

Artificial Neural Network (ANN) Modeling for Prediction of Pesticide Wastewater Degradation by FeGAC/H₂O₂ Process

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Abstract. The study examined artificial neural network (ANN) modeling for the prediction of chlorpyrifos, cypermethrin and chlorothalonil pesticides degradation by the FeGAC/H₂O₂ process. The operating condition was the optimum condition from a series of experiments. Under these conditions; FeGAC 5 g/L, H₂O₂ concentration 100 mg/L, pH 3 and 60 min reaction time, the COD removal obtained was 96.19%. The ANN model was developed using a three-layer multilayer perceptron (MLP) neural network to predict pesticide degradation in terms of COD removal. The configuration of the model with the smallest mean square error (MSE) of 0.000046 contained 5 inputs, 9 hidden and, 1 output neuron. The Levenberg–Marquardt backpropagation training algorithm was used for training the network, while tangent sigmoid and linear transfer functions were used at the hidden and output neurons, respectively. The predicted results were in close agreement with the experimental results with correlation coefficient (R²) of 0.9994 i.e. 99.94% showing a close agreement to the actual experimental results. The sensitivity analysis showed that FeGAC dose had the highest influence with relative importance of 25.33%. The results show how robust the ANN model could be in the prediction of the behavior of the FeGAC/H₂O₂ process.

1 Introduction

Pesticide pollution is a potential problem to surface and ground water. Pesticide presence in surface water including streams and ditches opposite farmlands and inland rivers have been recorded [1-2]. Part of the larger scale contamination results from non-agricultural uses of pesticides [3] or from point sources, including discharge from farmyards following filling and washing activities [4]. Diffusion of pesticides in both air and water are also noteworthy. Diffusion occurs during pesticide application in farmlands or when they find their way into drains and are transported into the natural environment [5]. Possible chronic effects of pesticide pollution are reported to include neurotoxicity [6] carcinogenesis [7] affect reproduction [8] and cell development [9]. This is very prominent in the early stages of life.

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Pesticide concentration in wastewater may vary; however, effective treatment is required irrespective of the concentration. Biological processes are normally chosen for treatment of pesticide wastewater. However, this method of treatment is liable to deactivate microbial organisms. An advisable method is to carry out pretreatment of the pesticide wastewater before application of the biological treatment [10].

Advanced oxidation process (AOP) is a promising technology whereby chemical reactions generate hydroxyl radicals ($\text{OH}\cdot$) in large quantity and oxidizes pollutants in water or wastewater in room temperatures [11]. The Fenton process is typically a reaction between iron salts and hydrogen peroxide (H_2O_2) to produce hydroxyl ($\text{OH}\cdot$) radicals. This occurs due to the catalytic decomposition of hydrogen peroxide in acidic pH [12-13].

Ferrous ions and hydrogen peroxide react and produce $\text{OH}\cdot$ iron sludge and it is inevitably produced in addition to complex agents and intermediate products [14]. This generates an added handling cost with regards to disposal after the treatment [15]. Therefore, Fe-granular activated carbon/hydrogen peroxide (FeGAC/ H_2O_2) process has been recently put forward as an alternative [16]. In the reaction between FeGAC and H_2O_2 , the GAC adsorbs the contaminants in the waste stream and provides support for the reaction between the ferric iron and hydrogen peroxide to catalyse other contaminants remaining in the wastewater. Additionally, the GAC catalyses the wastewater owing to the presence of functional groups and surface graphitic structure [17]. On another hand, the hydrogen peroxide oxidizes the GAC and ferric salt catalytic properties to degrade the contaminants in the wastewater. The application of FeGAC/ H_2O_2 includes Acid Black 24 decolorization [18], removal of humic substances (and fulvic acids) in municipal landfill leachate [18] and crystal violet degradation [16].

Wastewater treatment by AOP is tasking due to the complex nature required to solve equations that may involve radiant energy balance, spatial distribution of the absorbed radiation, mass transfer, and other mechanisms of photochemical or photocatalytic degradation processes. Because of the multiple factors this process depends on, the modeling approach is very important. The ANN is capable to simulate such complex interactions that could exist between an input variable and output variable in a typical wastewater treatment plant [19 – 22].

Artificial neural network has been taught to carry out very complex tasks in a variety of fields. This includes identification, pattern recognition, classification, classification, vision, and control systems [19; 22]. The advantages of ANN is such that mathematically describing the phenomena involved in a process is not necessary and this makes it useful for the simulation and up-scaling AOP treatment processes. In addition, less time is needed for development of the model in comparison to traditional mathematical models and their prediction ability using very few laboratory data [23-24]. The ANN has been applied in biological wastewater treatment [25-26] and physicochemical wastewater treatment [27-28]. Some studies have also reported the use of ANN for modeling full scale biological wastewater treatment plant and for removal of nitrogen and phosphorus from wastewater [29-30]. However, at present there is no report on ANN modeling for prediction of chemical oxygen demand (COD) removal from chlorpyrifos, cypermethrin and chlorothalonil pesticides in aqueous solution. This study investigated the application of ANN for predicting COD removal from pesticide aqueous solution by the FeGAC/ H_2O_2 process. A comparison of the model outputs and experimental results is also reported.

2 Materials and methods

2.1 Chemicals

The chemicals used were supplied by R&M Marketing, Essex, U.K. This includes H₂O₂ (30%, w/w) and (Fe(NO₃)₃·9H₂O). A commercial supplier provided the pesticides used during this study.

2.2 Fe-granular activated carbon (FeGAC)

The GAC purchased from Calgon Corporation, Pittsburgh, PA was blended to reduce it to 425 µm size. The preparation of the FeGAC was according to a previous study [18].

2.3 Analytical methods

Measurements of COD were done in accordance to Standard Methods [31]. In an effort to minimize an interference of COD values obtained, pH was raised above 10 immediately after the treatment. This was to enable hydrogen peroxide to decompose to oxygen and water [32-33]. The pH meter (HACH sension 4) was used in measuring pH during the entire process.

2.4 Pesticide aqueous solution

Preparation of the pesticide aqueous solution was done using distilled water and was stored at 4 °C until required. Its constituents were CPF 100 mg/L, CPT 50 mg/L and CTN 250 mg/L. The COD was 1130.0 mg/L, TOC was 274.39 mg/L and BOD₅/COD ratio was zero.

2.5 Experimental procedure

FeGAC/H₂O₂, laboratory study was conducted using 200 mL of the pesticide aqueous solution placed inside a 250 mL conical flask. The quantity of iron salt needed was added to this solution. Thereafter, an adjustment of solution pH was done as maybe needed using H₂SO₄ or NaOH. Stirring the solution to appropriate mix was done using a magnetic stirrer for good homogeneity. The required amount of H₂O₂ was thereafter added to the solution. At known time intervals, a conical flask was removed and a portion of the solution was filtered using a 0.45 µm size filter for COD measurement.

2.6 Artificial neural network

The ANNs are known mathematical models having the ability of learning, simulation and prediction of data based on past observations in complex systems without knowledge of any fundamental principles of any system [34]. They are biologically inspired computer programs designed to simulate the way the human brain processes information [35]. The disadvantage of ANN is its “black box” nature. The relationship between the input and output variables are not built on engineering principles and thus the model is referred to as ‘black box’. There is also a problem of overfitting along with its computational burden and large sample size requirement [36-38]. The network has a lot of single processing units referred to as neurons and these are usually interconnected using a variety of architectural structures. The interconnection strength is determined by the weight associated with neurons. The ANN modeling consists of two major stages (i) training and (ii) testing. In

training stage the input and targets (outputs) are both presented to the network, whereas in testing stage only inputs are presented to the network and outputs are predicted based on the learned examples. A program code written by MATLAB 2009a neural network toolbox was used for modeling the COD removal from the pesticide aqueous solution.

3 Results and discussion

3.1 Effect of FeGAC

To study the effect of FeGAC on COD removal, the FeGAC dose was varied between 1 to 5 g/L. Figure 1 shows the effect of FeGAC dose on the removal of COD from the pesticide aqueous solution. It was observed that an increase in FeGAC dose from 1 to 5 g/L led to an increase in COD removal from 56.9 to 85.75% in 60 min. This could be due to increase in the generation rates of ferrous ions as the FeGAC is increased [17].

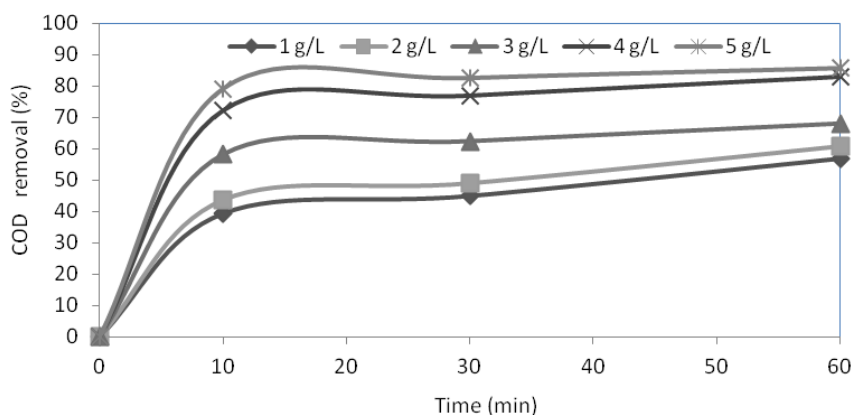


Fig. 1. Effect of FeGAC in terms of COD removal

3.2 Effect of H₂O₂ addition to FeGAC

In heterogeneous Fenton-like process, combining ferric ions and H₂O₂ leads to a reaction which occurs at the solid surface of the catalyst and it could also depend on the nature of the specific area of the catalyst [39]. In order to observe the effect of FeGAC with H₂O₂ addition on COD removal, H₂O₂ dose was varied between 10 to 300 mg/L and the FeGAC dose was kept fixed at 5 g/L. Figure 2 shows the effect of H₂O₂ addition on COD removal. The COD removal increased from 51.68 to 96.19% in 60 min when H₂O₂ dose increased from 10 to 100 mg/L, but reduced when H₂O₂ concentration was further increased from 100 mg/L to 300 mg/L. The maximum COD removal was 96.19% at H₂O₂ dose 100 mg/L. The improvement with the addition of H₂O₂ was probably due to the increased catalytic reaction between the coated iron and H₂O₂. The decrease in degradation above 100 mg/L was probably due to competing reaction of GAC, OH· and ferrous/ferric ions upon H₂O₂ degradation [18]. This has been reported by another study to be probably as a result of the scavenging effect of excess OH· by hydrogen peroxide [40].

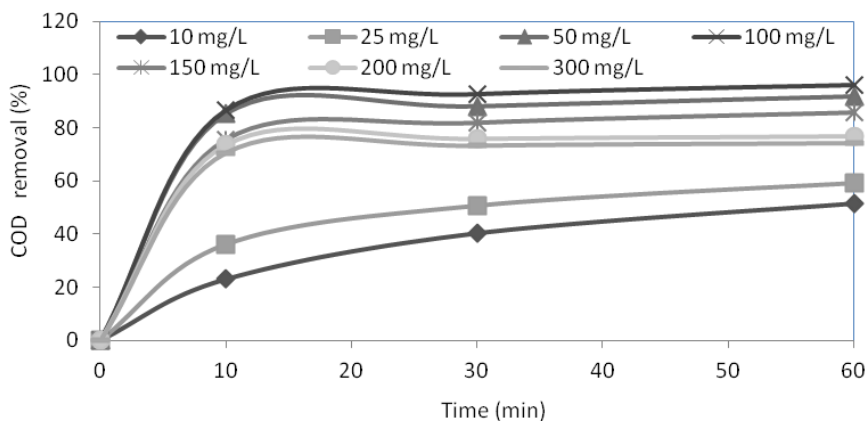


Fig. 2. Effect of H₂O₂ addition to FeGAC in terms of COD removal

3.3 Effect of pH

The solution pH has a major effect upon the catalytic activity in decomposition of hydrogen peroxide and OH[•] production [41]. In order to observe the effect of pH on COD removal, pH was varied between 2 and 8, and H₂O₂ and FeGAC were kept constant at 100 mg/L and 5 g/L, respectively. Between pH 2 and 3 the COD removal increased, but from 4 to 8 there was reduction in COD removal (Fig. 3). Typical Fenton-like reaction process has been reported to achieve a higher removal of COD in the acidic range of pH 3-4 [12].

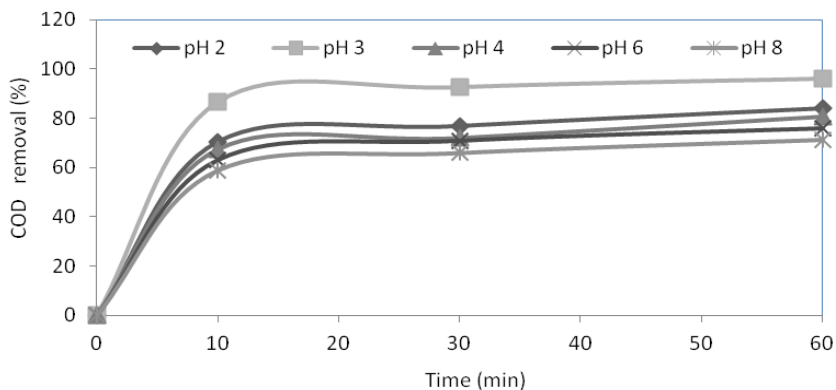


Fig. 3. Effect of pH on COD removal

3.4 Effect of initial pesticide concentration

To investigate the effect of the initial pesticide concentration on COD removal, various initial concentration of the pesticide (400, 800 and 1200 mg/L) were used. Other parameters were pH 3, H₂O₂ 100 mg/L and FeGAC 5 g/L. At high initial pesticide concentration, net removal was more but percentage removal was less (Fig. 4). In heterogeneous Fenton process such as the FeGAC/H₂O₂ process, the reaction occurs at the surface of FeGAC

between OH^\cdot produced at the active sites and pesticides molecules adsorbed on the surface. Therefore, where pesticide concentration increased, the number of active sites available decreased due to the competitive adsorption on the catalytic surface by the pesticide molecules. Added to this, intermediate products of oxidized pesticide can also compete for the limited adsorption sites with parent pesticide molecules, which limit their interactions with Fe(II)/Fe(III) active sites [42]. Therefore, concentration of FeGAC is an important factor in the application of FeGAC/ H_2O_2 process for varying COD loadings.

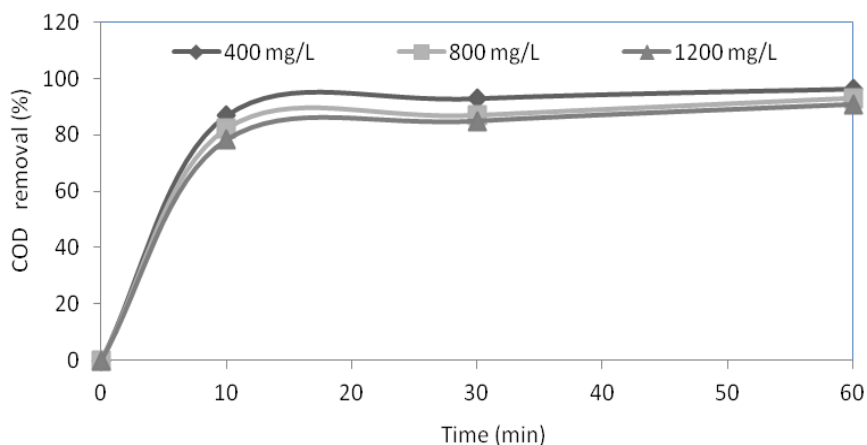


Fig. 4. Effect of initial concentration on COD removal

3.5 Input data selection

The screening of input variable data before selection is an important part of the network development. This is because the ANN modeling seriously needs to depend on the input data as it represents both the non-linearity and complexity of the whole data during training of the network [43]. The available data should be divided into training and testing data sets in such a way that the data set presented during training should contain maximum variations of the available data. In the present study, the available data was limited to 60 sets which were presented to the network during the training stage, whereas the preceding 30 sets were tested during the testing stage for model validation. The input vectors were, FeGAC, H_2O_2 , pH, time and pesticide concentration. The output vector was the percentage of COD removal.

3.6 Selection of backpropagation training algorithm

The main objective of training algorithm is to minimize or limit the error function by finding a set of connection weights that creates a condition for the ANN to produce outputs equal or close to the target values. Backpropagation algorithms minimize error function between the observed and predicted output through two phases [43]. Several algorithms were studied (data not shown). During the training of the network, the Levenberg–Marquardt backpropagation algorithm was applied. The tangent sigmoid and linear transfer functions were used at the hidden and output neurons.

3.7 Selection of ANN structure and optimization

A three-layered MLP back propagation neural network with tangent sigmoid (tansig) in hidden layer and a purelin transfer function at output layer were used. The numbers of inputs were five as described in the section 3.5 (input data selection). The number of hidden neurons was initially determined by trial and error procedure and the comparison of mean square error at various hidden neuron was performed. The optimum number of hidden neurons is based on the minimum value of mean square error of the training and prediction set [26]. Mean square error can be described by a mathematical function and usually it is used as the error function. The MSE measures the performance of the network expressed by Eq. (1) [26].

$$MSE = \frac{\sum_{I=N}^{i=N} (y_{i,pred} - y_{i,exp})^2}{N} \tag{1}$$

where, N is the number of data point, $y_{i, pred}$ is the network prediction, $y_{i, exp}$ is the experimental response and i is an index of data. The optimization was done by varying the neuron number. Thus by increasing from one to twelve, the MSE was decreased. This was possible using the Levenberg–Marquardt backpropagation training algorithm. Hence, 9 neurons were selected as the optimum number of neurons. The network had one output neuron because it was associated with COD removal only. Therefore, the network architecture containing five input neurons, nine hidden neurons and one output neuron can be denoted (Fig. 5).

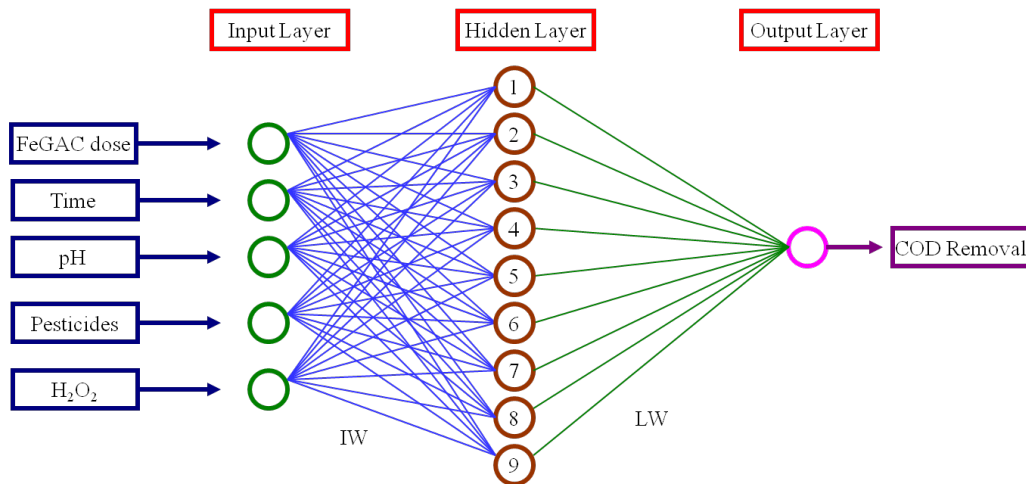


Fig. 5. The optimized artificial neural network structure

3.8 Testing and validation of the model

Data obtained from observations during the experimental study were normalized and thereafter feed to the optimized artificial neural network in an attempt to test and validate the model. The experimental and predicted COD removal values were compared using the network for both trained and test data. The number of iterations and MSE values were used as the performance criteria and monitored during training. Each input parameter had equivalent number of iterations and MSE during the training. Fig. 6 and 7 describe a good line of best fit for the data points in both the training and testing phases. The best linear fit for training correlation coefficient (R^2) was 0.9950 and for corresponding testing was

0.9994 with a MSE of 0.000046 when 9 neurons were applied to the ANN structure (Fig. 8). Predicted and experimental values for training and testing phases (Fig. 9 and 10). The values were in close agreement with little variations as shown in the COD removal for the predicted and experimental testing data (Table 1). Similar results have been reported for prediction of effluent TOC from an activated sludge process [26] effluent volatile suspended solids and methane yield in sludge digestion [44] and for BOD and suspended solids removal in wastewater treatment [43].

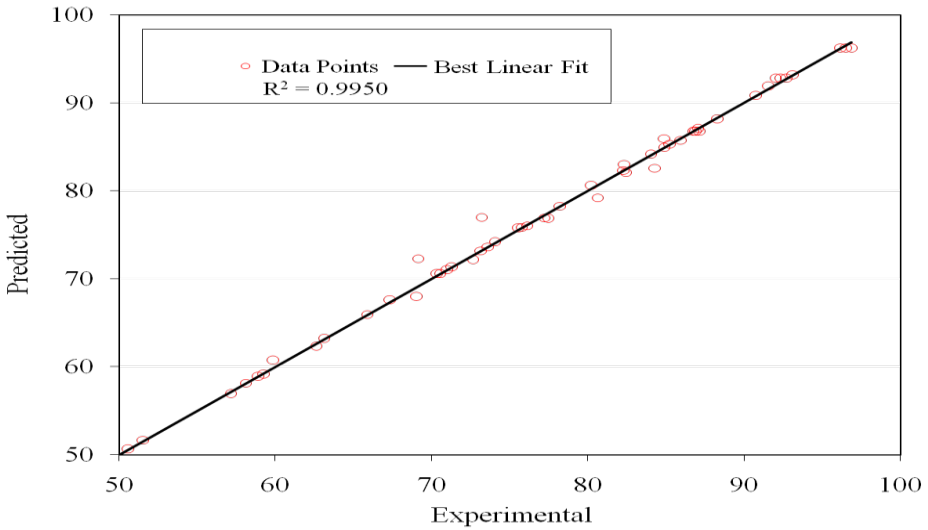


Fig. 6. Predicted vs. experimental data points during training

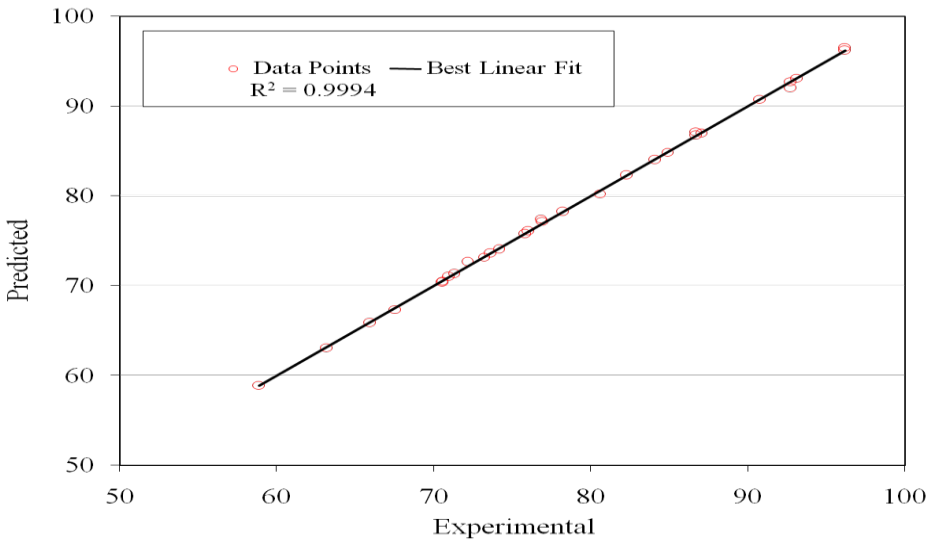


Fig. 7. Predicted vs. experimental data points during testing

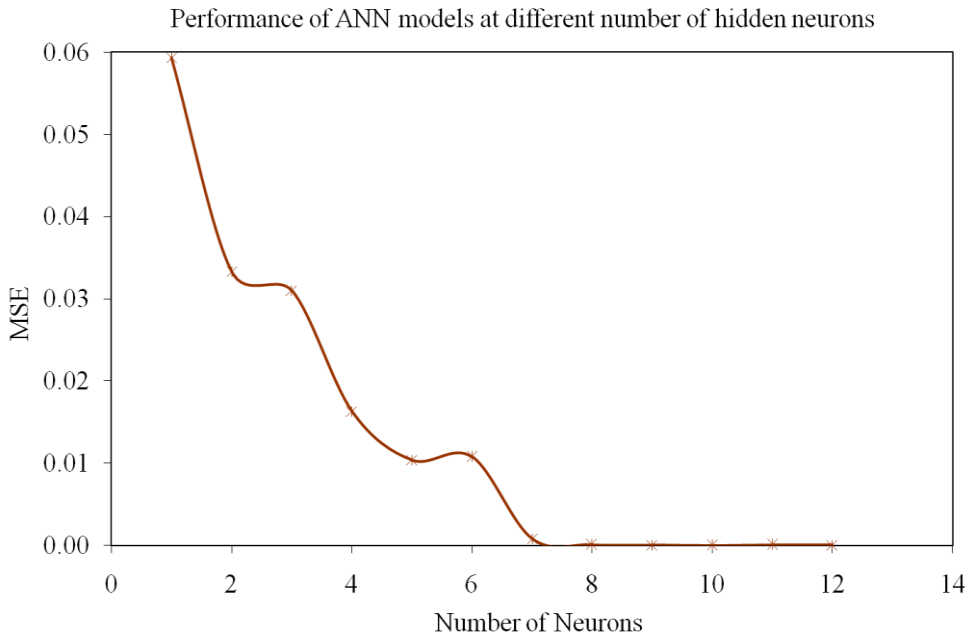


Fig. 8. Mean square error for optimum neurons

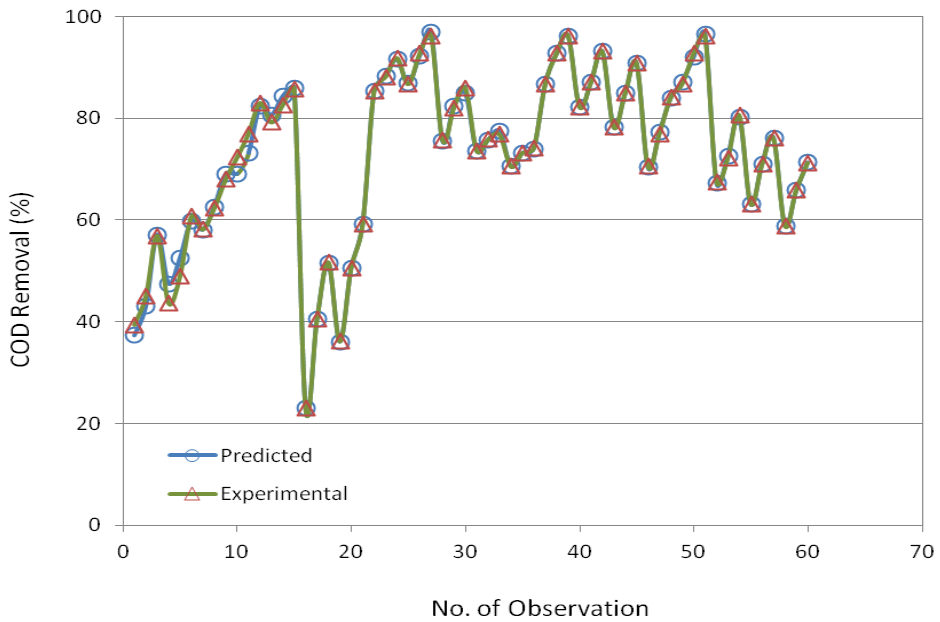


Fig. 9. COD removal for predicted and experimental data during training

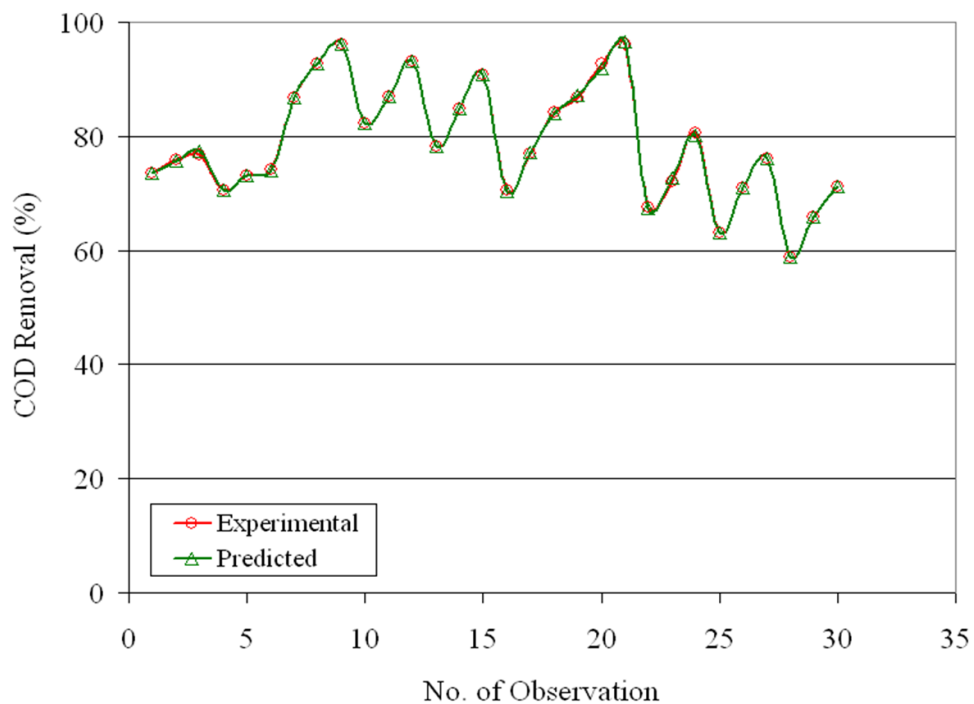


Fig. 10. COD removal for predicted and experimental data during testing

Table 1. Experimental and predicted values for COD removal using five model input variables during testing phase

No. of Observ.	Input Variables					COD Removal (%)	
	FeGAC dose	Time	pH	Pesticide conc.	H ₂ O ₂ conc.	Exp.	Pred.
1	5	10	3	400	200	73.63	73.63
2	5	30	3	400	200	75.84	75.77
3	5	60	3	400	200	76.81	77.46
4	5	10	3	400	300	70.53	70.53
5	5	30	3	400	300	73.19	73.19
6	5	60	3	400	300	74.16	74.04
7	3	10	5	400	100	86.73	86.73
8	3	30	5	400	100	92.74	92.75
9	3	60	5	400	100	96.19	96.19

10	3	10	5	800	100	82.31	82.31
11	3	30	5	800	100	87.04	87.04
12	3	60	5	800	100	93.13	93.13
13	3	10	5	1200	100	78.25	78.25
14	3	30	2	1200	100	84.88	84.88
15	3	60	2	1200	100	90.78	90.78
16	5	10	2	400	100	70.56	70.36
17	5	30	3	400	100	76.93	77.21
18	5	60	3	400	100	84.12	84.03
19	5	10	3	400	100	86.73	87.15
20	5	30	4	400	100	92.74	92.00
21	5	60	4	400	100	96.19	96.54
22	5	10	4	400	100	67.55	67.36
23	5	30	6	400	100	72.15	72.64
24	5	60	6	400	100	80.58	80.23
25	5	10	6	400	100	63.19	63.11
26	5	30	8	400	100	70.98	71.03
27	5	60	8	400	100	76.03	76.10
28	5	10	8	400	100	58.87	58.91
29	5	30	8	400	100	65.94	65.87
30	5	60	8	400	100	71.29	71.31

3.9 Sensitivity analysis

The relative importance of the data of the input variables on the output variable was evaluated on the basis of the neural net weight matrix. These weights are analogous to synapse strengths between the axons and dendrites in typical biological neurons. Thus, each weight is able to decide what portion or part of the entire incoming signal to transmit into the neuron’s body [41]. An equation based on partitioning of connection weights has been proposed by Garson [45] in Eq. 2.

$$I_j = \frac{\sum_{m=1}^{m=N_h} \left(\left(\frac{|W_{jm}^{ih}|}{\sum_{k=1}^{N_i} |W_{km}^{ih}|} \right) \times |W_{mn}^{ho}| \right)}{\sum_{k=1}^{k=N_i} \left\{ \sum_{m=1}^{m=N_h} \left(\frac{|W_{km}^{ih}|}{\sum_{k=1}^{N_i} |W_{km}^{ih}|} \right) \times |W_{mn}^{ho}| \right\}} \quad (2)$$

where, I_j is the relative importance of the j th input variable on output variable, N_i and N_h are the number of input and hidden-neurons, respectively, W is connection weights, the superscripts ‘ i ’, ‘ h ’ and ‘ o ’ refer to input, hidden and output layers, respectively and subscripts ‘ k ’, ‘ m ’ and ‘ n ’ refer to input, hidden and output neurons, respectively. Kasiri et al. [46] have used this equation to evaluate the relative importance of the input variables on colour removal from dye solution by the photo-Fenton process. They found that among the input variables studied, initial concentration of H_2O_2 with a relative importance of 48.89% was the most influential parameter. Table 2 shows the weights between the artificial neurons produced by the ANN model used in this work. Table 3 indicates the relative importance of the input variables calculated by Eq. (2). All variables had varying degree of effect on pesticide degradation in terms of COD removal. The FeGAC dose was the most influential parameter with relative importance of 25.33% and was closely followed by H_2O_2 dose with 20.88%. Others were time 19.11%, pH 17.52% and pesticide concentration 17.20%. The pesticide degradation in terms of COD removal agrees well with the sensitivity analysis using Garson’s equation.

Table 2. Weight matrix, weights between input and hidden layers (IW) and weights between hidden and output layers (LW)

Hidden neurons	hidden and output layers					LW Output
	(IW) Input Variables					
	FeGAC dose	Time	pH	Pesticide conc.	H_2O_2 conc.	COD Removal
1	0.8822	18.4423	-14.8835	7.0716	-9.4230	-2.2235
2	-30.4677	4.6959	8.0149	1.8914	0.8725	23.4970
3	-0.5347	4.3721	-4.0547	9.6229	-2.8131	5.6285
4	-0.4456	0.2298	-1.1318	7.9803	5.5135	31.2896
5	-5.1542	-19.0251	-12.6388	5.1403	1.2278	28.7780
6	1.2890	-0.1664	3.1365	-1.6466	-6.3421	33.2929
7	-3.1190	25.7100	-10.1029	-3.4215	-9.4206	24.0238
8	-74.9063	-81.2668	1.0315	-11.3778	-2.2434	-5.4806
9	7.6741	0.6914	-0.7206	0.3638	-0.9746	24.2266

Table 3. Sensitivity analysis showing relative importance of input variables

Input Variables	Importance (%)
FeGAC dose	25.33
H ₂ O ₂ conc	20.84
Time	19.11
pH	17.52
Pesticide Conc.	17.20
Total	100

4 Conclusion

The ANN modeling for predicting COD removal from pesticide aqueous solution by the FeGAC/H₂O₂ process was feasible using a multilayer perceptron neural network. The data collected from the laboratory had high accuracy with a minimum MSE of 0.000046 using Levenberg–Marquardt backpropagation training algorithm for training and tangent sigmoid and linear transfer functions with 5 inputs, 9 hidden and, 1 output neuron at the hidden and output layers, respectively. The predicted results were in agreement with the experimental results with correlation coefficient (R²) of 0.9994. The sensitivity analysis showed that all variables (FeGAC, H₂O₂, pH, time and pesticide concentration) have an effect on pesticide degradation, but FeGAC dose was the most influential parameter with relative importance of 25.33%. The ANN modeling can therefore be used to predict COD removal from combined chlorpyrifos, cypermethrin and chlorothalonil pesticides in aqueous solution by the FeGAC/H₂O₂ process.

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