

Article

# Prediction and Optimization of the Fenton Process for the Treatment of Landfill Leachate Using an Artificial Neural Network

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**Abstract:** In this study, the artificial neural network (ANN) technique was employed to derive an empirical model to predict and optimize landfill leachate treatment. The impacts of  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  ratio,  $\text{Fe}^{2+}$  concentration, pH and process reaction time were studied closely. The results showed that the highest and lowest predicted chemical oxygen demand (COD) removal efficiency were 78.9% and 9.3%, respectively. The overall prediction error using the developed ANN model was within  $-0.625\%$ . The derived model was adequate in predicting responses ( $R^2 = 0.9896$  and prediction  $R^2 = 0.6954$ ). The initial pH,  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  ratio and  $\text{Fe}^{2+}$  concentrations had positive effects, whereas coagulation pH had no direct effect on COD removal. Optimized conditions under specified constraints were obtained at pH = 3,  $\text{Fe}^{2+}$  concentration = 781.25 mg/L, reaction time = 28.04 min and  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  ratio = 2. Under these optimized conditions, 100% COD removal was predicted. To confirm the accuracy of the predicted model and the reliability of the optimum combination, one additional experiment was carried out under optimum conditions. The experimental values were found to agree well with those predicted, with a mean COD removal efficiency of 97.83%.

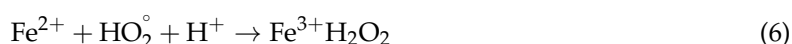
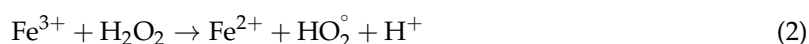
**Keywords:** artificial neural network (ANN); chemical oxygen demand (COD); Fenton treatment; landfill leachate; wastewater treatment

## 1. Introduction

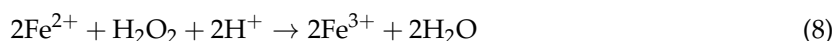
Solid waste management (SWM) is an increasingly complex task, absorbing a huge amount of resources and having a major environmental impact [1]. Municipal solid waste (MSW) is defined as waste from residential, multifamily, commercial and institutional sources [1,2]. Worldwide, approximately 1.3 billion tons of MSW is now generated per year, and this number is expected to reach 2.2 billion tons by 2025 [3]. Overall, 90% of MSW is disposed of in open dumps and landfills unscientifically, creating problems for public health and the environment [4]. If landfills are not properly managed, these can generate uncontrolled gaseous and liquid emissions as leachate [5]. Percolation of rainwater through waste layers in municipal landfills generates leachate [6]. The most important persistent pollutants in landfill leachate that pose a long-term threat to surrounding ground and surface waters are rich in organic matter, ammonia, heavy metals and toxic materials such as xenobiotic organic compounds and refractory humic substances. Waste type and compaction, landfill

hydrology, climate and, particularly, landfill age have an influence on the amount and composition of landfill leachate [7,8].

Fenton oxidation is a process under acidic conditions that use the decomposition of hydrogen peroxide catalysed by a ferrous ion to generate hydroxyl radicals [9]. The Fenton treatment is performed at ambient temperatures in a series of continuous steps and has two components, catalytic chemicals and chemical oxidation. During a Fenton reaction, hydroxyl radicals are produced and will react to pollutants, decomposing and oxidising organic molecules to provide  $\text{H}_2\text{O}_2$  and  $\text{CO}_2$  [10]. The classical Fenton process (FP) involves a sequence of the following reactions [11–13]:



The generation of hydroxyl radicals (Equation (1)) is very rapid. The net reaction (1) to (7) can overall be defined as the dissociation of  $\text{H}_2\text{O}_2$  in the presence of iron as a catalyst [13].



All parameters in the Fenton oxidation process are modified to increase the reduction of pollutants and hydroxyl radicals. Fenton reduction has advantages over other advanced oxidation processes (AOPs). Hydrogen peroxide, which easily decomposes into water and oxygen, is plentiful and easy to remove from water, which makes  $\text{Fe}^{2+}$  the most commonly used metal for the application of Fenton reactions [14,15]. In addition, Fenton reactions generate lower harmful by-products than AOPs [16]. The Fenton process has some remarkable advantages over other chemical treatment methods including high efficiency, biodegradability improvement, simplicity in operation, and treatment capability of a wide range of substances [17–19]. However, some operational problems such as sludge production and a high concentration of remaining sulphates are encountered [20]. The removal efficiency is dependent on various factors such as initial pH, reaction time, the initial concentration of pollutant, dosages of Fenton reagents, reagents mole ratio, coagulation pH, mode of reagent addition and temperature [21,22]. For example, Wadley and Waite [23] reported that when the pH is between 2 and 4, the Fenton oxidation is efficient, especially at pH of 2.8, due to the formation of ferric oxyhydroxide. The role of iron in Fenton process can be considered as a catalyst, and the reaction of a ferrous ion with  $\text{H}_2\text{O}_2$  produces a high rate constant. Transmission of electrons happens among  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{3+}$ . The oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  occurs in a range of a few seconds to a few minutes if there is an excess of  $\text{H}_2\text{O}_2$ . The  $\text{Fe}^{3+}$  generated can further react with excess hydrogen peroxide to form more OH radicals and  $\text{Fe}^{2+}$  in Fenton-like reaction.

Artificial neural networks (ANN) are now commonly employed in many areas of science and engineering due to their ability and flexibility to model highly non-linear phenomena. The ANN is a powerful method in multivariate calibration. As an alternative to physical models, an ANN is a valuable forecast tool in environmental sciences [24]. The ANN can be used effectively due to its learning capabilities and its low computational costs [25]. Because of their reliable, robust, and salient characteristics in capturing the non-linear relationships between variables (multi-input/output) in multivariate systems, numerous applications of ANN-based models have been successfully utilized in the field of environmental engineering in the past decade [26–28]. There is a limited number

of experimental studies investigating the use of the ANN for the treatment of landfill leachate. Biglarijoo et al. [29] explored the use of the analytic hierarchy process (AHP) for landfill leachate treatment and optimization of the process using an ANN. AHP was used to select the favorable catalyst between  $\text{FeSO}_4$  and  $\text{FeCl}_2$  and central composite design (CCN) was used for test design of the experiments along with response surface methodology (RSM) and an ANN for modeling. Chemical oxygen demand (COD) was one of the effective variables in this study. Sabour et al. [30] explored a comparative study of an ANN and RSM for simultaneous optimization of multiple targets in the Fenton treatment of landfill leachate. Three targets were used to cover different aspects of post-treatment products such as supernatant and sludge: mass content ratio (MCR) and mass removal efficiency (MRE). Their results showed low deviation from predicted values with maximum errors of 8% and 9% for RSM and ANN, respectively. Arabameri et al. [31] investigated the use of an ANN for the prediction of COD removal from landfill leachate by the ultrasonic process. The results showed that modeling a neural network could effectively predict COD removal from landfill leachate by the ultrasonic process. The above literature review shows that each investigation is unique and requires a specific investigation.

The aim of this study was to optimize and predict the Fenton treatment for landfill leachate by utilizing the ANN as a tool to achieve the optimum parameters. Four experimental factors such as  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  ratio,  $\text{Fe}^{2+}$  concentration, pH and process reaction time were selected as the input parameters and COD removal was selected as the output parameter of the ANN model. Although there are few studies utilizing ANN for landfill leachate, however, each landfill leachate has its own characteristics and depends on various factors e.g., type of waste, leachate age, seasonal variations and many others. Accordingly, each investigation is unique and requires a specific investigation. In the current study, a matured landfill leachate was used in the experiment which was unique in nature and has not been explored by other researchers. Moreover, a model was proposed in this study to predict the responses for the treatment of matured landfill leachate.

## 2. Material and Methods

### 2.1. Landfill Leachate

Landfill leachate samples were collected from Jeram Landfill, which is located in an oil palm plantation at Kuala Selangor, Malaysia. Table 1 shows the characterisation of the landfill leachate.

**Table 1.** Characteristics of landfill leachate.

Test Parameters	Units	Values
pH	-	7.5
Temperature	°C	40
Chemical oxygen demand (COD)	mg/L	10,516
Total Suspended Solid	mg/L	810
Oil and Grease	mg/L	9.5
Zinc as Zn	mg/L	2.48
Iron as Fe	mg/L	4.8
Chromium as Cr	mg/L	0.15
Arsenic as As	mg/L	0.17
Aluminium as Al	mg/L	20
Barium as Ba	mg/L	2.75
Formaldehyde	mg/L	1.9
Ammonia Nitrogen	mg/L	715
Colour Original pH	ADMI	>500
Colour adjusted to pH 7.0	ADMI	>500

## 2.2. Fenton Process and Optimisation Phase

To evaluate and optimise the Fenton process, a random experimental design was chosen to assess at laboratory scale. Some variables such as pH, the concentration of  $\text{Fe}^{2+}$ , reaction time and the ratio of  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  were considered. All tests were conducted at room temperature ( $25 \pm 1$  °C) and atmospheric pressure. All experiments were carried out in a glass reactor with 1 L capacity using jar-test equipment with flat stirring vanes used as a batch reactor. Three hundred millilitres of leachate were placed into the glass reactor and then the pH (3, 4.5, 6, 7.5, and 9) was adjusted according to the provisions of the experimental design using 95–97%  $\text{H}_2\text{SO}_4$ . The pH condition was controlled with a pH meter and rapid mixing was conducted using the jar-test device. The Fenton reaction was carried out by the addition of powdered ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) (500 mg/L, 750 mg/L, 1000 mg/L, 1250 mg/L, 1500 mg/L) and an appropriate  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  ratio (2, 4, 6, 8 and 10) was prepared and mixed for 5 min to obtain a homogeneous solution. Afterwards, the designed amount of hydrogen peroxide solution ( $\text{H}_2\text{O}_2$ , 30% *w/w*) was added in one step and the Fenton reaction was initiated. The glass reactor was then carried to the jar-test (used for coagulation and flocculation) equipment where the sample was subjected to a rapid mixing at 250 rpm for 80 s and then slowly mixed for the adjusted contact time (5 min, 18.75 min, 32.5 min, 46.25 min, 60 min) at 50 rpm. The proposed values of pH, the concentration of  $\text{Fe}^{2+}$ , reaction time and the ratio of  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  above were based on some of the works that have been carried using Fenton treatment for landfill leachate [15,19,32,33]. Once the stirring time was finished, separate aliquots without filtration were taken at the same intervals and neutralized to about pH 7.5–8.0 with sodium hydroxide solution. The sample was allowed to precipitate and form sludge during a period of 1 h. The final sampling was made taking an aliquot of the supernatant liquid. The biodegradability improvement of the Fenton process was achieved through the COD ratio after the treatment was carried out and compared with the initial ratio. The expression used to determine the COD removal (%) achieved was as follows [33]:

$$(\text{COD}_{\text{initial}} - \text{COD}_{\text{final}} / \text{COD}_{\text{initial}}) \times 100 \quad (9)$$

## 2.3. Experimental Design and Statistical Model

The neural network used was a feed forward-like network, consisting of three layers (input, hidden and output). The feed-forward neural network fit criterion using a back-propagation algorithm was used in order to minimize the mean square error for training sets, validation and the test. A three-layered feed forward back propagation neural network (4–3–3) has been used for the modelling of landfill leachate treatment by the Fenton process [34]. The input layer of the network included four parameters, namely, the pH of the leachate, the concentration of  $\text{Fe}^{2+}$ , the ratio of  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ , and the reaction time. The output variable of the entire network was the removal of COD. Thus a 4–3–3 structure network was constructed. The parameters of the ANN experiments are shown in Table 2. The selected ANN model provided a best-fit model for the training data that are demonstrated in Table 3. Figure 1 presents the diagram of the implemented network with four neurons in the input layer, three neurons in the hidden layer and three neurons in the output layer (4–3–3 network) for the modelling. As seen in Figure 1, each neuron is connected to several of its neighbours, with varying coefficients or weights representing the relative influence of the different neuron inputs to other neurons. The weighted sum of the inputs is transferred to the hidden neurons, where it is transformed using an activation function, such as a tangent sigmoid activation function. In turn, the outputs of the hidden neurons act as inputs to the output neuron where they undergo another transformation [35].

**Table 2.** Parameters of artificial neural network (ANN) experiments.

Run	Time (min.)	Fe <sup>2+</sup> Concentration (mg/L)	H <sub>2</sub> O <sub>2</sub> Concentration (mg/L)	pH	H <sub>2</sub> O <sub>2</sub> :Fe <sup>2+</sup> Ratio
1	46.25	750	3000	4.5	4
2	46.25	1250	10,000	7.5	8
3	32.5	1000	6000	6	6
4	32.5	1000	6000	6	6
5	32.5	1000	6000	6	6
6	32.5	1000	6000	6	6
7	32.5	1000	6000	6	6
8	32.5	1000	6000	6	6
9	32.5	1000	6000	6	6
10	32.5	1000	6000	6	6
11	18.75	750	3000	7.5	4
12	18.75	750	6000	4.5	8
13	32.5	1000	6000	6	6
14	46.25	1250	5000	4.5	4
15	32.5	1000	6000	6	6
16	18.75	1250	10,000	7.5	8
17	32.5	1000	6000	6	6
18	32.5	1000	6000	6	6
19	32.5	1000	6000	6	6
20	46.25	1250	5000	7.5	4
21	32.5	1000	6000	6	6
22	32.5	1000	6000	6	6
23	46.25	1250	10,000	4.5	8
24	18.75	1250	5000	4.5	4
25	18.75	750	6000	7.5	8
26	18.75	1250	5000	7.5	4
27	32.5	1000	6000	6	6
28	46.25	750	6000	7.5	8
29	32.5	1000	6000	6	6
30	46.25	750	6000	4.5	8
31	18.75	1250	10,000	4.5	8
32	32.5	1000	10,000	6	6
33	32.5	1000	10,000	6	6
34	18.75	750	3000	4.5	4
35	32.5	1000	6000	6	6
36	46.25	750	3000	7.5	4
37	32.5	500	3000	6	6
38	60	1000	6000	6	6
39	32.5	1500	9000	6	6
40	32.5	1000	6000	3	6
41	5	1000	6000	6	6
42	32.5	1000	6000	9	6
43	32.5	1000	2000	6	2
44	32.5	1000	10,000	6	10

**Table 3.** ANN training parameters.

Parameter	Magnitudes
Number of input nodes	4
Number of hidden neurons	3
Number of outputs nodes	3
Maximum number of epochs	5000
Learning rate (lr)	0.01
Learning rule	Back-propagation

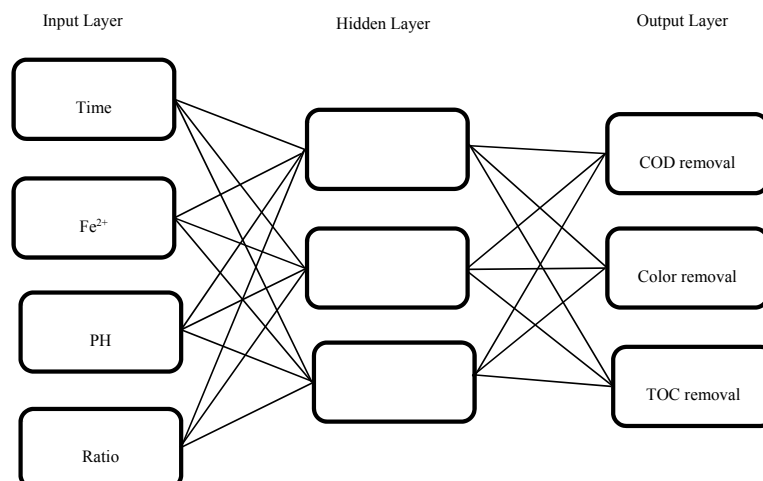


Figure 1. Schematic representation of neural network.

### 3. Results and Discussion

#### 3.1. Investigation of the Chemical Oxygen Demand (COD) Treatment Efficiency

The effects of four parameters, namely pH, Fe<sup>2+</sup> concentration, H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> ratio and experimental time of degradation, were studied using Matlab software; the subsequent statistical analysis was performed by the ANN method. A total of 44 runs of experiments were conducted to examine the prediction accuracy of the developed ANN model. Four experimental factors were selected as the input parameters and COD removal was selected as the output parameter of the ANN model. The experimental variables and the observed response ( $Y_1$ ) are presented in Table 4. The maximum COD removal occurred in run 40 with 94.41% and the lowest COD removal occurred in run 26 with 12.4% removal. The highest predicted COD removal percentage was 78.9% and the lowest predicted removal percentage was 9.3%. To validate the precision of the predicted values, a comparison of the COD removal obtained from the proposed model with the experimental results was performed and the results are presented in Figure 2. It was found that the overall prediction error using the developed ANN model was within  $-0.625\%$ . Thus, the ANN model's prediction accuracy was acceptable for the purpose of this study. The plots of the predicted values versus the actual data demonstrate acceptable agreement between the observed data and the fitted model. Figure 3 shows that the predicted values of the responses from the models agreed well with the observed values; the data points are distributed relatively close to the straight line ( $y = x$ ). Consequently, the model could be used to navigate the design space.

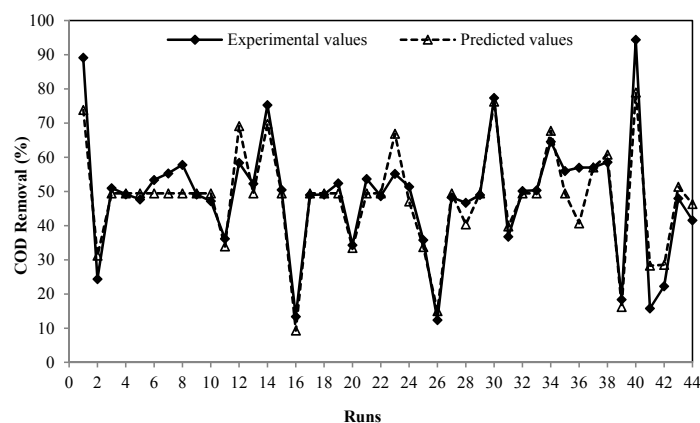
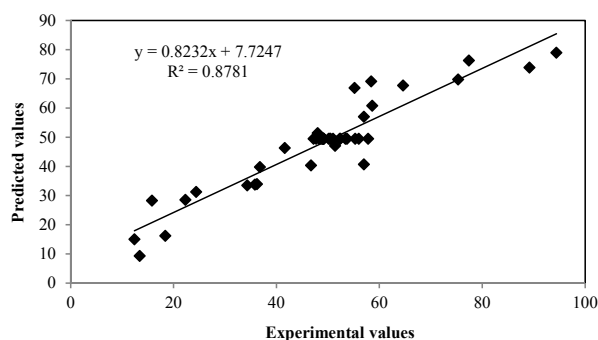


Figure 2. Comparison between experimental and prediction values for COD removal using the ANN method.

**Table 4.** ANN design magnitudes and experimental results for COD removal.

Run	Time (min.)	Fe <sup>2+</sup> Concentration (mg/L)	pH	H <sub>2</sub> O <sub>2</sub> :Fe <sup>2+</sup> Ratio	Experimental COD Removal %	Predicted COD Removal %	Error %
1	46.25	750	4.5	4	89.16	73.878	17.139
2	46.25	1250	7.5	8	24.4	31.247	-28.062
3	32.5	1000	6	6	51	49.468	3.003
4	32.5	1000	6	6	49.2	49.468	-0.544
5	32.5	1000	6	6	47.7	49.468	-3.706
6	32.5	1000	6	6	53.4	49.468	7.363
7	32.5	1000	6	6	55.3	49.468	10.546
8	32.5	1000	6	6	57.81	49.468	14.430
9	32.5	1000	6	6	49.15	49.468	-0.647
10	32.5	1000	6	6	47.2	49.468	-4.805
11	18.75	750	7.5	4	36.2	33.934	6.258
12	18.75	750	4.5	8	58.4	69.144	-18.398
13	32.5	1000	6	6	52.3	49.468	5.414
14	46.25	1250	4.5	4	75.3	69.790	7.316
15	32.5	1000	6	6	50.5	49.468	2.043
16	18.75	1250	7.5	8	13.4	9.331	30.365
17	32.5	1000	6	6	49	49.468	-0.955
18	32.5	1000	6	6	49.13	49.468	-0.687
19	32.5	1000	6	6	52.4	49.468	5.595
20	46.25	1250	7.5	4	34.31	33.484	2.405
21	32.5	1000	6	6	53.7	49.468	7.880
22	32.5	1000	6	6	48.67	49.468	-1.639
23	46.25	1250	4.5	8	55.17	66.921	-21.299
24	18.75	1250	4.5	4	51.4	47.087	8.390
25	18.75	750	7.5	8	35.8	33.766	5.681
26	18.75	1250	7.5	4	12.4	15.035	-21.256
27	32.5	1000	6	6	48.3	49.468	-2.418
28	46.25	750	7.5	8	46.7	40.371	13.552
29	32.5	1000	6	6	49	49.468	-0.9551
30	46.25	750	4.5	8	77.41	76.310	1.420
31	18.75	1250	4.5	8	36.79	39.777	-8.121
32	32.5	1000	6	6	50.15	49.468	1.359
33	32.5	1000	6	6	50.36	49.468	1.77
34	18.75	750	4.5	4	64.6	67.755	-4.884
35	32.5	1000	6	6	56	49.468	11.664
36	46.25	750	7.5	4	57	40.696	28.602
37	32.5	500	6	6	57	57.042	-0.075
38	60	1000	6	6	58.6	60.795	-3.746
39	32.5	1500	6	6	18.4	16.230	11.790
40	32.5	1000	3	6	94.41	78.969	16.355
41	5	1000	6	6	15.8	28.303	-79.135
42	32.5	1000	9	6	22.3	28.553	-28.042
43	32.5	1000	6	2	48	51.403	-7.089
44	32.5	1000	6	10	41.6	46.336	-11.386

**Figure 3.** Predicted versus actual values plot for COD removal using the ANN model.

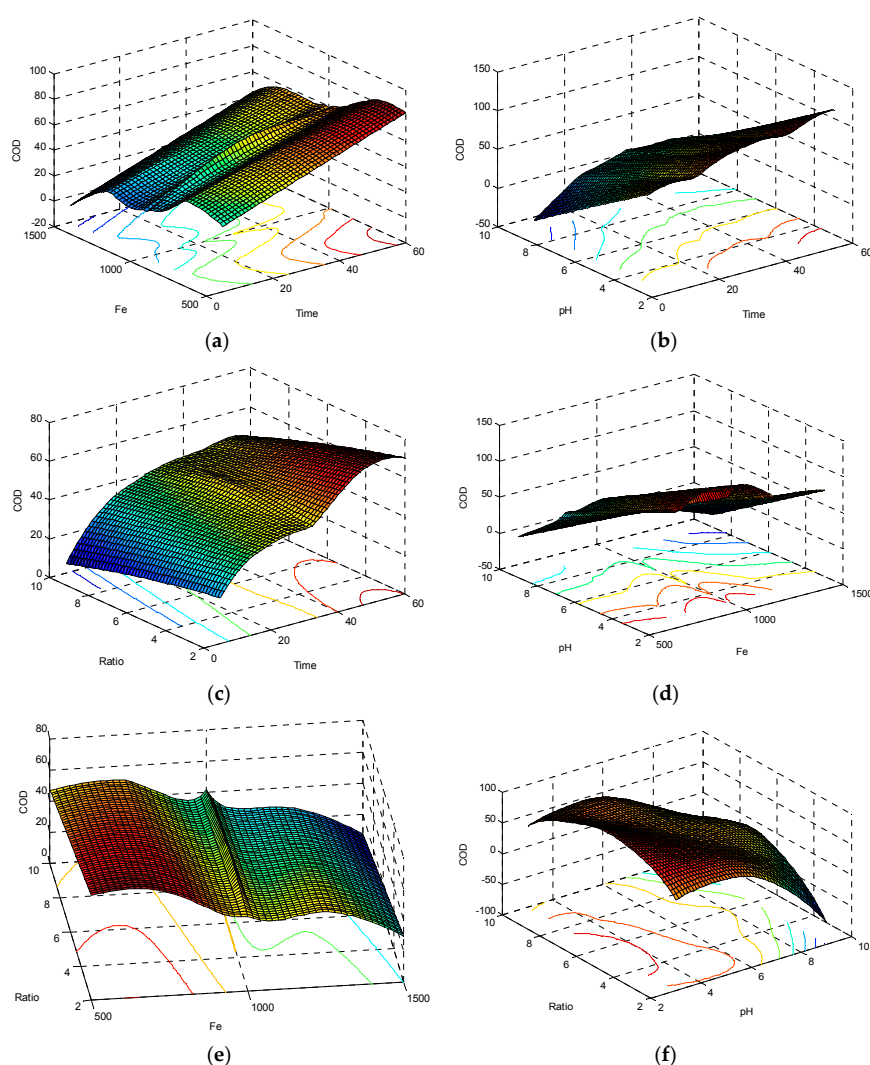
### 3.1.1. Interactive Effect of Time and Fe<sup>2+</sup> Concentration on COD Reduction

Figure 4a presents the 3D response surface from the ANN algorithm for COD reduction as a function of contact time and Fe<sup>2+</sup> concentration. It is obvious that reaction time had a positive effect on the mineralization of the leachate. It was observed that with an increase in reaction time and a decrease in Fe<sup>2+</sup> concentration, COD removal could be effectively increased. Increasing residence

time from 5 min to 32.5 min increased COD removal from 15.80% to 57.81%. Most organic removal occurred in the first 32.5 min, at which point the COD removal efficiency reached 57.81%, which is the common result of oxidation and coagulation. After 32.5 min, the change in COD removal efficiency became insignificant.

### 3.1.2. Interactive Effect of Contact Time and pH on COD Reduction

The pH of the leachate had a significant influence on COD removal. It was found that with a decrease in pH, the COD removal increased as the time increased (Figure 4b). Thus, the pH has to be in the acidic range to generate the maximum amount of hydroxyl radicals to oxidize the organic compounds. A similar phenomenon was observed in previous studies [36,37]. However, the pH should not be too low since at very low pH values (<2.0) the reaction will slow down due to the formation of complex iron species and oxonium ions  $[H_3O_2]^+$  [38]. On the other hand, at high pH (pH > 4), iron ions precipitate, especially  $Fe^{3+}$ , which inhibits the regeneration of ferrous ions. Therefore, the amount of catalyst available for the Fenton reaction decreases. Hydrogen peroxide is also unstable in a basic solution and may decompose into oxygen and water and lose its oxidation ability.



**Figure 4.** (a) 3D-response surfaces for COD reduction as a function of contact time and  $Fe^{2+}$  concentration; (b) contact time and pH; (c) contact time and  $H_2O_2:Fe^{2+}$  ratio; (d)  $Fe^{2+}$  concentration and pH; (e)  $Fe^{2+}$  concentration and  $H_2O_2:Fe^{2+}$  ratio; and (f) pH and  $H_2O_2:Fe^{2+}$  ratio.



### 3.1.3. Interactive Effect of Time and $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ Ratio on COD Removal

In the Fenton process, hydrogen peroxide and iron are the two major chemicals that determine the operating costs as well as the efficacy of the process. In order to maximize the effectiveness of the process, it is very important to determine the optimal operational  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  ratio. The results demonstrate that with an increase in reaction time, COD removal increased as the ratio decreased (Figure 4c).

### 3.1.4. Interactive Effect of $\text{Fe}^{2+}$ Concentration and pH on COD Removal

It can be seen in Figure 4d that the Fenton efficiency of COD removal increased with augmenting the  $\text{Fe}^{2+}$  concentration. The maximum  $\text{Fe}^{2+}$  concentration for COD removal was 1000 mg/L. A further increase in  $\text{Fe}^{2+}$  concentration resulted in a decrease in COD removal efficiency. Based on operational costs and organic material removal efficiency, the optimal dosage of Fenton reagents can be determined. Generally, the removal of organic matter improves with increasing concentrations of iron salt. However, the removal increment may be marginal when the concentration of iron salt is high. The use of a much higher concentration of  $\text{Fe}^{2+}$  could lead to the self-inhibition of OH radicals by  $\text{Fe}^{2+}$  ions and decrease the degradation rate of pollutants [39].

pH is an important parameter in the Fenton process because the pH of the solution controls the production of hydroxyl radicals and the concentration of ferrous ions. As can be seen in Figure 4d, the maximum removal of COD was obtained at pH 3 and decreased with an increase in pH. Thus, the pH value has to be in the acidic range to generate the maximum amount of hydroxyl radicals to oxidize organic compounds. The highest COD removal happened at pH = 3 and a  $\text{Fe}^{2+}$  concentration of 1000 mg/L. Increasing the pH value and the  $\text{Fe}^{2+}$  concentration decreased COD removal. Thus, there is a clear interaction between pH and  $\text{Fe}^{2+}$  concentration, with significant effects on COD reduction.

### 3.1.5. Interactive Effect of $\text{Fe}^{2+}$ Concentration and Ratio of $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ on COD Removal

$\text{Fe}^{2+}$  dosage has a considerable effect on the COD removal efficiency. The removal of organics directly decreased with the concentration of  $\text{Fe}^{2+}$  added to the critical dosage (Figure 4e). The optimum  $\text{Fe}^{2+}$  concentration for maximum COD removal was 1000 mg/L. A further increase in the  $\text{Fe}^{2+}$  concentration resulted in a decrease in COD removal efficiency. Moreover, it was seen that the Fenton efficiency of COD removal increased with a reduction in the  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  ratio. Any increase in the  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  ratio beyond 6 decreased the removal efficiency. This may be due to the fact that the Fenton reaction mechanisms change and some side reactions may occur. It seems that excessive hydrogen peroxide has a scavenging effect on hydroxyl radicals. On the other hand, when the ratio was above 6, COD removal decreased because of the scavenging effect of excess  $\text{Fe}^{2+}$ . It was noted that the maximum COD removal was obtained with a molar ratio located near the centre of the experimental region.

### 3.1.6. Interactive Effect of pH and Ratio of $\text{H}_2\text{O}_2:\text{Fe}^{2+}$ on COD Reduction

The influence of the  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  ratio and pH on COD removal efficiency was significant (Figure 4f). In the Fenton process, iron and hydrogen peroxide are the two major chemicals that determine operational costs as well as efficiency. Determination of the most favorable amount of Fenton reagents is very important. The results show that removal efficiencies increased with an increase in the  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  ratio, but a further increase in the  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  ratio (above 6) produced less efficient improvements in removal. The overall COD removal efficiency showed strong reductions when the initial pH was set out of the interval, i.e., ranging between 3.0 and 4.5.

## 3.2. Response Optimization and Validation of the Experimental Model

Numerical optimization was used to determine the optimum process parameters for maximum leachate mineralization. The optimized conditions under specified constraints were obtained for pH = 3,

$\text{Fe}^{2+}$  concentration = 781.25 mg/L, after 28.04 min of reaction time and at a ratio of 2. Under these optimized conditions, 100% COD removal was predicted. In order to confirm the accuracy of the removal predicted by the model and the reliability of the optimum combination, one additional experiment was carried out under the optimum conditions. The experimental values were found to agree well with the predicted ones, with a mean COD removal efficiency of 97.83%.

#### 4. Conclusions

In industrial applications, the determination of the operating conditions to optimize the process response is of special significance. An innovative technique to predict the response optimization of the experimental models is essential to measure the optimum operating conditions. In the current study, the ability of ANN model was evaluated to predict the COD of landfill leachate treatment using the Fenton oxidation process. The overall prediction error for COD using the developed ANN models were  $-0.625\%$  and, thus, the ANN model's prediction accuracy was acceptable. The derived model was adequate in predicting responses,  $R_{\text{COD}}^2 = 0.8781$ . The optimized conditions for COD removal under specified constraints were obtained at pH = 3,  $\text{Fe}^{2+}$  concentration = 781.25 mg/L, reaction time = 28.04 min and  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  ratio = 2.

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