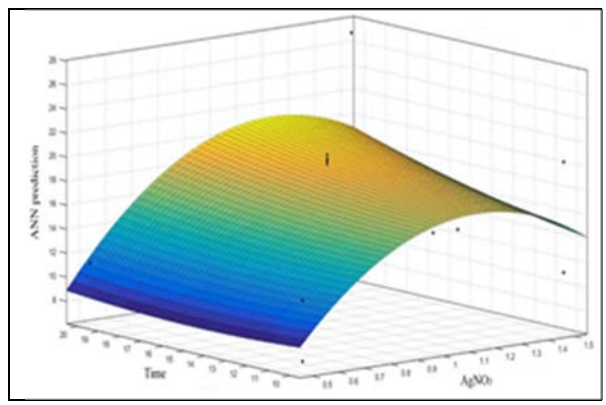

Figure-3. 3D interaction plot of ANN predicted AgNPs yield, interaction of $AgNO_3$ and stirring time.

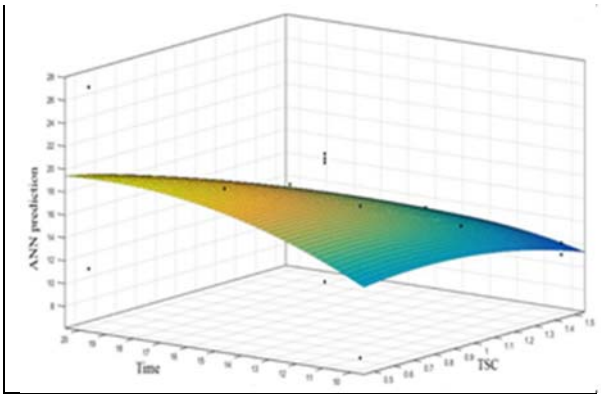

Figure-4. 3D interaction plot of ANN predicted AgNPs yield, interaction of TSC and stirring time.

Characterization of AgNPs using spectroscopic analysis and FESEM

UV-vis spectroscopy is a technique used to quantify the light that is absorbed and scattered by a sample (a quantity known as the extinction, which is defined as the sum of absorbed and scattered light). These measurements were compared at each wavelength to quantify the sample's wavelength-dependent extinction spectrum. The data was typically plotted as extinction as a function of wavelength. Each spectrum was background corrected, using a buffer blank, to guarantee that spectral features from the buffer was not included in the sample extinction spectrum. However, the sample presented the characteristics of surface plasmon resonance; 5-50 nm silver nanoparticles presented a narrow band with a maximum at approximately 404 nm, which is almost similar in this study as shown in Figure-1. It is reported that the absorption spectrum of spherical silver nanoparticles presented a maximum peak at 420 nm wavelength [10] and the suspension colour is pale yellow [11], as seen in Figure-1.

The FESEM image in Figure-5 confirmed that small and uniform AgNPs exist, which also confirmed that the average particle size is around 10-20 nm in diameter and the AgNPs shape is spherical silver. Large particles are also available in the image due to the aggregation property of AgNPs [12].

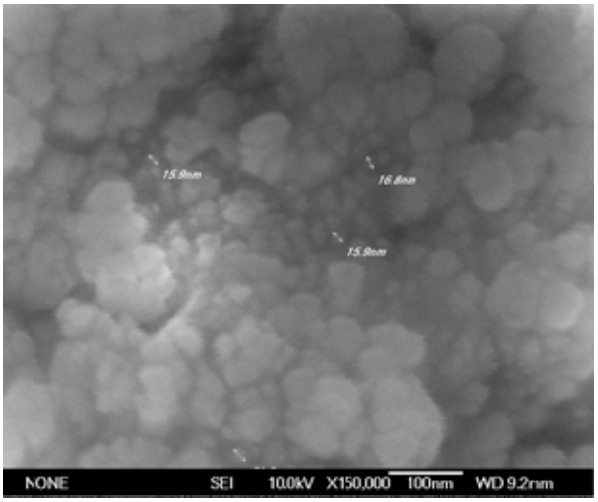

Figure-5. FESEM image of silver nanoparticle with diameter.

CONCLUSIONS

In this study, the impact of $AgNO_3$ concentration, stirring time and tri-sodium citrate concentration was investigated for silver nanoparticle production and the artificial neural network was used for modeling and predicting the production rate of silver nanoparticles. The developed ANN model gave the smallest MSE, a two-layer feed-forward network with sigmoid tangent (Tanh) hidden neuron function, linear output neuron function, and a model containing 30 hidden neurons and LMBP algorithm. However, the optimal and maximal AgNPs production was 20.62 of yield, experimentally at 1mM $AgNO_3$ concentration, 15 min of stirring time and 1% tri-sodium citrate, which was calculated using area under the curve from UV-vis analysis in the wave length range of 350 to 420 nm. On the other hand, the ANN predicted value is 19.84 of AgNPs yield with 3.95% error at optimum condition. Thus, ANN is a very powerful and flexible tool for the modeling the optimization process.

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