

Journal of Applied Research in Water and Wastewater

E-ISSN: 2476-6283

Journal homepage: https://arww.razi.ac.ir

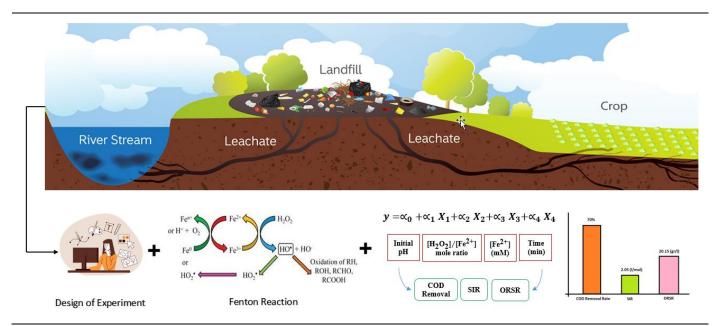


Multivariate modeling of the Fenton process for enhanced COD removal and low sludge generation in landfill leachate treatment

Nader Biglarijoo 📵, Amin Shams 🗓

Civil Engineering Department, School of Civil Engineering, Semnan University, Semnan, Iran.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article type:

Research Article

Article history:

Received 9 July 2024 Received in revised form 5 November 2024 Accepted 7 November 2024 Available online 12 November 2024

Keywords:

Fenton process Landfill leachate COD removal Sludge generation Multivariate modeling



ABSTRACT

Biological treatment methods are not practical when it comes to landfill leachate treatment. Fenton as a physiochemical pretreatment technique is used in this research to increase the BOD/COD ratio. Conventionally, the main purpose of Fenton reaction has been the removal of organic pollutants, but in this paper, two other factors including sludge to iron ratio (SIR) and organic removal to sludge ratio (ORSR) are examined to generate low amounts of sludge as well. For the design of the experimental procedure, central composite design was used to not only minimize the required tests, but also observe the interactions between factors. Therefore, pH, $[H_2O_2]/[Fe^{2+}]$, Fe^{2+} dosage and reaction time were considered as critical parameters while COD removal rate, SIR, and ORSR were introduced as targets. In order to have a clearer understanding of the process, multivariate modeling was applied to three targets to provide better predictions of the reaction. According to the statistical results, models can acceptably predict the target responses with R² above 0.95 and standard error and F-values were within suitable ranges. To reach high COD removal rates, the critical factors were [H₂O₂]/[Fe²⁺] and [Fe²⁺] while for lower SIR and higher ORSR, the role of pH and [H₂O₂]/[Fe²⁺] were more significant. The reaction time was not a determining factor based on our observations for all three targets.

1. Introduction

In recent years, industrial practices, agricultural activities, and the rise of urbanization have led to the production of large quantities of municipal waste (Abbas *et al.*, 2009). Sanitary landfills are known to be promising facilities to provide a suitable place for the disposal of generated municipal solid waste (MSW) (Clemente *et al.*, 2024). Since most of the waste is disposed without sufficient treatment, it can cause significant environmental problems (Mojiri *et al.*, 2021). The uncontrolled release of effluents called landfill leachate (LFL) is a **Corresponding author Email: nader.biglary@semnan.ac.ir

serious concern which leads to the contamination of water streams (Biglarijoo *et al.*, 2017). Leachate is generally formed via the percolation of rainwater into the waste, biological reactions which happen in the landfill, and inherent moisture of the waste (Amiri and Sabour, 2014). A number of parameters including the temperature (Dhanda *et al.*, 2023), elapsed time (Saber *et al.*, 2014), landfill hydrology (Pilli *et al.*, 2016), depth of site (Silva *et al.*, 2016), and moisture content (Qiu *et al.*, 2015) may affect the quantity and quality of leachates, so the characteristics of leachates vary depending on the region and climate (Oulego *et al.*, 2016). Leachates sound notorious for their large amounts of

ammoniacal nitrogen, remarkable concentrations of recalcitrant mixtures and low BOD₅/COD ratios (Li *et al.*, 2010). In case they are not treated sufficiently (Zhang *et al.*, 2009), they may mix with surface or ground water which results in the pollution of water and soil (Bolobajev *et al.*, 2014). Therefore, one practical method for the rehabilitation of landfills (Kavitha and Palanivelu, 2004) is the selection of practical methods of leachate treatment to minimize the adverse impacts they could have on soil and water on the site (Bouranene *et al.*, 2021; Rusdianasari *et al.*, 2017).

There are several methods to treat leachates (Kattel, Trapido and Dulova, 2016), but could be summarized into biological approaches (e.g. bioremediation, bioreactors, and phytoremediation) (Feng et al., 2024) and physicochemical methods (e.g. adsorption, advanced oxidation (Clemente et al., 2024), membrane filtration (Wu et al., 2015), and coagulation/flocculation) (Umar, Aziz and Yusoff, 2010). Among these techniques, advanced oxidation processes (AOPs) have gained more acceptance because of their efficiency to produce hydroxyl radicals to oxidize stable organic matters and degrade polluting agents into solid waste leachate which turns them into harmful materials (Bolobajev et al., 2014). Fenton processes are one of AOP methods that easily treat leachates that are biologically recalcitrant. This method possesses some benefits such as high removal rate, biodegradability improvement, simple operation, and flexibility in the type of influents (Biglarijoo et al., 2017). Several researches have focused on the use of photo-Fenton, electro-Fenton, and conventional Fenton to treat different wastewaters in recent decades(Meddah et al., 2021; Beryani et al., 2017).

The function of the conventional Fenton process is simple and takes advantage of the presence of the reagent solution called hydrogen peroxide (H_2O_2) and an iron catalyst (usually FeSO₄). This AOP method has been applied frequently to treat pharmaceutical, petroleum refinery, cosmetics, pesticide, and dye wastewaters (Wu *et al.*, 2015). This method takes benefit of the creation of highly reactive hydroxyl radicals (OH $^\circ$) and oxidizes complex organic substances (RH) that forms fixed ferric-hydroxo complexes (Amiri and Sabour, 2014):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\circ} + OH^{-}$$
 (1)

$$RH+OH^{\circ} \rightarrow H_2O+R^{\circ}$$
 (2)

$$R^{\circ} + Fe^{3+} \rightarrow R^{+} + Fe^{2+} \tag{3}$$

The summary of Eqs. 1 to 3 could be expressed as Eq. (4):

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$$
 (4)

While the Fenton process has been widely studied for its effectiveness in removing COD from landfill leachate, most research has focused primarily on COD reduction without adequately addressing two critical factors: the quantity of sludge generated and the amount of iron used in the process. These factors are crucial because the Fenton process relies on catalysts, producing significant amounts of ferric hydroxide sludge, which poses its own environmental and operational challenges. Therefore, optimizing the process to minimize sludge production while maintaining high COD removal efficiency is an essential yet underexplored area.

Conventionally, when it comes to the test design, one factor is examined while the rest are kept unchanged. In this approach, the interaction between different variables is not considered (Khourshidi and Qaderi, 2023). However, when experiments are designed via the use of a helpful device, the interactions between elements are considered and the number of tests is reduced (Amiri and Sabour, 2014). One of these helpful methods is the central composite design (CCD) which is a popular fractional factorial design. In this approach, the center points are augmented with a number of axial points named star points. With the help of this method, first-order and second-order terms could be estimated. In CCD, every factor possesses five levels: (-1) which is low factorial, (+1) which is high factorial, (0) which is central point, $(-\alpha)$ which is low axial, and $(+\alpha)$ which is high axial. The value of α depends mainly on the factor number (k) (Jalili et al., 2018). This test design method enables researchers to run the minimum possible experiments while the interaction of different factors is simultaneously seen. In addition, introducing a multivariate formula to represent the function of the Fenton process could shed light on researchers to have logical predictions of the efficiency of Fenton processes.

In this paper, the Fenton process is used to treat the landfill leachate achieved from Kahrizak site situated in the south of Tehran in Iran. Four factors including pH, [H₂O₂]/[Fe²⁺] mole ratio, [Fe²⁺] dosage and running time were considered as influential elements while the removal rate of COD, sludge to iron ratio (SIR), and organic removal to sludge ratio (ORSR) were investigated as targets. The main reason for considering the SIR and ORSR as indicators of the amount of sludge is

that Fenton process takes benefit of catalysts for treatment, and a considerable volume of ferric hydroxide sludge is produced, which should be considered in the final decision of optimum operational conditions. Therefore, the target of this paper is to examine the COD removal rate while the minimum volume of the generated sludge is achieved. To gain a better understanding of the process, a multivariate regression is proposed to achieve a math formula and a prediction for the results.

2. Materials and method 2.1. Experimental procedure

The lab samples were prepared from Kahrizak site (Tehran) in Iran. They were all taken manually from ponds on the Kahrizak site in polyethylene containers which were taken to the lab and kept in the fridge at 4°C . The characteristics of the leachate is mentioned in Table 1. One of the determining factors of classifying leachate is the BOD $_5/\text{COD}$ of the leachate, and in this study was about 0.21 which indicates the low biodegradability. In other words, this leachate is categorized as medium aged and chemical pretreatment is absolutely necessary. In fact, advanced oxidation methods such as Fenton are used as pretreatment methods to enhance the BOD $_5/\text{COD}$ ratio.

Table 1. Important characteristics of the collected leachate.

Parameter (unit)	Mean Value
рН	7.6
COD (mg/l)	9560
BOD₅ (mg/l)	2010

Chemicals used in this research were prepared from Merc Company in Germany. The pH of solution was measured via the use of WTW SERIES, pH730 instrument while Lovibond spectrophotometer was used to measure COD.

All laboratory tests were performed at room temperature and atmospheric pressure. One-liter glasses preserved from the infiltration of ultra-violet beams were used to run experiments. It is notable that sufficient space was considered to avert from the overflow of foaming resulting from the initial stages of the reaction. In the beginning of the experiment, the adjustment of the initial pH was done using 1 M sulfuric acid and 10 M sodium hydroxide solution. Then, the beaker was filled with 400 ml of the leachate sample and mixing procedure started. A Jartest device was used for rapid mixing at 175 rpm. Next, the necessary amount of powered FeSO₄.7H₂O was added to the beaker and mixed for 5 minutes to reach a homogeneous solution. Thereafter, the require amount of hydrogen peroxide solution (H₂O₂, 30% w/w) was added to the mixture and the Fenton reaction started. The reaction continued until the designated time was passed, then to adjust the pH to around 7, NaOH was added. Next, the solution of 10M NaOH was used dropwise to the pH of 8 and the solution was mixed slowly at 30 rpm for 20 minutes for flocculation. Thereafter, a 100 ml sample of the final solution was dispended to a graduated cylinder to determine the volume of the sludge. It should be noted that lab samples' temperature increased in a 50°C water bath for 30 minutes to eliminate the residual H_2O_2 in the solution as it may interfere the COD analysis. The sedimentation took 60 minutes and the height of the sludge was recorded. The COD of the solution was examined from the supernatant of the beaker.

2.2. Test design procedure

In order to minimize the number of laboratory tests and make sure that sufficient amount of information is provided to be examined for the lack of fit, central composite design (CCD) is an effective method which provides a reasonable estimation of the nonlinearity of dependent variable and allows for maximum information with minimum experimental result data, leading to fewer number of experiments to predict quadratic terms in the second-order model. For this purpose, the Design Expert Software (version 11) was applied to the experimental design. In this research, four influencing factors include pH, [H₂O₂]/[Fe²⁺] ratio, [Fe²⁺] and time were considered while COD removal rate, sludge to iron ratio (SIR) and organic removal to sludge ratio (ORSR) were opted as targets. Table 2 shows the factor levels for the test design. To the best of our knowledge, in the literature, COD or TOC were seen as the most crucial response in the Fenton reaction. Nevertheless, the efficiency of COD removal does not consider the amount of generated sludge or the quantity of added ferrous iron to the experiment.

Therefore, SIR and ORSR are examined in this paper as other important targets proposed by Amiri and Sabour (Amiri and Sabour, 2014):

Sludge to iron ratio (SIR)=
$$\frac{\text{produced sludge volume (I)}}{\text{added ferrous iron (mole)}}$$
 (5)

Table 2. Factor levels for the test design.

Tuble 11 actor levels for the tool deeligh							
Experimental	Symbol	Coded values					
variable (unit)	Symbol	-2	-1	0	+1	+2	
Initial pH	X ₁	2	3	4	5	6	
$[H_2O_2]/[Fe^{2+}]$ mole ratio	X_2	4	8	12	16	20	
[Fe ²⁺], mM	X_3	80	120	160	200	240	
Reaction time, min	X_4	30	60	90	120	150	

The test design included the following parts: (a) sixteen tests of the two-stage factorial design (b) eight tests at the star nodes and (c) one central node and five repetitions for it to calculate the test error and any potential repercussions of a curvature in the response surfaces. Table 3 illustrates the details of the CCD test design.

Table 3. The proposed test design.					
Test design	pН,	[H ₂ O ₂]/[Fe ²⁺],	[Fe²+],	Time,	
rest design	-	mole ratio	mM	min	
1	4	12	160	150	
2 3	5	8	120	60	
3	3	16	200	60	
4	4	20	160	90	
5	3	16	129	60	
6	5	8	120	120	
7	5	16	200	60	
8	3	16	120	120	
9	5	8	200	120	
10	2	12	160	90	
11	4	12	160	30	
12	4	12	160	90	
13	3	16	200	120	
14	3	8	120	120	
15	5	8	200	60	
16	4	12	160	90	
17	5	16	120	120	
18	4	4	160	90	
19	4	12	80	90	
20	4	12	160	90	
21	5	16	200	120	
22	4	12	240	90	
23	3	8	200	60	
24	5	16	120	60	
25	3	8	120	60	
26	4	12	160	90	
27	4	12	160	90	
28	6	12	160	90	
29	4	12	160	90	
30	3	8	200	120	

2.3. Multivariate regression

Multivariate multiple regression is a tool to model multiple responses (known as dependent variables) while a single set of independent (predictor) variables is used; i.e. four factors mentioned above (X1 to X₄) can affect the value of COD removal, SIR, and ORSR. For this purpose, a built-in data analysis tool was used. This tool can propose a formula for the prediction of the process and reveals important features of the correlation such as the fitting quality of the model (correlation coefficient R2) and the importance of linear terms as F-values. The schematic relation in the type of regression is shown in Eq. 7:

$$y = \alpha_0 + \alpha_1 X_1 + \alpha_2 X_2 + \alpha_3 X_3 + \alpha_4 X_4 \tag{7}$$

3. Result and discussion

3.1. COD removal

In this paper, COD as the most critical factor is removed to improve the BOD₅/COD ratio. The higher value of BOD₅/COD ratio could represent the potential of rehabilitation in landfill sites. Therefore, COD removal efficiency was measured as a valuable tool to evaluate the overall pollution level as well as organic content of water. The results of COD removal are shown in Figs. 1 and 2. According to the information in the

graphs, as the value of X_1 (pH) increases, a slight reduction could be seen in the rate of COD removal. This observation was mentioned in previous studies that Fenton performance was better in acidic pH values (Umar, Aziz and Yusoff, 2010; Oulego et al., 2016). The values they recommended were restricted to pH values of 2 to 3. Meanwhile, there are some studies that recommended high pH values that COD removal was quite acceptable (Li et al., 2010). In this paper, the pH of about 6 was selected as appropriate. However, the influences of X₂ $([H_2 O_2]/[Fe^{2^+}])$ and X_3 $([Fe^{2^+}])$ were more critical since their higher values increased the removal of COD remarkably. The main reason for this observation is that more reagent (H₂O₂) is available in the process and more ferrous could be consumed as the catalyst. Therefore, the removal efficiency increases significantly. As it could be seen in Figs. 1 and 2, the excess amount of X2 and X3 does not affect the removal rate, which helps to limit the amount of chemical use, resulting in better financial management of the project. This issue was already seen in the literature (Amiri and Sabour, 2014). The reason is that scavenging actions that occur in the presence of excessive amount of reagents and catalysts brings about a drop in destruction rate of pollutants and restrict the removal process. The last factor is X4 (time) which is shown in Fig. 2. The effect of this parameter is negligible as a slight increase could be seen in the COD removal rate by the passage of time. The possible explanation is that initial minutes of the process are more effective than the final minutes. However, in the literature, time was introduced as an important factor to reach the highest amount of COD removal (after 120 minutes) (Bocos et al., 2015) while the other study mentioned the insignificant impact of time (Biglarijoo et al., 2016).

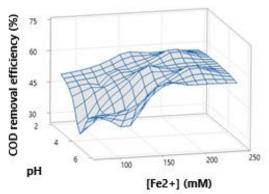


Fig. 1. Surface plot of COD removal efficiency as a function of X_1 and

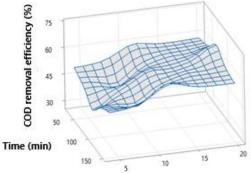


Fig. 2. Surface plot of COD removal efficiency as a function of X_2 and

[H2O2]/[Fe2+] (mole ratio)

To obtain a formula that shows the impact of independent variable $(X_1 \text{ to } X_4)$, a multi-variate regression is proposed with the aid of the regression tool in Data Analysis section (Excel). Eq. 8 shows the COD removal rate as a function of X_1 to X_4 . In this formula, X_1 represents pH, X_2 represents $\frac{H_2O_2}{Fe^{2+}}$, X_3 represents Fe^{2+} , and X_4 represents time while Y_1 indicates the rate of COD removal rate.

$$Y_1 = -2.07X_1 + 1.70X_2 + 0.24X_3 + 0.03X_4 \tag{8}$$

Since the correlation coefficient (R2) is around 99% and the multiple R is almost 99%, the relation can create an image for prediction of results. Table 5 illustrates the ANOVA results of COD removal rate formula. F-value can indicate the statistical significance of the regression Eq. as a whole. According to this table, since the F-value is greater than 4 (is around 528), the model is statistically significant. The value for significance-F should be less than 0.05, which is completely suitable in this model. Proposing such models can facilitate the initial predictions of the process for future studies to have a clearer imagination of the reaction and affecting factors.

Table 4. The regression statistics for COD removal rate.

Multiple	R	Adjusted R	Standard	Observations
R	Square	Square	Error	
0.994	0.988	0.948	6.58	30

Table 5. The ANOVA results for COD removal rate.

Parameter	df	SS	MS	F	Significance F
Regression	4	91400.2	22850.1	527.7	9.56E-07
Residual	26	1125.8	43.3		
Total	30	92525 9			

3.2. SIR

The amount of sludge generated in the Fenton reaction should be considered as a determining factor of the Fenton process performance. SIR value can show the volume of the generated sludge to the added iron as shown in Eq. 5. Figs. 3 and 4 illustrate the SIR value. It is notable than minimum amount of SIR could be more favorable as the generated sludge is minimized while the amount of added ferrous could still be remarkable. Based on these Figs., with the increase of pH, the value of SIR decreased noticeably; i.e. in case the SIR should be minimized, the highest possible pH could be applied. Meanwhile, the dosage of [Fe²⁺] reduced the value of SIR in the beginning but as the reaction continued, this ratio increased slightly. This means the lowest and the highest values of ferrous can be favorable. The possible explanation why higher pH quantities were more pleasant is that the higher pH quantities contributed to higher COD removal rate, but in terms of operational approaches, low values of ferrous are suggested. These findings were approved by Li et al. (Li et al., 2010) that reported pH values of 5.9, and Amiri and Sabour (Amiri and Sabour, 2014) that observed the optimum pH value of 5.7. In our study, the pH of around 6 is also favorable. In this paper, the favorable $[H_2O_2]/[Fe^{2+}]$ was 20 mole ratio and favorable †] was 170 mM. Li et al. proposed [H₂O₂]/[Fe²⁺] of 2.4 and [Fe²⁺] of 9.6 mM which were in contrast with the findings of our paper (Li et al., 2010). The effect of $[H_2O_2]/[Fe^{2+}]$ was very important as with the introduction of more value of X₃, the SIR value decreased as a whole. The repercussion of time was not noticeable which dictates the effective required time for the process does not need to be prolonged. This can be an important conclusion, because the shorter the time of the process, the more preferable for the operators.

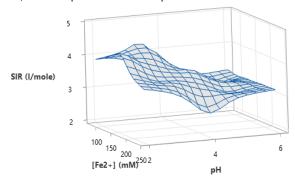


Fig. 3. Surface plot of SIR as a function of X_1 and X_3 .

A formula is also introduced to examine the impact of independent variable (X_1 to X_4) on SIR. Eq. 3 shows the SIR as a function of X_1 to X_4 . In this formula, X_1 represents pH, X_2 represents $\frac{H_2O_2}{Fe^{2+}}$, X_3 represents Fe^{2+} , and X_4 represents time while Y_2 indicates SIR.

$$Y_2 = -0.05X_1 - 0.06X_2 - 0.01X_3 + 0.01X_4$$
(9)

According to Table 3, the correlation coefficient (R^2) is 0.95 and the multiple R is almost 0.97, so the results can be somewhat predicted, and the standard error is within the acceptable range. Table 7 illustrates the ANOVA results of SIR formula. As the F-value can indicate the statistical significance of the regression equation. The value greater than 4 (is around 122) shows that the model is statistically significant. Moreover, when the significance-F is less than 0.05, the model is meaningful; i.e. the null hypothesis is rejected, and input variables can predict output ones, Overall, the lower values of SIR are more favorable in terms of economics and operation.

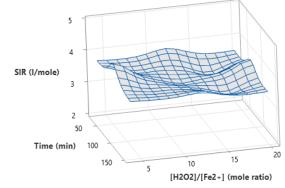


Fig. 4. Surface plot of SIR as a function of X_2 and X_4 .

Table 6. The regression statistics for SIR.

Multiple R	R Square	Adjusted R Square	Standard Error	Observations
0.974	0.950	0.905	0.88	30

Т	able	7. The Al	NOVA r	esults for	· SIR.
Parameter	df	SS	MS	F	Significance F
Regression	4	381.4	95.3	122.7	4.78E-016
Residual	26	20.2	0.8		
Total	30	401 6			

3.3. ORSR

One practical method to evaluate the removal rate of organic pollutants and at the same time having the minimum amount of generated sludge is the term of ORSR which indicates the organic removal to sludge ratio as described in Eq. 6. In other words, it is an index to indicate that only the high removal efficiency of COD is not the most favorable choice for leachates and the generated sludge amount must be simultaneously considered. Figs. 5 and 6 illustrate the surface plots for ORSR. With the addition of pH and $[H_2O_2]/[Fe^{2^+}]$ in the experiment, the value of ORSR increased remarkably. On the other hand, the increase in the reaction time and the dosage of [Fe2+] were not significant factors in ORSR. It could be concluded that oxidation had the key role in the treatment process whereas the coagulation's role was not important (Amiri and Sabour, 2014). In fact, high amounts of [H₂O₂]/[Fe²⁺] brought about the domination of the coagulation and the impact of coagulation was low, and this could interpreted that the influence of oxidation stage was positive and the coagulation stage was negative. The aforementioned observations were seen by Amiri and Sabour too (Amiri and Sabour, 2014). The result that can be seen is that high quantities of pH is operationally and technically pleasant. It means lower amounts of chemicals are needed (economic perspective) for pH adjustment in the experiment. More interestingly, high dosage of [Fe2+] does not necessarily lead to higher ORSR values, but the role of [H₂O₂] to [Fe²⁺] ratio can play the critical role.

The third formula is presented to predict the impact of independent variable (X₁ to X₄) on ORSR. Eq. 4 shows the ORSR as a function of X₁ to X₄. In this formula, X₁ represents pH, X₂ represents $\frac{H_2O_2}{Fe^{2+}}$, X₃ represents Fe^{2+} , and X₄ represents time while Y₃ indicates ORSR.

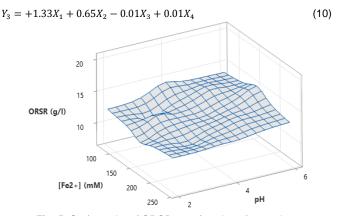


Fig. 5. Surface plot of ORSR as a function of X_1 and X_3 .

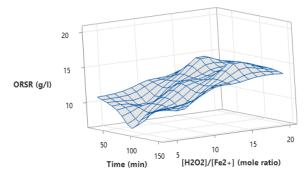


Fig. 6. Surface plot of ORSR as a function of X_2 and X_4 .

Table 8. The regression statistics for ORSR

Multiple R R Square		R Square	Adjusted R Square	Standard Error	Observations
	0.993	0.987	0.947	1.57	30

The correlation coefficient (R^2) is 0.76 and the multiple R is 0.87, so the results can be logically predicted, and the standard error is within the acceptable range (less than 2%). Table 9 illustrates the ANOVA results of ORSR formula. F-value is 19, which is greater than 4, and indicates that the model is statistically significant. Significance-F also indicates the predictability of the formula.

Table 9. The ANOVA results for ORSR.

Parameter	df	SS	MS	F	Significance F
Regression	4	4896.14	1224.04	496.2	2.02E-023
Residual	26	64.14	2.46		
Total	30	4960.28			

3.4. BOD/COD improvement

As one of the major targets of this paper is to enhance the ratio of $\mathsf{BOD}_{\mathsf{5}}/\mathsf{COD}$, in this part it is proved that the Fenton reaction could potentially improve this ratio. Before treatment, the $\mathsf{BOD}_{\mathsf{5}}/\mathsf{COD}$ was 0.21, but after the treatment at the best condition, the rate of COD removal improved significantly. In this condition, the highest COD removal rate was accomplished: pH: 3, [H₂O₂]/[Fe²⁺]: 16, [Fe²⁺]: 200, and reaction time: 120 min. At this condition, COD removal rate was around 70% and reached the value of 2868 mg/l. In this condition, the BOD₅/COD is almost 0.7 which is favorable and hopefully suitable biodegradable.

4. Conclusions

The Fenton process, in this paper, was used as a pretreatment method to treat landfill leachates. Although most articles in this area have paid attention only to the removal of organic pollutants in Fenton reaction, the main purpose here was to reach high COD removal efficiency rate while the minimum amount of sludge is generated. Hence, COD removal rate, SIR (sludge to iron ratio), and ORSR (organic removal to sludge ratio) were evaluated as targets whereas affecting factors were introduced as: pH, [H₂O₂]/[Fe²⁺], Fe²⁺ dosage and reaction time. The following results could summarize the important achievements of this research:

- 1. Multi-variant modeling was used to introduce a predictive model for COD, SIR, and ORSR. The models could acceptably predict the result with R^2 values higher than 0.7, and standard error and F-values within acceptable ranges.
- 2. The importance of considering SIR and ORSR as targets could help reach the high removal rate while the sludge generated is minimized.
- 3. The determining factors for COD removal rate were $[H_2O_2]/[Fe^{2+}]$ and $[Fe^{2+}]$ which indicates the importance of oxidation rate and the use of appropriate dosage of the catalyst.
- 4. To have low values of SIR, the value of pH and the [Fe²⁺] dosage were significant, which indicates the importance of the amount of the generated sludge. The lower dosage of ferrous and high pH values could decrease this target.
- 5. $[H_2O_2]/[Fe^{2+}]$ and pH were significant factors influencing ORSR, which is a suitable index to check the importance of high oxidation but low sludge generation.
- 6. When it comes to operational purposes, high quantities of pH may lead to lower COD removal efficiency (slight impact) but could help to reach favorable values of SIR and ORSR. Meanwhile, in practice, lower amounts of chemicals must be used to adjust the pH values.

Nomenclature	
BOD	biological oxygen demand
COD	chemical oxygen demand
RSM	response surface methodology
SIR	sludge to iron ratio
ORSR	organic sludge to iron ratio
CCD	central composite design
SD	standard deviation
R^2	coefficient of determination
RMSE	root mean squared error
MS	mean square
F	F-value
Р	probability error
Adj. R²	adjusted R ²
Pred. R ²	prediction R ²
df	degrees of freedom
SS	sum of squares
MS	mean square

Author Contributions

Nader Biglarijoo: Conceptualization, methodology, supervision, experimental work, writing & revision.

Amin Shams: Conceptualization, methodology, experimental work & revision.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgement

The authors acknowledge Prof. Ahmad Mirbagheri from the School of Civil Engineering, University of Khaje Nasir Toosi of Technology, Tehran, for helping the research plan.

Data Availability Statement

Data will be available on request.

References

Abbas, A.A. et al. (2009) 'Review on landfill leachate treatments', American Journal of Applied Sciences, 6(4), pp. 672–684. doi: https://doi.org/10.3844/ajas.2009.672.684

Amiri, A. and Sabour, M.R. (2014) 'Multi-response optimization of Fenton process for applicability assessment in landfill leachate treatment', *Waste Management*, 34(12), pp. 2528–2536. doi: https://doi.org/10.1016/j.wasman.2014.08.010

Beryani, A. et al. (2017) 'Benzene and MTBE removal by Fenton's process using stabilized Nano Zero-Valent Iron particles', Journal of Applied Research in Water and Wastewater, 8(2), pp. 343–348. doi: https://doi.org/10.22126/arww.2017.788

Biglarijoo, N. et al. (2016) 'Optimization of Fenton process using response surface methodology and analytic hierarchy process for landfill leachate treatment', *Process Safety and Environmental Protection*, 104, pp. 150–160. doi: https://doi.org/10.1016/j.psep.2016.08.019

Biglarijoo, N. et al. (2017) 'Assessment of effective parameters in landfill leachate treatment and optimization of the process using neural network, genetic algorithm and response surface methodology', Process Safety and Environmental Protection, 106, pp. 89–103. doi: https://doi.org/10.1016/j.psep.2016.12.006

Bocos, E. et al. (2015) 'Application of a new sandwich of granular activated and fiber carbon as cathode in the electrochemical advanced oxidation treatment of pharmaceutical effluents', Separation and Purification Technology, 151, pp. 243–250. doi: https://doi.org/10.1016/j.seppur.2015.07.048

Bolobajev, J. et al. (2014) 'Reuse of ferric sludge as an iron source for the Fenton-based process in wastewater treatment', Chemical Engineering Journal, 255, pp. 8–13. doi: https://doi.org/10.1016/j.cej.2014.06.018

Bouranene, S. et al. (2021) 'Comparative study of leachate treatment by coagulation-flocculation process using iron-based coagulants: A case study on Souk-Ahras city', *Journal of Applied Research in Water and Wastewater*, 8(1), pp. 71–76. doi:

https://doi.org/10.22126/arww.2021.1817

- Clemente, E. et al. (2024) 'European and African landfilling practices: an overview on MSW management, leachate characterization and treatment technologies', *Journal of Water Process Engineering*, 66, p. 105931. doi: https://doi.org/10.1016/j.jwpe.2024.105931
- Dhanda, M. et al. (2023) 'Biological treatment of compost leachate: Assessing the efficacy of composting process and bioaugmentation of composting piles', *Journal of Alloys and Compounds*, p. 169738. doi: https://doi.org/10.1016/j.eti.2024.103859
- Feng, W. et al. (2024) 'Unlocking the application potential of superabsorbent polymers in landfill leachate treatment', *Polymer Testing*, 138, p. 108537. doi: https://doi.org/10.1016/j.polymertesting.2024.108537
- Jalili, B. et al. (2018) 'Optimization of adsorption removal of ethylene glycol from wastewater using granular activated carbon by response surface methodology', Journal of Applied Research in Water and Wastewater, 10(2), pp. 421– 430. https://doi.org/10.22126/arww.2018.982
- Kattel, E., Trapido, M. and Dulova, N. (2016) 'Treatment of landfill leachate by continuously reused ferric oxyhydroxide sludgeactivated hydrogen peroxide', *Chemical Engineering Journal*, 304, pp. 646–654. doi: https://doi.org/10.1016/j.cej.2016.06.135
- Kavitha, V. and Palanivelu, K. (2004) 'The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol', Chemosphere, 55(9), pp. 1235–1243. doi: https://doi.org/10.1016/j.chemosphere.2003.12.022
- Khourshidi, A. and Qaderi, F. (2023) 'The use of response surface methodology for modeling and optimizing of pnitrophenol contaminated water treatment process conducted by the nonthermal plasma discharge technology', *Journal of Applied Research in Water and Wastewater*, 10(1), pp. 80–90. doi: https://doi.org/10.22126/arww.2023.8527.1275
- Li, H. et al. (2010) 'Application of response surface methodology to the advanced treatment of biologically stabilized landfill leachate using Fenton's reagent', Waste Management, 30(11), pp. 2122–2129. doi: https://doi.org/10.1016/j.wasman.2010.03.036
- Meddah, S. *et al.* (2021) 'Optimization of the operating parameters and their effects on the degradation of naphthol blue black by the Fenton process', *Journal of Applied Research in Water and Wastewater*, 8(2), pp. 133–139. https://doi.org/10.22126/arww.2021.6153.1200

- Mojiri, A. *et al.* (2021) 'Treatment of landfill leachate with different techniques: An overview', *Journal of Water Reuse and Desalination*, 11(1), pp. 66–96. doi: https://doi.org/10.2166/wrd.2020.079
- Oulego, P. et al. (2016) 'Impact of leachate composition on the advanced oxidation treatment', Water Research, 88, pp. 389–402. doi: https://doi.org/10.1016/j.watres.2015.09.048
- Pilli, S. et al. (2016) 'Fenton pre-treatment of secondary sludge to enhance anaerobic digestion: Energy balance and greenhouse gas emissions', Chemical Engineering Journal, 283, pp. 285–292. doi: https://doi.org/10.1016/j.cej.2015.07.056
- Qiu, S. *et al.* (2015) 'Kinetic modeling of the electro-fenton process: quantification of reactive oxygen species generation', *Electrochimica Acta*, 176, pp. 51–58. doi: https://doi.org/10.1016/j.electacta.2015.06.103
- Rusdianasari et al. (2017) 'Treatment of landfill leachate by electrocoagulation using aluminum electrodes', MATEC Web of Conferences, 101, pp. 435–440. doi https://doi.org/10.1051/matecconf/201710102010
- Saber, A. *et al.* (2014) 'Optimization of Fenton-based treatment of petroleum refinery wastewater with scrap iron using response surface methodology', *Applied Water Science*, 4(3), pp. 283–290. doi: https://doi.org/10.1007/s13201-013-0144-8
- Silva, T.F.C.V. et al. (2016) 'Scale-up and cost analysis of a photo-Fenton system for sanitary landfill leachate treatment', *Chemical Engineering Journal*, 283, pp. 76–88. doi: https://doi.org/10.1016/j.cej.2015.07.063
- Umar, M., Aziz, H.A. and Yusoff, M.S. (2010) 'Trends in the use of Fenton, electro-Fenton and photo-Fenton for the treatment of landfill leachate', Waste Management, 30(11), pp. 2113–2121. doi: https://doi.org/10.1016/j.wasman.2010.07.003
- Wu, D. et al. (2015) 'Ferric iron enhanced chloramphenicol oxidation in pyrite (FeS 2) induced Fenton-like reactions', Separation and Purification Technology, 154, pp. 60–67. doi: https://doi.org/10.1016/j.seppur.2015.09.016
- Zhang, H. et al. (2009) 'Multivariate approach to the Fenton process for the treatment of landfill leachate', *Journal of Hazardous Materials*, 161(2–3), pp. 1306–1312. doi: https://doi.org/10.1016/j.jhazmat.2008.04.126