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Prediction of Methylene blue Degradation by γ-Fe_2O_3-ZnO/RHA using Response Surface Model (RSM) and Artificial Neural Networks (ANN)

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Abstract

The photocatalytic degradation of methylene blue was successfully predicted using response surface model and artificial neural network. The catalyst dosage, initial methylene blue concentration and irradiation time were the input factors with percentage degradation of the methylene blue as the singular response. Experiments were conducted as generated by experimental design, the data were used for model development from response surface model and artificial neural network with R^2 values as 0.9956 and 0.9999. Also, relative importance of input factors to the response for artificial neural network (ANN) was computed with catalyst dosage having the best ranking of 42% which is agreement with the result from response surface model (RSM).

1. Introduction

Industrialization come with a price tag which is environmental pollution, especially water pollution which is gradually becoming a concern globally [1]. Large quantities of contaminants (such as dyes, oil, particulates) are being released into water bodies without pre-treatment, thus threatening plant and animal life. Dyes are mostly used in printing and paper, leather and tannery, textile and recently pharmaceutical industries because it adds colour to material it is being applied to. After operations the unfixed dyes are discharged into mostly water bodies without treatment and dyes are not easily broken down because of their complex nature and high organic composition [2].

The growing animosity due to the ever-increasing volume of waste water being disposed into the environment and receding water resources, necessitated the development and application of different

waste water treatment techniques to ensure industrial water reuse, thus avoiding further depletion of global water resources. One of these numerous methods is advanced oxidation processes (AOPs) of which photocatalysis is an example. Photocatalysis uses some semi-conductor metallic oxide and the visible or ultraviolet spectrum of light to degrade of a wide variety of organic pollutants into carbon (IV) oxide and water through generation of superoxide and hydroxyl radical under ambient conditions [3]. Although artificial source of light is mostly used, solar energy can be applied depending on the intensity of sunlight [4].

The abilities of semi-conductors such as iron III oxide [5], zinc oxide [6], copper II oxide [7]etc, to degrade contaminants in industrial waste water had been investigated and have proven to degrade polluted effluent in the presence of artificial light because of their band gaps, but little consideration has been given to sunlight which is an inexhaustible energy source. Also, rice husk ash and its adsorptive capabilities has been extensively studied [8]but each have shown individual deficiencies therefore, doping these semiconductors has shown special capabilities by tapping into the advantages of the constituent semiconductors with lower band gap.
The input factors of photocatalytic degradation are not limited to pH, catalyst dosage, and initial concentration of the contaminant, irradiation time, amount of energy consumed, with the degradation efficiency, mostly used as the response. As the amounts of this input factors are varied, the value of the degradation efficiency changes in response to this change in the input factors.

Artificial neural network is defined as a system of simple processing elements called neurons, which are connected to a network by a set of weights [9]. Artificial neural network is an example of multivariate technique used for modelling production processes [10]. Their ability to recognize and reproduce cause-effect relationship through training for multiple input-output systems makes them efficient to represent most complex systems [11].
This work is interested in modelling the photocatalytic degradation of methylene blue using an in-situ synthesized agro-based catalyst with artificial neural networks.

2. Methodology

2.1. Sourcing of Materials

All reagents used were of analytical grade, they were procured from a local chemical store in Zaria, Kaduna state, Nigeria, nitric acid (Merck), zinc (II) acetate dihydrate (BDH Chemicals), ethylene glycol (Merck), citric acid (BDH Chemicals), iron (III) nitrate nonahydrate (Aldrich), distilled water, methylene blue (LabChem), Design Expert 13.0 software (Stat-Ease Inc.), MATLAB R2018a software (MathWorks Inc), Huske Flux 2.0 Pyranometer app, all catalyst samples were synthesized and characterized as reported in earlier works [12].

2.2. Experimental Design

Center composite design was used for the design of experiment, three input factors were studied viz, catalyst dosage, initial methylene blue concentration and irradiation time with percentage degradation as the response as shown in **Table 1**. The total number of experiments (N) conducted was computed using **Eqn. 1**

Table 1. Independent variables and levels used

Variables	Level		
	-1	0	1
Catalyst dosage (g)	0.1	0.2	0.3
Initial MB. conc. (mg/l)	5	17.5	30
Irradiation time (hrs)	0.5	1.75	3.0

$$N = 2^k + 2k + C \qquad \textbf{Eqn. 1}$$

Where, 2^k is the star points, 2k is the axial points and C is the center points.

2.3. Photocatalytic activity

The best performing catalyst sample was selected by carrying out preliminary screening of the produced catalyst samples [14]. 100ml of methylene blue solution with 17.5mg/l concentration was measured into a beaker and initial absorbance (A_o) of the solution was read and recorded.

0.3g of produced γ-Fe_2O_3-ZnO/1g RHA was sprinkled into the methylene blue solution and stirred for 30 minutes in the dark to attain adsorption-desorption equilibrium. 4ml of the suspension was subsequently withdrawn and centrifuged for 30 minutes at speed of 2500rpm, the decanted liquid was then placed in a UV- spectrophotometer and the absorbance at 664nm was read and recorded and concentration was evaluated

The solution was then placed under sunlight and stirred continuously for 105 minutes, after 30minutes, 4ml of the suspension was withdrawn and centrifuged, then the absorbance at 664nm was read and recorded, with the final concentration computed.

The final percentage degradation for the after 1.75hrs was calculated using **Eqn. 2**.

$$\%\, Degradation = \frac{C_o - C_t}{C_o} \times 100 \qquad \textbf{Eqn. 2}$$

Where C_o *and* C_t are initial methylene blue concentration and final methylene blue concentration.

The above procedure was repeated for the remaining 17 runs, and the respective absorbance at 664nm was recorded, the final methylene blue concentration and final percentage degradation was evaluated. The experimental set-up for the runs is as shown in **Figure 1**

2.4. Artificial Neural Network

The values of catalyst dosage, initial methylene blue concentration and irradiation time as derived from design of experiment were used as the input data sets and percentage degradation (response) was used as the output data set. The main program codes containing these data sets were keyed into MATLAB 2018a.

The network architecture was obtained as developed by MATLAB, the neural network learning was achieved with Levenberg-Marquardt backpropagation algorithm after 10,000 epochs, the training algorithm was run for about three times to get the best fit for the R^2 value. Also, the predicted response by neural network was generated. The values of the predicted percentage degradation and actual percentage degradation were used to plot the error histogram which was generated by the neural network interface on MATLAB.

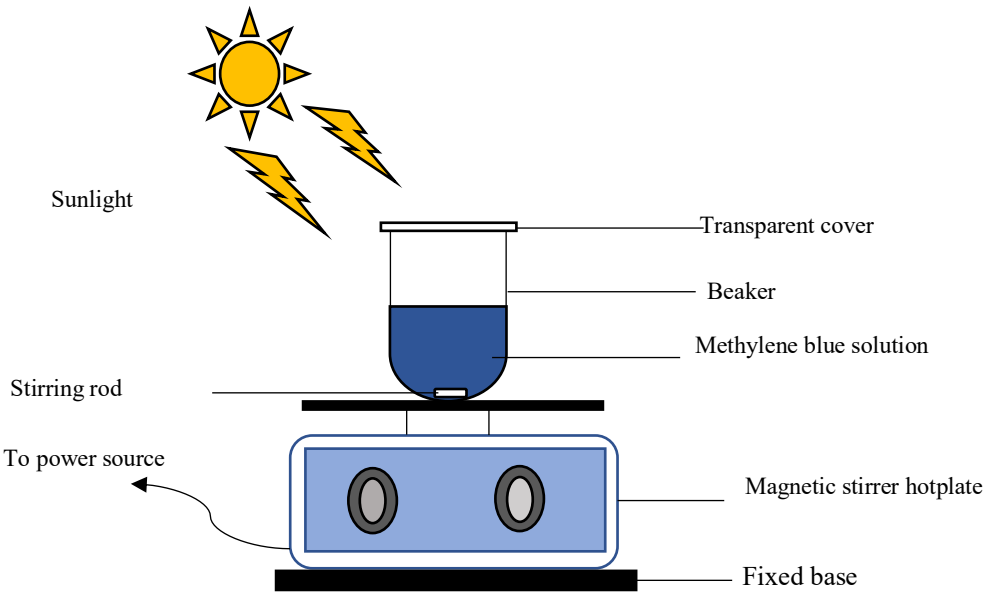

Figure 1. Experimental set-up

During learning 'tan' sigmoidal *("tansig")* transfer function was used between the input layer and hidden layers while the linear transfer function was applied between the hidden layer and output layer, as expressed in **Eqn. 3** and **4** respectively.

$$f(x) = \frac{2}{(1 + e^{-2x})} - 1 \qquad \textbf{Eqn. 3}$$

$$f(x) = x \qquad \textbf{Eqn. 4}$$

The weights in the neural networks were used to determine the relative importance of the various input variables with respect to the output variable using **Eqn. 5**.

$$I_j = \frac{\sum_{m=1}^{m=N_h}\left[\left(\left|W_{jm}^{ih}\right| / \sum_{k=1}^{N_i}\left|W_{km}^{ih}\right|\right) \times \left|W_{mn}^{ho}\right|\right]}{\sum_{k=1}^{k=N_i}\left[\sum_{m=1}^{m=N_h}\left(\left|W_{km}^{ih}\right| / \sum_{k=1}^{N_i}\left|W_{km}^{ih}\right|\right) \times W_{mn}^{ho}\right]} \times 100 \qquad \textbf{Eqn. 5}$$

Where, I_j is the relative importance of the j^{th} input variable on the output variable, N_i and N_h are the input and hidden neurons, respectively W_i, W_h, W_o are the connection weights of input, hidden and output layers respectively, the superscripts 'i', 'h', and 'o' refer to input, hidden and output layers respectively and subscripts 'k', 'm', and 'n' are the input, hidden and output neurons respectively [14].

3. Results and Discussion

3.1 RSM Modelling

The 20 experimental runs were generated with 8-star points, 6 axial points and 6 center points; however, 18 experimental runs were conducted because 2 axial points were negative, the values of the responses are illustrated in **Table 2**. The statistical model ($p \leq 0.05$) was developed using analysis

of variance (ANOVA), which suggested a quadratic model which was confirmed to be significant as shown in **Table 3**. The regression (R^2) of the model was generated by Design Expert® to be 0.9956, which explains the reason why the standard deviation is 1.34, the predicted R^2 of 0.9230 is in consensus with the adjusted R^2 of 0.9906; that is the difference is less than 0.2. Adeq precision which measures the signal to noise ratio, with the ratio of 51.517, (for a ratio which is > 4) illustrates adequate signal, therefore the quadratic model generated can be applied in the design space.

Table 2. Experimental design with the observed and predictive responses

Run	Catalyst Dosage (g)	MB Conc. (mg/l)	Irradiation Time (hrs.)	Response (% Degradation)		
				Observed	Predicted	
					RSM	ANN
1	0.2	17.5	1.75	78.2	78.15	78.202
2	0.2	17.5	1.75	78.14	78.10	78.142
3	0.2	38.5	1.75	67.61	68.72	67.612
4	0.1	30	3	80.63	78.49	80.632
5	0.2	17.5	1.75	78.18	78.13	78.182
6	0.2	17.5	1.75	78.20	78.17	78.202
7	0.1	5	3	91.47	91.57	91.472
8	0.2	17.5	1.75	78.27	78.23	78.272
9	0.3	5	3	94.94	94.05	94.942
10	0.37	17.5	1.75	86.70	86.32	86.702
11	0.1	30	0.5	47.37	47.47	47.372
12	0.3	30	3	97.49	97.91	97.492
13	0.03	17.5	1.75	69.64	71.13	69.642
14	0.2	17.5	1.75	78.20	78.16	78.202
15	0.1	5	0.5	62.37	61.17	62.372
16	0.2	17.5	3.85	98	99.11	98.002
17	0.3	5	0.5	58.46	59.81	58.462
18	0.3	30	0.5	63.94	63.05	63.942

The response surface model generated model equation as presented in eqn. 6 shows with respect to the coefficient of the actual factors and the response means changes in catalyst dosage and irradiation time has significant corresponding effect on the response which is percentage degradation and this assertion is corroborated by ANN calculations:

$$\%\ Degradation = 91.66 + 101.12(Cat.\ dosage) - 0.70(MB\ conc.) + 16.03(Irradiation\ time) + 3.30(Cat.\ dosage \times MB\ conc.) + 5.16(Cat.\ dosage \times Irradiation\ time) + 0.21(MB\ conc. \times Irradiation\ time) - 304.26(Cat\ dosage)^2 - 0.025(MB\ conc)^2 - 3.13(Irradiation\ time)^2 \quad \textbf{Eqn. 6)}$$

Table 3. ANOVA table

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3241.79	9	360.20	199.17	< 0.0001	significant
A-Cat. Dosage	278.58	1	278.58	154.04	< 0.0001	
B-MB Conc.	52.84	1	52.84	29.21	0.0006	
C-Irradiation Time	2324.64	1	2324.64	1285.37	< 0.0001	
AB	143.40	1	143.40	79.29	< 0.0001	
AC	7.35	1	7.35	4.07	0.0785	
BC	0.1891	1	0.1891	0.1046	0.7547	
A^2	0.5386	1	0.5386	0.2978	0.6001	
B^2	26.33	1	26.33	14.56	0.0051	
C^2	39.43	1	39.43	21.80	0.0016	
Residual	14.47	8	1.81			
Lack of Fit	14.46	3	4.82	2062.29	< 0.0001	
Pure Error	0.0117	5	0.0023			
Model statistics						
R^2	0.9956					
Predicted R^2	0.9230					
Adjusted R^2	0.9906					

3.2 Artificial Neural Network Modelling

In the ANN model development, the input and output data sets were successfully trained with the neural network model and the schematic of the multi-layer structure is illustrated in figure 2, which is the architectural model containing 3 input factors (catalyst dosage, initial methylene blue concentration and irradiation time), 20 neurons in the layer between input layer and hidden layer, 1 neuron in the layer between the hidden layer and the output, as well as 1 output which is the % degradation of methylene blue as well as the biases between the layers. In the unseen (hidden) layer, "tan" sigmodal transfer function was used because of the few experimental runs, while "purelin" transfer function was used between the hidden layer and the output.

Levenberg-Marquardt training algorithm which is an example of backpropagation algorithm was adopted for training, the optimal regression value (R^2) was 0.99999 which implies that 0.00001% of

the variation in the percentage of methylene blue degraded were not explained by the model developed by ANN, also a minimal error margin between the predicted (by ANN) and the experimental values indicating the predictability of the process by ANN which validates the model as shown in **figure 3**.

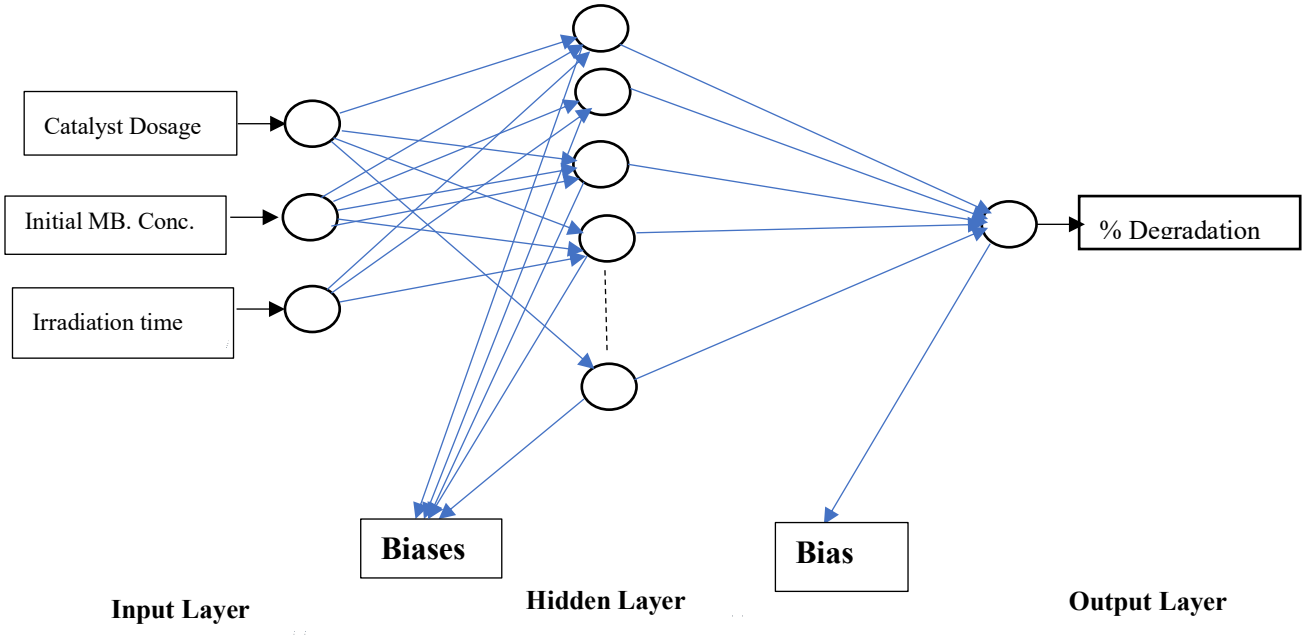

Figure 2. ANN architecture

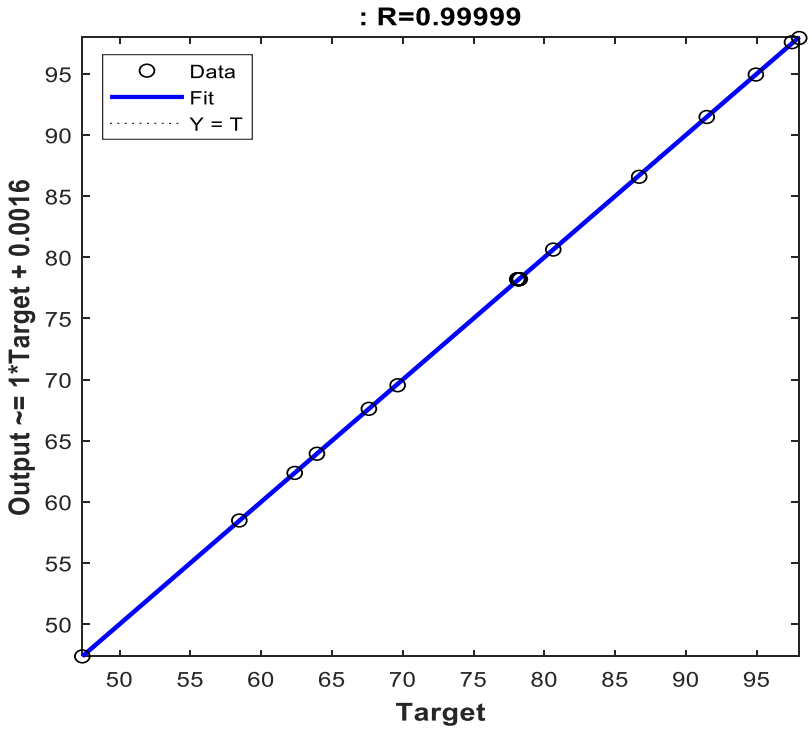

Figure 3. Regression plot (Predicted vs Experimental % Degradation).

The R^2 value was corroborated by **figure 4** which is the histogram plot on **figure 4**, where the error hovers around zero, also the data sets in which the fit is worse, which are 18 iterations are of the zero error (difference between ANN predicted output and experimental output) and on 7 instances we have the error at 0.000215, which is an indication that the data set fits significantly.

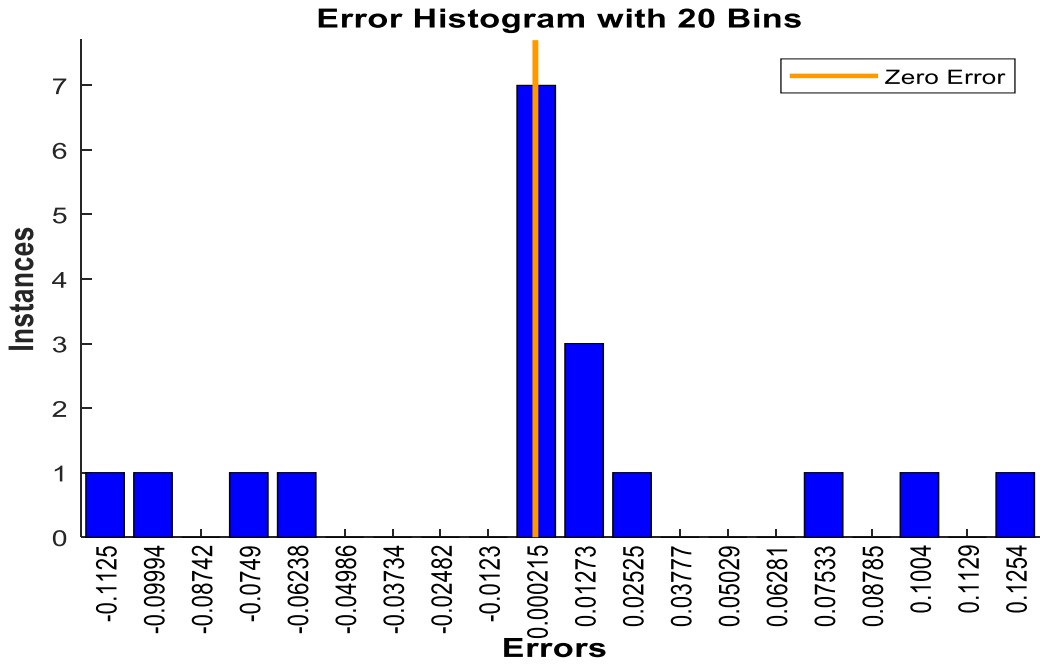

Figure 4. Histogram plot

The neural network generated weights and biases are shown in **Table 4**, the weights are synonymous to the synapse strengths between the axons and dendrites in the biological neural systems (Aleboyeh *et al.,* 2008). The relative importance of the various variables with the output was calculated using **Eqn. 5** and illustrated in **figure 5**.

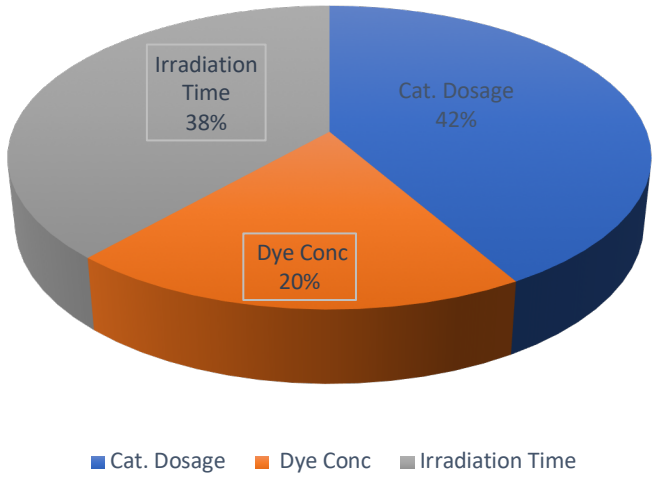

Figure 5. Relative importance of input variables to the percentage degradation.

Table 4. Matrix of weights

Input Layer to Hidden Layer Weights					Hidden Layer to Output Layer Weights		
Neurons	W1 (Cat. Dose)	W1(MB. Conc.)	W1 (Irradiation Time)	Bias	Neurons	W2	Bias
N1	13.43	0.33	1.31	-13.82	N1	38.88	-0.0084
N2	21.77	5.21	1.6	14.21	N2	-1.73	
N3	19.59	-4.27	14.55	20.99	N3	-40.15	
N4	11.89	-2.05	-1.5	11.41	N4	48.65	
N5	14.29	-1.8	-2.53	-0.43	N5	5.56	
N6	31.01	-7.97	23.12	-17.92	N6	18.84	
N7	-9.66	12.89	10.63	4.35	N7	-15.19	
N8	-108.02	62.39	128.63	-318.91	N8	115.41	
N9	30.1	-3.77	-9.19	3.147	N9	2.1	
N10	8.05	-7.32	-1.23	-13.738	N10	10.62	
N11	22.47	3.69	4.43	-3	N11	-1.8	
N12	41.28	6.16	1.23	12.3	N12	-52.88	
N13	-30.92	-8.45	-8.72	-1.44	N13	4.86	
N14	-16.38	-0.61	-16.25	-12.55	N14	-0.58	
N15	37.72	51.82	-10.35	11.61	N15	-16.65	
N16	-7.75	-13.62	-45.61	18.16	N16	23.75	
N17	5.86	9.06	2.03	6.85	N17	0.52	
N18	26.08	-1.38	9.48	-4.98	N18	58.34	
N19	-0.78	-3.45	-31.02	19.66	N19	14.01	
N20	-8.07	-1.54	-2.52	-12.176	N20	9.1	

As illustrated in **figure 5**, all the input variables have a corresponding effect on the percentage degradation, although the catalyst dosage has the greatest influence on the percentage degradation with a relative importance of 42%, which shows that increase in the catalyst dose will have a significant effect on the photocatalytic degradation process.

Conclusion

Both response surface method (RSM) and artificial neural network (ANN) were able to successfully predict the degradation of methylene blue in the presence of sunlight and both approaches have their unique advantages. The resulting model for the photocatalytic degradation process using RSM had R^2 value for 0.9956 with standard deviation to be 1.34, also the quadratic model selected had a significant fit. Catalyst dosage and the irradiation time were more significant factors when compared with initial methylene blue concentration in the actual model equation.

Using ANN, the process was modelled using a multi-layered neural network structure containing 3-20-1 architecture with the R^2 value for neural network generated was 0.9999. Furthermore, the significance of the input factors with respect to the response shows that the catalyst dosage is an important factor to be considered in the photocatalytic degradation of methylene blue, and this assertion was in agreement with RSM.

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Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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