

Electro-Fenton Oxidation to test the values of COD in the treatment of oily wastewater of petroleum refinery

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Abstract

Petroleum refinery wastewater contains organic pollutants that resist conventional treatment. This study applied Response Surface Methodology with Box Behnken Design to optimize the electro-Fenton process for chemical oxygen demand (COD) removal. Three operational factors were systematically varied: applied voltage, total dissolved solids, and conductivity. A cubic polynomial model emerged as statistically significant, explaining 99.97% of observed variance in COD removal. The results reveal an unexpected relationship between operational parameters and treatment efficiency that contradicts conventional assumptions about maximizing voltage and conductivity. Optimal conditions diverge substantially from apparent maximum values, suggesting a delicate balance between oxidant generation and competing side reactions. The developed model provides quantitative guidance for parameter optimization in electrochemical wastewater treatment, with practical implications for refinery operations seeking enhanced COD removal efficiency.

1.0 Introduction

Wastewater treatment is a global issue that's been around for a long time, this is due to its significant effects on the environment and human health (APHA, 1998; World Health Organization, 2024). Advanced oxidation processes (AOPs) are potent treatment procedures for the efficient elimination of refractory organic pollutants via oxidation with hydroxyl radicals (OH) (Ammar et al., 2015). The Electro-Fenton process is an innovative technology for the treatment of water and wastewater. Electro-Fenton employs hydroxyl radicals to oxidize hazardous pollutants and is particularly effective for treating recalcitrant chemicals that resist degradation in traditional water and wastewater treatment facilities (Annabi et al., 2016). The development of AOPs in the past few decades has helped scientists and engineers to develop a comprehensive understanding of their oxidation mechanisms and to improve their efficacy in pollutant removal. The Fenton process is regarded as one of the most appealing methods for advanced oxidation (AOPs) and has been utilized for water and wastewater treatment, biomedical applications, atmospheric processes, and biogeochemistry (Atmaca, 2009). Fenton technology is appealing because of its simplicity, affordability, great efficiency, and the non-toxic nature of Fenton's reagents (Zhou et al., 2007). During the past three decades, its development has advanced as a clean and efficient method for wastewater treatment.

While conventional electro-Fenton (EF) has demonstrated efficacy in the decomposition and mineralization of hazardous and persistent organic pollutants, it has multiple restrictions for industrial scale use. Recent research has focused on enhancing effectiveness and relevance, primarily through the modification of specific operating parameters, advancements in electrode materials and reactor configurations, and integration with alternative treatment approaches (Arellano et al., 2020). In an electro-Fenton process, pollutants are eliminated through the application of Fenton's reagents in conjunction with anodic oxidation at the anode surface. Despite the considerable benefits of electro-Fenton compared to the traditional Fenton process, the sluggish generation of H_2O_2 resulting from the poor solubility of oxygen, diminished current efficiency at elevated pH levels, and increased operational expenses have constrained the implementation of electro-Fenton (Adnan et al., 2022). The electro-Fenton (EF) technique is an environmentally harmless electrochemical advanced oxidation process (EAOP) particularly effective in reducing persistent and harmful pollutants from water. However, its relatively high cost arises from the energy consumption necessary for complete mineralization of the treated solutions (Banuelos et al., 2015).

Fenton's reagent is an intriguing and efficient technique for the degradation of numerous hazardous organic pollutants, characterized by the non-toxicity of the reagents, the simplicity of the procedure, and the absence of residuals (Gomes et al., 2007). The oxidation of maleic acid was the inaugural Fenton reaction documented by Fenton (Mollah et al., 2001). The key phases of the Fenton process are (i) oxidation, (ii) neutralization, (iii) flocculation, and (iv) sedimentation. A pH near 3 is ideal for the Fenton reaction (Igwegbe et al., 2025). Organic chemicals are generally removed via oxidation and coagulation using the Fenton (EF) process. Ting et al. categorized the EF process into four distinct types: Type 1) An external ferrous ion is utilized, and hydrogen peroxide is generated by an oxygen sparging cathode; Type 2) A ferrous ion is derived from a sacrificial iron anode, while hydrogen peroxide is introduced externally; Type 3) Fenton's reagent (Fe^{2+} , H_2O_2) is incorporated into the electrolytic cell to produce hydroxyl radicals, with ferrous ion replenished through the reduction of ferric ion at the cathode; and Type 4) Ferrous ion and hydrogen peroxide are electro-generated via a sacrificial anode and an oxygen-sparging cathode (Can et al., 2003).

In the current investigation, hydrogen peroxide was externally introduced while the ferrous ion was generated in situ at the iron anodes, corresponding to Type 2 electro-Fenton in the classification above. The Fe^{2+} concentration was not directly measured; its availability is inferred from the applied voltage and anodic dissolution rate, consistent with how comparable sacrificial anode electro Fenton studies report Fe^{2+} generation without direct measurement (Zhao et al., 2022; Xiaodong et al., 2021). Furthermore, electricity serves as a clean energy source, so preventing the generation of secondary pollutants during the total process. The EF process employs no hazardous reagents, rendering it an environmentally sustainable solution for water and wastewater treatment. Hydrogen peroxide (H_2O_2) is produced in this process.

The aim of this study was to examine the utilization of electro-Fenton processes in the treatment of petroleum refinery wastewater (PRW).

2.0 Material and Method

2.1 Collection of Materials

A sample of refinery wastewater (PRW) was obtained from the Samawah oil refinery in Iraq and preserved in a 1-liter container at ambient laboratory temperature. The reagents used for this experimental study including hydrogen peroxide (H_2O_2 98%), potassium chloride (KCl), and distilled water were of analytical grade without requiring further dilution.

2.2 Experimental Procedure

The Electron-Fenton system is designed with an entrance tube to allow transit of materials (oil, water, hydrogen peroxide, and potassium chloride) and an output drain for waste expulsion. A container for material placement is fitted with inlet and output valves, while locally produced carbide electrodes near the base, composed of iron and acting as the sacrificial anode from which Fe^{2+} is generated through anodic dissolution, are equipped with valves to regulate oxidation within the system. The electrodes have a total surface area of approximately 80.11 cm², with a lateral surface area of 78.54 cm², consistent with the geometric surface area reporting practice adopted in comparable petroleum refinery electro-Fenton studies (Fahim & Abbar, 2020; Jiad & Abbar, 2023). This research involved the fabrication and utilization of a locally produced electro-Fenton unit, shown in Fig. 1. The experimental procedure was carried out by measuring 150 mL was poured in the system container, and one drop each of hydrogen peroxide and diluted potassium chloride (KCl) was added. The system was activated at the power source, with the voltage configured to 30V and the communication duration established at 20 minutes for the initial phase (This 20 minute reaction time was held constant across all 15 experimental runs). We await the results, as the acidity was measured at pH 7, rather than adjusted to the conventionally ideal pH of approximately 3 for homogeneous Fenton chemistry; the electro Fenton systems can remain effective near neutral pH through localized pH depression at the electrode surface and related interfacial mechanisms that sustain the Fe(III)/Fe(II) cycle outside the classical acidic window (Heidari et al., 2023; Ye et al., 2019), and the concentration of dissolved particles in the water was 1100 mg/L. We replicate the procedures for the subsequent stages, incrementally raising the voltage to 5V, until it reaches the final limit of 90 volts.

To investigate the effect of voltage, the procedures were replicated for subsequent stages with voltage incrementally increased by 5V at each step until reaching 90V. Throughout each run, pH was monitored using a pH meter and contact duration was tracked with a stopwatch.

2.3 Experimental Design

Response surface methodology (RSM) was applied to optimize treatment performance using Box-Behnken design (BBD) matrix with three factors voltage (volt), TDS content (mg/g), and conductivity (S/m). The experimental variables voltage (volt), TDS content (mg/g), and conductivity were varied to 3-levels and replicated and translates to 15 experimental runs. This study examined the utilization of the electro-Fenton process in the treatment of refinery wastewater. Response Surface Methodology (RSM) based on a Box-Behnken design (BBD) space was applied to determine the relationships between the process response across three operational factors: Voltage coded (A) was varied to a range of 30–90 volts which was selected as the control variable rather than current density; which was not measured or reported in this study, and the relationship between applied voltage and resulting current density across runs is not established and is recommended for future research. Total Dissolved Solids, TDS (B) 964–2144 mg/L, and Conductivity (C) from 988–2212 S/m. The objective was to optimize Chemical Oxygen Demand (COD) removal within the ranges of experimental variables detailed in Table 1, with corresponding design matrix presented in Table 2.

Table 1
Range of Experimental process variables in terms of coded and actual variable ranges

Factor	Name	Units	Minimum	Maximum	Coded Low	Coded High	Mean	Std. Dev.
A	Voltage	V	30.00	90.00	-1 ↔ 30.00	+ 1 ↔ 90.00	60.00	22.68
B	TDS	Mg/L	964.00	2144.00	-1 ↔ 964.00	+ 1 ↔ 2144.00	1605.00	458.85
C	Conductivity	S/m	998.00	2212.00	-1 ↔ 998.00	+ 1 ↔ 2212.00	1554.00	446.00

Table 2
Experimental design matrix of the CCD space in terms of actual values

Run order	Volt	Cond	TDS	Final COD
1	30	998	1554	195
2	90	998	1554	164
3	30	2212	1554	57
4	90	2212	1554	639
5	30	1605	964	65
6	90	1605	964	70
7	30	1605	2144	41
8	90	1605	2144	127
9	60	998	964	245
10	60	2212	964	135
11	60	998	2144	98
12	60	2212	2144	85
13	60	1605	1554	67
14	60	1605	1554	60
15	60	1605	1554	53

Table 2
Physiochemical characteristics of refinery wastewater

Run order	Volt	Cond	TDS	Final COD
1	30	998	1554	195
2	90	998	1554	164
3	30	2212	1554	57
4	90	2212	1554	639
5	30	1605	964	65
6	90	1605	964	70
7	30	1605	2144	41
8	90	1605	2144	127
9	60	998	964	245
10	60	2212	964	135
11	60	998	2144	98
12	60	2212	2144	85
13	60	1605	1554	67
14	60	1605	1554	60
15	60	1605	1554	53

2.4 The Initial Chemical Oxygen Demand (COD)

The initial Chemical Oxygen Demand (COD) concentration of real oily wastewater discharged from the Al-Muthanna (Samawah) Middle Petroleum Refineries Company - Al Samawah Refinery typically ranges from 240 mg/L to 710 mg/L depending on the specific process unit and physical separation efficiency. Local environmental research on this specific refinery effluent shows that after basic physical separation, the baseline COD remains around 240 mg O₂/L, while heavily contaminated streams can reach up to 710 mg/L. The initial COD for the specific batch used across the 15 experimental runs in this study was 710 mg/L. Many factors affect this rate, including the vapor content resulting from the refining process, which was used as a physical separator in atmospheric distillation towers. These factors include the type of crude oil being refined, the degree of contact with the distillation tower trays, and the time of foam formation, extraction, and condensation.

3.0 Results and Discussion

3.1 Characterization of Refinery Wastewater

Table 3 shows the result of the physiochemical properties of the petroleum refinery wastewater (PRW) used in this study characterized prior to treatment. The findings proved that the petroleum refinery wastewater (PRW) exhibited pH 7.59, total dissolved solids (TDS) of 2562 mg/L, conductivity of 2921 micro siemens per centimeter, and turbidity of 57.6 NTU. These values position the raw PRW in the high pollution category. Refinery wastewater from Morocco demonstrated total suspended solids (TSS) ranging from 5420 to 10200 mg/L, turbidity exceeding 2500 NTU, pH values between 9.3 and 10.38, and COD concentrations of 43.5 to 53.6 g/L (Dkhissi et al., 2018). Petroleum refinery treatment plant effluents have shown pH ranging from 7.90 to 9.92 at different distances from discharge points (Musa et al., 2013). The high organic and inorganic content of untreated PRW, characterized by elevated TDS and conductivity, is typical of petroleum refinery streams and necessitates optimization of electrochemical treatment parameters before effective degradation of organic pollutants can be achieved.

Table 3
Physiochemical characteristics of refinery wastewater

Parameter	value
COD	240 mg/L – 710 mg/L
TDS	2562 ppm
Turbidity	57.6 NTU
PH	7.59
Dissolved oxygen content	-
density	998 kg/ m ⁰
conductivity	2921 µs/cm

3.2 RSM Model Selection for the Optimization of Electro Fenton Process

The summary of model selection for the RSM optimization modeling of the electro-fenton process is presented in Table 4. The finding confirmed a sequential model sum of squares analysis was performed to determine how factor effects and interactions would be interpreted in downstream analysis. The linear ($p = 0.4843$), 2FI ($p = 0.2501$), and quadratic ($p = 0.1552$) models were all non-significant, indicating that these lower order formulations could not adequately describe COD removal across the experimental domain. The cubic model, by contrast, returned an F-value of 404.85 and a p-value of 0.0025, making it statistically significant at a 99.75% confidence level and establishing it as the most appropriate model for further analysis (Varank et al., 2020; Akkaya et al., 2018; Chiedu et al., 2024; Ichie et al., 2025).

This outcome is consistent with electro-Fenton chemistry for Cod removal as recent studies using RSM also require at least quadratic models to explain the system (Pilco-Núñez et al., 2026; Ugonabo et al., 2024; Igwegbe et al., 2024). The process involves simultaneous electrochemical reactions: cathodic oxygen reduction to generate hydrogen peroxide, anodic iron dissolution to supply ferrous ions, and the homogeneous Fenton reaction yielding hydroxyl radicals, all of which were explained in detail in the previous section.

Table 4
Sequential Model Sum of Squares (Type I) for COD Response

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	2.943E + 05	1	2.943E + 05			
Linear vs Mean	60607.00	3	20202.33	0.8731	0.4843	
2FI vs Linear	97934.75	3	32644.92	1.67	0.2501	
Quadratic vs 2FI	96970.68	3	32323.56	2.71	0.1552	
Cubic vs Quadratic	59512.50	3	19837.50	404.85	0.0025	Suggested
Residual	98.00	2	49.00			
Total	6.094E + 05	15	40626.87			

3.3 ANOVA Statistic for the Reduced Cubic Model

The overall model F-value of 535.76 with a p-value of 0.0019 confirms that the reduced cubic model is statistically significant as shown in the ANOVA analysis in Table 5. The model explains 99.97% of observed variance in COD removal ($R^2 = 0.9997$, Adjusted $R^2 = 0.9978$), and an Adequate Precision of 91.77 far exceeds the minimum acceptable threshold of 4, confirming the model is reliable for navigating the experimental design space (Fazeli Burestan et al., 2020; Chiedu et al., 2024). The coefficient of variation of 5.00% further indicates excellent reproducibility across experimental runs.

Table 5
ANOVA for Reduced Cubic Model, COD Response

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3.150E + 05	12	26252.08	535.76	0.0019	significant
A-Voltage	618.32	1	618.32	12.62	0.0709	
B-TDS	10114.75	1	10114.75	206.42	0.0048	
C-Conductivity	14112.63	1	14112.63	288.01	0.0035	
AB	67908.98	1	67908.98	1385.90	0.0007	
AC	1640.25	1	1640.25	33.47	0.0286	
BC	2352.25	1	2352.25	48.01	0.0202	
A ²	15044.64	1	15044.64	307.03	0.0032	
B ²	66670.67	1	66670.67	1360.63	0.0007	
C ²	10617.75	1	10617.75	216.69	0.0046	
A ² B	26450.00	1	26450.00	539.80	0.0018	
A ² C	6612.50	1	6612.50	134.95	0.0073	
AB ²	26450.00	1	26450.00	539.80	0.0018	
Pure Error	98.00	2	49.00			
Cor Total	3.151E + 05	14				

3.4 Optimization and Analysis of Electro Fenton Process

The goal of the optimization was to find the optimal combination of each varied factor required to minimize COD content in the oily wastewater. The finding based on the developed model equation transcends to the predicted optimum operating conditions presented in the optimization ramp in Fig. 2. The selected reduced cubic model predicted optimum operating condition required to achieve the optimization goal translates to a 71.8432 volts, 1610.4 mg/g TDS, and conductivity value of 1981.36 S/m respectively, corresponding to a minimum COD content of 28.8593 mg/g, lower than the experimentally derived value. The model equation in coded factors is given by:

$$\text{\textbackslash varvec{C}\textbackslash varvec{O}\textbackslash varvec{D}\textbackslash varvec{r}\textbackslash varvec{e}\textbackslash varvec{m}\textbackslash varvec{o}\textbackslash varvec{v}\textbackslash varvec{e}\textbackslash varvec{c}\textbackslash varvec{l}} = 58.70 + 12.44A - 49.80B - 62.30C + 130.18AB + 20$$

The predicted optimum was lower than the experimental center-point average of 60.0 mg/L recorded across the three replicate runs at the design center (runs 13 to 15: 67, 60, and 53 mg/L). The deviation reflects the model's capacity to identify a more favorable operating point within the design space than the pre-selected center point, which is precisely the utility of RSM over traditional one factor at a time approaches (Varank et al., 2020; Akkaya et al., 2018). The optimal voltage of 71.84 V sits between the design center (60 V) and upper bound (90 V), consistent with the parabolic voltage response visible from the one-factor plots, where COD reaches a minimum at moderate voltage before rising steeply at the high end. Similarly, the optimal TDS of 1,610.4 mg/L falls near the design center of 1,554 mg/L, confirming that mid-range ionic strength balances current efficiency against radical scavenging. The optimal conductivity of 1,981.36 μ S/cm is notably above the design center of 1,605 μ S/cm, suggesting that within the context of the other two parameters set at their optimal values, somewhat elevated conductivity is tolerable before parasitic losses dominate (Pilco-Nuñez et al., 2026).

The predicted optimum (71.84 V, 1610.4 mg/L TDS, 1981.36 μ S/cm) corresponds to a minimum COD of 28.86 mg/L, which falls below the 125 mg/L COD guideline value for treated petroleum refinery effluent set by the IFC/World Bank Group Environmental, Health, and Safety Guidelines for Petroleum Refining (2016), representing an apparent removal margin of approximately 96 mg/L relative to this benchmark. A specific enforced Iraqi national numeric COD limit for refinery discharge was not identified in the available literature; this international guideline is cited as the applicable benchmark in its absence. This predicted value has not yet been confirmed by a dedicated validation run at the exact optimum conditions; such confirmatory experimentation is recommended as a next step to verify that actual performance matches model prediction, consistent with standard practice in Box-Behnken RSM studies (Aziz & Aziz, 2018; Manohar et al., 2013; Sandani et al., 2021).

3.5. Main Effects of modelled variables on Electro-Fenton Process

3.5.1 Anatagonistic Effect of Modelled variables on COD Removal

The outline Fig. 3 shows the antagonistic effect of experimental variables in terms of actual and predicted outcome. The result based on the findings from the ANOVA, the antagonistic effect of voltage (A) was not significant as a linear main effect, returning an F-value of 12.62 and p-value of 0.0709. This does not mean voltage is unimportant. It means voltage acts on COD removal through curvature and interaction rather than a simple additive linear trend. At 30 V, H_2O_2 generation was limited by cathodic reduction kinetics, while at 90 V, side reactions including hydrogen evolution and parasitic oxygen discharge reduced current efficiency and hydroxyl radical availability. The true influence of voltage is therefore nonlinear and becomes visible only through higher order terms.

Second-order degree of the A^2 term (F-value = 307.03, p-value = 0.0032, SS = 15,044.64) reveals that voltage peaks in the middle rather than just going up or down. Beyond an optimal potential, over-potential drives side reactions that consume electrons without contributing to oxidant generation. The C^2 term (F-value = 216.69, p = 0.0046, SS = 10,617.75) shows conductivity follows a similar parabolic pattern with an optimum near 1,605 S/m, beyond which competing reactions suppress hydroxyl radical availability.

Because voltage drives both cathodic oxygen reduction to generate H_2O_2 and anodic iron dissolution to supply Fe^{2+} ions, effect of model parameters Across the experimental range of 30 to 90 V, COD removal did not increase monotonically with voltage. Instead, the response followed a parabolic pattern with a peak near the design center of 60 V, consistent with the highly significant A^2 term (F-value = 307.03, p-value = 0.0032). At 30 V, cathodic current was insufficient to produce H_2O_2 at rates high enough to sustain the Fenton reaction. As voltage increased toward 60 V, hydroxyl radical generation improved and COD removal climbed accordingly.

Beyond 60 V, however, competing side reactions took over. Hydrogen evolution at the cathode and parasitic oxygen discharge consumed electrons that would otherwise drive H_2O_2 generation, reducing the faradaic efficiency of the system. This explains why the voltage main effect was not significant on its own (p-value = 0.0709): its influence on COD removal is almost entirely expressed through curvature and through its interaction with TDS, not through a simple linear trend. The practical takeaway is that operating at the maximum available voltage does not deliver the best performance. Intermediate voltage around 60 V balances oxidant generation against side reactions and gives the highest COD removal, while also offering energy savings over maximum voltage operation.

TDS (B) was highly significant as a main effect (F-value = 206.42, p-value = 0.0048, SS = 10,114.75). Its negative main effect coefficient indicates that increasing TDS from 964 to 2144 mg/L reduces COD removal when considered alone. This occurs due to elevated dissolved solids promote competing ionic reactions and suppress hydroxyl radical formation despite improving solution conductivity (Munirathinam et al., 2000).

The individual effect of conductivity (C) on COD content of the water was also highly significant (F-value = 288.01, p-value = 0.0035, SS = 14,112.63) with a negative main effect that mirrors TDS but with greater magnitude. As conductivity increased from 998 to 2212 S/m, secondary reactions and reduced oxidant efficiency were observed. Although both TDS and conductivity being significant main effects tells us that these parameters individually exert a measurable direct influence on COD removal, and their management is important even before considering interactions.

3.3.1 Synergistic Effects of Parameters on COD Levels

The ANOVA results establish that no single parameter governs COD removal in isolation. The interaction and cubic terms collectively account for the dominant share of model variance, and the three pairwise combinations of voltage, TDS, and conductivity each produce distinct combined effects on treatment outcome. These combined responses are illustrated in the surface plots presented as Figs. 4 (a-c)

3.5.4 Synergistic Effect of modeled variables

The outline of the 3-D surface plots in Fig. 4 confirmed the synergistic effect of voltage by conductivity interaction (AC) in combined interaction was significant (F-value = 33.47, p-value = 0.0286, SS = 1,640.25) but considerably weaker than voltage and TDS (AB). At high conductivity, voltage more efficiently drives the electro-Fenton reactions because ohmic resistance is minimized. The reduced interaction intensity compared to AB reflects that conductivity and TDS overlap conceptually as measures of solution composition.

While single effect of conductivity was statistically significant with its main effect exhibiting the largest negative coefficient among the three factors at 62.30 in coded units. This magnitude reflects conductivity's direct role as a measure of the current-carrying capacity of the solution. Conductivity also interacts with voltage through the AC and A²C terms, meaning its effect on COD removal shifts depending on what voltage is applied. At high conductivity and high voltage together, the system is not simply better: the interaction changes the shape of the response surface, making it essential to co-optimize these parameters rather than adjust them independently.

The synergistic effect of TDS and Conductivity (BC) in combined interaction was significant (F-value = 48.01, p-value = 0.0202, SS = 2,352.25). Both parameters influence the electrochemical environment simultaneously: at high levels of both, the system benefits from enhanced current flow but suffers from increased radical scavenging. This interaction captures that balance across the experimental domain.

All three quadratic terms were highly significant. The B² term (F-value = 1,360.63, p-value = 0.0007, SS = 66,670.67) was the most influential quadratic term in the entire model, indicating TDS exerts the strongest nonlinear influence on COD removal. This parabolic response means there is an optimal TDS window around the design center (1,554 mg/L) where ionic strength is sufficient for efficient electrolysis but low enough that radical scavenging remains manageable. Above or below this window, performance drops substantially.

The cubic terms A²B and AB² were each highly significant (F-value = 539.80, p = 0.0018, SS = 26,450.00). These terms tell us that the voltage-TDS synergy established in the AB interaction is not constant across the design space: it strengthens at moderate voltages and TDS levels and weakens at the extremes. Specifically, near 60 V and 1,554 mg/L TDS, the synergy is maximized. The equal F-values for A²B and AB² indicate that curvature is symmetric in both dimensions of this interaction.

The A²C term (F-value = 134.95, p = 0.0073, SS = 6,612.50) captures a similar higher-order coupling between voltage and conductivity. Though smaller in magnitude than the voltage-TDS cubic terms, it remains highly significant and confirms that the voltage-conductivity relationship also varies across the experimental domain in a nonlinear fashion. Together, these cubic terms provide the model with the flexibility needed to represent the complex, multi-reaction electro-Fenton system accurately.

The effect of voltage and TDS interaction (AB) was extraordinarily significant (F-value = 1,385.90, p-value = 0.0007, SS = 67,908.98), the largest contributor among all two factor terms. The voltage-TDS interaction (AB) was the single most influential term in the entire model (F-value = 1,385.90, p = 0.0007, SS = 67,908.98), exceeding every main effect and outweighing even the dominant B² quadratic term. Its significance at p < 0.001 confirms that the effect of voltage on COD removal cannot be interpreted without accounting for TDS level, and vice versa. The cubic terms A²B (F-value = 539.80, p = 0.0018) and AB² (F-value = 539.80, p = 0.0018) extend this interaction into higher-order curvature, indicating that the synergy intensifies near the center of the design space and weakens at the extremes (Varank et al., 2020).

The experimental data in Table 3 illustrate this clearly. At 30 V and mid-range TDS (1,554 mg/L), COD was 195 mg/L; at 90 V and the same TDS, it fell modestly to 164 mg/L. At 30 V and high TDS (2,144 mg/L), COD dropped sharply to 41 mg/L, while at 90 V and the same high TDS it rose to 127 mg/L. This reversal at high voltage and high TDS occurs because elevated dissolved solids accelerate anodic oxidation of ionic species rather than organic contaminants, and simultaneously promote hydroxyl radical recombination before reaction with COD-contributing molecules (Munirathinam et al., 2000). The interaction is therefore antagonistic at the extremes and synergistic near the optimal center of 71.84 V and 1,610 mg/L TDS, as shown in Fig. 4b (Akkaya et al., 2018).

3.5.2 Combined Effect of Voltage and Conductivity on COD Removal

The voltage-conductivity interaction (AC) was statistically significant (F-value = 33.47, p-value = 0.0286, SS = 1,640.25), and its higher-order counterpart A²C was highly significant (F-value = 134.95, p = 0.0073, SS = 6,612.50). The smaller magnitude of AC relative to AB reflects the conceptual overlap between TDS and conductivity as correlated measures of solution ionic content, which reduces their independent contributions to the interaction with voltage (Adnan et al., 2022).

At 60 V and low conductivity (998 μ S/cm), COD values of 245 mg/L and 98 mg/L were recorded for runs 9 and 11 respectively, depending on TDS level. At 60 V and high conductivity (2,212 μ S/cm), COD fell to 135 and 85 mg/L, reflecting reduced ohmic resistance enabling more efficient current delivery. However, at 90 V and high conductivity (run 4: 90 V, 2,212 μ S/cm, 1,554 mg/L TDS), COD rose to 639 mg/L, the highest value across all runs. This confirms that high voltage combined with high conductivity destabilizes the electrochemical environment: excess ions at elevated potential drive parasitic electrode reactions and accelerate radical scavenging simultaneously (Banuelos et al., 2015; Munirathinam et al., 2000). Figure 4c captures this behavior, with the optimal

conductivity of approximately 1,981 $\mu\text{S}/\text{cm}$ under the predicted optimal voltage representing the balance between current efficiency and radical stability (Pilco-Nuñez et al., 2026).

The TDS-conductivity interaction (BC) was statistically significant ($F\text{-value} = 48.01$, $p\text{-value} = 0.0202$, $SS = 2,352.25$). Although TDS and conductivity are physically related, their interaction term remained significant in the model, indicating their combined effect on COD removal exceeds what either explains individually. At high levels of both simultaneously, the system faces compounded radical scavenging pressure that neither variable alone fully captures (Munirathinam et al., 2000).

At 60 V, run 12 (2,212 $\mu\text{S}/\text{cm}$, 2,144 mg/L TDS) recorded a COD of 85 mg/L, lower than run 9 (998 $\mu\text{S}/\text{cm}$, 964 mg/L) at 245 mg/L. At 60 V, which is near the current efficiency optimum, moderately high ionic concentrations still provide net benefit through improved electrolyte conductivity. The detrimental interaction becomes most pronounced when voltage is also elevated, as discussed in Section 3.3.1.2. Within the 60 V plane, Fig. 4a shows a broad favorable zone at low-to-mid levels of both TDS and conductivity, with COD rising steeply when both exceed their respective optima, consistent with electrochemical literature on ionic strength management in electro-Fenton systems (Munirathinam et al., 2000; Akkaya et al., 2018; Varank et al., 2020).

4.0 Conclusion

This study demonstrates that electro-Fenton optimization for petroleum refinery wastewater cannot be achieved through simple parameter maximization. The cubic response surface model reveals a fundamental truth: operating at maximum voltage or conductivity actively degrades treatment performance. Instead, COD removal follows a precisely defined optimal window where voltage, TDS, and conductivity interact synergistically. The voltage-TDS interaction dominates the system response, establishing that these parameters cannot be tuned independently. Most critically, the natural TDS of untreated refinery wastewater (2562 mg/L) significantly exceeds the optimal ionic strength (approximately 1554 mg/L), placing industrial operation in a performance-suppressed regime unless pretreatment is applied. The developed cubic model provides quantitative prediction across the experimental domain and serves as a design tool for scaling electro-Fenton treatment to industrial capacity. Future work should validate these findings at pilot scale and examine pretreatment integration as an economically viable pathway to enhanced COD removal in refinery operations.

Declarations

Conflicts of interest

The authors declare that there are no conflicts of interest relevant to the content of this research publication.

Ethical approval

Ethical considerations were observed in the overall experimentation. Approval covered the collection and processing of industrial wastewater samples from the Al-Samawah refinery; this is an industrial sampling permission and not a human-subjects (IRB) clearance.

Consent to participate

The authors received permission from Midland Refineries Company (Al-Samawah Refinery) to collect and use the wastewater samples in this industrial research (no human participants were involved)

Consent to publish

All authors agreed to the submission of the manuscript for publication.

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Authors' contributions:

(E.I.A): Conceptualization, methodology, writing the original draft, data curation, formal analysis, visualization, Writing the original draft. (T.O): Project Management, Supervision, Conceptualization, Resources, Writing reviews, and Editing the manuscript

Data availability statement:

Data generated or analysed within this study are included in this article. Data will be made available on request with the corresponding author.

Code availability:

Not applicable

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Figures

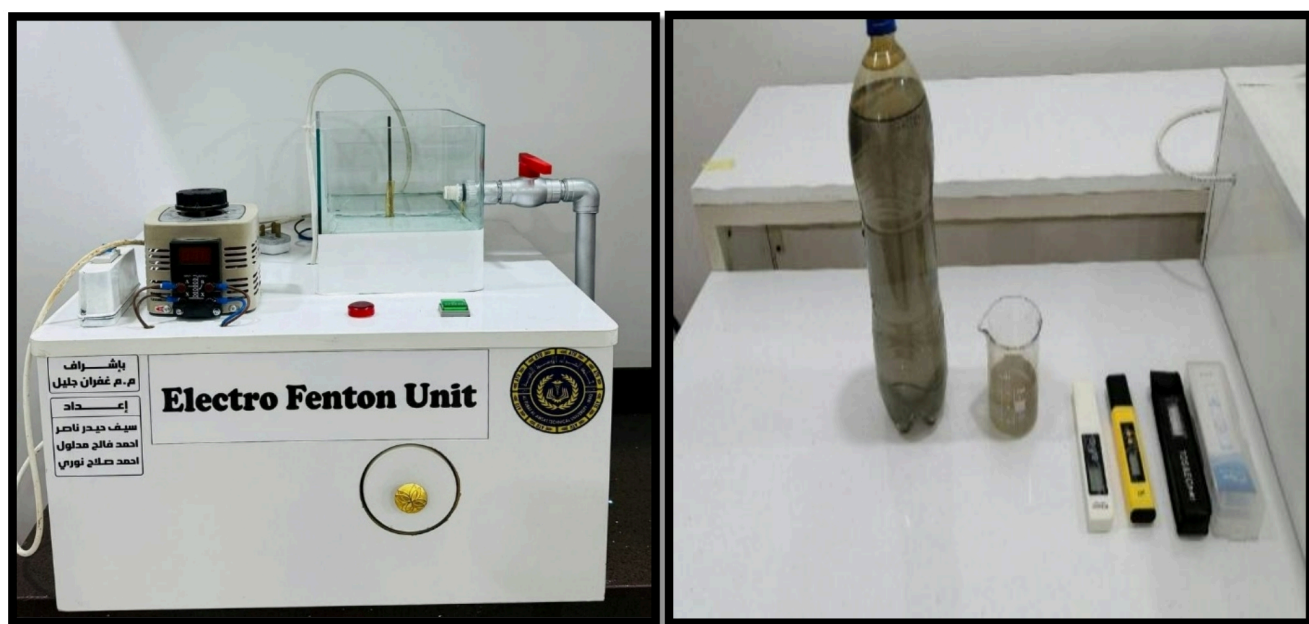


Figure 1

Electro Fenton Unit, (b) sample of refinery wastewater

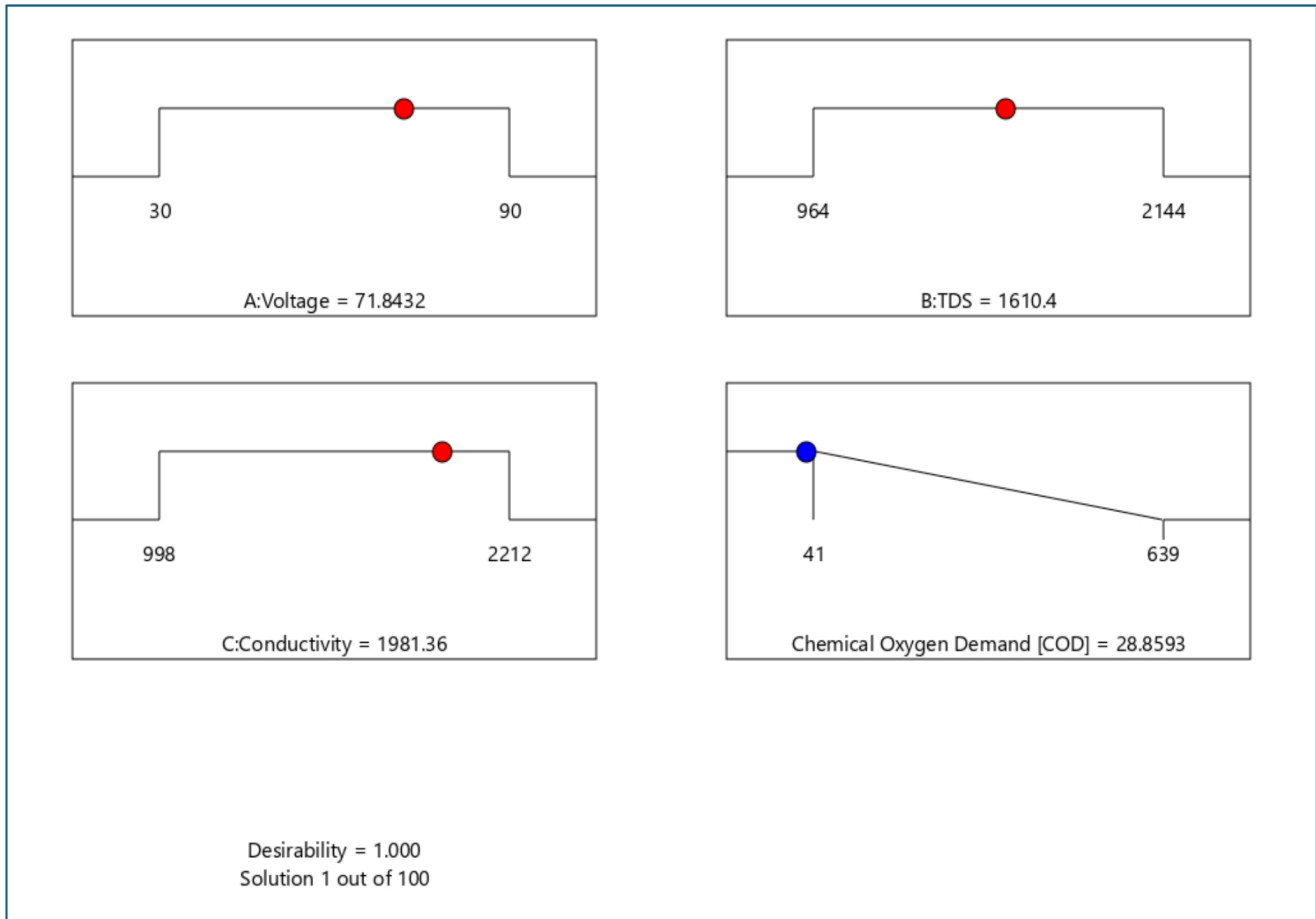


Figure 2
Optimization Ramp showing optimum conditions for Electro Fenton Process

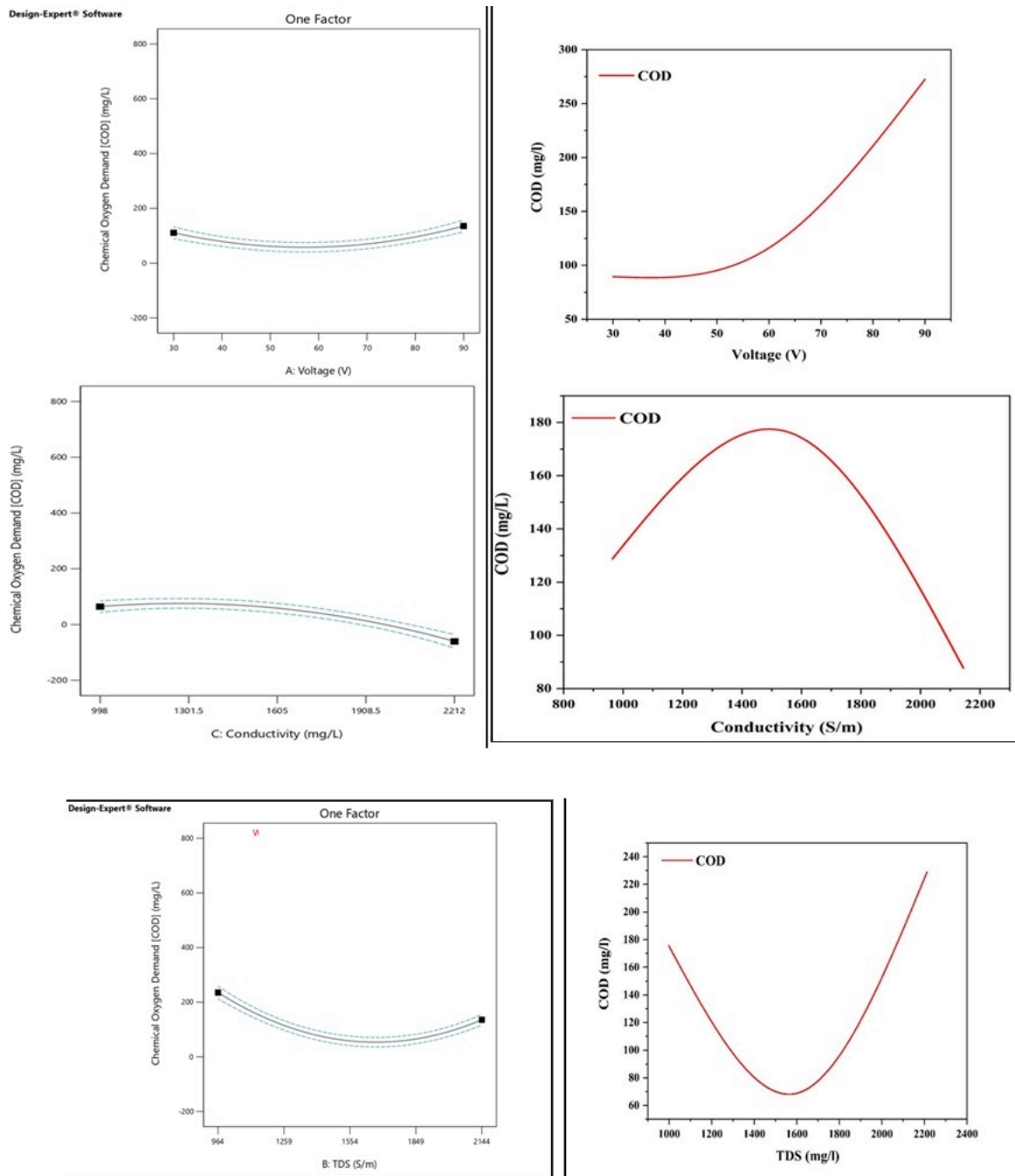


Figure 3

Anatagonistic Effect of modelled variables optimal operating conditions

Factor Coding: Actual

Chemical Oxygen Demand [COD] (mg/L)

Design Points:

● Above Surface

○ Below Surface

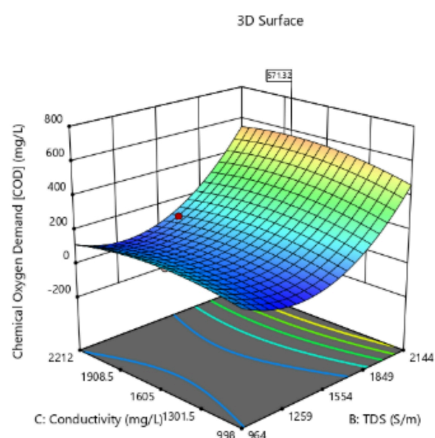
41 639

X1 = B

X2 = C

Actual Factor

A = 90



Factor Coding: Actual

Chemical Oxygen Demand [COD] (mg/L)

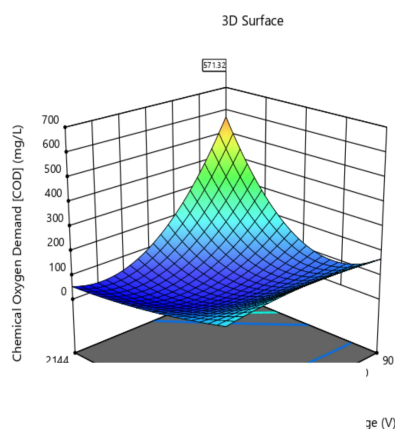
41 639

X1 = A

X2 = B

Actual Factor

C = 1605.02



Factor Coding: Actual

Chemical Oxygen Demand [COD] (mg/L)

41 639

X1 = A

X2 = C

Actual Factor

B = 2144

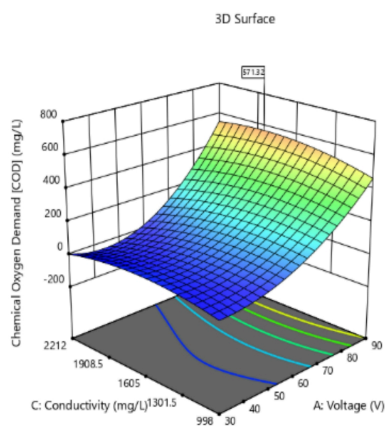


Figure 4

(a): Three-dimensional response surface plot showing the combined effect of TDS and conductivity on COD at a fixed voltage of 60 V. (b) Three-dimensional response surface plot showing the combined effect of voltage and TDS on COD at a fixed conductivity of 1,605 $\mu\text{S}/\text{cm}$, and (c) Three-dimensional response surface plot showing the combined effect of voltage and conductivity on COD at a fixed TDS of 1,554 mg/L .

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- floatimage1.png