

Response Surface Modelling for Cod Removal in Electroplating Effluent Using Sacrifical Electrodes by Electro Fenton Process - Optimization and Analysis

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Abstract

The effluent produced by the electroplating industry contains hazardous and toxic chemicals that pose a threat to living organisms and ecosystems. Consequently, it is essential to employ advanced treatment technologies to remove the toxicants from the wastewater. Over the past two decades, the concept of Electro Fenton has been developed and demonstrated as an effective method for significantly alleviate pollutants in wastewater, making it a promising solution for treating wastewater. In the present investigation, the efficiency of the Electro Fenton (EF) process in removing Chemical oxygen demand (COD) from electroplating wastewater using stainless steel as the sacrificial electrode was examined. The influence of various operating parameters, including pH, hydrogen peroxide concentration, reaction time, and Fe²⁺ concentration, was investigated with the help of Box-Behnken design (BDD) in Response surface methodology (RSM). Notably, EF treatability studies demonstrated that optimal conditions of pH 2, Fe²⁺ concentration of 0.005M, H₂O₂ concentration of 0.5M, and RPM of 450 resulted in more than 75% COD removal. Hence, the sacrificial electrodes can be effective in removing COD from the wastewater.

Key Words	Electroplating wastewater, Chemical oxygen demand, EF, Sacrificial electrodes,
	kinetics, Response surface methodology, Box-Behnken design
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INTRODUCTION

The swift growth of industrialization and urbanization has resulted in the generation of a wide range of pollutants, which has raised concerns about the environment and human health (Xing *et al.*, 2022). Currently, the world is grappling with significant environmental challenges, particularly water contamination, which is primarily driven by various industrial activities. The electroplating industry is one of the most impactful pollution-generating industries, producing a vast amount of wastewater which contains heavy metals and toxic substances which are persistent (Guan *et al.*, 2022). The electroplating process involves applying a thin layer of metal to an object's surface by immersing or suspending the object in an electrolytic solution. The

cathode is used for the electrolytic deposition process, while the plate of the metal to be deposited acts as the anode. A substantial amount of freshwater is consumed during the process, with about 40% of the water used being discharged as electroplating effluent, into the Groundwater (Prajapati et al., 2016). Further, the effluents consist of a variety of heavy metals, including copper, zinc, nickel, chromium, and lead, as well as calcium salts, organic compounds, and other toxic substances. The release of these heavy metals into the environment has detrimental effects on human health, the ecosystem, and other living organisms, due to their potential for bioaccumulation (Yong et al., 2021). As a result, effective measures are necessary to reduce the threats of these toxins pose to ecosystems and humans. Preventative measures are necessary to mitigate the harmful consequences of water discharge. Although sedimentation techniques are often utilized in the electroplating industry, they may result in increased sludge production, which leads to the transportation of sludge and the recovery of metals unfeasible. Therefore the wastewater treatment methods such as coagulation (Wei et al., 2013), biosorption (Abdel-Shafy et al., 2019), adsorption (Boddu et al., 2022), reverse osmosis (Alharthi et al., 2022), ion exchange, electro dialysis (Zelinski et al., 2023) and electro deposition (Klishchenko & Chebotarova, 2023) and chemical precipitation (Verma & Balomajumder et al., 2020) were used. They do not completely degrade the pollutants in the effluent and it is expensive.

Advanced oxidation processes (AOPs) have been developed in recent decades to convert various refractory organic molecules with strong oxidant into water, CO_2 and inorganic salts (Mustafa& Aziz 2023). Among the AOPs, the Fenton process has demonstrated its effectiveness in reducing harmful contaminants in industrial effluents through electroplating, out of all the examined AOPs. On the other hand, hydroxyl radicals have the ability to regulate the rate of reaction and are highly reactive, non-selective, easily developed, powerful oxidants, short-lived, and harmless (Zhu *et al.*, 2019). In case of adsorption and Reverse Osmosis, both techniques are basically the removal processes rather than degradation methods. Adsorption concentrates pollutants on the adsorbent surface (Boddu *et al.*, 2022), while RO separates them, often resulting in a brine or concentrate that requires further treatment (Alharthi *et al.*, 2022). In contrast, EF actively degrades pollutants rather than simply removing them. The hydroxyl radicals generated in EF process, target the pollutants, breaking down their molecular structure, which leads to mineralization. This degradation reduces the further waste management (Shokri *et al.*, 2023).

As the reaction shows, continuous in-situ electrochemical production of H_2O_2 takes place in an acidic medium via oxygen reduction at the cathode (Brillas *et al.*, 2009) produces OH which has a strong oxidation potential (2.8 V/SHE) which oxidizes any organic pollutant which leads to the complete mineralization of organics in the wastewater (Oturan *et al.*, 2021).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

The classical Fenton process involves the homogeneous treatment by adding Fenton's reagent, which consists of iron (II) and hydrogen peroxide to the wastewater. On the other hand, the EF process is a heterogeneous treatment that uses an electrochemically assisted Fenton process.

The process can continue because Fe^{2+} can be regenerated through chemical or electrochemical processes. (Eq. (2-7) (Asaithambi *et al.*, 2022).

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

$$OH \bullet + RH \xrightarrow{\rightarrow} R^{\cdot} + H_2O$$
 (3)

$$Fe^{3+} + H_2O_2 \supseteq Fe^{2+} + HO_2 \bullet + H^+$$
(4)

$$Fe^{3+} + e^{-} \overrightarrow{F}e^{2+}$$
(5)

$$Fe^{3+} + HO_2 \xrightarrow{\frown} Fe^{2+} + HO_2^+$$
(6)

$$\mathbf{R.} + \mathbf{F}\mathbf{e}^{3+} \xrightarrow{\longrightarrow} \mathbf{R}^{+} + \mathbf{F}\mathbf{e}^{2+} \tag{7}$$

Electro-Fenton process as an increasingly viable option for sustainable industrial wastewater treatment, particularly for industries dealing with persistent, complex pollutants like those in electroplating effluent. It relies on electro-chemical generation of hydrogen peroxide (H₂O₂) and ferrous ions (Fe²⁺) in situ, which react to produce hydroxyl radicals capable of oxidizing various contaminants leading to the generation of smaller chemical foot prints eventually decrease the reagent cost, make it as cost effective (Shokri et al., 2023). In the EF process, the performance of the electrolytic system is heavily dependent on the electrode material, as it is the source of the OH radical, which is generated on the surface of the electrode when it oxidizes with water. Stainless steel electrodes are commonly used in the EF process due to their affordability, high catalytic conductivity, corrosion resistance and simplicity. During the EF process, a significant amount of iron is sacrificed, which reacts with the existing Fenton reagents and results in the demineralization of pollutants (Radwan et al., 2018). In this study, stainless steel was employed as a sacrificial electrode and evaluated for its effectiveness in treating electroplating wastewater using the electro-Fenton (EF) process. Investigations were conducted on the impacts of several operating parameters that affect the EF process, including pH, Fe²⁺ concentration, H₂O₂ concentration, temperature, and time. In addition, reaction kinetics and response surface methodology (RSM) with Box-Behnken design (BBD) are studied in detail.

Materials and Methods:

Materials:

Electroplating effluent was collected from the Zinc electroplating industry in Coimbatore, Tamil Nadu. The effluent samples were collected in pre-cleaned polyethylene bottles, sealed, and subsequently transported to the laboratory for analysis. The samples were stored at 4°C. All the chemicals utilized in the experiments were of the highest analytical grade. All solutions were prepared using double-distilled water. The physico-chemical parameters such as pH, electrical conductivity, acidity, chloride, nitrate, phosphate, sulphate, COD, Iron and zinc, of the wastewater samples were assessed as per APHA 2017 guidelines. Concentration of heavy metals such as Iron (Fe) and Zinc (Zn) were determined using Atomic Absorption Spectroscopy (AAS). Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were utilized to adjust the pH. Sodium sulphate (Na₂SO₄) served as the electrolyte. Hydrogen peroxide (H₂O₂) and ferrous sulphate hepta hydrate (Fe₂SO₄.6H₂O) were used as oxidants and catalysts, respectively.

Experimental procedure:

The main components of the EF process are electrodes, a reactor, and a power supply. Electrodes play a crucial role in the Electro-Fenton (EF) process, as they are directly involved in generating the essential reactants and facilitating pollutant degradation. Both the anode and cathode serve specific functions in the process, influencing the generation of hydrogen peroxide, the regeneration of ferrous ions, and, ultimately, the overall efficiency of pollutant removal (Zhou et al 2024). The cathode in the Electro-Fenton process is primarily responsible for generating hydrogen peroxide (H₂O₂) and regenerating ferrous ions (Fe²⁺), which are essential for producing hydroxyl radicals. At the cathode, dissolved oxygen (O₂) is reduced to form H₂O₂, a key reactant for hydroxyl radical production. The pH range of 2 to 5 is crucial for the Electro-Fenton process because it ensures the optimal generation of hydroxyl radicals (•OH) (Sirés & Brillas, 2017). At lower pH values, the formation of ferric ions (Fe³⁺) is favored, which are essential for the Fenton reaction (Xu et al., 2020). Additionally, a lower pH helps in maintaining the stability of hydrogen peroxide (H₂O₂). Studies have shown that the degradation efficiency of contaminants is highest within this pH range (Nidheesh et al., 2018). The concentration of ferrous ions (Fe²⁺) is another critical parameter. A concentration range of 0.001 M to 0.005 M is optimal because it provides enough Fe²⁺ to react with H₂O₂ and generate hydroxyl radicals without causing excessive iron precipitation (Xu et al., 2020). Higher concentrations can lead to the formation of insoluble iron hydroxides, which can reduce the efficiency of the process (Sirés & Brillas, 2017). The concentration of hydrogen peroxide (H₂O₂) is also important for the generation of hydroxyl radicals. A concentration range of 0.1 M to 0.5 M ensures that there is sufficient H₂O₂ to react with Fe²⁺ ions, but not so much that it leads to the scavenging of hydroxyl radicals or excessive consumption of H₂O₂ (Nidheesh et al., 2018). This range balances the need for effective radical generation with the practical considerations of cost and reagent availability (Xu et al., 2020). These parameters are supported by various studies and reviews on the Electro-Fenton process, which highlight the importance of optimizing pH, Fe²⁺ concentration, and H₂O₂ concentration to achieve efficient degradation of contaminants (Sirés & Brillas, 2017). The electro fenton setup was shown in Fig 1.The electrodes should be cleaned before and after each run by washing with acetone, and after rinsing with aqua distillate. The next step was to add 0.5 L of effluent to a glass reactor. The pH of 2 - 4 (acidic) is ideal for the EF reaction (Zhao et al., 2020), therefore, the pH of the wastewater is regulated using H Cl. During the electro catalytic reaction, the reaction mixture was kept uniform by employing a magnetic stirrer. Wastewater was stirred constantly at the speed of 450 rpm. The appropriate amount of Na₂SO₄ was added which is necessary to increase the wastewater sample's conductivity and enable simultaneous electrical current passage

through it. Electrodes are positioned inside the reactor, and the electrodes are wired to the DC supply. The anode-cathode electrode pairs used in this experiment were separated by a 1 cm inter-electrode gap. A precision DC power supply provided the current for the trials. After a pre-determined time, the electricity was shut off, and samples of the reactor were removed for further analysis. Following the completion of the run, wastewater sample generated was filtered and 100ml of sample was then collected for COD analysis (APHA 2017). The removal efficiency of the COD was calculated using the Equation (8)

$$CODRemoval = (1 - rac{CODi}{CODt}) imes 100$$
 (8)

Where COD_i is the initial COD and COD_t is the final COD of the electroplating effluent.



Fig 1: Electro Fenton setup with Sacrificial stainless steel electrodes

Optimization analysis using RSM

To determine the optimum number of parameters for the effective degradation of COD in electroplating wastewater, RSM was used in this study. RSM is a more systematic approach to experimentation that simultaneously predicts outcomes which are called a response; it depends on the independent variables (Nu *et al.*, 2021). The concentrations of Fe^{2+} , H₂O₂ and the initial pH of the solution, among the process variables that were optimized. The Box-Behnken Design (BBD) within Response Surface Methodology (RSM) provides distinct advantages by reducing the number of experimental trials needed to identify potential interactions between parameters and their effects on the electro-Fenton (EF) degradation of electroplating effluent (Rajoria *et al.*, 2024). BBD was used to optimize the process variables, with three components set at levels -1 and 1, representing low and high values, respectively (Table 1). The high and low values for

each factor varied from the factorial design to identify the optimal range for maximizing degradation efficiency.

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Factor	Variable	Unit	Low value	High Value
А	Initial pH	-	2	5
В	Fe ²⁺	М	0.004	0.006
С	H_2O_2	М	0.1	0.5

Table 1: Independent input variables for Box-Behnken design

Utilizing Design-Expert® software version 13.0 (Stat-Ease Inc., Minneapolis, Minnesota, USA), the experimental design and statistical analysis were completed. The software also generated the trial runs at random. At the 5% level of significance, the ANOVA was utilized to ascertain the model's significance as well as the main effects and higher-order interactions of the components. The experimental validation of the model was evaluated by comparing the experimental results with the predicted values obtained under optimal conditions, which were tested in replicates. A second-order polynomial equation (9) was used to fit the experimental data and identify the significant variables in the model

COD Removal efficiency =
$$\beta o k + \Sigma \beta_i Z_i + \Sigma \beta_{ii} Z_i^2 + \Sigma \beta_{ij} Z_{ij} + e$$
 (9)

The variables in this case are k, the intercept is denoted by $\beta 0$, the input factor Zi's linear effect is represented by βi , the linear-by-linear interaction between Zi and Zj is represented by $\beta i j$, the input factor Zi's quadratic effect is represented by $\beta i i$, and the statistical error is denoted by e. To investigate the link between the process components and the replies, ANOVA was employed. Second degree polynomials were employed to characterize the data, and regression analysis, variance coefficient of regression (R²), and p-value of the ANOVA were used to assess the acceptability of the model with the best fit (9).

RESULTS AND DISCUSSION:

CHARACTERISTICS OF WASTEWATER:

The physicochemical characteristics of the electroplating wastewater were analyzed and tabulated (Table 2):

PARAMETER	VALUE
pH	4.8
Electrical conductivity (mS/cm)	2.2
Total Dissolved Solids(mg/L)	1538
Acidity (as CaCO ₃) (mg/L)	30
Chloride (mg/L)	301.32
Nitrate (mg/L)	2.12
Phosphate (mg/L)	1.70

Table 2: Characteristics of Electroplating effluent

Sulphate (mg/L)	13.23
Iron (mg/L)	2.68
Zinc (mg/L)	5.17
COD (mg/L)	1080

OPTIMIZATION ANALYSIS

The BBD technique was applied to maximize COD degradation at the initial pH, Fe^{2+} , and H_2O_2 conditions. The removal efficiency was taken into consideration as the surface responses to the variables in the intended experiment, which comprised fifteen distinct runs. The outcomes of the trials carried out with BBD, along with the predicted and observed removal percentages, are mentioned in Table 3.

 Table 3: Experimental matrix and observed responses of Electroplating wastewater in

 BBD

		Factor	Factor	Factor	Desmanae 1
		1	2	3	Response 1
Std	Run	A: Initial pH	B: Fe	C: H2O2	COD Degradation
			М	М	%
8	1	6	0.005	0.5	78.34
2	2	6	0.004	0.3	75.16
9	3	4	0.004	0.1	71.99
15	4	4	0.005	0.3	78.61
6	5	6	0.005	0.1	76.31
12	6	4	0.006	0.5	73.17
10	7	4	0.006	0.1	72.54
7	8	2	0.005	0.5	80.45
14	9	4	0.005	0.3	78.61
1	10	2	0.004	0.3	75.12
4	11	6	0.006	0.3	74.32
3	12	2	0.006	0.3	76.86
13	13	4	0.005	0.3	76.61
11	14	4	0.004	0.5	74.76
5	15	2	0.005	0.1	78.89

A second-order polynomial regression model was used to establish the relationship between the independent variables and the response variable (Rajoria *et al.*, 2024).

COD Degradation (mg/L) = +77.94 - 0.8988A - 0.0175 **B** + 0.8738C + 1.40A²-3.98B² - 0.8479C² - 0.6450AB + 0.1175AC - 0.5350BC

Where A is the Initial pH, B is the ferrous ion concentration, and C is the H_2O_2 concentration, respectively. The 2% nonconformity of the observed and the predicted values depict that the model was fit to the data (Nu *et al.*, 2021).

Statistical Analysis

The statistical ANOVA of COD degradation for the EF treatment of electroplating wastewater is shown in Table 4. Fisher's distribution test (F-test) and Regression coefficient (R^2) were used to assess the models' sufficiency and significance. Consequently, the computed F-values came out to be 12.83, which is significant because it is less than the *p*-value < 0.005. These results can be explained by a suitable correlation between the factors and degradation efficiency. A, C, A² and B² are important model terms in this instance. Additionally, the nonsignificant Lack of Fit mean squares indicate that there are no extra interactions affecting the performance of the second-degree model or its removal efficiency. The non-significance of AC means that H₂O₂ levels can be optimized independently, similarly, AB and BC is non significant implies that Fe²⁺ and H₂O₂ can be optimized independently, which may lead to more efficient use of H_2O_2 and Fe^{2+} without compromising the process efficiency which makes the process cost effective. The Prob > F values, which are below 0.05 with a 95% confidence level, demonstrate the significance of the model parameters and the accuracy of the regression model. The low coefficient-of-variation (C.V.) value of 1.14 for COD degradation percentages reflects a high level of precision. The sequential F-test and other adequacy indicators support the use of a quadratic model. Analysis of the sequential model sum of squares and model summary statistics showed that P-values for A, C, A², and B² were all below 0.01, indicating a strong relationship between these terms and the response variable. According to the Response Surface Methodology (RSM), there was no significant interaction between the two factors (2FI) and the linear model. The quadratic model, as indicated by the model summary statistic (Table 4), provided the highest regression coefficients ($R^2 = 0.9585$ for % COD degradation). The close agreement between the observed and predicted values is evidenced by the minimal difference of less than 0.2 between the adjusted R² value of 0.8838 and the expected R² value of 0.7428 (Fig. 2). The near alignment of the points to the straight line suggests that the model's predictions were largely consistent with the experimental results.



Fig 2 : Predicted vs Actual Plots for COD degradation.

Adequate Precision (AP) is characterized by a signal-to-noise ratio, with a preferred value of at least 4. In other words, AP is defined as the range in the expected response related to its associated error. Since all of the AP values for COD degradation were greater than 4 (11.9342), it may conclude that the system is performing effectively (Kacem *et al.*, 2024).

Source	Sum of	df	Mean	F-value	p-value	
	Squares		Square			
Model	86.42	9	9.60	12.83	0.0059	significant
A-Initial	6.46	1	6.16	8 61	0.0222	
pН	0.40	1	0.40	0.04	0.0323	
B-Fe	0.0024	1	0.0024	0.0033	0.9566	
C-H ₂ O ₂	6.11	1	6.11	8.16	0.0355	
AB	1.66	1	1.66	2.22	0.1961	
AC	0.0552	1	0.0552	0.0738	0.7967	
BC	1.14	1	1.14	1.53	0.2710	
A ²	7.26	1	7.26	9.70	0.0264	
B ²	58.50	1	58.50	78.18	0.0003	
C ²	2.65	1	2.65	3.55	0.1183	
Residual	3.74	5	0.7482			
Lack of Fit	1.07	3	0.3582	0.2686	0.8461	not significant

1	Table 4:	ANOVA	for O	uadratic	model
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Pure Error	2.67	2	1.33		
Cor Total	90.16	14			

Table 5: Fit Statistics

Std. Dev.	0.8650	R ²	0.9585
Mean	76.12	Adjusted R ²	0.8838
C.V. %	1.14	Predicted R ²	0.7428
		Adeq Precision	11.9342

Interaction of Process parameters:

Three-dimensional response surface graphs generated by RSM were analyzed to investigate the effects caused by factor interactions, including initially pH, Fe^{2+} , and H_2O_2 (Fig 3).The interaction parameters were discussed individually as follows:



(c)



Fig 3. 3-D surface graph for the Electroplating effluent (a-c) COD degradation vs Initial pH, Fe²⁺, H₂O₂

EFFECT OF pH ON COD REMOVAL:

To investigate the impact of pH on COD removal, the range of pH values from 2 to 5 was studied. The COD removal efficiency of 80.45% is maximum and it was observed at pH of 2 after 30 minutes of treatment. It is evident that the effect of pH decreased with higher pH values from 2 to 5, and COD removal decreased leveling off after wards. This occurrence can be attributed to the fact that higher pH, leads to the precipitation of dissolved iron ions as Fe^{2+} , leading to the formation of Fe(OH)_n, which can only decrease the concentration of dissolved Fe²⁺ and these ions accumulated on the surfaces of the electrodes, preventing the further regeneration of Fe²⁺. On the other hand, low pH level lead to increase hydroxyl radical radiation which oxidize the compounds. A similar trend was observed in a study by Latha et al., (2024), where COD removal decreased from 85 to 45 % by increasing the pH from 3 to 6. This can be explained by the increased concentration of OH• radicals generation in the reactor over time. In acidic solutions, the presence of additional protons facilitates the conversion of dissolved oxygen into hydrogen peroxide, in conditions of higher pH; hydrogen evolution is enhanced, leading to a decrease in the availability of protons for the generation of hydrogen peroxide and its decomposition. Furthermore, at higher pH levels, the formation of various hydroxide species of iron ions occurs, along with increased scavenging effects of hydroxyl radical which leads to auto decomposition, resulting in a decrease in removal efficiency.

EFFECT OF Fe²⁺ ON COD REMOVAL:

The concentration of Fe²⁺ plays a crucial role in regulating the rate of the Fenton's reaction for the production of •OH. The highest COD removal efficiency of 80.45% was attained at a Fe²⁺ concentration of 0.005M. The lower concentration of Fe²⁺ slower the hydroxyl radical formation resulted decrease in removal efficiency. As the Fe²⁺ concentration increased up to 0.005M, COD removal efficiency significantly improved; however, it decreased at higher concentrations and leads to iron sludge formation. Nguyen *et al.*, (2021) also reported, the Fe²⁺ concentration was increased, resulting in higher removal efficiency for various pollutants. Although the increase was negligible at higher Fe^{2+} concentrations, it was still significant. Additionally, high Fe^{2+} concentrations may exceed the desired levels. Excessive application of Fe^{2+} ions can also increase the amount of sludge produced and associated sludge disposal costs. It can be inferred that increasing the relative concentration of Fe^{2+} in relation to the organic substrate enhance hydroxyl radical formation, thereby accelerating substrate degradation. However, this enhancement also requires more electrical charge due to the intensification of competing reactions during electrolysis. Fenton's reaction produces more •OH when the Fe^{2+} content rises; nevertheless, greater concentrations may even somewhat suppress the radical's generation, decreasing the process's potency. The increase in the rate of waste response explains the deleterious effects of this excess of Fe^{2+} ions (10), which consequently consumes •OH.

 $Fe^{2+}+OH \rightarrow Fe^{3+}+OH \bullet$

(10)

EFFECT OF H₂O₂ ON COD REMOVAL:

In order to investigate the influence of hydrogen peroxide (H_2O_2) concentration on COD and its removal from electroplating wastewater, A range of H_2O_2 values, from 0.1 M to 0.5 M, was investigated. It is crucial to determine the optimal H_2O_2 concentration in the EF process for both efficiency of COD removal and economic feasibility, particularly with respect to the cost of H_2O_2 . The results indicate that the highest COD removal efficiency was achieved with a 0.5 M H_2O_2 concentration after a 30-minute treatment. As the H_2O_2 concentration increased from 0.3 M to 0.5 M, COD removal efficiency improved. This improvement is likely due to the increased generation of hydroxyl radicals in the system resulting from the higher H_2O_2 concentration. A study by Dokhani *et al.*, (2024), on the Fenton process observed that COD removal improved as the H_2O_2 concentration increased from 20 to 170 µL/L. This increase is attributed to the acceleration of the Fenton reaction and the generation of a higher amount of •OH radicals. However, further increasing the H_2O_2 concentration reduced removal efficiency due to the deactivation of OH radicals and greater depletion of oxidizing agents. Therefore, a 0.5 M H_2O_2 concentration, which achieved the highest COD removal efficiency, was deemed optimal for subsequent experiments.

REACTION KINETICS FOR COD REMOVAL

The effectiveness of the EF process for eliminating COD was assessed at pH 2, a Fe^{2+} concentration of 0.005M, H₂O₂ concentration of 0.5M, and RPM of 450, which resulted in COD removal of over 80%. Furthermore, the COD removal kinetics model was investigated at optimum operating conditions (Fig 4) using equations 11 and 12.

$$\ln (\text{Co/C}) = -k_1 t \tag{11}$$

$$1/C = 1/Co + K_2 t$$
 (12)

Where $k_1 \text{ (min}^{-1)}$ and K2 (mg/L/min) are the apparent first and second order rate constant, respectively. Also, C (mg/L), Co (mg/L), and 't' are the COD dosages at the final and initial electrolysis time (t), respectively.

The relationship between $\ln (Co/C)$ and time during the EF process exhibited a precise linear correlation, with an R² value of 0.9068. This finding is compared to the relationship between 1/C - 1/Co and time, which had an R² value of 0.8132 which is shown in Table 6. The kinetic model for COD removal followed pseudo-first-order kinetics. A study conducted by Jiad *et al.*, 2024 also demonstrated first-order kinetics, indicating that the reaction proceeds rapidly, leading to a significant reduction in pollutant concentration over time. This enhanced reactivity may result from the generation of highly reactive hydroxyl radicals (•OH) through the EF process. Therefore, high rate constants suggest that the rate-limiting step is favourable, resulting in efficient pollutant degradation.

A high R^2 value, or coefficient of determination, is crucial in practical applications as it indicates a strong fit between the kinetic model and experimental data, enhancing the predictability and control of the treatment process. The pseudo-first-order model accurately describes the degradation rate when the R^2 value approaches 1, enabling precise estimation of the time required for pollutant reduction (Eilertsen *et al.*, 2024). A strong R^2 value enables the detection and correction of deviations from expected rates, ensuring efficiency and stability in real-time operations (Bhangare *et al.*, 2022; Subash *et al.*, 2022).





(b)



(c)



Fig 4 Kinetics for COD removal in electroplating effluent (a) Zero order Kinetics (b) First order Kinetics (c) Second order Kinetics

Table 0. Relieves for COD relievant in cleen oplating enfuent				
Kinetics	Rate constants	Precision (R ²)		
Zero order	K = -16.08 (mg/L)	0.8508		
First order	$k_1 = 0.027 (min^{-1})$	0.9068		
Second Order	$K_2 = -0.001 (mg/L/min)$	0.8132		

Table 6	: Kinetics	for COD	removal in	electroplating	effluent
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CONCLUSION:

In the present study, the performance EF process for the removal of COD in the electroplating wastewater using stainless steel electrodes were analysed and the effect of pH, Fe²⁺, H₂O₂ were investigated. The cathode and anode made up of stainless steel were used. The observations of these investigations clearly demonstrate the significance of selecting the ideal parameters to achieve high COD elimination efficiency, which is crucial for any practical applications. The operating variables of the EF process that impact the COD removal efficiency are assessed; at optimal conditions of pH 2, Fe²⁺ concentration of 0.005 M, H₂O₂ concentration of 0.5 M, and RPM of 450, the COD removal efficiency of 80.45%. The kinetics study obeys the pseudo first order kinetics with the precision of R^2 value of 0.9068. The results showed that the EF method can be applied successfully in COD removal. The developed treatment procedure with the optimal conditioning parameters was employed for the effective removal of COD from electroplating wastewater. There are certain drawbacks in the system, including the formation of iron sludge due to the Fenton reagents therefore the sludge is isolated and can be processed further without risk of contamination. Although the experiment was conducted on a lab scale, scaling up to the industrial level presents major challenges. Key areas needing further study include energy consumption, the durability and resistance of stainless steel and iron-based electrodes, and the handling and disposal of iron sludge, which can introduce secondary pollution concerns. Additionally, process optimization is required to address potential decreases in treatment efficiency due to sludge buildup, as well as to minimize operational costs associated with sludge management. Addressing these challenges is essential to ensure the process's feasibility and sustainability on a larger scale.

Declaration of Competing Interest

The authors declare that they have no known competing financial or personal interests that might have influenced the work reported in this paper.

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References

Abdel-Shafy, H. I., Hewehy, M. A., Razek, T., Hamid, M., & Morsy, R. M. (2019). Treatment of industrial electroplating wastewater by electrochemical coagulation using carbon and aluminum electrodes. *Egyptian Journal of Chemistry*, *62*(Special Issue (Part 1) Innovation in Chemistry), 383-392. DOI <u>10.21608/ejchem.2019.11667.1742</u>

Alharthi, S., Alharthy, S. A., Manaa, E. S. A., Abd El-Magied, M. O., & Salem, W. M. (2022). High adsorption performance of Cr (VI) ions from the electroplating waste solution using surface-modified porous poly 2-((methacryloxy) methyl) oxirane polymers. *Zeitschrift für*

anorganische und allgemeine Chemie, 648(19), e202100327.<u>https://doi.org/10.1002/zaac.202100327</u>

Asaithambi, P., Yesuf, M. B., Govindarajan, R., Hariharan, N. M., Thangavelu, P., & Alemayehu, E. (2022). A review of hybrid process development based on electrochemical and advanced oxidation processes for the treatment of industrial wastewater. *International Journal of Chemical Engineering*, 2022. https://doi.org/10.1155/2022/1105376

Bhangare, D., Rajput, N., Jadav, T., Sahu, A. K., Tekade, R. K., & Sengupta, P. (2022). Systematic strategies for degradation kinetic study of pharmaceuticals: an issue of utmost importance concerning current stability analysis practices. *Journal of Analytical Science and Technology*, *13*(1), 7. https://doi.org/10.1186/s40543-022-00317-6

Boddu, S., Chandra, A., & Khan, A. A. (2022). Biosorption of Cu (II), Pb (II) from electroplating industry effluents by treated shrimp shell. *Materials Today: Proceedings*, 57, 1520-1527.<u>https://doi.org/10.1016/j.matpr.2021.12.052</u>

Brillas, E., Sirés, I., & Oturan, M. A. (2009). EF process and related electrochemical technologies based on Fenton's reaction chemistry. *Chemical reviews*, *109*(12), 6570-6631.<u>https://doi.org/10.1021/cr900136g</u>

Dokhani, A., Kalantar-Neyestanaki, D., Rokhbakhsh-Zamin, F., Dolatabadi, M., & Ahmadzadeh, S. (2024). Removal of Staphylococcus aureus using EF, UV/H2O2, and combination of EF and UV/H2O2 processes; optimization of operational parameters. *Applied Water Science*, *14*(5), 1-9.https://doi.org/10.1007/s13201-024-02151-0

Eilertsen, J., Schnell, S. & Walcher, S. The Michaelis–Menten Reaction at Low Substrate Concentrations: Pseudo-First-Order Kinetics and Conditions for Timescale Separation. *Bull Math Biol* **86**, 68 (2024). https://doi.org/10.1007/s11538-024-01295-z

Guan, Z., Guo, Y., Li, S., Feng, S., Deng, Y., Ou, X., ... & Liang, J. (2020). Decomplexation of heterogeneous catalytic ozonation assisted with heavy metal chelation for advanced treatment of coordination complexes of Ni. *Science of the Total Environment*, 732, 139223.<u>https://doi.org/10.1016/j.scitotenv.2020.139223</u>

Jiad, M. M., & Abbar, A. H. (2024). Petroleum refinery wastewater treatment using a novel combined EF and photocatalytic process. *Journal of Industrial and Engineering Chemistry*, *129*, 634-655.<u>https://doi.org/10.1016/j.jiec.2023.09.018</u>

Kacem, S. B., Clematis, D., Elaoud, S. C., & Panizza, M. (2024). Response surface methodology for low-energy consumption EF process for xanthene dye electrochemical degradation. *Journal of Applied Electrochemistry*, 1-16. https://doi.org/10.1007/s10800-024-02087-y

Klishchenko, R., & Chebotarova, R. (2023). Removal of Nickel from Electroplating Wastewater by a Combination of Electrodialysis and Electrodeposition. *Journal of Water Chemistry and Technology*, 45(4), 378-382.https://doi.org/10.3103/S1063455X23040070

Latha, A., Ganesan, R., Sai Bharadwaj, A. V. S. L., & Barmavatu, P. (2024). An experimental investigation of textile dyeing wastewater using modified EF process with optimization by response surface methodology. *Environmental Quality Management*, *33*(3), 421-432.<u>https://doi.org/10.1002/tqem.22135</u>

Mustafa, F. S., & Aziz, K. H. H. (2023). Heterogeneous catalytic activation of persulfate for the removal of rhodamine B and diclofenac pollutants from water using iron-impregnated biochar derived from the waste of black seed pomace. *Process Safety and Environmental Protection*, *170*, 436-448.<u>https://doi.org/10.1016/j.psep.2022.12.030</u>

Nguyen, M. K., Pham, T. T., Pham, H. G., Hoang, B. L., Nguyen, T. H., Nguyen, T. H., ... & Ngo, H. H. (2021). Fenton/ozone-based oxidation and coagulation processes for removing metals (Cu, Ni)-EDTA from plating wastewater. *Journal of water process engineering*, *39*, 101836.<u>https://doi.org/10.1016/j.jwpe.2020.101836</u>

Nidheesh, P. V., Olvera-Vargas, H., Oturan, N., & Oturan, M. A. (2018). Heterogeneous electro-Fenton process: principles and applications. *Electro-Fenton Process: New Trends and Scale-Up*, 85-110.https://doi.org/10.1007/698_2017_72

Nu, C. E., Nwabanne, J. T., Ohale, P. E., & Asadu, C. O. (2021). Comparative analysis of RSM, ANN and ANFIS and the mechanistic modeling in eriochrome black-T dye adsorption using modified clay. *South African Journal of Chemical Engineering*, *36*, 24-42.<u>https://doi.org/10.1016/j.sajce.2020.12.003</u>

Oturan, N., Bo, J., Trellu, C., & Oturan, M. A. (2021). Comparative Performance of Ten Electrodes in Electro-Fenton Process for Removal of Organic Pollutants from Water. *ChemElectroChem*, 8(17), 3294-3303.<u>https://doi.org/10.1002/celc.202100588</u>

Prajapati, A. K., Chaudhari, P. K., Pal, D., Chandrakar, A., & Choudhary, R. (2016). Electrocoagulation treatment of rice grain based distillery effluent using copper electrode. *Journal of Water Process Engineering*, *11*, 1-7.<u>https://doi.org/10.1016/j.jwpe.2016.03.008</u>

Radwan, M., Alalm, M. G., & Eletriby, H. (2018). Optimization and modeling of EF process for treatment of phenolic wastewater using nickel and sacrificial stainless steel anodes. *Journal of water process engineering*, *22*, 155-162.<u>https://doi.org/10.1016/j.jwpe.2018.02.003</u>

Rajoria, S., Vashishtha, M., & Sangal, V. K. (2024). Electroplating wastewater treatment by electro-oxidation using synthesized new electrode: Experimental, optimization, kinetics, and

cost analysis. *Process Safety and Environmental Protection*, 183, 735-756..<u>https://doi.org/10.1016/j.psep.2024.01.023</u>

Shokri, A., Nasernejad, B., & Sanavi Fard, M. (2023). Challenges and future roadmaps in heterogeneous electro-fenton process for wastewater treatment. *Water, Air, & Soil Pollution, 234*(3), 153. https://doi.org/10.1007/s11270-023-06139-5

Sirés, I., & Brillas, E. (2018). Electro-Fenton process: fundamentals and reactivity. *Electro-Fenton Process: New Trends and Scale-Up*, 1-28. <u>https://doi.org/10.1007/698_2017_40</u>

Subash, M., Chandrasekar, M., Panimalar, S., Inmozhi, C., Parasuraman, K., Uthrakumar, R., & Kaviyarasu, K. (2023). Pseudo-first kinetics model of copper doping on the structural, magnetic, and photocatalytic activity of magnesium oxide nanoparticles for energy application. *Biomass Conversion and Biorefinery*, *13*(4), 3427-3437. https://doi.org/10.1007/s13399-022-02993-1

Verma, B., & Balomajumder, C. (2020). Hexavalent chromium reduction from real electroplating wastewater by chemical precipitation. *Bulletin of the Chemical Society of Ethiopia*, 34(1), 67-74. DOI <u>10.4314/bcse.v34i1.6</u>

Wei, X., Kong, X., Wang, S., Xiang, H., Wang, J., & Chen, J. (2013). Removal of heavy metals from electroplating wastewater by thin-film composite nanofiltration hollow-fiber membranes. *Industrial & Engineering Chemistry Research*, 52(49), 17583-17590.<u>https://doi.org/10.1021/ie402387u</u>

Xing, L., Wei, J., Zhang, Y., Xu, M., Pan, G., Li, J., ... & Li, Y. (2022). Boosting active sites of protogenetic sludge-based biochar by boron doping for EF degradation towards emerging organic contaminants. *Separation and Purification Technology*, *294*, 121160.<u>https://doi.org/10.1016/j.seppur.2022.121160</u>

Xu, M., Wu, C., & Zhou, Y. (2020). Advancements in the Fenton process for wastewater treatment. *Adv. Oxid. Process*, *61*(61.10), 5772.

Yong, Y., Hua, W., & Jianhang, H. (2021). Co-treatment of electroplating sludge, copper slag, and spent cathode carbon for recovering and solidifying heavy metals. *Journal of Hazardous Materials*, *417*, 126020.<u>https://doi.org/10.1016/j.jhazmat.2021.126020</u>

Zelinski, R., Silvestre, W. P., Duarte, J., Livinalli, N. F., Zeni, M., & Baldasso, C. (2023). Evaluation of the use of reverse osmosis in the treatment of galvanic effluents. *Journal of Membrane Science and Research*, 9(1). DOI <u>10.22079/jmsr.2022.562616.1565</u>

Zhao, M., Cui, Z., Fu, L., Ndayisenga, F., & Zhou, D. (2020). Shewanella drive Fe (III) reduction to promote EF reactions and enhance Fe inner-cycle. *ACS ES&T Water*, *1*(3), 613-620.<u>https://pubs.acs.org/doi/10.1021/acsestwater.0c00126</u>.

Zhou, X., Yang, J., Guo, J., Xiong, W., & Leung, M. K. (2024). Advances and Prospects in Electrocatalytic Processes for Wastewater Treatment. *Processes*, *12*(8), 1615. https://doi.org/10.3390/pr12081615

Zhu, Y., Fan, W., Zhou, T., & Li, X. (2019). Removal of chelated heavy metals from aqueous solution: A review of current methods and mechanisms. *Science of the Total Environment*, 678, 253-266.<u>https://doi.org/10.1016/j.scitotenv.2019.04.416</u>