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CAR WASHES WASTEWATER TREATMENT AND REUSE TECHNOLOGY: AOP APPROACH AND RSM OPTIMIZATION

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Abstract

Nowadays, in our modern daily life, car-washing stations play a great role. Car-washing stations are among the activities that consume large capacities of fresh water on daily basis. Oil-contaminated wastewater can have a detrimental effect on municipal biological treatment processes. Fenton's reagent; one of the advanced oxidation processes (AOPs) has been applied in this study. The experiments were planned and conducted according to the factorial Box-Behnken design based on the experimental surface methodology to treat a real car washing wastewater. Lab-scale experiments with UV source, coupled with Fenton's reagent, suggested the hydrocarbon oil is readily degradable. Moreover, the Fenton dose was optimized and the COD is maximized to reach to more than 93% removal after only one hour of reaction time. The optimum Fenton's reagent dose is 48.4 and 403.9 mg/L for Fe^{2+} and H_2O_2, respectively. However, the optimum pH is 3.5.

Keywords: car wash technology, oily wastewater, Fenton's reagent, Chemical oxygen demand (COD), Response surface methodology.

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1. Introduction

Car driving the process very disposed to contamination, body and glass is mainly dirt by adhesion of dust, soot incomplete combustion of fuel and air in a variety of floating particles. Chassis and wheel dirt adhesion is mainly sand, road asphalt, coal tar and burning oil. It can be seen car wash wastewater pollutant composition varies according to the way of washing (mechanical car washing and artificial high-pressure water washing) or the type of vehicles (small cars and large trucks). However, car washing water quality is essentially the same. In some cases, car wash wastewater may also contain heavy metals [1-3] NEETF, 1999).

Petrol stations play a great role in our modern daily life and usually consume large amounts of water in many activities such as car washing and floor cleaning. Carwash stations located in Egypt, and in any country, and outdoor car washing are among those activities discharge a large volume of wastewater which can pollute lakes, rivers, and drinking water if not properly managed. River Nile suffers from discharge of untreated wastewater [4]. Outdoor car washing has the potential to result in high loads of nutrients, metals and hydrocarbons, as the detergent-rich water used to wash the dust off our cars flows down the street and into the storm drain. Commercial car wash facilities often recycle their water or are required to treat their wash water discharge prior to release to the sanitary sewer system, so most storm water impacts from car washing are from residents, car wash systems that discharge polluted wash water to the storm drain system. However commercial car washes spend much more soap and hot water than hand washing. In order to improve the quality of water that eventually seeps back into the Nile, the Egyptian government have authorized various legislative acts with the object of reduction and elimination of water and land pollution. However, operation sector utilities were not applied so far. To facilitate and accomplish these authorizations, effective control and remediation methods must be developed and realized. Considering the large volume of wastewater generated from the car washing process, wastewater treatment coupled with recycling may possibly be an essential alternative. Some countries have made considerable progress in reusing the wastewater by setting up rules and regulations, while other countries still lack sufficient planning and regulation. Such countries, Switzerland, Germany and Netherlands which no longer allow for outdoor car washing away from car washing stations [5]. Therefore, there has been an increase in research activity focused on treating this kind of wastewaters. The need for new technology is a considering research topic.

The development of novel treatment methods encompasses investigations of advanced oxidation processes (AOPs), which are characterized by production of the hydroxyl radical (·OH) as a primary oxidant [6]. Examples of AOPs include the use of hydrogen peroxide with ultraviolet light (H_2O_2/UV) to treat hazardous compounds [7], Fenton and photo-Fenton reagent (H_2O_2/Fe^{2+}) [8-10], semiconductor photocatalysis [11], and the sonlysis process using the ultrasonic irradiation [12]. Among various AOPs, the Fenton reagent is one of the most effective methods in treating various industrial effluents including wastewater treatment [13-14], oily wastewater effluents [15]. Previous work by the authors demonstrates the application of Fenton's and the photo-Fenton's reagent in the case of the treatment water polluted with diesel oil emulsion wastewaters [10-16].

To address this problem, oil wastewater treatment methods traditionally have included phase-separation and skimming, evaporation, filtration and dissolved air flotation. However, these methods transform the pollutants from one phase to another without mineralizing them. In other words, these methods are non-destructive and generate lower volumes of more concentrated waste. Furthermore, these methods are also less effective in removing the smaller oil droplets and emulsion [10].

Although Fenton reagent has been reported extensively in the literature, there is a scarcity of literature published in the case of car washes wastewater treatment. Factors to control the Fenton reaction process are the amounts of Fe^{2+} and H_2O_2, and the working pH. Optimising such parameters plays a key role towards the achievement of the Fenton reaction. The experimental design using a statistical-based technique commonly known as RSM (response surface methodology) [17] has been increasingly applied in many fields including wastewater treatment to study the optimization of the treatment process [18-20].

The main aim of the study presented below is to explore the possibility of treating and upgrading car-washing water to an acceptable level that can be recycled and reused for the same application. The application of the Photo-Fenton reagent to the mineralization of a real car-wash wastewater was illustrated. Hence, the outcome would render several benefits to Egypt, including water conservation and abating water pollution. The effect of the reaction operating conditions was investigated and the optimization of Fenton reaction conditions (Fe^{2+}, H_2O_2 and pH) using RSM to maximize COD removal rates.

2. Materials and methods

2.1. Car-wash wastewater

Real' wastewater samples were collected from a car washing wastewater tank at a petroleum filling station in the south of Egypt. The principal properties of this wastewater are: 82 mg-COD/L, and a turbidity of 28.1 NTU, pH 8.2 and suspended solids of 55 mg/L.

2.2. Experimental Materials

Fe^{2+} in Fenton's reagent (Fe^{2+}/H_2O_2) is prepared by making a solution from Fe^{2+} salt. H_2O_2 was obtained in liquid (30% of H_2O_2, wt) from a commercial supplier. Sulfuric acid is used for adjusting the pH of the sludge samples during conditioning. Properties of chemicals used in this study are listed in Table1.

Table 1 Properties of chemicals used in this study[1]

Compound	Molecular weight	Formula	Manufacturer	Purity
Iron chloride tetrahydrate	198.8	$FeCl_2.4H_2O$	Sigma-Aldrish	98.0%
Hydrogen peroxide	134.01	H_2O_2	Sigma-Aldrish	30 wt%
Sulfuric acid	98.08	H_2SO_4	Sigma-Aldrish	97.0%

[1]Hydrogen peroxide solution with a stabilizer
(Dipicolinic acid (approximately 40 mg/l))

2.3. Methodology

All photochemical experiments were carried out in a batch mode laboratory scale using a 250 mL beaker. Initially, the desired pH of 100 mL of the car wash wastewater samples was adjusted with sulphuric acid before oxidation. Then, ferrous ions solution and hydrogen peroxide were added to produce hydroxyl radicals. Subsequently, the mixture was subjected to magnetic stirring and UV radiation (254 nm wavelength), as illustrated in Figure 1. Samples were taken at regular time intervals in the discontinuous experiments and were analyzed immediately to avoid further reaction.

2.4. Analytical Determinations

The COD measurements were performed using HACH analyser (model HACH DR-2400). Turbidity was undertaken using a HACH 2100N IS Turbidimeter (ISO method 7027). The pH of the wastewater was adjusted using a digital pH-meter (model PHM62 Radiometer) supplied by Copenhagen.

2.5. Experimental design

The Fenton oxidation process was optimized by applying the response surface methodology (Montgomery, 1991). COD removal, defined by Eq. (1), of the effluents was used as the variable to be optimized. The amounts of H_2O_2, Fe^{2+}, and pH were chosen as the control factors to be optimized. The initial design involved 15 tests, based on a three-level factorial Box-Behnken factorial design (Montgomery, 1991).

$$\eta\ (\%) = \frac{COD_o - COD}{COD_o} \times 100 \qquad (1)$$

where η, percentage of COD removal; COD_o, measured COD in supernatant before oxidation (mg-O_2/L); COD, is the COD value after the treatment.
The first step in the RSM is to find a suitable approximation for the true functional relationship between the response (η) and the set of independent variables. The following response function (2) was used to correlate the dependent and independent variables in the response surface:

$$\eta = \beta_o + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i} \sum_{j=i+1} \beta_{ij} X_i X_j \qquad (2)$$

Where η is the predicted response; ; i = 1 ,2, 3 and j = 1, 2, 3; β_o the constant coefficient (intercept); β_i the linear coefficients; β_{ij} the crossproduct coefficients; ; and X_i is the input controlling coded variable. In addition, the natural variables of the operating system (ξ_i) were transferred to coded variables (X_i) according to Eq. (3) [17] to simplify the model calculations. The results of COD removal and the turbidity were analyzed through the statistical analysis software package of SAS Institute, Inc., [18] by performing the analysis of variance (ANOVA) and fitted with a second-order polynomial model.

$$x_i = \frac{(\delta_i) - (\text{its upper level} + \text{its lower level})/2}{(\text{its upper level} - \text{its lower level})/2} \qquad (3)$$

The combined effect of the three independent variables, i.e. Fe^{2+} concentration, H_2O_2 concentration and initial pH as δ_1, δ_2 and δ_3 respectively. The range of the experimental variables investigated in this study and the time of reaction (1 hr) were chosen according to preliminary tests. Therefore, each variable ranged between -1 and 1, the lower and upper levels, respectively. These ranges and levels are presented in Table 2. Fifteen runs were required for a complete set of the experimental design.

Table 2 Range and levels of natural and corresponded coded variables for RSM

Variable	Symbols		Range and levels		
	Natural	**Coded**	**-1**	**0**	**1**
Fe^{2+} (mg/l)	δ_1	x_1	30	40	50
H_2O_2 (mg/l)	δ_2	x_2	350	400	450
pH	δ_3	x_3	3.5	6	8.5

3. Results and discussions

3.1. Model fitting

The three-level experiments were carried out according to the Box-Behnken design and the experimental plan is shown in Table 3 as coded and natural levels. The data shows the results of the photo-Fenton experiments as an average of the duplicate experimental results at each operating condition. The following second-order fitting polynomial equation of coded factors:

$$\eta(\%) = 29.30 + 6.48X_1 + 0.60X_2 - 7.70X_3 + 30.86X_1^2 - 5.50X_1X_2 - 0.75X_1X_3 + 24.63X_2^2 + 1.85X_2X_3 + 27.18X_3^2 \quad (2)$$

Table 3: RSM for the three experimental variables in coded units and its corresponding natural values

Experiment No.	Natural variable			Coded variable		
	Fe^{2+} (mg/l)	H_2O_2 (mg/l)	pH	x_1	x_2	x_3
1	30	350	6	-1	-1	0
2	30	450	6	-1	1	0
3	50	350	6	1	-1	0
4	50	450	6	1	1	0
5	40	350	3.5	0	-1	-1
6	40	350	8.5	0	-1	1
7	40	450	3.5	0	1	-1
8	40	450	8.5	0	1	1
9	30	400	3.5	-1	0	-1
10	50	400	3.5	1	0	-1
11	30	400	8.5	-1	0	1
12	50	400	8.5	1	0	1
13	40	400	6	0	0	0
14	40	400	6	0	0	0
15	40	400	6	0	0	0

The values of COD of the car washes wastewater as the responses obtained from the experiments and the predicted values are shown in Table 4 and plotted in Fig. 2. It can be seen from Table 4 that a good agreement of the data between the experimental and the predicted is obtained. This can be confirmed in Fig. 2 with regression coefficient R^2 value of 0.97 (the model being rejected if the R^2 value is less than 0.8 [17]). Thus, it is reasonable to believe that the polynomial model (Eq. (2)) is a reliable model to describe the Fenton reaction behaviour in car washing wastewater treatment.

Table 4 Experimental and predicted achieved removal responses for RSM

Experiment No.	η(%)	
	Experimental results	Predicted response
1	68	72
2	88	84
3	93	96
4	90	86
5	98	90
6	71	71
7	88	88
8	68	76
9	84	88
10	98	102
11	78	74
12	89	85
13	29	29
14	31	29
15	28	29

3.2. Statistical analysis

The effect of a factor is the change in response produced by a change in the level of the factor. When the effect of a factor depends on the level of another factor, the two factors are said to be interacting. In order to further assess the polynomial model (Eq. (5)), statistical analysis of variance (ANOVA) using SAS software was conducted and the statistical significance of the factors towards the response (η) of the process was determined by Fisher's 'F' test (F-value is the ratio of mean square of regression to the mean square of the error) [17, 18]. The Student't' test was used to determine the significance of the regression coefficients of the parameters. The probability values, (P-values) were used as a tool to check the significance of the model. In general, if the significance probability value ($P>F$) is small (below than 0.05) and the P value lower than 0.01, the model is acceptable [17]. ANOVA of the tested model is listed in Table5, which indicating that the model is significant as the F-model is 19.94 and a low probability value ($P>F= 0.002105$).

The response surfaces of two-dimensional contour plots and three-dimensional curves of the response (COD removal, %), generated by MATLAB 7.0, is a significant and noticeable illustration to facilitate the relations between two interacting factors with the response (η), while third factor was kept constant at its zero level. Fig. 3 demonstrated the response under the variable concentrations of Fe^{2+} and H_2O_2. It can be seen that a considerable enhancement of COD removal (%) is observed when the H_2O_2 concentration was increased. However, at higher concentrations of H_2O_2 the reduction rate was negatively affected. The effect of higher H_2O_2 concentrations than the optimum, which get an opposite effect on the % COD removal, is clearer when the iron concentration is low. Thus, an excess of this reagent does not mean a continuous increase in COD removal of the treated wastewater. Similarly, the reduction percentage of COD increased with increasing the Fe^{2+} concentration to a certain limit after which it became slower. Clearly, there is an optimal dosage for both Fe^{2+} and H_2O_2 concentrations. In the similar way, the 3D surface and the corresponding contour plot in Fig. 4 shows that the combination of Fe^{2+} concentration and pH has a significant effect on COD removal. The detrimental effect of higher H_2O_2 concentration is probably due to the both auto-decomposition of H_2O_2 into oxygen and water, and the recombination of OH radicals [21]. If either of H_2O_2 and Fe^{2+} is not present in optimal dosage, it will scavenge OH radicals and reduce their available amount in solution [20]. Fig. 5 demonstrated that the increase in pH with the increase in the H_2O_2 concentration enhanced the rate of COD removal certain region, beyond that region the less reduction of COD is observed. Therefore, optimising the Fe^{2+} and H_2O_2 concentrations as well as pH was conducted to achieve the highest COD removal as the system is a sensitive to those parameters.

Table 5 ANOVACoefficient of Regression and t Checking[1]

Variable	Standard deviation	*t*	*P* > *t*	Coefficient
X_1	2.405956	2.691238	0.043235	6.475
X_2	2.405956	0.249381	0.812987	0.6
X_3	2.405956	-3.20039	0.023985	-7.7
$X_1 X_1$	3.541472	8.704009	0.000331	30.825
$X_1 X_2$	3.402536	-1.61644	0.166922	-5.5
$X_1 X_3$	3.402536	-0.22042	0.834259	-0.75
$X_2 X_2$	3.541472	6.953324	0.000945	24.625
$X_2 X_3$	3.402536	0.543712	0.609995	1.85
$X_3 X_3$	3.541472	7.673364	0.000599	27.175

[1]R^2, Coefficient of determination, values were 0.97 for CD percent removal

Table 6 Analysis of Variance (ANOVA) for the RSM Model

Source	Degree of freedom (df)	Sum of squares (SS)	Mean Squares (MS)	F statistics	*P*>*F*
Model	9	8309.248	923.2498	19.93673	0.002105
Linear	3	812.605	812.605	17.547452	0.880207
Square	3	3631.609	3631.609	78.42124	1.001512
Interaction	3	4979.369	4979.369	107.52485	0.611539
Error	5	231.545	46.309		
Total	**14**	**8540.793**			

3.3. Optimization analysis

Using the method of experimental factorial design and response surface analysis, the optimal conditions to obtain the optimum COD removal percent by photo-Fenton's reagent could be determined. The optimum values of selected variables could be obtainable by solving the regression equation (using MATHEMATICA software (V 5.2)). The optimum vales of the test variables in coded were as follows: Fe2+ dosage, x_1 = H_2O_2 dosage, x_2 = and pH, x_3 = 3.5 while the response predicted was 91.7 %. According to relation between δ_i and x_i, the natural values of the test variables are shown in Table 7.

The optimal molar ratio H_2O_2:Fe2+ in this study is 12:1. This optimal ratio is higher than the ratio recommended [20] who give the ratio of 4.5:1 in the treating of laboratory wastewater. However, it is lower than the ratio obtained by [19] in the treatment of cellulose bleaching effluent who recommended the value of 26:1 as a molar ratio. While this value is near to the value given by Tang and Hung [22] who give a molar ratio of 11:1 for 2,4-dichlorophenol degradation. Hence, the hydrogen peroxide should be in excess. The recommended pH value in this investigation agrees with the suggested value of 3.0 by [23] in the treatment of wastewater from textile industry. However, it slightly differs to the value obtained by [24] who reported that pH above 5 increases the reaction rate of landfill leachate treated by Fenton's reagent. This means the optimal ratio of the reagent concentration and the pH value differs according to the trend of the substance to be treated.

Table 7 Optimum value of the process parameter for maximum efficiency

Parameter	Optimum value
η (COD removal rate, %)	91.7
Fe^{2+} (mg/l)	48.4
H_2O_2 (mg/l)	403.9
pH	3.5

3.4. Verification of the results

To confirm the model sufficiency, three additional experiments using these optimum operating conditions (Table 7) were conducted. The duplicate experiments yielded an average COD removal percent 47.878% (Table 8).

Table 8 Predicted and experimental value for the responses at optimum conditions

	COD removal %
Predicted	91.7
Experimental	93.4

4. Conclusion

The results from the present study have demonstrated the effectiveness of the application of Fenton reagent (Fe^{2+}/H_2O_2) in the treatment of wastewater delivered from car washing. Response surface methodology for optimising such process parameters was applied. This experimental design methodology was shown to be a valuable tool in optimizing the process, and to achieve with a minimum number of experiments. The three statistically variables, Fe^{2+}, H_2O_2 concentrations and pH, showed optimal values, giving maximum % COD removal reaches to 93% in treating such car washing water used in the study. The optimal molar ratio of H_2O_2:Fe^{2+} 12:1 (48.4 and 403.9 mg/L for Fe^{2+} and H_2O_2) and the optimum pH is 3.5. This demonstrates the usefulness and effectiveness of the Fenton's reagent as an advanced technique in the treatment.

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Figures

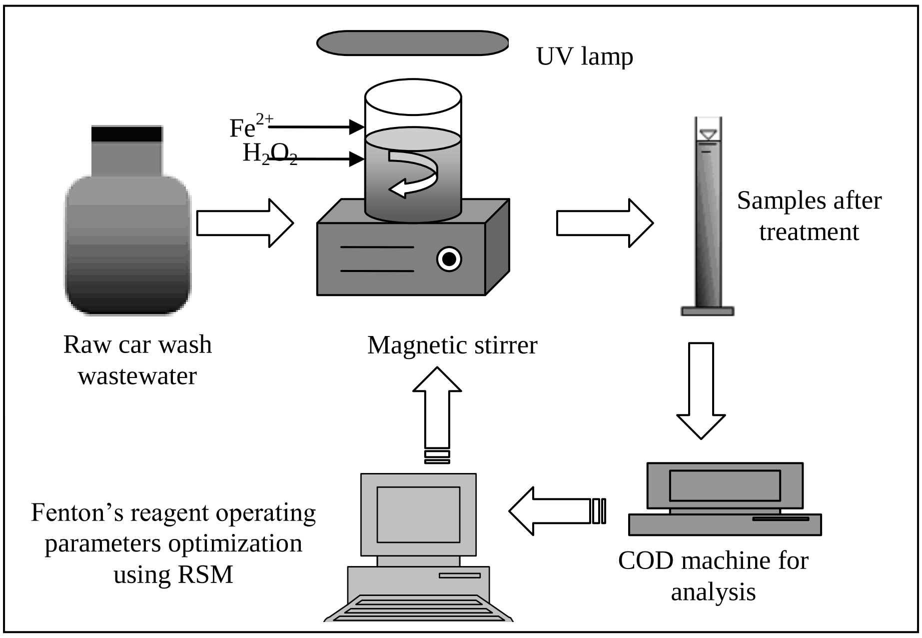

Fig. 1. Schematic diagram of lab-scale photo-Fenton test

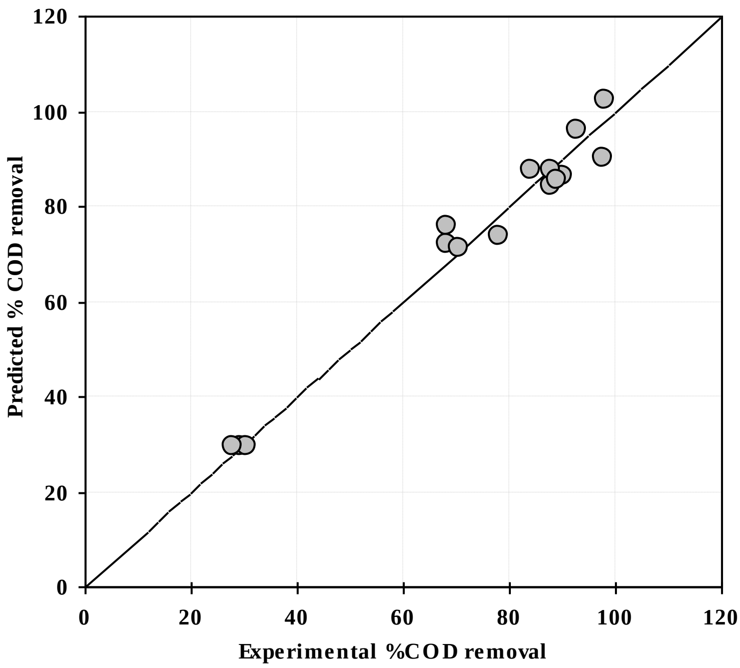

Fig.2. Predicted vs. experimental data for COD removal (%) (R^2 =0.97)

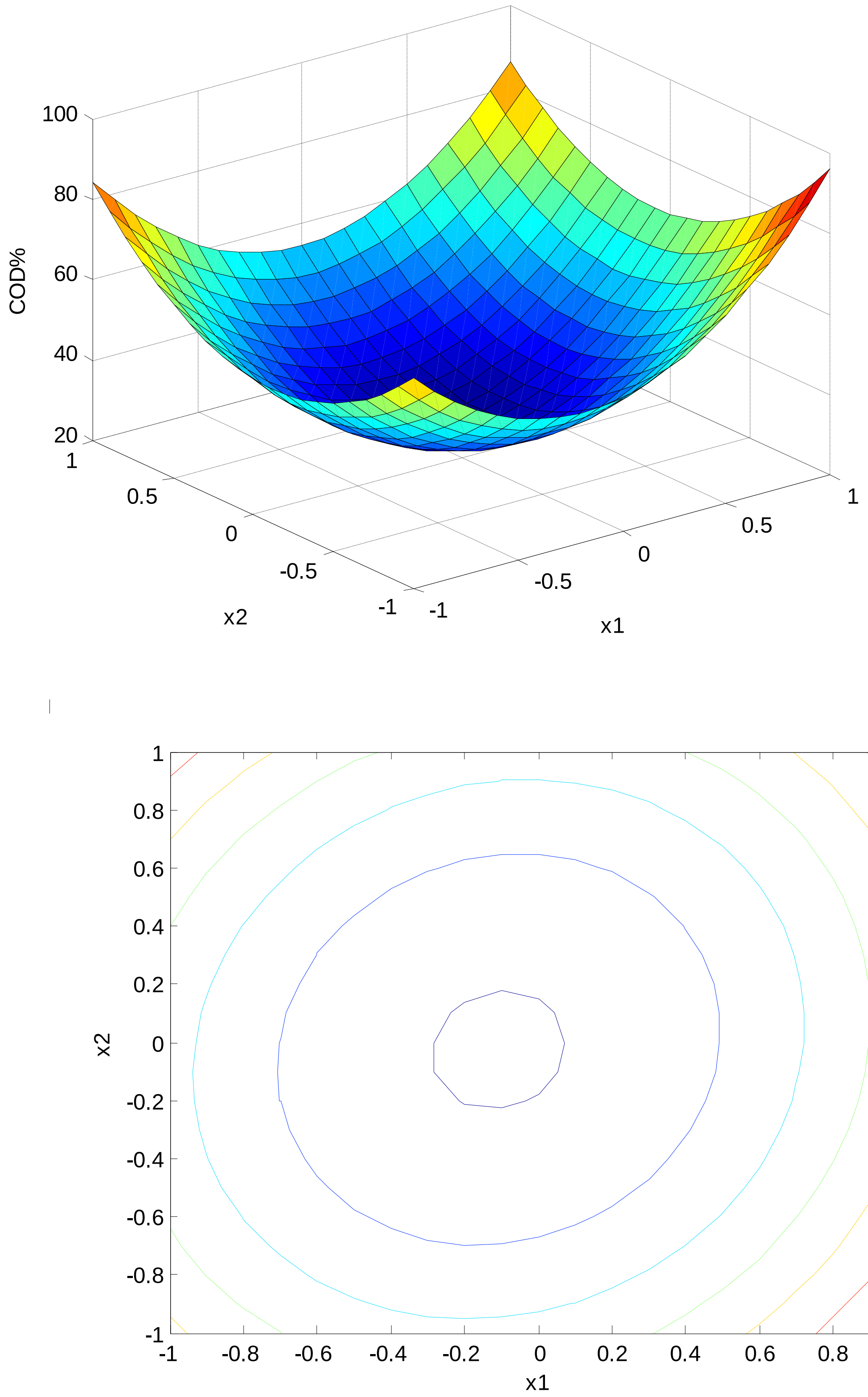

Fig.3. 3-D of surface and contour plot of response surface curve for COD removal showing interaction between A: Fe^{2+} and B: H_2O_2

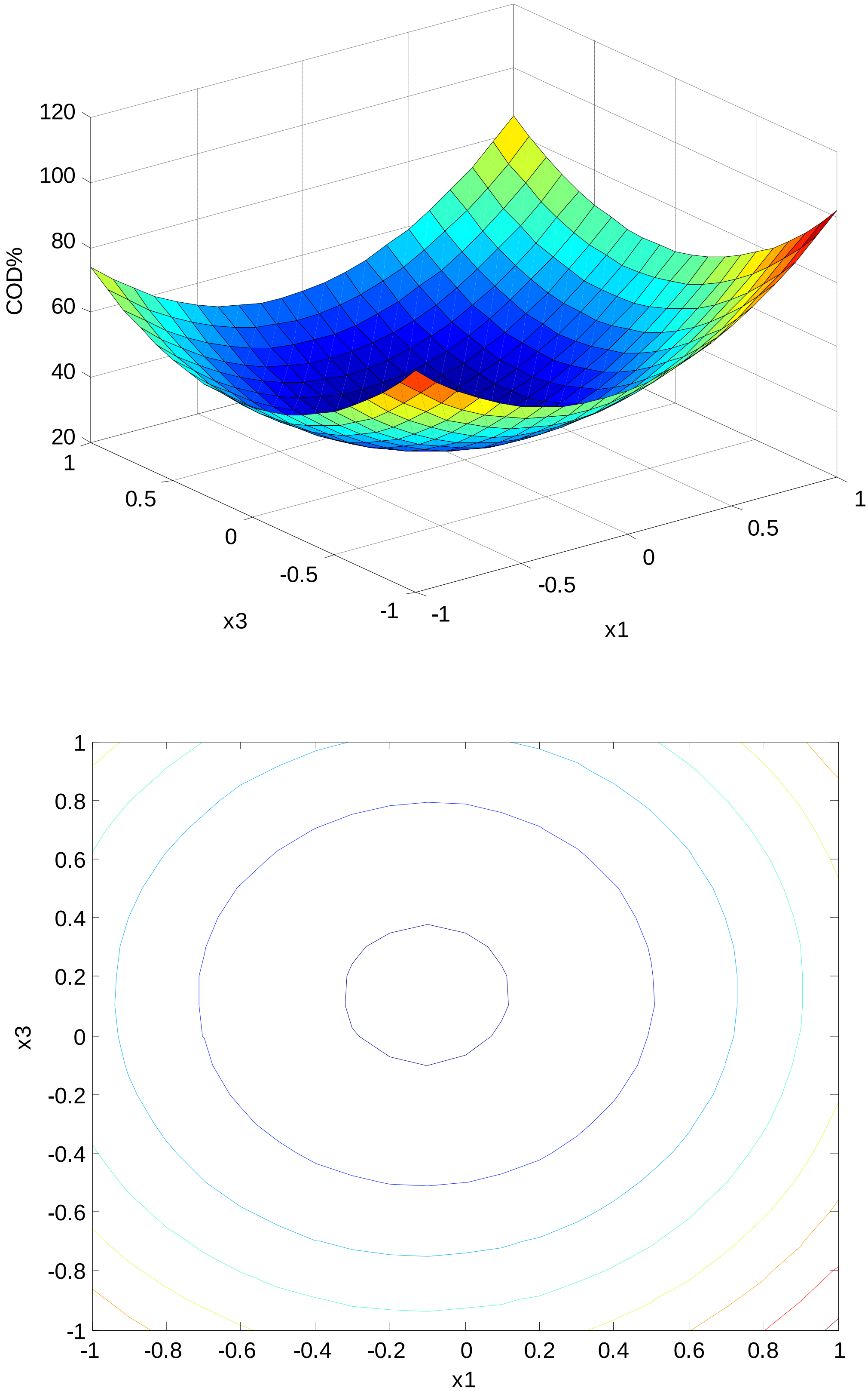

Fig.4. 3-D of surface and contour plot of response surface curve for COD removal showing interaction between Fe^{2+} and pH

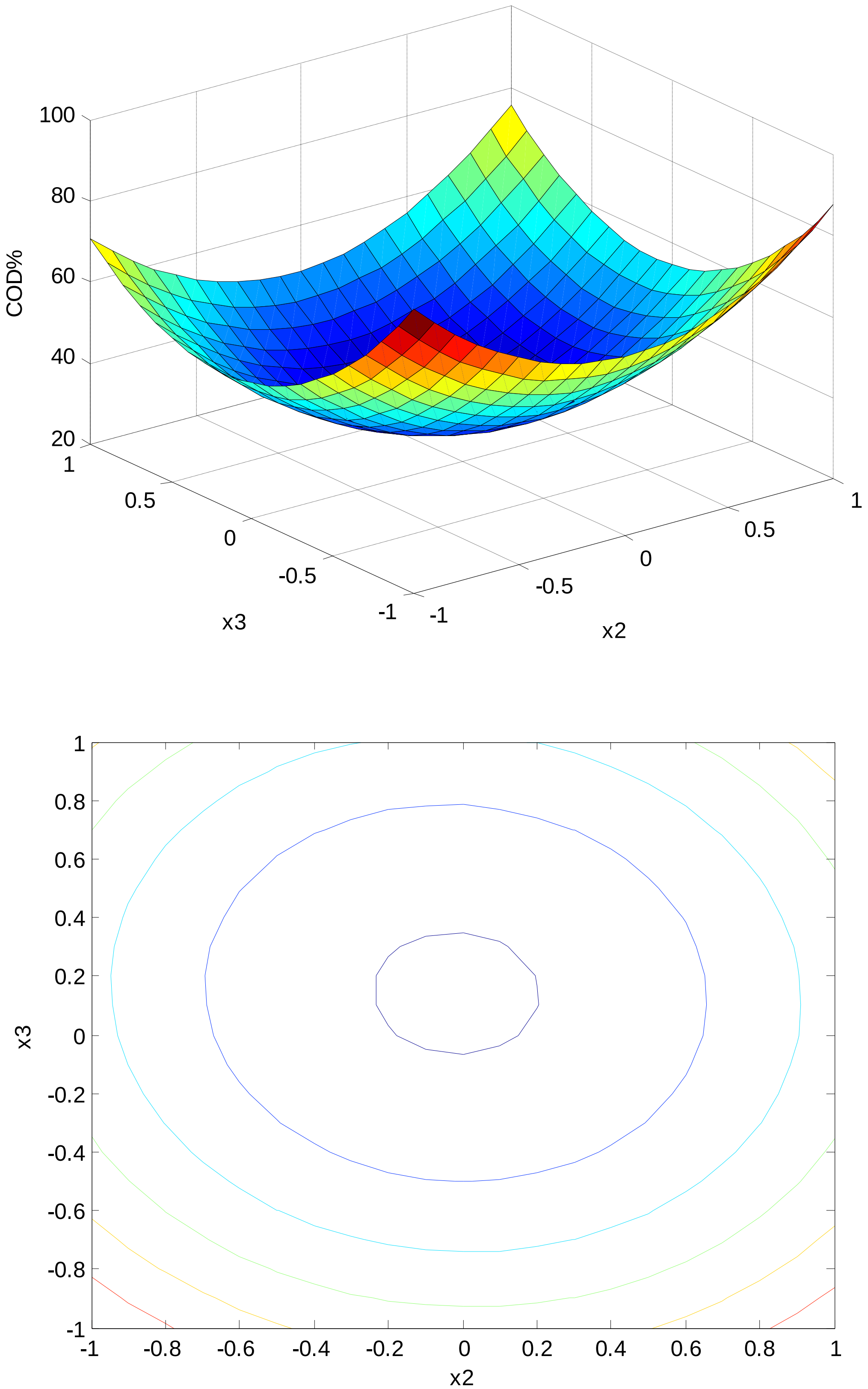

Fig. 5. 3-D of surface and contour plot of response surface curve for COD removal showing interaction between $H_2O_2$and pH