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Studies on the Applicability of Artificial Neural Network (ANN) in Evaluation of Photocatalytic Performance of TiO_2 thin Film Doped by SiO_2

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Abstract: Nanocrystalline films of TiO_2 and TiO_2:SiO_2 with high photocatalytic activity were prepared on glass substrates by the application of sol-gel method. Then the films were subjected to a high temperature treatment at 500˚C, which resulted in growth of TiO_2 crystals. Afterwards the TiO_2:SiO_2 films were in contact with an aqueous solution (10 $mg.L^{-1}$) of methyl orange (MO) and irradiated under UV. The resulted films showed a high photocatalytic activity. In the current study the photocatalytic activity of TiO_2 crystals was studied by an Artificial Neural Network (ANN). This was achieved by predicting the concentration of MO in various values of SiO_2 concentration and time of degradation. In order to perform the modeling, Multi-layer Perceptron (MLP) network was used in this work, with its learning algorithm being Levenberg-Marquardt (LM). The outcome of modeling showed that there was an excellent agreement between the results of simulation and the data obtained from the experiments. It is worth noting that in the current work, the methods applied in recent papers and patents for the preparation of nanocrystalline films and determination of their photocatalytic performance and also modeling of such processes have been studied.

Keywords: Photocatalytic activity, thin film, Artificial Neural Network, Sol-gel, Multi-layer Perceptron, Simulation.

1. INTRODUCTION

The result of interactions between the electrons and holes that are generated in an activated solid (semiconductor) and its surrounding medium (electrolyte) is photocatalysis phenomenon [1-3]. Recently, the application of this phenomenon has been focused on environment protection processes such as purification and air and water treatment [4-6]. Photocatalitic activation occures as a result of light absorption. Electron–hole pairs, which are formed in semiconductor as the result of light absorption, may recombine or participate in reductive and oxidative reactions [1]. TiO_2, ZnO, MoO_3, CeO_2, ZrO_2, WO_3, α-Fe_2O_3, SnO_2 and various metal oxide semiconductors are used as catalysts in photocatalytic reactions [1, 7]. There are many patents that studied photocatalytic activity of TiO_2 films. Anazaki *et al.* produced TiO_2 photocatalyst by their coverage on substrates of SiO_2 and ZrO_2. The resulted photocatalyst had a homogeneous surface and also could be used in optic applications [8]. Prochazka *et al.* doped TiO_2 photocatalyst using phosphorus, which improved its efficiency [9]. Yu *et al.* produced TiO_2 photocatalyst by sol gel method, which then was used to remove the virus and bacteria [10]. In the present study, nanocrystalline thin films of TiO_2:SiO_2 were prepared by sol-gel method and then their photocatalytic activity was measured based on the degradation of methyl orange (MO). Sol-gel method is a type of polymerization process; in fact it is the synthesis of mineral networks as a result of chemical reactions in a solution at relatively low temperatures.

Many researches have been performed on the prediction of the efficiency of photocatalytic activity of TiO_2 [11-16]. Most of equations which were used in these modeling studies are not applicable for a wide range of conditions in various processes, because they are only appropriate for a certain set of conditions and they could be used under some specific assumptions. Therefore the significance of techniques which are based on experimental data and their development to predict the result of processes seems to be obvious. Among these techniques, artificial neural network (ANN) is an excellent tool to predict the results of processes using experimental data. Similar studies have proved this fact [17-20]

The purpose of this study is to simulate the behavior of photocatalytic activity of TiO_2 using ANN. ANN has a wide range of applications in various fields, including finance and economics, robotics, material science, chemistry, chemical engineering, and etc. [21]. Because of the capability of ANN in simulation of several processes, the number of researches about its applications in chemical engineering has been increased recently.

In this contribution we tried to train a network with an appropriate architecture that was trained to simulate the concentration of MO. The experimental data resulted from laboratorial experiments of photocatalytic activity measurement were used to train the multi-layer perceptron (MLP)

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network by Levenberg -Marquardt (LM) learning algorithm. The agreement between the results of the modeling and the experimental data was acceptable.

2. THEORY

The application of ANN as an accurate and powerful tool to solve the problems, in which the mathematical modeling is neither possible nor practical has been developed in recent two decades. In such problems the information about the effective parameters may not be available or the relations between the data are very complex.

A neural network (NN) is considered as a processor that stores the experiential data for further applications. NNs obtain their knowledge during the training step. Then, the information will be stored using connections between neurons. ANNs can be different from each other in different aspects such as architecture, topology and the algorithms applied during the learning procedure [21]. Each ANN has three layers that neurons are arranged in these layers: input layer, hidden or intermediate layer, and output layer. A network can consist of many neurons that are connected to each other. Each connection has a specific weight. The input layer collects the signals and then distributes them, while the neurons in the hidden layers do the actual processing.

In mathematical terms, a neuron k can be described by the equations as below:

$$u_k = \sum_{j=1}^{m} w_{kj} x_j \tag{1}$$

$$y = \varphi(u_k + b_k) \tag{2}$$

Where x_j is the input signal, w_{kj} is the weight of neuron k, u_k is the linear combiner output due to the input signal, b_k is the bias, $\varphi(\bullet)$ is the activation function and y_k is the output signal of the neuron.

Due to its structure, MLP network is one of the most widely used networks to design the controllers and other systems. The number of hidden layers of MLP network can be considered more than one, but several researches have shown that a network with one hidden layer can be used to predict the procedure of non-linear problems [22, 23]. During the modeling procedure the output value is compared with the desired output and the error between them is used to adapt the weights. The structure of a typical MLP network is illustrated in (Fig. **1**).

In comparison with the Gradient Descent (GD) method, Levenberg-Marquardt method is more stable and would converge faster during the training step [24]. Therefore, in this study the LM training algorithm is applied for training step. During the training step, the weights are determined using the following equation:

$$W_{k+1} = W_k - [J_{W_k}^T J_{W_k} + \mu_k I]^{-1} * J_{W_k}^T V_{w_k} \tag{3}$$

Where W_{k+1} and W_k are the matrixes of weights in $K+1^{th}$ and K^{th} repetition, J is the Jacobian matrix, V is the vector of accumulated errors, I is the identity matrix, and μ_k is used to define a specification of LM in changing the searching method between Gauss-Newton and Steepest Descent Algorithms [25].

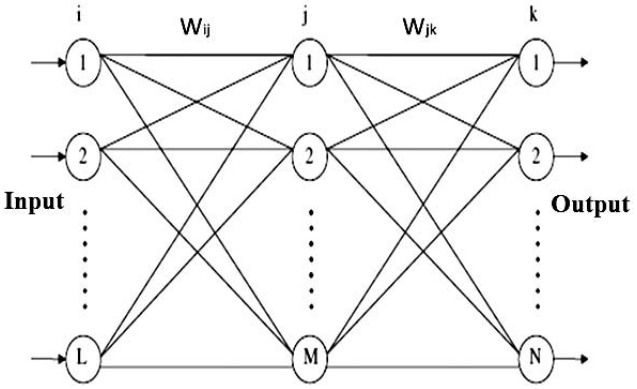

Fig. (1). Schematic of MLP Structure.

In the current study, the number of hidden layers is considered one. The optimized number of neurons in the hidden layer is determined by the trial and error technique; it is worth noting that the transfer functions of hidden and output layers are linear.

In order to investigate the efficiency of ANN for studying the photocatalytic activity of TiO_2, the statistical parameters including squared correlation coefficient (R^2), standard squared error (SSE), mean squared error (MSE), root mean squared error (RMSE) and normalized bias (NB) were calculated. The equations of these parameters are as the followings:

$$R^2 = \frac{\sum_{i=1}^{n}(Y_{\exp,i} - Y_{Model-Mean})^2 - \sum_{i=1}^{n}(Y_{Model,i} - Y_{\exp,i})^2}{\sum_{i=1}^{n}(Y_{\exp,i} - Y_{Model-Mean})^2} \tag{4}$$

$$SSE = \sum_{i=1}^{n}(Y_{Model,i} - Y_{\exp,i})^2 \tag{5}$$

$$MSE = \frac{\sum_{i=1}^{n}(Y_{Model,i} - Y_{\exp,i})^2}{n} \tag{6}$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(Y_{Model,i} - Y_{\exp,i})^2}{n}} \tag{7}$$

$$NB\% = \sum_{i=1}^{n}\frac{(Y_{Model,i} - Y_{\exp,i})/Y_{\exp,i}}{n} \tag{8}$$

In these equations $Y_{exp,i}$ is the concentration of MO obtained from the experiments, $Y_{Model,I}$ is the concentration of MO calculated by the model, $Y_{Model\text{-}Mean}$ is the average of data predicted by the model, and n is the number of data which is used in the modeling process. Time of degradation of MO and the concentration of SiO_2 were considered as the inputs of the network and MO concentration was the output.

3. MATERIAL AND METHOD

Tetra isopropoxy titanium (TTIP, Merck), tetraethyl orthosilicate (TEOS, Merck), ethanol, hydrochloric acid, and

acetylacetone (ACAC, Merck) were commercially obtained and used for the preparation of the target solution without further purification [1-4]. For the synthesis of the starting solution, TTIP (8.8 ml) was dissolved in ethanol (143 ml) solution that contained hydrochloric acid (0.5 ml) and water, then TEOS (5, 10, 15 mole percent) was added to the resulted solution. Afterwards, ACAC (2 ml) was added to stabilize TiO_2. The solution then was mixed magnetically for 2.5 hr [1, 2]. Finally, the sols were aged in a sealed beaker for 24 hours [1].

TiO_2:SiO_2 thin films were prepared by dipping the glass slides in the aged solution at a drawing speed of 70 cm min^{-1}. These films were dried at room temperature for 15 minutes, followed by calcination at 500 ˚C and for 4 hours. Finally they were cooled in the oven to room temperature. The double and multi-layer films are obtained by repeating the above procedures properly. Four types of films were prepared. In order to measure the concentration, 5ml of MO was added to them; afterwards the sampling was done from the resulted solution every 60 minutes. The volume of SiO_2 which was used to prepare the films of 5% SiO_2, 10% SiO_2, and 15% SiO_2 were 0.35ml, 0.7ml, and 1ml, respectively.

3.1. Photocatalytic Activity Measurement

MO solution and a high pressure mercury lamp (125 W) were used for measuring the photocatalytic activity of TiO_2 thin film. MO powder ($C_{14}H_{14}N_3NaO_3S$) was dissolved in distilled water at 10 $mg.L^{-1}$ concentration, after that the films (2 mm×2 mm) of TiO_2:SiO_2 were drawn off and settled in 5 ml MO under UV irradiation, while one side of TiO_2 thin films were irradiated with UV lamp. The average intensity of UV irradiance was 6.8 $mW.cm^{-2}$, which was measured by a UV irradiance meter. The photocatalytic decolorization of MO is a pseudo-first order reaction, and its kinetic may be expressed by the following equation [5, 26]:

$$\ln\left(\frac{C_0}{C}\right) = kt \tag{9}$$

Where k is the reaction rate constant, C_0 and C are initial and final concentration of MO, respectively. During the photocatalytic reaction the presence of oxygen and moisture on the photocatalyst surface stimulates the activation of the photoreaction during light irradiation. The photocatalyst surface is excited by the light photons and adsorbs dye molecules. Consequently, the singlet excited state can be produced.

In this paper, four films with different concentrations of SiO_2 (0%, 5%, 10%, and 15%) were used as photocatalysts. UV spectrophotometry technique was used to monitor the degradation of MO (in contact with the films) by the reduction of main absorbance peak at 464 nm. As mentioned above, Concentration of MO was measured every 60 minutes with UV spectrophotometer system. Fig. (**2**) shows the procedure of photocatalytic activity measurement schematically.

4. RESULTS AND DISCUSSION

In the current study, the data are normalized between 0 and 1 prior to training. The input variables to network are two operating variables including time of degradation of MO and the mole percentage of SiO_2, while the output is MO concentration. The structure of ANN that was used for this procedure is shown in (Fig. **3**).

As it can be seen, the network consists of three layers. The input layer has two input nodes corresponding to two operating variables (Mole percent of SiO_2 and Irradiation time). These input nodes are connected to neurons of the hidden layer (as mentioned above, this network has one hidden layer) which perform the actual processing. The input vales are straightly sent to hidden layer where the weighted sum of input is calculated. The output layer has one node corresponding to concentration of MO. The results of processing are sent to these output nodes by weighted connections. A set of weighted values are estimated initially, then they are gradually corrected during the training step where the predicted values are compared to actual vales. In order to determine the appropriate weight adjustments (for the minimization of the errors), the errors are back propagated.

75% of these data (12 samples) are used for training. The difference between the value of validation data and the data calculated by the network must be minimum to adjust the number of neurons of hidden layer. The validation and testing are done using the remaining data, and the number of neurons of hidden nodes is adjusted in a way to achieve the minimum deviation between the validation data and the neural network output. As mentioned before, the MLP network is used in this study.

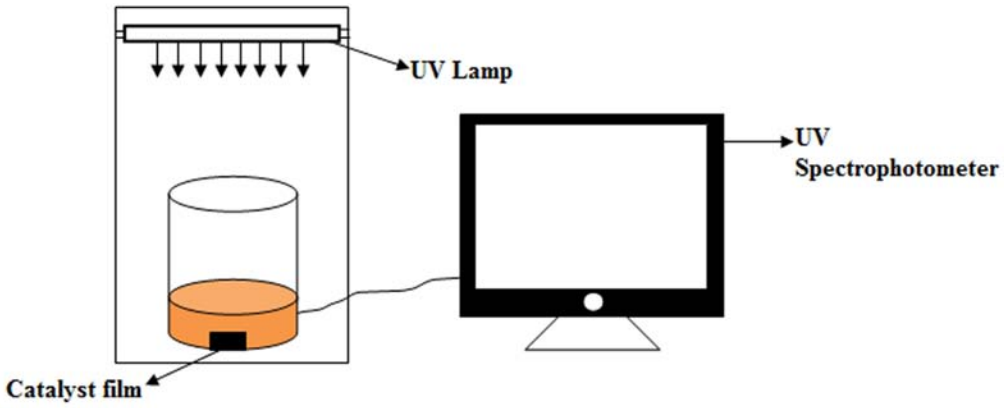

Fig. (2). Photocatalytic activity measuring system.

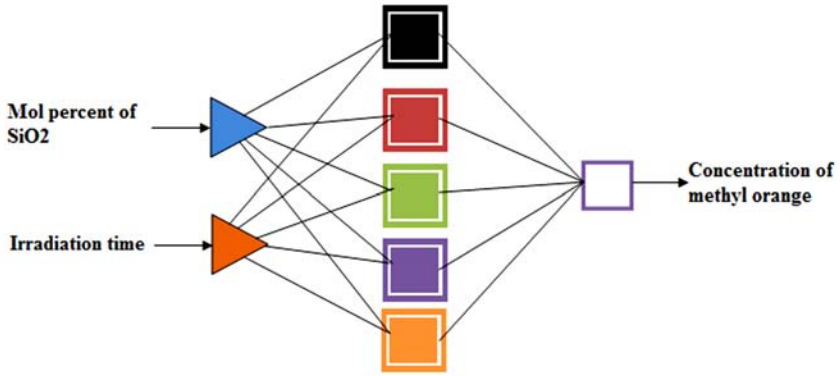

Fig. (3). A typical neural network architecture for two input variables.

In order to predict the values of MO concentration by ANN, the network was trained by the experimental data. In order to evaluate the capabilities of ANN, the model was presented with the new values of MO concentration that were not part of the training data set. Here, MO concentration values determined by the model were compared to the actual values of MO concentration resulted from the experiments. Fig. (**4**) allows easy visual comparison between the predicted MO concentration values and its actual values. The output tracks the targets very well and the R-value is over 0.99. In this case, the network response is satisfactory. According to this figure and Table **1**, the results of the modeling have the R-value of 0.99908 for the training data and 0.99446 for all of sets of data, which indicates the accuracy of ANN to predict the MO concentration. Additionally, the reported errors (SSE, MSE, RMSE) in Table **1** reveal a minor error in prediction of MO concentration, which is the mark of the capability of the model in predicting the values of this parameter. NB value shows that the data predicted by the model are a little higher than the experimental set of data.

Fig. (**5**) presents the ANN predictions versus the actual data of MO concentration. The squared correlation coefficient, R^2, shows how well the variation in the output was illustrated by the target. The determination coefficient (R^2 = 0.9996) reveals a good agreement between actual and the predicted data, which confirms the accuracy of ANN and is a measure of good fitting between the experimental and predicted data.

Table 1. Statistic Information and Number of Optimized Neurons in Hidden Layer

Value	Parameter
0.999517	R^2
0.000470794	SSE
3.92328×10^{-5}	MSE
0.006263611	RMSE
0.010937019	NB%
5	Optimized neurons in hidden layer

Comparison between the simulation results from AAN model and the experimental data (actual data) is illustrated in

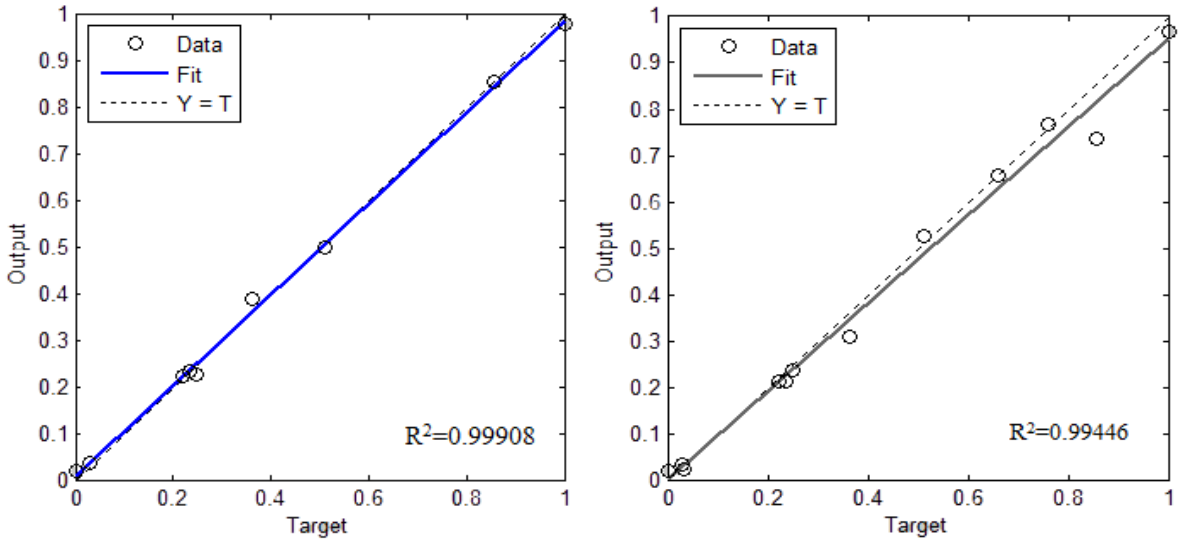

Fig. (4). Regression plot of the training data set and all the prediction set.

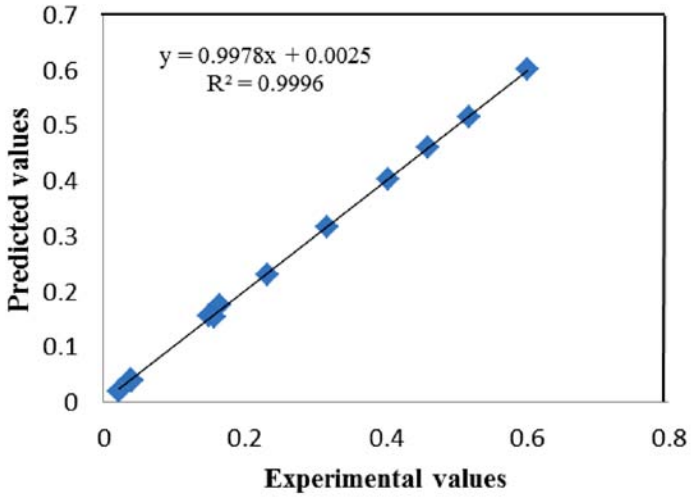

Fig. (5). Correlation between experimental and predicted values of MO concentration calculated by ANN.

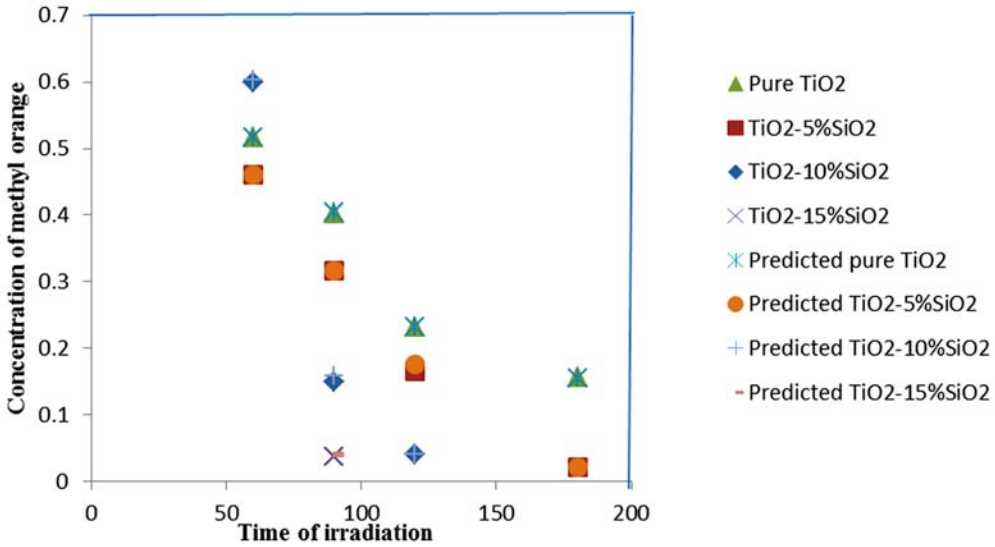

Fig. (6). Comparison between experimental data and predicted data by ANN for MO concentration.

(Fig. **6**). It can be observed that the sampling procedure for the 0% and 5% SiO_2 films was done every 60 minutes for 4 hours, for 10% SiO_2 film was done every 60 minutes for 3 hours, and finally the experiments was done only in 90 minutes for 15% SiO_2 film. The results indicated that there is an acceptable agreement between the simulation results and the actual data.

It is worth noting that the solution which was in contact with 15% SiO_2 film has made the solution colorless in a period shorter than 2 hours (90 minutes), therefore the reaction was finished after this period; apparently there would not be a reaction after this point.

Fig. (**7**) is represented here in order to illustrate the performance of ANN. It shows the evolution of training, validation and test errors as a function of the number of learning epochs. The training stopped when the network converged and the mean squared error is relatively constant over 7 iterations. In this study, the network was trained for 7 epochs to obtain the acceptable output errors.

5. CONCLUSION

The main conclusion of this study is that ANN can be a powerful tool for the prediction of MO concentration during the measurement of photocatalytic activity of TiO_2 in various conditions of irradiation time and mole percentage of SiO_2. In the present study the MLP network has one hidden layer with two input nodes and one output node. For the ANN model, the independent predicted target values were compared to measured MO concentrations and excellent correlation was found (R^2> 0.99). The figures reported for errors (SSE, MSE and RMSE) show minor error in prediction of MO concentration. In other words, the network has successfully followed the experimental concentration of MO in the system.

6. CURRENT & FUTURE DEVELOPMENTS

Considering the recent developments in production of photocatalysts, their applications in removal of pollutants in

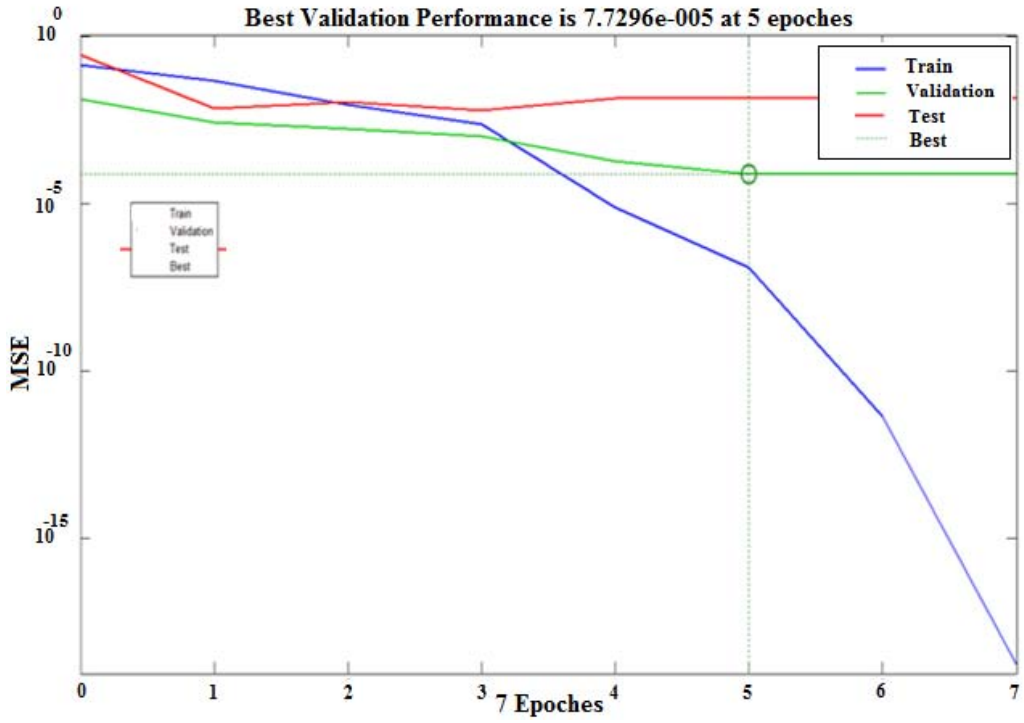

Fig. (7). Evolution of training, validation and test errors as a function of the number of learning epochs during ANN training.

short time is interested more than other related fields. Actually the future purpose is to use them as a tool to remove the pollutants spontaneously. Additionally it is expected that the techniques that are effective for the stabilization of photocatalysts on surfaces and also the improvement of their performance are the future developments of the current filed.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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NOMENCLATURE

Symbol

x_j	=	Input signal
w_{kj}	=	Weight of neuron *k*
u_k	=	Linear combiner output
b_k	=	Bias
$\varphi(\bullet)$	=	Activation function
y_k	=	Output signal of the neuron
W_k	=	Matrixes of weights in K^{th} repetition
J	=	Jacobian matrix
V	=	Vector of accumulated errors
I	=	Identity matrix
μ_k	=	Model Specification
$Y_{exp,i}$	=	MO Concentration (Experimental)
$Y_{Model,I}$	=	MO Concentration (Model)
$Y_{Model-Mean}$	=	Average of data predicted by the model
n	=	Number of data
k	=	Reaction rate constant
C_0	=	Initial concentration of MO
C	=	Final concentration of MO

Abbreviations

MO	=	Methyl orange
ANN	=	Artificial Neural Network
MLP	=	Multi-layer perceptron
LM	=	Levenberg -Marquardt
NN	=	Neural Network
GD	=	Gradient Descent
R^2	=	Squared correlation coefficient
SSE	=	Standard squared error
MSE	=	Mean squared error
RMSE	=	Root mean squared error
NB	=	Normalized bias

TTIP = Tetra isopropoxy titanium

TEOS = Tetraethyl orthosilicate

ACAC = Acetylacetone

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