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RESEARCH ARTICLE

The use of artificial neural network (ANN) for the prediction and simulation of oil degradation in wastewater by AOP

Yasmen A. Mustafa · Ghydaa M. Jaid · Abeer I. Alwared · Mothana Ebrahim

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Abstract The application of advanced oxidation process (AOP) in the treatment of wastewater contaminated with oil was investigated in this study. The AOP investigated is the homogeneous photo-Fenton ($UV/H_2O_2/Fe^{+2}$) process. The reaction is influenced by the input concentration of hydrogen peroxide H_2O_2, amount of the iron catalyst Fe^{+2}, pH, temperature, irradiation time, and concentration of oil in the wastewater. The removal efficiency for the used system at the optimal operational parameters (H_2O_2=400 mg/L, Fe^{+2}= 40 mg/L, pH=3, irradiation time=150 min, and temperature=30 °C) for 1,000 mg/L oil load was found to be 72 %. The study examined the implementation of artificial neural network (ANN) for the prediction and simulation of oil degradation in aqueous solution by photo-Fenton process. The multilayered feed-forward networks were trained by using a backpropagation algorithm; a three-layer network with 22 neurons in the hidden layer gave optimal results. The results show that the ANN model can predict the experimental results with high correlation coefficient (R^2=0.9949). The sensitivity analysis showed that all studied variables (H_2O_2, Fe^{+2}, pH, irradiation time, temperature, and oil concentration) have strong effect on the oil degradation. The pH was found to be the most influential parameter with relative importance of 20.6 %.

Keywords Advanced oxidation process · Homogeneous photo-Fenton · Oil degradation · Artificial neural network · Sensitivity analysis

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Y. A. Mustafa (✉) · G. M. Jaid · A. I. Alwared
Department of Environmental Engineering, University of Baghdad, P.O. Box 47121, Jadria, Baghdad, Iraq
e-mail: yasmen.mustafa@gmail.com

M. Ebrahim
Ministry of Environment, Baghdad, Iraq

Introduction

Oil-contaminated wastewater can cause serious environmental problems due to its hazardous nature. The volume of oil-contaminated wastewater from petroleum filling stations has increased in line with the number of such stations required to cater for the growing number of vehicles. In Iraq, there are 507 car-wash facilities, excluding the region of Kurdistan (Ministry of Environment report 2011, Iraq), and some of them discharge their oily wastewater (almost an emulsion) to the sewer system without treatment.

Also, there are many accidental discharges of hydrocarbon oil to the natural environment during its processing, transportation, and storage. Oil-spills cause many problems in the environment depending on the volume of the oil spilled. For instance, water resources as well as habitats where fish, birds, and other wildlife live can be damaged. As a result, there has been an increase in research activity focusing on treating oily wastewaters.

Several conventional techniques such as gravity separation, dissolved air flotation, demulsification, coagulation, and flocculation have been employed for the treatment of oily wastewater.

However, these processes can only transform the pollutants from one phase to another without destroying them. Also, these processes result in concentrated sludge which requires further processing and disposal. In addition, conventional treatment processes have difficulty in fully removing emulsified oil or small oil droplets.

Advanced oxidation processes (AOPs) have been investigated for the treatment of oil-contaminated wastewater, as an alternative to conventional treatment techniques, by many researchers (Tiburtius et al. 2005; Galvao et al. 2006; Mater et al. 2007; Mota et al. 2008; Tony et al. 2009; Yu et al. 2011; Tony et al. 2012).

AOPs are characterized by the use of highly reactive intermediates, hydroxyl radicals ($HO^{\bullet}$), which attack the organic pollutants in the wastewater and mineralize them. Advanced oxidation processes have the advantage of rapid oxidation of pollutants to harmless end-products. These processes include homogenous processes such as Fenton's reagent and H_2O_2, and heterogeneous photocatalysis using semiconductors such as TiO_2 and ZnO. Fenton process has received much attention especially when induced by ultraviolet radiation (Neyens and Baeyens 2003).

The AOPs are expensive processes, owing to the high cost of the reagents involved such as H_2O_2 and electric energy when UV radiation is applied. Therefore, a balance must be maintained between excess and low levels of reagents.

Treatments of recalcitrant wastewater by AOPs are influenced by several factors. Due to the complexity of the process, it is difficult to be modeled and simulated using conventional mathematical techniques. Application of artificial neural network (ANN) to solve environmental engineering problems has been reported in many articles. However, few studies on application of ANN in advanced oxidation processes have been reported (Aleboyeh et al. 2008; Oguza et al. 2008; Duran et al. 2006), especially in the oil contamination domain.

In the present work, the effectiveness of $UV/H_2O_2/Fe^{+2}$ system in the degradation of oil in wastewater was studied. To achieve the experimental objectives, different variables were chosen to be followed throughout the treatment, H_2O_2, Fe^{+2}, pH, temperature, irradiation time, and oil concentration. The implementation of ANN model for the prediction of oil degradation was investigated. The ANN modeling outputs were compared with the experimental data. Additionally, the ANN model was used to confirm the optimum experimental amount of H_2O_2 and Fe^{+2} required for the oil degradation process.

Materials and methods

Chemicals

Commercial gas oil was used in this study as a model pollutant for the degradation of oil from wastewater by AOP. The gas oil was analyzed at the Petroleum Research and Development Center, Ministry of Oil. The chemical composition was Paraffins 62.5 %, Aromatics 18.7 %, and Naphthenes 18.8 %. Hydrogen peroxide H_2O_2 (30 % wt/wt from Scharlau) and ferrous chloride tetrahydrate $FeCl_2.4H_2O$ (97 % purity from BDH) were used in the experimentation. All samples were prepared by dissolving requisite quantity in distilled water. The pH of the solution was adjusted by using sulfuric acid H_2SO_4 solution (99 % purity from Riedel-deHaen).

Equipment

The experiments were carried out in a batch mode laboratory-scale reactor .The reactor consisted of Pyrex glass cylinder 3 L volume with a magnetic stirrer and a heater (MSH-300N, BOECO, Hamburg, Germany). UV radiation (254 nm) was generated from UV lamp (TUV 11W 4P-SE, Philips, Guildford, Surrey, England), which was fixed vertically at the top of the reactor. The lamp was totally immersed in the content of the cylindrical reactor. UV lamp was sheathed in quartz sleeve for protection. The distance between the lamp and the reactor wall was fixed at 5 cm to ensure maximum light irradiation as mentioned by Chiu et al. (1999). The turbidity of the solution was measured using turbidity meter (Hanna microprocessor, Padua, Italy). Initial pH of the solution was monitored using a pH meter (INOLAB 72, WTW Co., Weilheim, Germany).

Experimental procedure

The desired concentration of gas oil (500–2,000 mg/L) was prepared and the pH was adjusted, before adding the reagents, by adding a dilute H_2SO_4 solution to the reactor contents.

The Fenton reagents were introduced to the solution by adding ferrous chloride (10–100 mg/L) and then the hydrogen peroxide (100–800 mg/L). The solution was then subjected to stirring using magnetic stirrer at 200 rpm for 150 min. The heater was adjusted at the required temperature. Samples at a regular time intervals (30 min) were taken for COD analysis.

Analysis

Chemical oxygen demand (COD) was used to monitor the oil concentration. COD of samples was analyzed by using COD Photometer. The appropriate amount of sample (0.2 mL) was introduced into commercially available digestion solution (HR-Rang 0–15,000 mg/L) containing potassium dichromate, sulfuric acid, and mercuric sulfate. The mixture was then incubated for 120 min at 150 °C in a COD reactor (model RD-125, Lovibond, Dortmund, Germany). After oxidation is complete, the COD concentration was measured colorimetrically at 605 nm using a DR/2010 spectrophotometer (model MD 100, Lovibond, Dortmund, Germany).

Artificial neural network

Artificial neural networks are computational tools which have the ability to learn the behavior of a process and the relationship between groups of variables without any phenomenological model of the system. They are a powerful tool for discovering relationships between sets of data. This artificial intelligence method has attracted considerable attention because it can handle complex, nonlinear problems and requires less processing time than conventional methods (Khataee and Kasiri 2010).

A computational neural network consists of simple processing units called neurons. A neural net is a interconnected parallel structure consisting of (1) an input layer of neurons (independent variables), (2) a number of hidden layers, and (3) an output layer (dependent variables). The number of input and output neurons effectively represents the number of variables used in the prediction and the number of variables to be predicted, respectively. Hidden layers act like feature detectors, and theoretically, the existence of more than one hidden layer is possible. However, universal approximation theory suggests that a network with a single hidden layer with a sufficiently large number of neurons can interpret any input–output structure (Darioush et al. 2009). The hidden layer's task is to transform the inputs into something that the output layer can use.

To develop an accurate process model using ANN, the learning process or training, validation, and testing are among the important steps. In the training process, a set of input–output patterns is repeated to the ANN. From that, weights of all the interconnections between neurons are adjusted until the specified input yields the desired output. Through these activities, the ANN learns the correct input–output response behavior. For validation, the ANN is subjected to input patterns unseen during training and introduced adjustment to make the system more reliable and robust. It is also used to determine the stopping point before over fitting occurs. After the training phase, the ANN is used to simulate the output of a set of test data. If the ANN returns the values of the output for the test data within an acceptable margin, then the ANN can be said to be successfully trained and may be used as a predictive tool (Emad and Malay 2011).

Topology of an artificial neural network is determined by the number of its layers, the number of nodes in each layer, and the nature of transfer functions. Optimization of ANN topology is probably the most important step in the development of the model. In the present work, a three-layered feed-forward backpropagation neural network (6:22:1) was used for modeling of oil degradation process (Fig. 1). The input variables to the feed-forward neural network were as follows: irradiation time (min), initial Fe^{+2} concentration (mg/L), initial H_2O_2 concentration (mg/L), pH, temperature (°C), and initial oil concentration (mg/L). Removal efficiency (%) was chosen as the experimental response or output variable.

In order to determine the optimum number of hidden nodes, a series of topologies was used, in which the number of nodes were varied from 2 to 22. Mean square error (MSE) was used as the error function. MSE measures the performance of the net network. In the present work, the mean square error was minimized when 22 neurons were used.

In the feed-forward neural net, all the neurons of a particular layer are connected to all the neurons of the layer next to it. The input layer of neurons acts as a distributer, and the input to this layer is directly transmitted to the hidden layer. The inputs to the hidden and output layers are calculated by performing a weighted summation of all the inputs received from the preceding layer. The weighted sum of the input is transferred to the hidden neurons, where it is transformed using an activation function. The output of hidden neurons, in turn, acts as inputs to output neurons where it undergoes another transformation.

In the present work, a three-layer ANN with tangent sigmoid transfer function (tansig) at the hidden layer with (22) neurons, linear transfer function (purelin) at output layer, and Levenberg–Marquardt backpropagation (LMA) training algorithm were used. A comparison between calculated and experimental values of the output variable for test sets using neural network model showed a correlation coefficient of 0.9949, which confirms that neural network model could effectively reproduce the experimental results.

Results and discussion

In the photo-Fenton process, H_2O_2 is dissociated to generate hydroxyl radical which is responsible for the degradation and mineralization of organic compounds. The formation of hydroxyl radical depends on several factors such as initial concentration of H_2O_2, dose of Fe^{+2}, pH, temperature, and the organic load. Therefore, the effects of these factors were investigated.

The effect of initial H_2O_2 concentrations

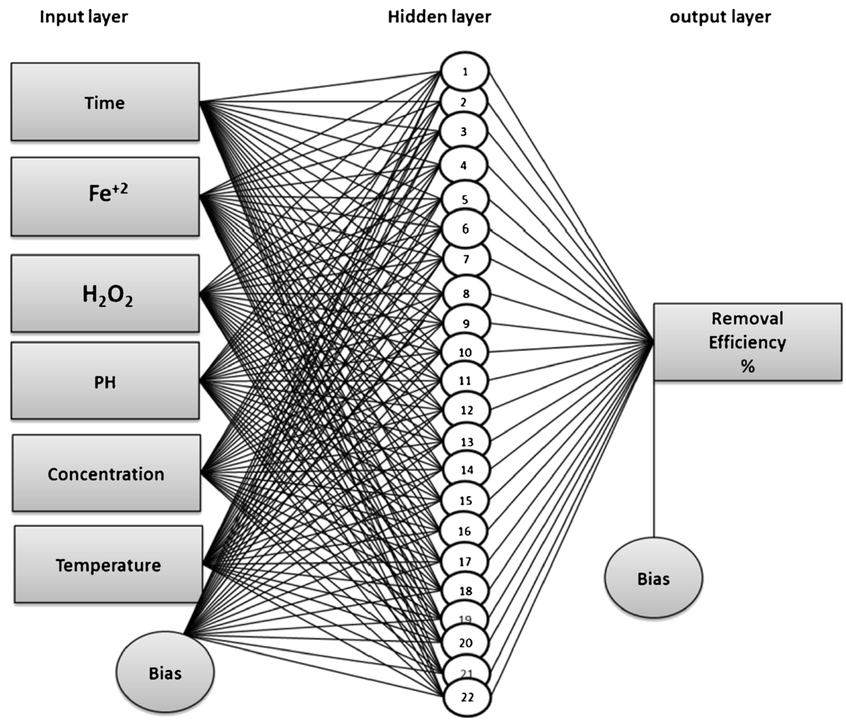
The effect of initial concentration of H_2O_2 (100, 200, 400, 600, and 800 mg/L) on photo-Fenton process was tested to optimize the amount of H_2O_2 required to degrade the oil. A fixed initial amount of Fe^{+2} (40 mg/L) was maintained throughout these experiments. The initial oil concentration was 1,000 ppm (1,550±60 COD), initial pH=7, and the temperature was maintained at 20 °C throughout the tests.

Figure 2 shows the relation between the removal efficiency and the irradiation time for different initial concentrations of H_2O_2. From this figure, it can be noticed that the percent of degradation increased to 54 % at 400 mg/L H_2O_2 then decreased to 47 % at 800 mg/L of H_2O_2 following 150 min of irradiation time.

It was expected that increasing the concentration of H_2O_2 results in a reduction in the rate of degradation due to many reasons among them (Ahmad 2011): the reaction of H_2O_2 with $HO^{\bullet}$ acts as an inhibiting agent (i.e., self-scavenging of $HO^{\bullet}$ by H_2O_2), Eq. 1.

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad (1)$$

Fig. 1 Optimized ANN structure



HO$^{\bullet}$ efficiently reacts with H_2O_2 and produce $HO^{\bullet}_2$. Since $HO^{\bullet}_2$ radicals are not as reactive as HO$^{\bullet}$, then low degradation may be obtained. Also, the hydroxyl radical may recombine and participate in radical–radical reactions to form H_2O_2, Eq. 2.

$$2HO^{\bullet} \rightarrow H_2O_2 \tag{2}$$

Additionally, at higher H_2O_2 concentrations, a lower light intensity is available for oil degradation, since H_2O_2 also absorbs light in the system. However, if H_2O_2 does is low, HO$^{\bullet}$ formation will also be low, decreasing the treatment efficiency. Therefore, a balance must be maintained between excess and low levels of H_2O_2.

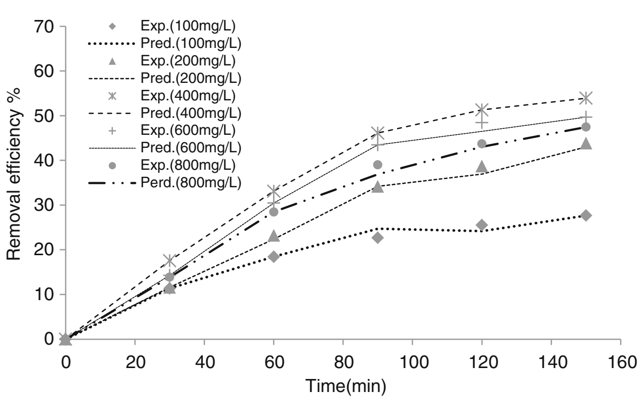


Fig. 2 Effect of initial H_2O_2 concentrations on the degradation of oil by photo-Fenton system at Fe^{+2}=40 mg/L, pH=7, oil concentration=1,000 mg/L, and temperature=20 °C. Experimental and predicted results

The predicted results are also shown in Fig. 2, for different H_2O_2 concentrations using ANN model. The figure shows that the predicted values are in good agreement with the experimental results.

Khataee and Kasiri (2010) and Emad and Malay (2011) have reviewed the early applications of ANNs in modeling and simulation of homogeneous photocatalytic processes in wastewater treatment. They illustrated that many researchers applying the photo-Fenton process (Elmolla et al. 2010; Yu et al. 2009; Giroto et al. 2006; Yu et al. 2010) obtained a good agreement between experimental and predicted output values, with high correlation coefficients of more than 95 %. The ANN predicted results in this research were very close to the experimental output of oil degradation with a correlation coefficient of 0.9949 which is in line with previous work.

An optimum value of H_2O_2 was obtained to be 400 mg/L experimentally after 150 min of irradiation time. To examine if this value represents the adequate amount of H_2O_2 required for best degradation using ANN model, the amount of H_2O_2 was varied around the optimum value as shown in Fig. 3. It can be seen from this figure that increasing the concentration of H_2O_2 from 400 to 410 and 430 mg/L gave approximately the same efficiency, and then, a slight increase in removal efficiency at 440 mg/L was observed. After that, a noticeable decrease in the removal efficiency was seen. This means that 400 mg/L of H_2O_2 is the optimum amount for the degradation process at the mentioned conditions.

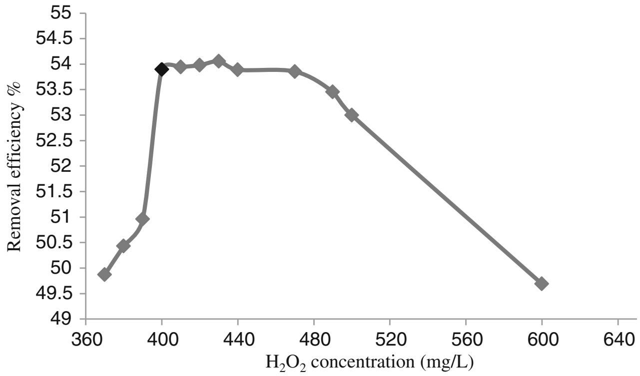


Fig. 3 Removal efficiency at different concentrations of H_2O_2, varied around the optimum value (400 mg/L) as predicted by ANN model

The effect of initial Fe^{+2} concentrations

Different concentrations of Fe^{+2} (10, 20, 40, 50, 60, and 100 mg/L) were tested in the present experiments. The optimum H_2O_2 concentration (400 mg/L) from the previous section was used. All the other parameters were maintained at their previous values. The results are plotted in Fig. 4. From this figure, it can be observed that the degradation rate of oil distinctly increased with the increasing amounts of iron salt; it reached its maximum value of 54 % at 40 mg/L after about 150 min of irradiation time. The addition of the iron salt above this value did not affect the degradation; rather, it had a negative effect, only 20 % removal was achieved at 100 mg/L Fe^{+2}. This finding is in agreement with the previous observation of Tony et al. (2009, 2012).

The negative effect can be explained as follows: the addition of ferrous ions increases wastewater brown turbidity during the photo-treatment, which hinders the absorption of UV light (Dincer et al. 2008). Excess ferrous ions can react with hydroxyl radical according to Eq. 3, decreasing the attack of hydroxyl radical on organic substrates.

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + HO^{-} \quad (3)$$

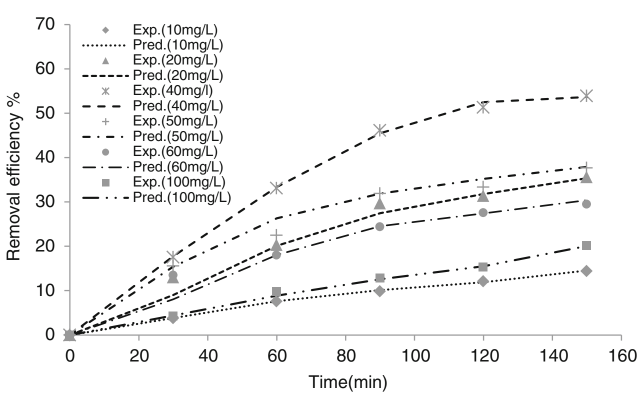


Fig. 4 Effect of initial Fe^{+2} concentration on the degradation of oil by photo-Fenton system at H_2O_2=400 mg/L, pH=7, oil concentration= 1,000 mg/L, and temperature=20 °C. Experimental and predicted results

Also, excess ferrous ions can react with OH radical producing compounds which inhibit reaction rate (Neyens and Baeyens 2003).

The predicted results by using ANN model are also shown in Fig. 4. These results confirm that the neural network models can effectively reproduce the experimental results.

An optimum value of Fe^{+2} (40 mg/L) was obtained experimentally. To examine if this value represents the adequate amount of Fe^{+2} using ANN model, the amount of Fe^{+2} was varied around the optimum value as shown in Fig. 5. It can be seen from this figure that increasing the concentration of Fe^{+2} from 40 to 41 and 42 mg/L gave nearly the same efficiency; after that, the efficiency tends to be decreased distinctly. Hence, 40 mg/L is the optimum amount of Fe^{+2} at the mentioned conditions.

The effect of initial pH

The effect of pH plays an important role in the photo-Fenton treatment process. Different values of pH were examined in this study (2, 3, 4, 5, 7, and 8), keeping the other parameters and dosage constant (Fe^{+2}=40 mg/L, H_2O_2=400 mg/L, oil concentration=1,000 mg/L, and temperature=20 °C). Figure 6 shows that a maximum removal efficiency at 66 % was obtained at pH=3. Above this value, the removal efficiency decreased gradually, except for pH=8, where a marked decrease in removal efficiency of 28 % was observed.

The optimum pH, as observed, was 3 which is in agreement with previous studies using photo-Fenton process (Benitez et al. 2001; Tiburtius et al. 2005; Tony et al. 2012).

The pH affects the activity of both the speciation of iron and hydrogen peroxide decomposition. The decrease in removal efficiency can be explained as follows: at lower pH (<2.5), the formation of $[Fe(H_2O)_6]^{2+}$ complex occurs rather than $[Fe(OH)(H_2O)_5]^{+}$ complex, which reacts more slowly with hydrogen peroxide and therefore produces less amount of reactive hydroxyl radicals, thereby reducing the degradation efficiency as mentioned by Mota et al. (2008). In addition,

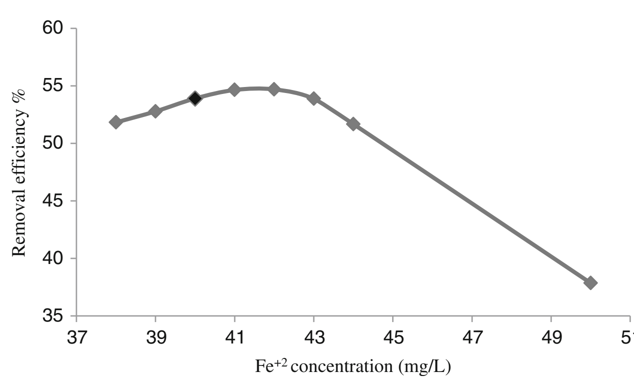


Fig. 5 Removal efficiency at different concentrations of Fe^{+2}, varied around the optimum value (40 mg/L) as predicted by ANN model

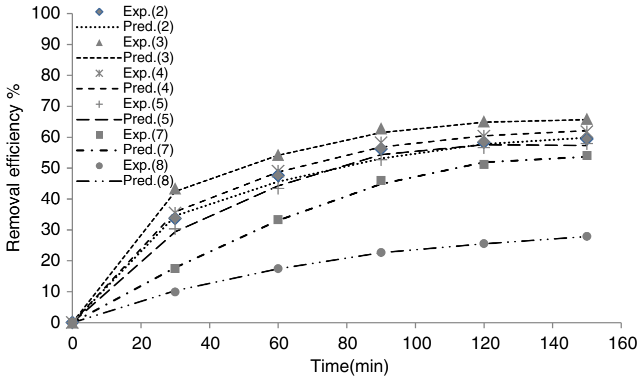


Fig. 6 Effect of difference initial pH values on the degradation of oil by photo-Fenton system at H_2O_2=400 mg/L, Fe^{+2}=40 mg/L, oil concentration=1,000 mg/L, and temperature=20 °C. Experimental and predicted results

the scavenging effect of hydroxyl radicals by hydrogen ions becomes important at a very low pH, and also, the reaction of Fe^{3+} with hydrogen peroxide is inhibited (Pignatello 1992).

At an operating pH of >4, iron reacts with the hydroxide ions (HO−), precipitating iron hydroxide $Fe(OH)_2$ or $Fe(OH)_3$, which does not react with H_2O_2, and precluding the Fenton reaction. Also, the oxidation potential of OH radical is known to decrease with an increase in the pH (Kwon et al. 1999).

A very good fitting between the predicted values and the experimental results can be observed for different pH values in Fig. 6.

The effect of temperature

Reaction temperature is another important process parameter that affects the degradation process. Different temperatures (20, 30, and 40 °C) were used. The dosage of the reagents and other parameters were kept constant (Fe^{+2}=40 mg/L, H_2O_2= 400 mg/L, oil concentration=1,000 mg/L, and pH=3). The results are plotted in Fig. 7. This figure shows that the removal efficiency of oil increases from 66 % at 20 °C to 72 % at 30 °C and then decreases to 69 % at 40 °C. The increase in temperature accelerated the decomposition of H_2O_2, thus increasing the generation of OH radicals which enhances the degradation process slightly. Rivas et al. (2004) have reported that the degradation efficiency is unaffected even when the temperature is increased from 10 to 40 °C. Above 40 °C, the efficiency of hydrogen peroxide utilization decreases due to accelerated decomposition of hydrogen peroxide into water and oxygen as mentioned by Nesheiwat and Swanson (2000).

Additionally, Fig. 7 shows a very good agreement between the predicted values of ANN model and the experimental values.

The effect of initial oil concentration

Different concentrations of gas oil (500, 1,000, and 2,000 °mg/L) were used with H_2O_2=400 mg/L, Fe^{+2}= 40 mg/L, pH=3, and temperature=30 °C. The results are plotted in Fig. 8. From this figure, it can be observed that the removal efficiency decreases from 79 to 50 % as the concentration of gas oil increases from 500 to 2,000 mg/L, respectively. This can be attributed to the increase in turbidity of the solution. The turbidity for 2,000 mg/L oil solution was measured to be 47 NTU, whereas for 500 mg/L oil solution the turbidity was only 6 NTU. Decreasing turbidity clearly enhances the penetration of UV light, resulting in enhanced oil removal; this observation was reported by Najjar et al. (2001).

Figure 8 confirms that the neural network model can effectively predict the experimental results.

Sensitivity analysis

In order to assess the relative importance of the input variables, sensitivity analysis was conducted based on the Garson

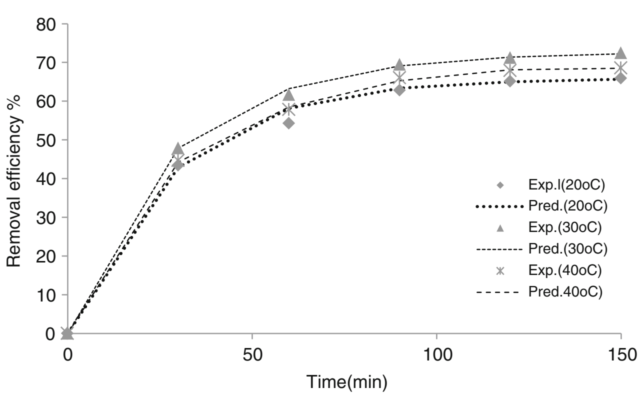


Fig. 7 Effect of different temperatures on degradation of oil by photo-Fenton system at H_2O_2=400 mg/L, pH=3, oil concentration=1,000 mg/L, and Fe^{+2}=40 mg/L. Experimental and predicted results

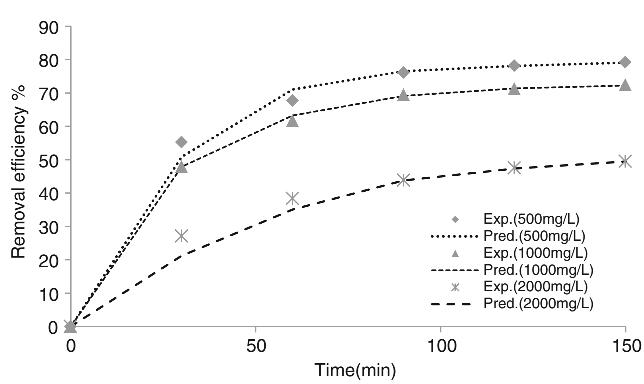


Fig. 8 Effect of different oil concentrations on the degradation of oil by photo-Fenton system at H_2O_2=400 mg/L, Fe^{+2}=40 mg/L, temperature= 30 °C, and pH=3. Experimental and predicted results

Table 1 Weight matrix, weights between input, and hidden layers *W1* and between hidden and output layers *W2*

Neuron	*W1*						*W2*
	Input						Output removal efficiency
	Time	Fe^{+2}	H_2O_2	pH	Temperature	Concentration	
1	0.074	−1.2287	1.4079	0.1123	0.8194	−1.2166	0.4139
2	0.0006	1.2271	0.8978	0.6385	1.7186	−0.0842	1.0085
3	−0.7775	−1.5063	1.68	0.0567	0.2417	−1.4488	1.4461
4	−2.5685	−0.5048	−0.4694	2.3759	1.5027	−0.1929	1.5725
5	1.1365	0.5833	0.3538	−0.9943	2.31	0.2087	0.7732
6	0.4473	−0.4432	0.0646	2.6564	1.4318	1.5292	−1.2890
7	−0.454	−0.1175	−0.1876	−0.1937	0.0413	−1.6799	0.4331
8	−1.7649	−0.8794	0.932	−0.4883	−0.4338	0.1091	0.7381
9	1.3475	1.6684	−1.1184	1.4551	1.5735	−0.4795	0.6531
10	−1.099	0.4118	0.6014	1.2003	−0.2165	1.091	0.3258
11	−2.1269	−0.6149	−0.9933	2.1928	1.2592	−0.3137	−1.8707
12	2.1671	−1.0603	1.2899	−2.2465	−1.8442	−1.3058	0.6504
13	−0.0765	−1.3239	−0.9012	4.1684	0.3216	−1.2305	0.8400
14	−0.446	3.5371	−0.8388	1.8283	−0.3713	−1.2131	−2.1613
15	−0.6529	−0.7292	0.9099	−0.0229	1.6426	0.9243	0.7674
16	0.0455	0.8619	0.3482	1.5888	−1.5156	−1.0472	1.8880
17	−2.2509	−0.5292	0.6256	2.7353	−0.0015	−1.1773	−0.5977
18	0.5551	3.6213	0.4745	0.6041	−0.7958	0.5588	2.2289
19	0.2415	1.924	−0.0695	0.3129	−1.816	0.1995	−0.0403
20	0.6519	−0.7632	1.5633	−1.9622	−2.1796	0.5395	2.0682
21	−2.426	0.4957	0.8348	−0.5804	0.1756	−0.1244	−3.0095
22	0.7928	0.7843	0.6314	−0.623	1.0546	−1.226	−0.5539

equation. Garson (1991) proposed an equation based on the partitioning of connection weights:

$$Ij = \frac{\sum_{m=1}^{m=\mathrm{Nh}}\left(\left(\frac{\left|w_{jm}^{ih}\right|}{\sum_{k=1}^{\mathrm{Ni}}\left|w_{km}^{ih}\right|}\right)\times\left|w_{mn}^{ho}\right|\right)}{\sum_{k=1}^{k=\mathrm{Ni}}\left\{\sum_{m=1}^{m=\mathrm{Nh}}\left(\frac{\left|w_{km}^{ih}\right|}{\sum_{k=1}^{Ni}\left|w_{km}^{ih}\right|}\right)\times\left|w_{mn}^{ho}\right|\right\}}, \qquad (4)$$

where Ij is the relative importance of the jth input variable on the output variable; Ni and Nh are the numbers 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.

Table 2 Relative importance of input variables

Input variables	Importance %
pH	20.6
Fe^{+2}	19.5
Time	18.4
Temperature	16.1
H_2O_2	13.3
Concentration	12.1

Table 1 shows the weights between input and hidden layers (*W1*) and weights between hidden and output layers (*W2*). Table 2 shows the relative importance of the input variables (irradiation time, H_2O_2, Fe^{+2}, pH, temperature, and oil concentration). It can be seen that all variables have strong effect on oil degradation.

pH was found to be the most influential parameter with a relative importance of 20.6 %. A number of researchers in their papers show different relative importance of input variables for the photo-Fenton degradation process (Aleboyeh et al. 2008; Khataee and Kasiri 2010; Elmolla et al. 2010). This variation may depend on the specific conditions and variables each researcher dealt with.

Conclusion

The removal efficiency of the system $UV/H_2O_2/Fe^{+2}$ (homogeneous photocatalysis) considered in this study, for the degradation of oil in wastewater was found to be 72 % at 400 mg/L H_2O_2, 40 mg/L Fe^{+2}, 30 °C temperature, pH=3, and 1,000 mg/L oil load.

A three-layer feed-forward backpropagation neural network was optimized to predict the degradation of oil in wastewater. The configuration of the backpropagation neural network giving the smallest MSE was a three-layer ANN, with tangent sigmoid transfer function (tansig) at a hidden layer with 22 neurons, linear transfer function (purelin) at an output layer, and Levenberg–Marquardt backpropagation training algorithm. ANN predicted results are very close to the experimental results with a correlation coefficient of 0.9949 and MSE of 0.0003. Sensitivity analysis showed that all studied variables in this work (H_2O_2, Fe^{+2}, pH, temperature, irradiation time, and oil concentration) have considerable effects on the degradation efficiency. pH was found to be the most influential parameter a with relative importance of 20.6 %. The result of the modeling confirmed that ANN model could effectively reproduce experimental data and predict the behavior of the process.

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