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Intelligent Techniques for Photocatalytic Removal of Pollution in Wastewater

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Abstract: This paper discusses the elimination of C.I. AY23 (Acid Yellow 23) using UV/Ag-TiO_2 process. To anticipate the photocatalytic elimination of AY23 with the existence of Ag-TiO_2 nanoparticles processed under desired circumstances, two computational techniques namely NN (neural network) and PSO (particle swarm optimization) modeling are developed. A summed up of 100 data are used to establish the models, wherein introductory concentration of dye, UV light intensity, initial dosage of nano Ag-TiO_2 and irradiation time are the four parameters applied as the input variables and elimination of AY23 as the output variable. The comparison among the predicted results by designed models and the experimental data proves that the performance of the NN model is comparatively sophisticated than the PSO model.

Key words: Modeling, NN, PSO.

1. Introduction

The developed countries are facing a serious problem of water pollution caused by dyes. Synthetic dyes are the significant water contaminants and industrial pollutants. Azo dyes, the greatest class of synthetic dyes utilized in the food industries, are specified by the appearance of one or more azo bonds $(-N=N-)$ at par with one or more aromatic systems. In general, these dyes cannot be eliminated by conventional water treatment systems [1]. Hence the elimination of dyes from wastewater has become a matter of concern for the relevant industries. The advancement of highly efficient techniques for the removal of dangerous pollutants from air, soil, and water is one of the most active fields in environmental research [2]. Therefore, it has become a necessity for the development of highly efficient techniques for the elimination of organic pollutants by transformation to less adverse compounds or by thorough mineralization [3]. Currently, chemical treatment techniques on the basis of generating hydroxyl radicals, known as AOPs (advanced oxidation procedures) have been expanded [1]. An intense study of TiO_2 as a photocatalyst has been done for the reason of its immense chemical stability, without any toxicity, low cost and exquisite deterioration for organic pollutants [4]. The growth of UV/TiO_2 process to attain entire mineralization of organic pollutants has been extensively tested for a broad variation of industrial dyes [5]. Heterogeneous photocatalysis through amalgamation of TiO_2 and UV light is considered as one of the promising AOPs for the devastation of water-soluble organic pollutants observed in water as well as waste water. The hydroxyl radical is a dominant oxidizing factor that assails organic pollutants existing at or close to the surface of the TiO_2. The ultimate result is the entire decay of toxic as well as bioresistant compounds into non-injurious species like CO_2 and H_2O [6].

Generally, the behavior associated with photochemical system is quite complicated. Therefore, the advancement of reliable and robust predictive models is still required for the elimination of organic pollutants. Numerable modeling techniques based on artificial intelligence, like NNs and PSO have appeared as adsorbent tools and have represented a better

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potential for modeling complicated systems [3, 7-11]. Artificial NN is considered to be generalized models related to the biological neuron system and it is incorporated with hugely parallel distributed processors with a naturalistic proneness for accumulating information and preparing its availability for utilization. The training of NNs can be done with real data in order to take up issues related to complex and nonlinear problems where mathematical modeling may be too unsuitable or complicated. NN is on the basis of the empirical risk minimization that can make the solution be captured in a local minimum and over-fitting of the network [12].

PSO is a searching algorithm that is utilized for searching large and non-linear spaces where the knowledge of investigators is lagged and conventional optimization methodologies are not of use [13-15]. It is a strong evolutionary algorithm having the global optimization capability. The method is initially designed and generated by Kennedy and Eberhart [16]. In PSO, a set of arbitrarily produced agents (called particles) spread in the design space towards the optimal solution via a number of iterations. Every particle demonstrates a candidate solution related to the optimization problem. The location of a particle is effected by the superior location visited by itself (i.e. its own experience) as well as the location of the superior particle in its total population. The excellent location which is extracted is considered as the global best particle. The performance of each particle (i.e. how near the particle is from the global optimum) is computed by employing a fitness function which changes based on the optimization problem [17, 18].

Since a very fewer research works have been done on the application of NN and PSO in water sector [19], so the primary aim of this paper is the generalization of two techniques based on the NN and PSO in order to estimate the elimination of C.I. AY23 by $UV/Ag-TiO_2$ process. Here we investigate the photocatalytic proficiency of the $Ag-TiO_2$ particles for elimination of AY23 (Acid Yellow 23) as a refractory pollutant. The consequence of utilizable key factors such as initial dye concentration, UV light intensity, irradiation time and dosage of $Ag-TiO_2$ nanoparticles has been discussed. A limited data set obtained from the literature has been utilized, and the NN and PSO techniques have been generalized on the basis of predictive models for the elimination of AY23 in water by using a set of selected water quality. Predictive potencies of the generalized models are verified by utilizing multiple statistical performance criteria parameters. This paper has a significant contribution and is the first attempt in initializing a superior starting point for the removal of AY23 in water by $UV/Ag-TiO_2$ process and PSO and NN modeling.

2. Materials and Methods

2.1 Materials

Tetraisopropyl orthotitanate $Ti(OC_3H_7)_4$, methanol (MeOH) as well as silver nitrate ($AgNO_3$) are extracted from Merck (Germany) and utilized without any additional purifications. Acid Yellow 23 is brought from Acros (USA) and utilized without additional purification. Fig. 1 displays the chemical structure of this dye. Deionized water is employed throughout the work.

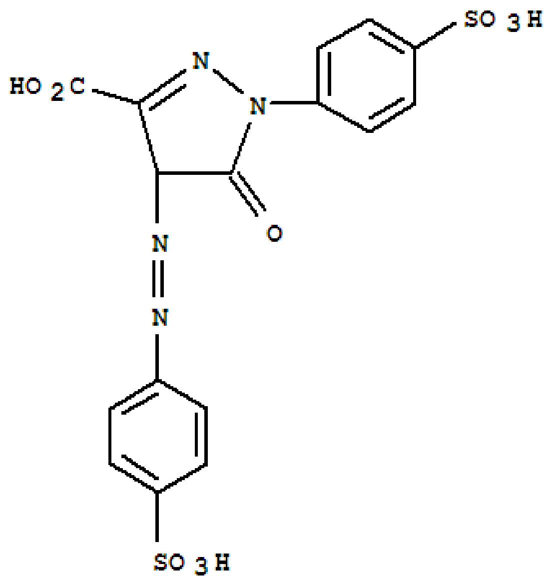

Fig. 1 Chemical formation of Acid Yellow 23 (AY23).

2.2. Ultrasonic Bath (T 460/H)

The ultrasonic bath Elma (GmbH) is utilized via the operating frequency of 34 KHz as well as a rate output power of 169 W. The bath contains the dimensions of 239 mm × 136 mm × 99 mm. The total internal structure is constructed from stainless steel.

2.3. Analytical Method

In the existence of Ag-TiO_2 as photocatalyst, AY23 is utilized as pollutant. Sample solutions are sonicated before irradiation for 4 min. At known irradiation time intervals, the samples (4 mL) are removed, afterward, analysis is carried out by UV-V which is spectrophotometer (Ultrospec 2000, Biotech Pharmacia, England) at 427 nm. A linear correlation is laid down in the midst of the AY23 concentration and the absorbance, in the range 0-50 mg/L having a correlation coefficient, $R^2 = 0.9981$. Eq. (1) is utilized in order to compute the photocatalytic eradication effectiveness (R, %) in the experiments

$$R = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \quad (1)$$

such that, C_0 (mg/L) as well as C_t (mg/L) are taken to be the initial concentration of AY23 and the concentration of AY23 at time *t* respectively.

2.4. Neural Network Method

In this paper, a three-layer feed-forward back propagation neural network is used for modeling the UV/Ag-TiO_2 process (Fig. 2). The input variables to the feed-forward neural network are stated as follows: initial concentration of dye (mg/L), UV light intensity (W/m^2), initial dosage of nano Ag-TiO_2 (mg/L), irradiation time (min). AY23 removal percentage (R, %) is chosen as the experimental response or output variable. The defined input-output variables in this proposed neural network have not been implemented in any other structures of neural network proposed by other researchers.

The MSE (mean square error) is utilized as the error function. MSE is calculated from the model predicted and actual measured values of the response variable as

$$MSE = 1/N \sum_{j=1}^{N} \left(A_j - Y_j\right)^2 \quad (2)$$

here, A_j and Y_j are the model predicted and measured values of the response variable, respectively, as well as *N* is total number of data points.

The train gradient descent is utilized with momentum and adaptive learning rate (traingdx), as a transfer function and the training-and-test technique to estimate the NN. Traingdx is a network training function which updates weight and bias values via gradient descent and an adaptive learning rate.

Here, feed-forward back propagation NN model is laid down to forecast the eradication of AY23 in water. The transfer functions in the hidden layer are considered to be linear, as well as in the output layer are taken to be log sigmoid. NN computations are carried out by utilizing Matlab 7.8 (2009R) mathematical software at par with NN toolbox.

2.5. Particle Swarm Optimization Method

PSO methodology is considered as an algorithm which utilizes plural points. The PSO on the basis of algorithm is generated in MATLAB environment. It is user friendly, also runs the algorithm for producing the outcomes more effectively with optimal error. One of the primary advantages of these kinds of concepts in comparison to other global minimization techniques is that the large number of members which generates the

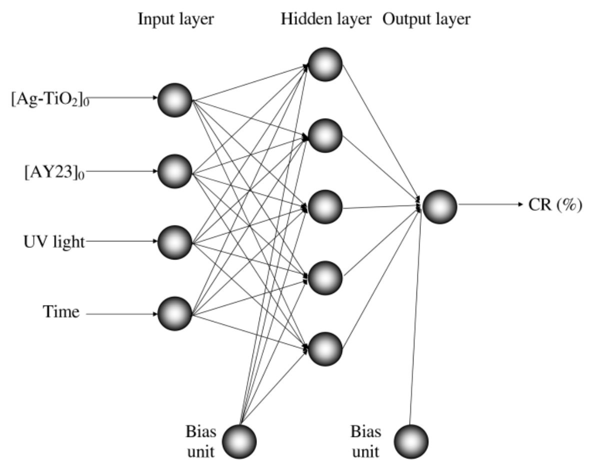

Fig. 2 Schematic diagram of the NN modeling approaches.

particle swarm causes the methodology impressively resilient to the problem of local minima.

Here, the capability of the PSO technique is proved to forecast the eradication of AY23 in water by utilizing the set of four operational variables termed as estimators. The total process of PSO is illustrated as a flowchart which is shown in Fig. 3.

2.6. The Dataset

This study attempts to generate artificial intelligence concept on the basis of predictive model for eradication of AY23 in water by utilizing a set of chosen variables termed as the estimators. Dataset which is utilized to generate the NN as well as PSO models in this paper, is based on the laboratory studies performed under statistical experimental design. Four parameters to be mentioned as primary dye concentration, UV light intensity, primary dosage of nano Ag-TiO_2 as well as irradiation time are selected as the input variables and eradication of AY23 as output variable. The range of variables which are discussed is summarized in Table 1. Out of the 100 data sets extracted via statistical design related to the study, 80 are utilized in order to train the models. The remaining 20 that were not included in the training, are demonstrated in order to test the models.

3. Models, Results and Discussion

In this work, two different techniques, NN and PSO have been applied in order to construct the predictive models for removal of AY23 in wastewater by implementing a set of four operational variables as the estimators.

3.1. Results and Discussion

Two different modeling methods NN and PSO are utilized in order to construct the predictive models for removal of AY23 in wastewater by implementing the same set of estimators. Here different numbers of neurons are tested from 2 to 16 in the hidden layer. Each topology is repeated six times to prevent random

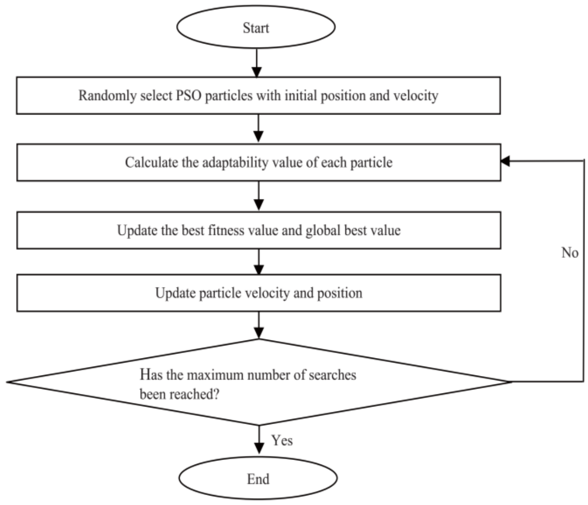

Fig. 3 Flowchart of PSO algorithm.

Table 1 Range of studied variables.

Variable	Range
Input layer	
Ag-TiO_2 initial dosage (g/L)	0.01-0.05
AY23 initial concentration (mg/L)	5-60
UV light intensity (W/m^2)	0-60
Irradiation time (min)	0-60
Output layer	
Removal of AY23 (%)	0-100

correlation considering random initialization of the weights. Figs. 4A and 4B state the relation between the network error and the number of neurons in the hidden layer in NN and PSO models respectively. It can be noticed that the performance of the network stabilized after inclusion of an adequate number of hidden units just about seven and six in NN and PSO models respectively. The network which includes more neurons in the hidden layer cannot approach effectively.

The training and validation outcomes extracted from NN along with PSO models are utilized to calculate several statistical validated specifications, as coefficient of determination (R^2), the root mean squared error (RMSE), the accuracy factor (A_f) as well as the Nash-Sutcliffe coefficient of efficiency (E_f). The chosen validated specifications are stated as mentioned below [20]:

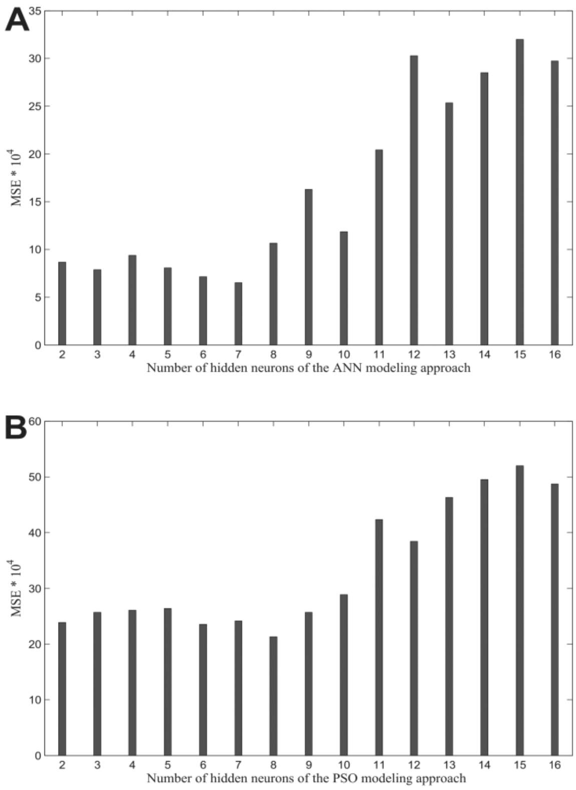

Fig. 4 Effect of the number of neurons in the hidden layer on the performance of the (A) NN and (B) PSO modeling approaches.

$$R^2 = \left[\frac{N\sum_{j=1}^{N} Y_j A_j - (\sum_{j=1}^{N} Y_j)(\sum_{j=1}^{N} A_j)}{\sqrt{\left[N\sum_{j=1}^{N} Y_j^2 - (\sum_{j=1}^{N} Y_j)^2\right] \times \left[N\sum_{j=1}^{N} A_j^2 - (\sum_{j=1}^{N} Y_j)^2\right]}}\right],$$

$$RMSE = \sqrt{\frac{\sum_{j=1}^{N}(A_j - Y_j)^2}{N}}, A_f = 10^{\left(\sum_{j=1}^{N}\frac{\left|\log\left(\frac{A_j}{Y_j}\right)\right|}{N}\right)},$$

$$E_f = 1 - \frac{\sum_{j=1}^{N}(A_j - Y_j)^2}{\sum_{j=1}^{N}(Y_j - \bar{Y})^2}$$

where, $\bar{Y}$ is the mean of the computed value related to the response variable. The coefficient of determination (R^2) exhibits the level of variability which is possible to be stated using the models along with RMSE which depicts an average measure of the error in forecasting related to the dependent variable. The preciseness factor (A_f), a straightforward multiplicative factor exhibits the diffusion of outcomes around the prediction. Forwardly, the greater the value of A_f, the minimal precise is the average estimate. The value of one designates that there exists a flawless consent between all the forecasted and the measured values [21]. The Nash-Sutcliffe coefficient of efficiency (E_f) which shows the model fit is a normalized measure (-∞ to 1) which compares the mean square error produced with the help of distinct model simulation to the variance of the target output sequence [22].

Considering both of the training as well as the validation sets, the model forecasted and experimentally computed values of the withdrawal of AY23 in water are displayed in Figs. 5 and 6, respectively. It distinctly reveals that the outcomes resulted from the NN model are in superior agreement along with corresponding experimental outcomes taking into account both the cases for the training (Fig. 5A) along with the validation sets (Fig. 6A).

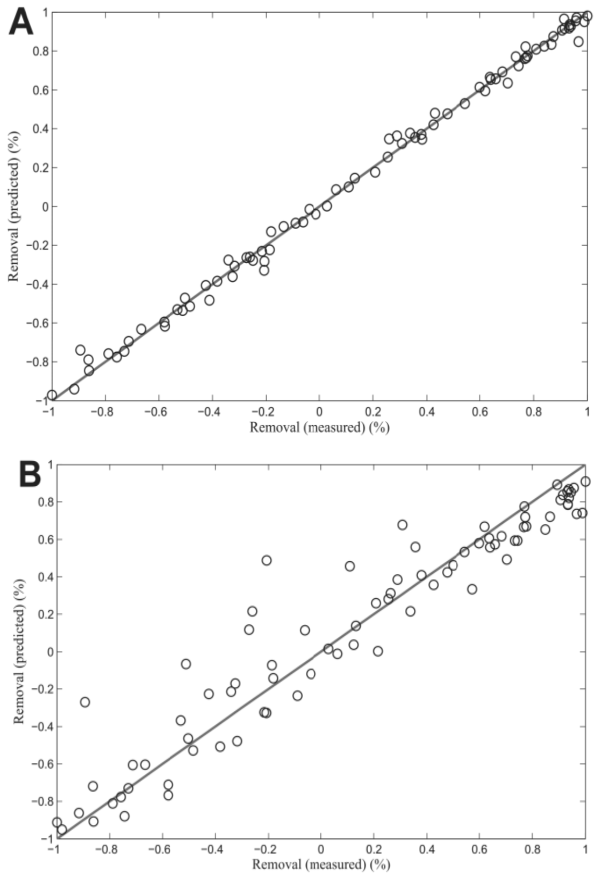

Fig. 5 Plot of the measured and predicted removal of AY23 in water by (A) NN, (B) PSO models in training set.

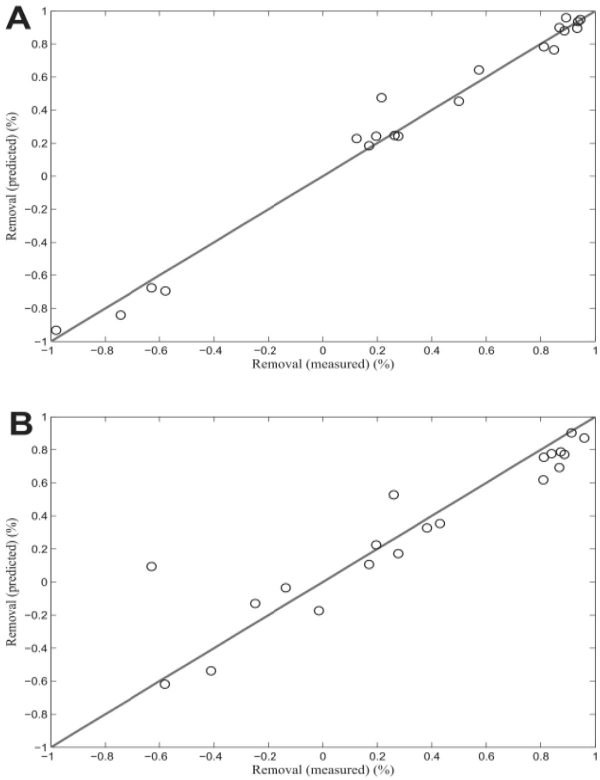

Fig. 6 Plot of the measured and predicted removal of AY23 in water by (A) NN, (B) PSO models in validation set.

Comparable values of the coefficient of determination (R^2) between the predicted and the measured levels of AY23 elimination authenticate the adequacy of the both modeling concepts for AY23 elimination forecast. The R^2 value of above 0.8 among two groups states that the two data are notably correlated [21]. Values related to A_f as well as E_f close to unity and low RMSE by NN and PSO models for both the training and validation sets affirm the superior extension and predictive capabilities of the two modeling techniques for the given data set.

Anyway, through the association amidst the measured and the predicted values of the response variable, both in the training and validation set (Table 2), it can be seen that the NN model carried out is relatively superior in comparison with PSO model.

The weights which are generated are listed in Tables 3 and 4 by gradient descent and PSO as training algorithms, respectively. The weights are coefficients among the artificial neurons, which are analogous to synapse strengths between the axons and dendrites in real biological neurons. Hence, every weight decides what proportion of the incoming signal will be transferred into the neuron's body [23].

The neural network weight matrix can be utilized in order to evaluate the relative importance of the multiple input variables on the output variables. An equation on the basis of the partitioning of connection weights is stated as follows [24]:

$$\boldsymbol{I_j} = \frac{\sum_{m=1}^{m=N_h}\left(\left(|W_{jm}^{ih}|/\sum_{k=1}^{N_i}|W_{km}^{ih}|\right)\times|W_{mn}^{ho}|\right)}{\sum_{k=1}^{k=N_i}\left\{\sum_{m=1}^{m=N_h}\left(\left(|W_{jm}^{ih}|/\sum_{k=1}^{N_i}|W_{km}^{ih}|\right)\times|W_{mn}^{ho}|\right)\right\}} \qquad (3)$$

where, I_j is termed as the relative significance of the j^{th} input variable on the output variable. W_s are termed as connection weights. N_i and N_h are the numbers of input as well as hidden neurons, respectively. The superscripts "i", "h" and "o" signify input, hidden as well as output layers, respectively. Subscripts "k", "m" and "n" signify input, hidden as well as output neurons, respectively.

The relative importance of input variables on the AY23 removal efficiency is exhibited in Fig. 7. It can be noticed that all variables have influences on the

Table 2 Performance statistics of the NN and PSO models.

Model	Sub-set	RMSE	E_f
NN	Training	0.04039	1.01256
	Validation	0.08076	1.04562
PSO	Training	0.17989	0.92895
	Validation	0.19699	0.91978

Model	Sub-set	A_f	R^2
NN	Training	1.00103	1.00685
	Validation	0.99001	1.02212
PSO	Training	0.96541	0.95131
	Validation	0.92142	0.91089

Table 3 Matrices of weights by gradient descent as training algorithm. W1: weights between input and hidden layers, W2: weights between hidden and output layers.

W1						W2	
Neuron	$[Ag\text{-}TiO_2]_0$	$[AY23]_0$	UV light	Time	Bias	Neuron	Weight
2	-0.082	3.940	14.211	1.286	9.752	2	-0.15
3	0.070	0.204	-0.092	0.221	-1.344	3	25.6
4	28.311	-15.42	-5.464	-13.37	-20.03	4	-0.10
5	-2.917	2.188	-2.978	0.235	-0.657	5	-0.27
6	3.043	1.473	2.946	2.971	1.648	6	0.29
7	-0.374	1.921	1.376	2.425	-3.305	7	-0.75
						Bias	21.2

Table 4 Matrices of weights by PSO as training algorithm. W1: weights between input and hidden layers, W2: weights between hidden and output layers.

W1						W2	
Neuron	$[Ag\text{-}TiO_2]_0$	$[AY23]_0$	UV light	Time	Bias	Neuron	Weight
2	-0.142	-0.719	0.951	-0.622	-0.999	2	0.462
3	0.012	-0.759	-0.379	0.832	0.867	3	0.497
4	-0.687	-0.251	0.101	-0.454	-0.002	4	-0.711
5	-0.549	-0.111	-0.571	0.291	-0.321	5	-0.402
6	-0.351	0.559	-0.889	-0.211	-0.101	6	-0.711
						Bias	-0.701

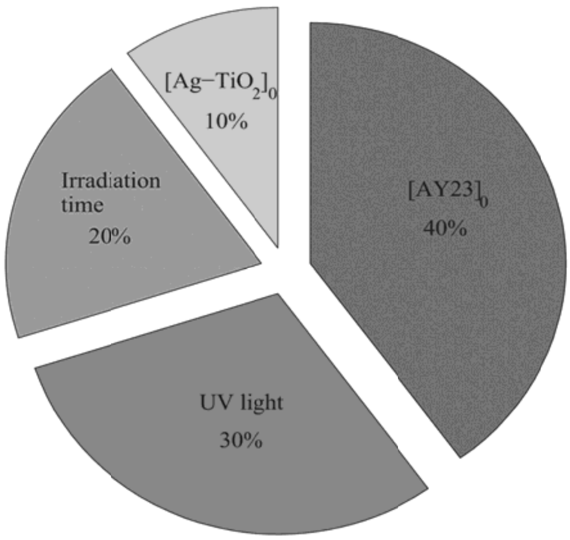

Fig. 7 Relative importance (%) of input variables on AY23 eradication effectiveness.

AY23 removal efficiency. However, the influence of AY23 initial concentration in comparison with others is more. So, none of the variables investigated in this paper could be neglected in the present analysis.

4. Concluding Remarks

In this paper, the withdrawal of AY23 by utilization of UV/$Ag\text{-}TiO_2$ operation is researched. Predictive and universalization abilities of the NN and PSO models in order to eliminate the AY23 in water are unearthed by the implementation of a statistically designed dataset gathered from the literature. The elimination of AY23 is successfully forecasted by implementing a three-layer neural network along with seven neurons related to the hidden layer in NN model as well as by implementing a three-layer neural network in addition to six neurons in PSO model. The comparison between the measured and the predicted values, in case of both training and validation set, shows that the NN model outperforms than the PSO model. As the progress of artificial intelligent methodology has been affected significantly from deficiency of training techniques, so it is taken into our consideration that our schemes cover up this emptiness and wish that they will result in several new applications.

References

[1] Behnajady, M. A., Modirshahla, N., and Ghanbary, F. 2007. "A Kinetic Model for the Decolorization of C.I. Acid Yellow 23 by Fenton Process." *J. Hazard. Mater*.

148: 98-102.

[2] Castro, A. L., Nunes, M. R., Carvalho, A. P., Costa, F. M., and Floreencio, M. H. 2008. "Synthesis of Anatase TiO_2 Nanoparticles with High Temperature, Stability and Photocatalytic Activity." *Solid State. Sci.* 10: 602-6.

[3] Cho, Y. R., Kim, H. S., Yu, Y. J., and Suh M. C. 2015. "Highly Efficient Organic Light Emitting Diodes Formed by Solution Processed Red Emitters with Evaporated Blue Common Layer Structure." *Scientific Reports* 5: 1-8. doi.10.1038/srep15903.

[4] Wang, H. W., Lin, H. C., Kuo, C. H., Cheng, Y. L., and Yeh, Y. C. 2008. "Synthesis and Photocatalysis of Mesoporousanatase TiO_2 Powders Incorporated Ag Nanoparticles." *J. Physics Chem. of Solids* 69: 633-5.

[5] Behnajady, M. A., Modirshahla, N., Daneshvar, N., and Rabbani, M. 2007. "Photocatalytic Degradation of an Azo Dye in a Tubular Continuous-Flow Photoreactor with Immobilized TiO_2 on Glass Plates." *J. Chem. Eng.* 127: 167-76.

[6] Khataee, A. R. 2009. "Photocatalytic Removal of C.I. Basic Red 46 on Immobilized TiO_2 Nanoparticles: Artificial Neural Network Modeling." *Environ. Tech.* 30: 1155-68.

[7] Chang, Y., Erera, A. L., and White, C. C. 2015. "Risk Assessment of Deliberate Contamination of Food Production Facilities." *IEEE Transactions on Systems Man & Cybernetics Systems* 47 (3): 381-93.

[8] Jafari, R., and Yu, W. 2015. "Fuzzy Control for Uncertainty Nonlinear Systems with Dual Fuzzy Equations." *Journal of Intelligent and Fuzzy Systems* 29: 1229-40.

[9] Jafari, R., Yu, W., and Li, X. 2017. "Numerical Solution of Fuzzy Equations with Z-Numbers Using Neural Networks." *Intell. Autom. Soft.* Doi: 10.1080/10798587.2017.1327154.

[10] Jafari, R., and Yu, W. 2017. "Fuzzy Differential Equation for Nonlinear System Modeling with Bernstein Neural Networks." *IEEE Access.* Doi: 10.1109/ACCESS.2017.2647920.

[11] Jafari, R., and Yu, W. 2017. "Uncertainty Nonlinear Systems Modeling with Fuzzy Equations." *Mathematical Problems in Engineering* 2017. https://doi.org/10.1155/2017/ 8594738.

[12] Kunwar, P., and Shikha, G. 2012. "Artificial Intelligence Based Modeling for Predicting the Disinfection By-Products in Water." *Chemometrics. Intell. Lab. Syst.* 114: 122-31.

[13] Chakraborty, P., Das, S., Roy, G. G., and Abraham, A. 2011. "On Convergence of the Multi-objective Particle Swarm Optimizers." *Information Sciences* 181: 1411-25.

[14] El-Wakeel, A. S., Hassan, F., Kamel, A., and Abdel-Hamed, A. 2013. "Optimum Tuning of Pid Controller for a Permanent Magnet Brushless DC Motor." *Int. J. Electr. Eng. Techno.* l4: 53-64.

[15] Fathi, V., and Montazer, G. A. 2013. "An Improvement in RBF Learning Algorithm Based on PSO for Real Time Applications." *Neurocomputing* 111: 169-76.

[16] Kennedy, J., and Eberhart, R. C. 1995. "Particle Swarm Optimization." In *Proceedings of IEEE International Conference on Neural Networks*, Perth. Australia 4: 1942-8.

[17] Delgarm, N., Sajadi, B., Kowsary, F., and Delgarm, S. 2016. "Multi-objective Optimization of the Building Energy Performance: A Simulation-Based Approach by Means of Particle Swarm Optimization (PSO)." *Applied Energy* 170: 293-303.

[18] Eberhart, R. C., and Kennedy, J. 2001. *Swarm Intelligence.* San Diego, CA: Morgan Kaufmann.

[19] Khajeh, M., Kaykhaii, M., and Sharafi, A. 2013. "Application of PSO-Artificial Neural Network and Response Surface Methodology for Removal of Methylene Blue Using Silver Nanoparticles from Water Sample." *J. Ind. Eng. Chem.* http://dx.doi.org/10.1016/j.jiec.2013.01.033.

[20] Karul, C., Soyupak, S., Çilesiz, A. F., Akbay, N., and Germen, E. 2000. "Case Studies on the Use of Neural Networks in Eutrophication Modeling." *Ecological Modeling* 134: 145-52.

[21] Smith, G. N. 1986. *Probability and Statistics in Civil Engineering.* London: Collins.

[22] Nash, J. E., and Sutcliffe, I. V. 1970. "River Flow Forecasting through Conceptual Models Part I: A Discussion of Principles." *J. Hydro.* 10: 282-90.

[23] Slokar, Y. M., Zupan, J., and Marechal, A. M. L. 1999. "The Use of Artificial Neural Network (ANN) for Modeling of the H_2O_2/UV Decoloration Process." *Dyes Pigments* 42: 123-35.

[24] Aleboyeh, A., Kasiri, M. B., Olya, M. E., and Aleboyeh, H. 2008. "Prediction of Azo Dye Decolorization by UV/H_2O_2 Using Artificial Neural Networks." *Dyes Pigment* 77: 288-94.