ORIGINAL ARTICLE

Improvement of Two Iranian Petrochemical Complexes' Wastewater Biodegradability from 2015 to 2017 Using H_2O_2/ Fe^{2+} and Optimization of the Conditions by RSM

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Received: 20 July 2017
Revised: 8 August 2017
Accepted: 20 September 2017

Abstract

Background: Petrochemical wastewaters are a critical environmental challenge in industrial zones due to the amount of pollutants they release into the environment. Therefore, finding a solution for treatment of the wastewater has become the priority of the researchers. The main objective of this research is improvement of petrochemical wastewaters' biodegradability using Fenton oxidation process and defining the effective parameters on the efficiency of this technique.

Methods: In this research, the capability of Fenton method for promoting the biodegradability of hardly-decomposable wastewaters of petrochemical complexes was studied. The actual wastewater of Karoon and Maroon petrochemical complexes were used in this research. Design of the experiments and also the analysis of the experimental results were carried-out using Response Surface Methodology (RSM) with four variables and four parameters. A rector with sizes of 60, 20 and 20 cm was designed and built. The ranges of COD_{in}, H_2O_2 concentration, Fe^{2+} dosage, and TDS variation were 1000-2500 mg/L, 1000-4000 mg/L, 500-3000 mg/L, and 4500-11500 mg/L, respectively, and the average ratio of BOD/COD in the inlet stream was 0.09.

Results: The range of BOD/COD in the outlet stream was 0.19-0.37 which decreased with the COD growth. The trend of biodegradability promotion with increase in H_2O_2 concentration and Fe^{2+} dosage was ascending, while the effect of TDS on biodegradability was not noticeable.

Conclusion: The optimum conditions for achieving maximum efficiency of the reactor were COD=1375 mg/L, $[H_2O_2]$=2509.27 mg/L, $[Fe^{2+}]$=1753.49 mg/L and TDS=8622.9 mg/L and the BOD/COD ratio was 0.32.

Please cite this article as: Derakhshan M, Fazeli M. Improvement of Two Iranian Petrochemical Complexes' Wastewater Biodegradability from 2015 to 2017 Using H_2O_2/ Fe^{2+} and Optimization of the Conditions by RSM. J Health Sci Surveillance Sys. 2017;5(4):144-152.

Keywords: Waste water, Hydrogen Peroxide, Biodegradation, Environmental

Introduction

Due to the presence of various kinds of compounds and contaminants in industrial wastewaters, their direct discharge into acceptable resources such as surface or underground waters and agricultural lands is usually impossible because of the hazards it may cause for the life of humans, animals, and plants.[1] Therefore, rigid environmental rules and regulations have been set for discharging industrial wastewaters into the environment and some considerations must be taken into account. Hence, a significant number of researches have been carried-out to propose and develop new methods of industrial wastewater management and treatment aiming at reducing or removing of hazardous materials or in some cases converting them into environmentally-compatible compounds.[2]

Wastewater of petrochemical industries is among the most hazardous and least-decomposable wastewaters due to the presence of a wide range of chemicals and organic matters such as aromatics, olefins and phenols.[3] Furthermore, the high amount of generated wastewater in these industries has made it impossible to use common methods of wastewater treatment.[4] Therefore, a combination of physical, chemical and biological methods is usually applied in order to reduce the biological oxygen demand (BOD), chemical oxygen demand (COD), and concentration of the pollutants.[5]

Advanced oxidation process (AOP) is an effective treatment method to deal with hardly-biodegradable pollutants in wastewaters from the petrochemical industry.[6] These processes are based on production of non-selective, highly reactive and strong oxidant free radicals.[7] Normally, free radicals are considered as the strong oxidants for breaking the indecomposable big molecules into the smaller ones, which usually have greater biodegradability.[8] In these processes, oxidants such as UV, O_3, TiO_2, H_2O_2 and ultrasound can be used merely or in combination with each other.[9] AOPs are mostly used as a supplementary method of treatment before or after the main wastewater treatment process which is normally a biological method.[6] High operational costs make it unfavorable to use AOPs for complete degradation of the pollutants; therefore, they are usually used for relative oxidation of hardly-decomposable compounds and facilitating biological wastewater treatment.[10]

Fenton is one of the AOPs with appropriate capability for being applied for hardly-decomposable compounds. Classic Fenton reaction is the combination of hydrogen peroxide (H_2O_2) and Fe^{2+} ions in acidic environment which results in decomposition of H_2O_2 to hydroxyl ion (OH^-) and hydroxyl radicals (OH°) and oxidation of Fe^{2+} to Fe^{3+}.[11] This reaction can be carried out under the normal temperature of the environment; no input energy is needed and it is usually quicker than other AOPs. Moreover, the reactants are easily available, storable and almost safe.[12]

Hydroxyl radicals are produced in the reactions 1-4.[13] As it is shown in equations 1 and 2, the reaction starts with Fe^{2+} and results in H_2O_2 decomposition and hydroxyl radical (OH°) production. However, newly-generated Fe^{3+} ions may decompose H_2O_2 into water and oxygen (Eq. 3 and 4). Basically, this method is based on hydroxyl radical (OH°) production, which can be used as a strong oxidant for decomposing the compounds which cannot be removed by common oxidants such as O_2, O_3 and chlorine. This radical reacts with dissolved compounds and starts a chain of oxidation reactions until the desirable level of oxidation is achieved. OH° has a noticeable oxidation power and low resistance in confrontation of most of the materials.[14]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\circ + OH^- \qquad \text{Eq. 1}$$

$$OH^\circ + Fe^{2+} \rightarrow OH^- + Fe^{3+} \qquad \text{Eq. 2}$$

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe\ OOH^{2+} + H^+ \qquad \text{Eq. 3}$$

$$Fe\ OOH_2+ \leftarrow HO_2^\circ + Fe^{2+} \qquad \text{Eq. 4}$$

Numerous studies have been carried out in this field and some of them are mentioned in the following part. In a research, electro-Fenton was used as a pre-treatment technique to a biological treatment for industrial wastewater. After 1hr in pH=3 and temperature of 18°C and I=200 mA, 94.2% of the sulfamethazine (SMZ) in the wastewater was removed. However, the rate of mineralization of the interior compounds was still low, which shows the significant durability of the organics in the sample. Then, the activated sludge method was used for completing the process of SMZ mineralization. The efficiency of SMZ removal after 0.5, 1 and 4 hours in this process was 61.4, 78.8 and 93.9%, respectively.[7]

In another research, the researchers worked on the wastewater of acrylic fibers production unit. They proposed Fenton-UASB (2-phase)-SBR hybrid under the conditions of pH=3, $[Fe^{2+}]$=300 mg/L, $[OH^-]$=500 mg/L, and retention time=2 hr. COD removal in their suggested system was 65.5%, and BOD/COD=0.529 was obtained.[15]

In this research, wastewaters from Maroon and Karoon petrochemical complexes, Iran, were used and the effectiveness of Fenton method on the promotion of biodegradability in these wastewaters was studied. As to their BOD/COD, these wastewaters are categorized as hardly-biodegradable wastes and the main objective of this research was to improve their biodegradability by Fenton technique. Fenton process has been widely used during recent years for increasing the biodegradability of hardly-decomposable wastewaters such as petrochemical wastewaters; however, an engineering study on the effective parameters on its efficiency and the optimum conditions for achieving the maximum biodegradability with minimum capital investment which is the most important approach of this research has not been conducted yet.

Materials and Methods

Chemicals

The chemicals used in this research were: H_2O_2,

$FeSO_4.7H_2O$, CH_3OH, NaOH and H_2SO_4 which were all bought from Merck™.

Experimental Setup

In this research, a glass rectangular reactor with length, width and height of 80, 20 and 20cm, respectively, was used. Figure 1 shows the schematic illustration of the reactor. The tests were carried out in different batches with retention time of 1hr. The height of the fluid in the reactor was kept at 5cm. Temperature and pH were set as 25°C and 3, respectively.

Wastewater Specifications

Table 1 displays the specifications of the raw wastewater which was sampled from Maroon and Karoon petrochemical complexes in Iran. Noticeable amounts of hardly-decomposable compounds and high TDS were the most significant characteristics of the wastewaters.

As shown in Table 1, the sampled wastewaters were employed with the outlined ratios to achieve qualitative characteristics required for mixture experiments. According to Eq.5, different parameters with experimental responses were compared to acquire mixed raw wastewater.

$$(P_{im}\times 2)+(P_{ik}\times 1)+(P_{sk}\times 0.5)=(P_m\times 3.5) \quad \text{Eq.5}$$

where P_{im} is the parameter regarding Maroon petrochemical industry wastewater, P_{ik} is the intended parameter corresponding to Karoon petrochemical industry wastewater, P_{sk} is the parameter related to Karoon sanitary petrochemical wastewater, and P_m is the parameter of interest associated with the mixed wastewater. The range of COD and TDS were 1000-2500 mg/L and 4500-11500 mg/L, respectively.

The Experiments and Procedure

The tests were conducted at 25±2°C, the standard temperature of the lab. pH was set to be 3 during all the tests, using NaOH 0.1 M and H_2SO_4 0.1 M.[16] Then, a specific amount of $FeSO_4.7H_2O$ was added to the reactor. The mixture was well-mixed using an electrical mixer which was provided in the setup. Fenton reaction started with gradual addition of H_2O_2. In order to prevent extra undesired reactions after the specified time, we used 0.1 mL methanol to stop the reactions. At the end, BOD and COD in the outlet stream were measured using HACH DR/ 2800 (USA) and HACH BOD (USA), respectively.

Design of Experiments and Statistical Analysis

Response surface method (RSM) has been widely used to carry out statistical analysis and define optimum conditions in experimental studies during recent years. The advantages of this method are the reduced number of necessary experiments for analysis of the results and decreased experimental attempts.[17, 18] Central composite design (CCD) is an approach in experiments using RSM which is capable of multi-parameter modelling and analysis.[19] The design of experiments in this study was performed through CCD method and by relying on four variable parameters of inlet COD concentration, H_2O_2 concentration, Fe^{2+} injected dosage and TDS concentration. Also, Design Expert® 10.01 software was used to devise the experiments, carry out statistical analysis, model and determine optimum conditions. Five different levels were introduced for variable analysis, as presented in Table 2.

The number of the random tests, considering six central repetitions and two repetitions in other points, was 54 and variable interactions study and analysis of variance (ANOVA) were performed using RSM. Moreover, the quality of predictions by the suggested model was determined by R^2 coefficient. Eq. 6 was the regression equation for the variables used in this research.

$$X_i = \frac{(x_i - x_{cp})}{\Delta x_i} \quad \text{Eq.6}$$

where X_i is the coded quantity of i-th independent parameter, x_i is the specific independent parameter, x_{cp} is the independent parameter in the central point, and $\Delta\Delta x_i$ is the parameter variation in each step. The general form of the fitted equation in RSM was according to Eq. 7:[20]

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i<j}^{k} \beta_{ij} X_i X_j + \varepsilon \quad \text{Eq. 7}$$

where Y is the variable response (BOD/COD in outlet stream), β_0 is a constant coefficient, β_i is the linear coefficient, β_{ii} is the second order impact, β_{ij} is the interaction coefficient, and ε is the statistical error.

Results

The tests were based on the range of variation of the independent variable which is defined according to literature. Design of experiments and measured responses are reported in Figures 2 and 3. According to Design Expert®, 54 random tests were designed and the results were obtained in each test. Based on the results, the experimental correlation between variables and responses wasobtained as Eq. 8:

$$Ln\left(\frac{BOD_5}{COD}\right) = -1.28 - 0.13 \times A + 0.099 \times B + 0.10 \times C + (4.891E-003) \times BC + (5.133E-003) \times A^2 - 0.036 \times B^2 - 0.031 \times C^2 \quad \text{Eq. 8}$$

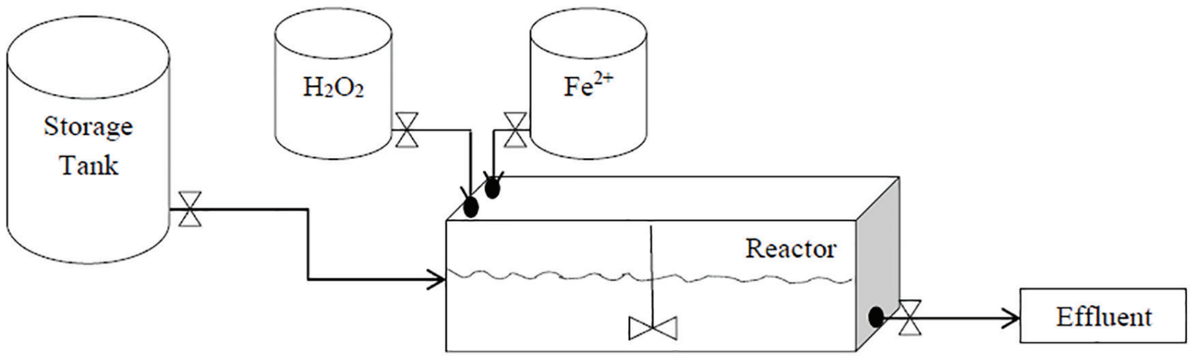


Figure 1: Schematic illustration of the experimental setup designed for Fenton process

Table 1: Specifications of wastewater samples from Maroon and Karoon petrochemical complexes, Iran

Parameter	Industrial wastewater		Sanitary wastewater	Mix wastewater for experimental
	Karoon petrochemical	Maroon petrochemical	Karoon petrochemical	
COD ($mg.L^{-1}$)	3980	742	81	2498
BOD_5 ($mg.L^{-1}$)	345	70	64	226
TDS ($mg.L^{-1}$)	7050	24350	1402	11186
pH	5	6.5	7	5.7
BOD_5/COD	0.09	0.09	0.8	0.09
Mix ratio	2	1	0.5	-

Table 2: The levels used in the parameters used in the test

Parameters	-alpha	Low	Center	High	+alpha
COD initial	1000	1375	1750	2125	2500
H_2O_2	1000	1750	2500	3250	4000
Fe^{2+}	500	1125	1750	2375	3000
TDS	4500	6250	8000	9750	11500
$(BOD/COD)_{IN}$	0.09				
pH	3				

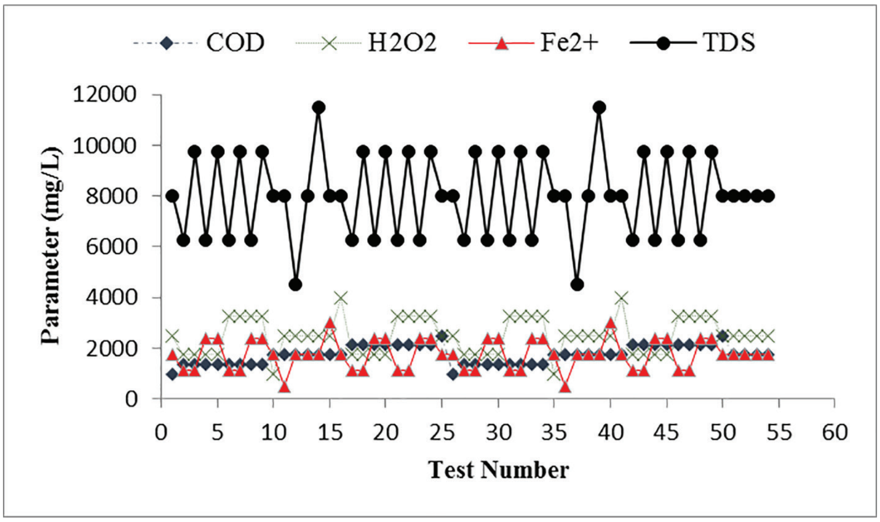


Figure 2: Design of Experiments using Design Expert®

In the developed second order equation, A, B and C are COD, H_2O_2 and Fe^{2+}, respectively. Eq. 8 shows the dependency of BOD/COD on the input variables as separate or interactive impacts. Variation of BOD/COD vs. COD, H_2O_2 and Fe^{2+} was linear and second order which shows the interactions between independent input variables.

As shown in Figure 3, BOD/COD ratio which is the index of wastewater biodegradability was measured 0.09 in the inlet stream. Fenton process increased this ratio in all the tests. This increase was observed more in lower concentrations of organic materials, showing that hydroxyl radicals are more effective in lower concentrations of hardly-decomposable materials.

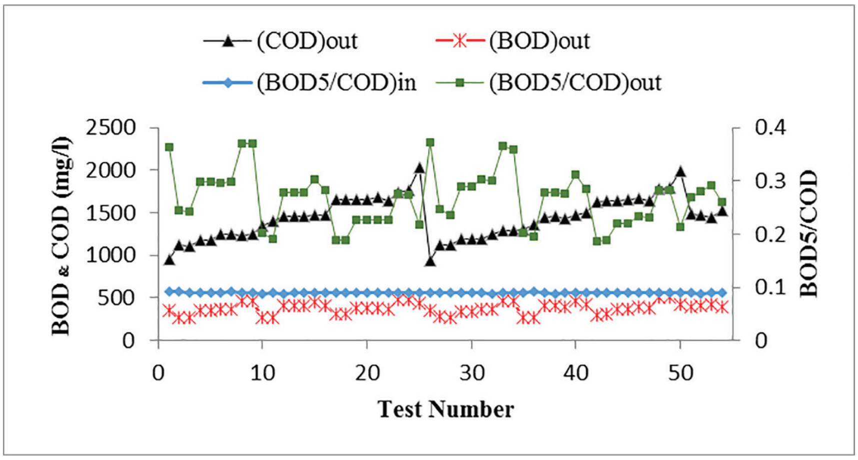


Figure 3: Impact of Fenton on wastewater biodegradability

Generally, the trend of biodegradability was desirable under all conditions, so that it varied between 0.19 and 0.37.

Discussion

Analysis of Variance (ANOVA)

As shown in previous section, Fenton method increased the petrochemical wastewater biodegradability from 0.09 to 0.37 under the optimum conditions. Comparison of the results with those of our previous study which focused on applicability of photo-Fenton technique on enhancement of petrochemical biodegradability[21] indicated that photo-Fenton technique can increase wastewater biodegradability twice as classic Fenton. However, due to the hazards that using UV light in photo-Fenton process can cause, using classic Fenton seems to be more reasonable for petrochemical wastewater treatment, especially in large scales.

Using Fenton technique in this study has quadrupled the wastewater biodegradability (300% increase), while Tekin et al. (2006) could achieve 100% increase under the optimum conditions.[22] It shows that the influential parameters are chosen correctly in this study and the design of experiments in order to define the optimum conditions has been selected appropriately.

Analysis of variance (ANOVA) is used to show model accuracy and the impacts of input factors on responses and each other as well.[23] The results of ANOVA are displayed in Table 3.

Validation of the results was conducted using F and P values and Lack of Fit. In cases where F and P values are significant in the model and Lack of Fit is not significant, the accuracy of the model is sufficient and model is proved to be trustful.[24]

F value in the model was 518.90 which is a significant number. Prob>F was less than 0.05 which shows that model parameters were significant ($P<0.001$). In this research, A, B, C, A^2, B^2 and C^2 were reported to be significant. F value in Lack of Fit was 1.45 which is negligible in comparison to pure error. Lack of significance of Lack of Fit is a good result

Table 3: ANOVA table for BOD/COD

Source	SUM of Square	Degree of Freedom	Mean Square	F Value	P value Prob>F	
Model	1.93	7	0.28	518.90	<0.0001	Significant
A-COD	0.85	1	0.85	1599.62	<0.0001	
B-H_2O_2	0.47	1	0.47	878.99	<0.0001	
C-Fe^{2+}	0.51	1	0.51	952.61	<0.0001	
BC	7.654E-004	1	7.654E-004	1.44	0.2358	
A^2	1.265E-003	1	1.265E-003	2.38	0.1294	
B^2	0.062	1	0.062	116.57	<0.0001	
C^2	0.047	1	0.047	88.96	<0.0001	
Residual	0.024	46	5.305E-004			
Lack of Fit	0.011	17	6.589E-004	1.45	0.1853	not significant
Pure Error	0.013	29	4.553E-004			
Cor Total	1.95	53				

R^2=98.75%

$R^2_{adj} = 98.56\%$

which shows the sufficiency of the model. This means that the statistical equations are meaningful and can predict the responses satisfactorily.

Model fitness was studied using R^2 coefficient which was 0.9875 in this research for BOD/COD. R_{adj}^2 was 0.9856 which was close enough to R^2 and showed desirable sufficiency of the model. R_{pred}^2 was also 0.9816 where the negligible deviation from R_{adj}^2 (less than 0.2) was an index of reasonability of the responses. Low value of C.V% (1.72) means that the results of the tests are valid enough.[24]

Moreover, the quantities were compared to the normal distribution graph to validate the design of the experiment procedure, as shown in Figure 4. As seen, the deviation of the data from the normal line is not noticeable, which is a very good proof for the model accuracy.

Interactions between Variables

The impacts of different variables including COD_{in}, H_2O_2, Fe^{2+} and TDS on enhancement of wastewater biodegradability were studied as well. Figure 5 shows the effects of interactions between variables on wastewater biodegradability. It can be concluded from Figure 5 that COD_{in}, H_2O_2 and Fe^{2+} have a noticeable impact on wastewater biodegradability, while TDS shows no significant impact.

Separate Study of Each Variable on Biodegradability

Figure 5 shows the separate impact of each variable on BOD/COD in the outlet stream. All tests were conducted in five different levels for each variable.

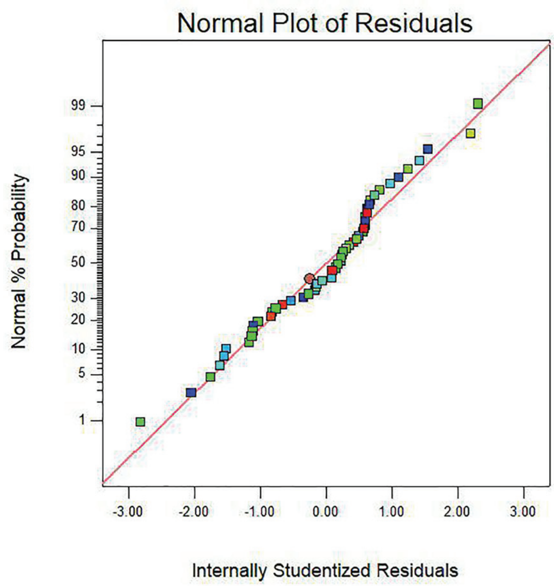
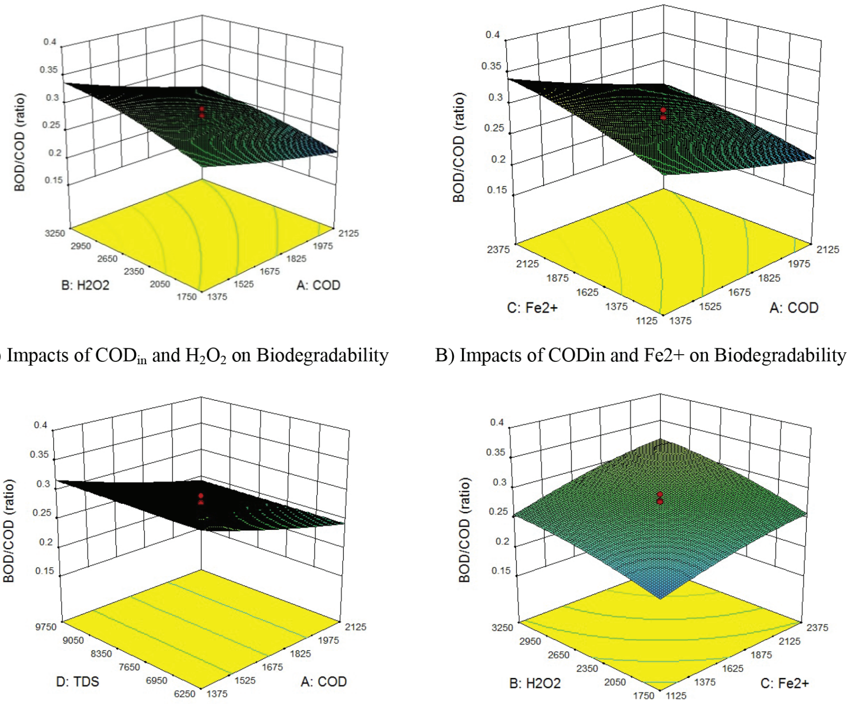


Figure 4: Normal plot of residuals for quantities in design of the experiment

In Figure 6 (A), wastewater biodegradabilitywas decreased with an increase in COD_{in} which is due to the increasing amount of hardly-decomposable materials with COD increase in the inlet stream. As the amount of hardly-decomposable organic materials decreased in the wastewater composition, the produced hydroxyl radicals reacted easily with them and retention time for achieving desirable biodegradability decreased consequently. BOD/COD ratio in this section was obtained between 0.21 and 0.37.

In Figure 6 (B), BOD/COD ratio was increased



A) Impacts of COD_{in} and H_2O_2 on Biodegradability

B) Impacts of CODin and Fe2+ on Biodegradability

C) Impacts of COD_{in} and TDS on Biodegradability

D) Impacts of Fe^{2+} and H_2O_2 on Biodegradability

Figure 5: The impacts of different variables on wastewater biodegradability; all units are mg/L.

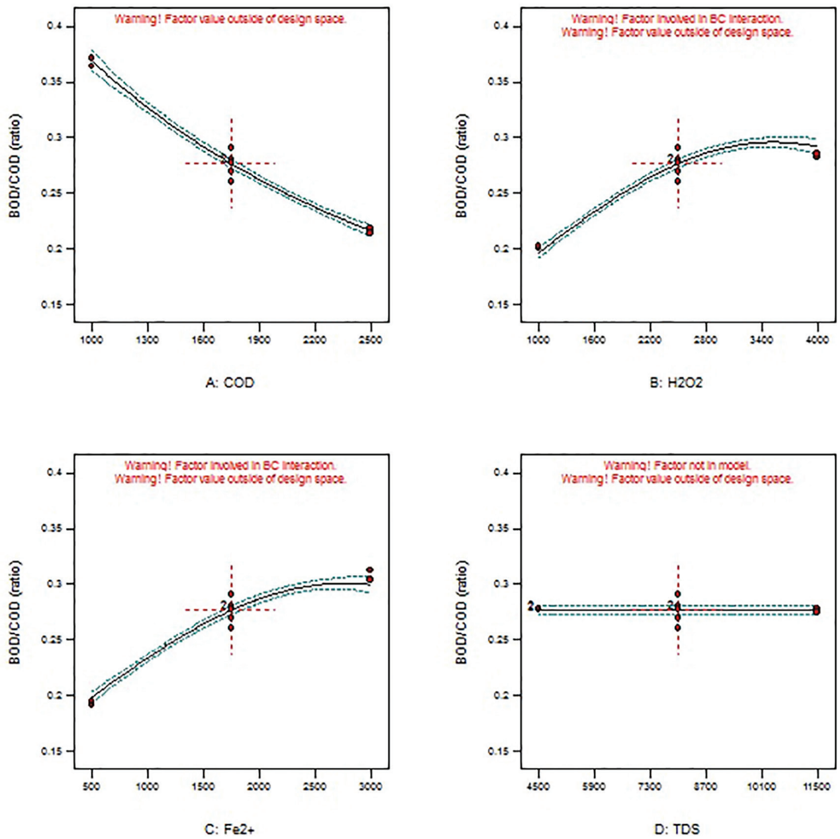


Figure 6: The impacts of each variable on wastewater biodegradability

with H_2O_2 growth until 3250 mg/L which is mainly due to higher rate of hydroxyl radical production in the environment. The range of biodegradability in this section was 0.19-0.28.

Figure 6 (C) shows the impacts of Fe^{2+} concentration on wastewater biodegradability. As shown, the trend of biodegradability with Fe^{2+} increase was ascending because of te hgrowing rate of hydroxyl radical production. In this case, the range of BOD/COD was 0.19 to 0.3.

The effect of TDS on Fenton efficiency was negligible which can be obviously seen in Figure 6 (D). The range of BOD/COD variation in all tests was 0.19–0.37.T distribution of the results is shown in Figure 7. As it is shown, more than 60% of the tests showed the BOD/COD greater than 0.25, so it can be concluded that Fenton process has a high potential for enhancement of biodegradability in petrochemical wastewater.

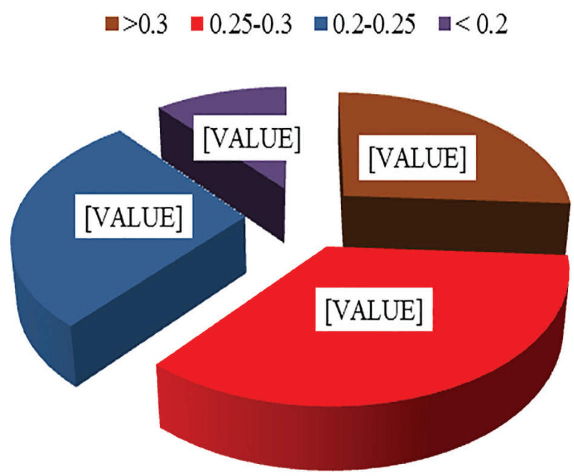


Figure 7: Distribution of different BOD/COD ratio in 54 tests

Optimum Conditions

With regard to the results, finding the optimum conditions is crucial in order to obtain the most efficient biodegradability regarding operational and economic conditions. Table 4 shows the optimum conditions achieved by the model in which H_2O_2 and Fe^{2+} concentrations is tried to be kept at minimum levels possible for minimizing the operational costs. 85 different optimum points were suggested by the model and the conditions presented in Table 5 are chosen in which H_2O_2 and Fe^{2+} concentrations are minimum.

It can be concluded from Table 5 that wastewater biodegradability under the optimum conditions was satisfactory and biological treatment could be easily applied after pre-treatment with Fenton process under the conditions proposed in Table 5.

Table 4: Criterion for choosing the optimum conditions

Parameter	Objective	Level of Importance
COD_{in}	In range	***
H_2O_2	Minimum	***
Fe^{2+}	Minimum	***
TDS	In range	***
BOD_{out}	In range	***
COD_{out}	In range	***
BOD/COD	Maximum	*****

Table 5: Optimum condition for achieving the most efficient results

COD_{in} (mg/L)	H_2O_2 (mg/L)	Fe^{2+} (mg/L)	TDS (mg/L)	COD_{out} (mg/L)	BOD_{out} (mg/L)	BOD/COD
1375	2509.27	1753.49	8622.9	1230.57	387.4	0.32

Conclusion

According to the results of this research and success of the proposed model by Design Expert on the basis of RSM, COD, H_2O_2 and $Fe^{2+,}$ significant impacts are shown by converting the hardy-decomposable compounds into more biodegradable ones. High TDS, which is an index of the salinity of the environment, showed no noticeable effect on the process of biodegradability enhancement by Fenton method. In all steps of the experiment, BOD/COD was varying between 0.19 and 0.37, and more than 26% of the tests were above 0.3; also, in 35% of the tests it was between 0.25 and 0.3 which shows the satisfactory capability of Fenton method in enhancement of petrochemical wastewater biodegradability. BOD/COD ratio in the outlet stream increased with a decrease in COD_{in} and increase in H_2O_2 and Fe^{2+}. Maximum BOD/COD in the outlet was 0.37 which proves the potential of Fenton method for enhancement of wastewater biodegradability.

Declarations

- Ethics approval and consent to participate: Not applicable

- Consent for publication: Not applicable

- Availability of data and material: All data generated or analysed during this study are included in this published article

- Competing interests: The authors declare that they have no competing interests

- Funding: The autors declare that they used no funding sources

- Authors' contributions:

1) First author

● Carrying out all of the experimental tests, producing the results and analyzing

● Preparing the first manuscript

2) Second author

● Supervising the experimental process and analyzing the resulta

● Final editing of the manuscript

Conflict of Interest: None declared.

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