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Response Surface Modeling for COD Removal in Electroplating Effluent Using Sacrificial 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 alleviating 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 Fe^{2+} 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, Fe^{2+} concentration of 0.005M, H_2O_2 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.

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 that 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 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 being unfeasible. Therefore, 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 electrodeposition (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 oxidants 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 can regulate the rate of reaction and are highly reactive, non-selective, easily developed, powerful oxidants, short-lived, and harmless (Zhu et al. 2019). In the case of adsorption and Reverse Osmosis, both techniques are removal processes rather than degradation methods. Adsorption concentrates pollutants on the adsorbent surface (Boddu et al. 2022), while RO separates them, often resulting in 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 the EF process target the pollutants, breaking down their molecular structure, which leads to mineralization. This degradation reduces 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).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad \ldots(1)$$

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).

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

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

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

$$Fe^{3+} + e- \rightarrow Fe^{2+} \quad \ldots(5)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + HO_2^{+} \quad \ldots(6)$$

$$R. + Fe^{3+} \rightarrow R^+ + Fe^{2+} \quad \ldots(7)$$

Electro-Fenton process is 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 the electrochemical generation of hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) in situ, which react to produce hydroxyl radicals capable of oxidizing various contaminants, leading to the generation of smaller chemical footprints that eventually decrease the reagent cost, making 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, Fe^{2+} concentration, H_2O_2 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. The concentration of heavy metals such as Iron (Fe) and Zinc (Zn) was determined using Atomic Absorption Spectroscopy (AAS). Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were utilized to adjust the pH. Sodium sulfate (Na_2SO_4) served as the electrolyte. Hydrogen peroxide (H_2O_2) and ferrous sulfate heptahydrate (Fe_2SO_4 .$6H_2O$) 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 (H_2O_2) and regenerating ferrous ions (Fe^{2+}), which are essential for producing hydroxyl radicals. At the cathode, dissolved oxygen (O_2) is reduced to form H_2O_2, 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 ($^{\bullet}OH$) (Sirés & Brillas 2017). At lower pH values, the formation of ferric ions (Fe^{3+}) 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 (H_2O_2). Studies have shown that the degradation efficiency of contaminants is highest within this pH range (Nidheesh et al. 2018). The concentration of ferrous ions (Fe^{2+}) is another critical parameter. A concentration range of 0.001 M to 0.005 M is optimal because it provides enough Fe^{2+} to react with H_2O_2 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 (H_2O_2) 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 H_2O_2 to react with Fe^{2} ions, but not so much that it leads to the scavenging of hydroxyl radicals or excessive consumption of H_2O_2 (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, Fe^{2+} concentration, and H_2O_2 concentration to achieve efficient degradation of contaminants (Sirés & Brillas 2017). The electro-Fenton setup is 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 HCl. During the electro-catalytic reaction, the reaction mixture was kept uniform by employing a magnetic stirrer. Wastewater was stirred constantly at a speed of 450 rpm. The appropriate amount of Na_2SO_4 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

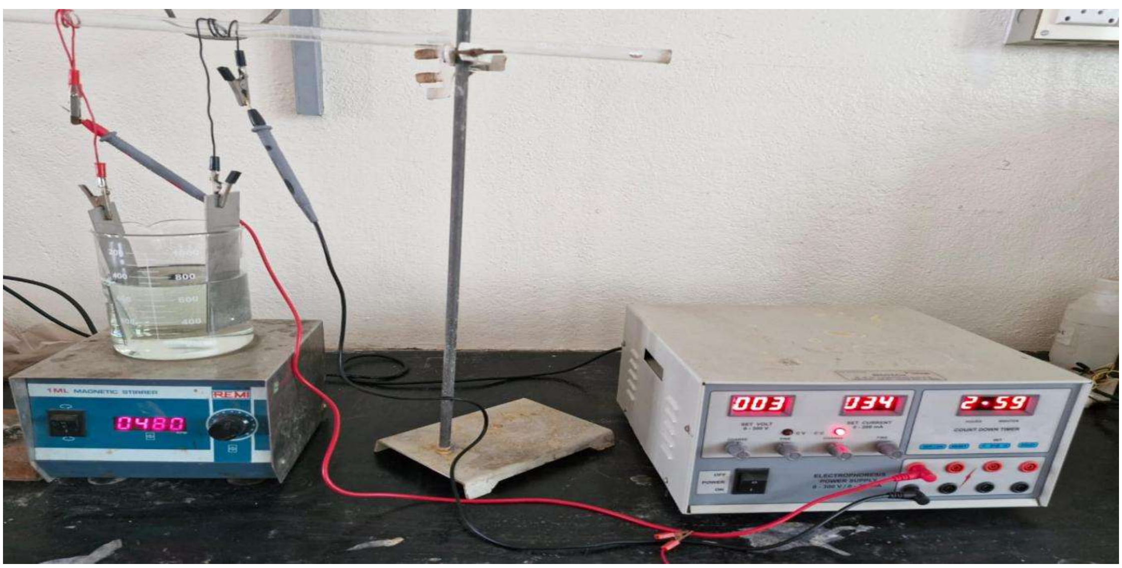


Fig. 1: Electro Fenton setup with Sacrificial stainless steel electrodes.

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, the wastewater sample generated was filtered, and 100 mL of the sample was then collected for COD analysis (APHA 2017). The removal efficiency of the COD was calculated using Equation (8)

$$CODRemoval = (1 - \frac{CODi}{CODt}) \times 100 \qquad \ldots(8)$$

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

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 responses; it depends on the independent variables (Nu et al. 2021). The concentrations of Fe^{2+}, H_2O_2, and the initial pH of the solution, were 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.

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.

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

The variables, in this case, are k, the intercept is denoted by β0, the input factor Zi's linear effect is represented by βi, the linear-by-linear interaction between Zi and Zj is represented by βij, the input factor Zi's quadratic effect is represented by βii, 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 (R^2), and p-value of the ANOVA were used to assess the acceptability of the model with the best fit (9).

Table 1: Independent input variables for Box-Behnken design.

Factor	Variable	Unit	Low value	High Value
A	Initial pH	-	2	5
B	Fe^{2+}	M	0.004	0.006
C	H_2O_2	M	0.1	0.5

RESULTS AND DISCUSSION

Characteristics of Wastewater

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

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.

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 ($mg.L^{-1}$) = +77.94 - 0.8988A - 0.0175 B + 0.8738C + 1.40A^2 - 3.98B^2 - 0.8479C^2 - 0.6450AB + 0.1175AC - 0.5350BC

Table 2: Characteristics of Electroplating Effluent.

Parameter	Value
pH	4.8
Electrical conductivity [$mS.cm^{-1}$]	2.2
Total Dissolved Solids [$mg.L^{-1}$]	1538
Acidity (as $CaCO_3$) [$mg.L^{-1}$]	30
Chloride [$mg.L^{-1}$]	301.32
Nitrate [$mg.L^{-1}$]	2.12
Phosphate [$mg.L^{-1}$]	1.70
Sulphate [$mg.L^{-1}$]	13.23
Iron [$mg.L^{-1}$]	2.68
Zinc [$mg.L^{-1}$]	5.17
COD [$mg.L^{-1}$]	1080

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

Std	Run	Factor 1	Factor 2	Factor 3	Response 1
		A: Initial pH	B:Fe	C:H_2O_2	COD Degradation
			M	M	%
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

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 depicts 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 the 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, $A^{2,}$ and B^2 are important model terms in this instance. Additionally, the non-significant Lack of Fit mean squares indicates 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 H_2O_2 levels can be optimized independently. Similarly, AB and BC are significant, implying that Fe^{2+} and H_2O_2 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, A^2, and B^2 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 & 5), provided the highest regression coefficients (R^2 = 0.9585

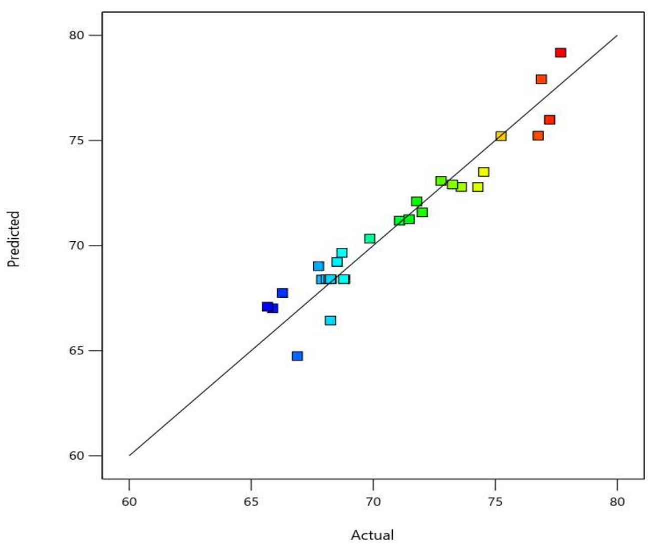


Fig. 2: Predicted vs Actual Plots for COD degradation.

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 R^2 value of 0.8838 and the expected R^2 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.

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 be concluded that the system is performing effectively (Kacem et al. 2024).

Interaction of Process Parameters

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

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 a pH of 2 after 30 min 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 afterward. 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 Fe^{2+}, and these ions accumulated on the surfaces of the electrodes, preventing the further regeneration of Fe^{2+}. On the other hand, low pH levels lead to an increase in hydroxyl radical radiation, which oxidizes 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.

Table 4: ANOVA for Quadratic model.

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	86.42	9	9.60	12.83	0.0059	significant
A-Initial pH	6.46	1	6.46	8.64	0.0323	
B-Fe	0.0024	1	0.0024	0.0033	0.9566	
C-H_2O_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
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

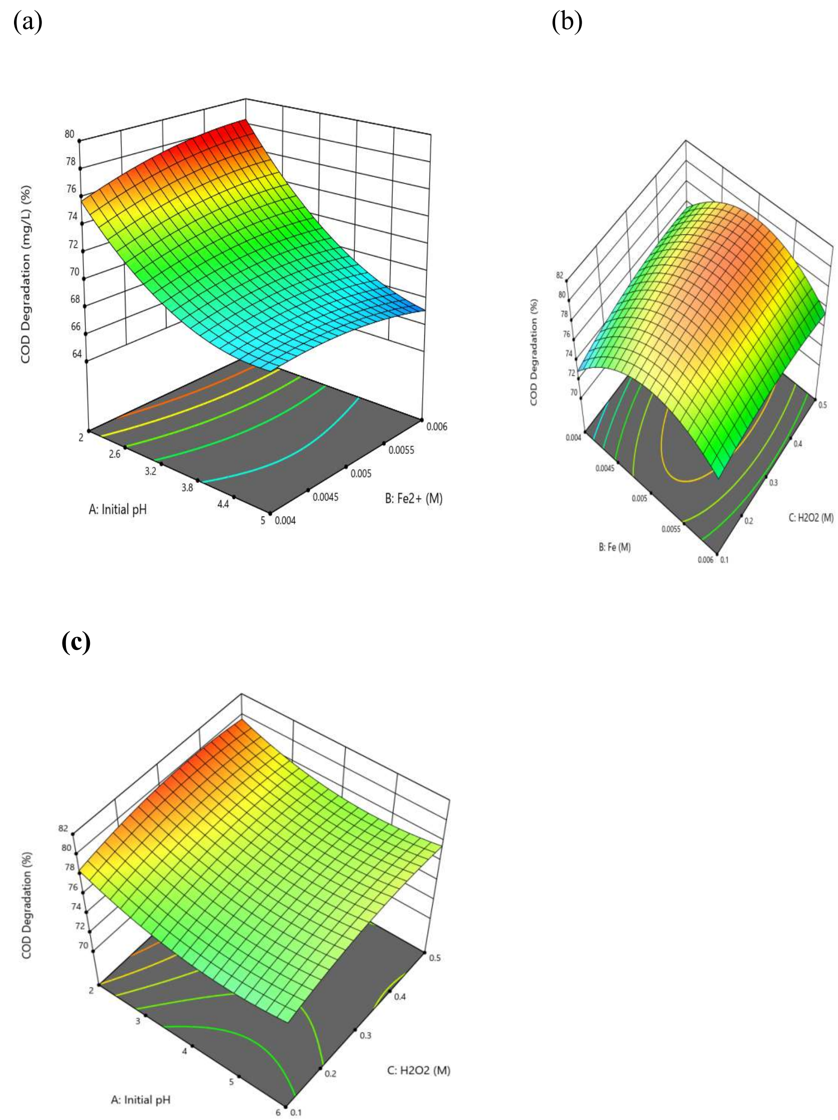


Fig. 3: 3-D surface graph for the Electroplating effluent (a-c) COD degradation vs Initial pH, Fe^{2+}, H_2O_2.

Effect of Fe^{2+} on COD Removal

The concentration of Fe^{2+} plays a crucial role in regulating the rate of the Fenton reaction for the production of •OH. The highest COD removal efficiency of 80.45% was attained at a Fe^{2+} concentration of 0.005 M. The lower concentration of Fe^{2+} slower hydroxyl radical formation, resulting in a decrease in removal efficiency. As the Fe^{2+} concentration increased up to 0.005M, COD removal efficiency significantly improved; however, it decreased at higher concentrations and led to iron sludge formation. Nguyen et al. (2021) also reported the Fe^{2+} 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.

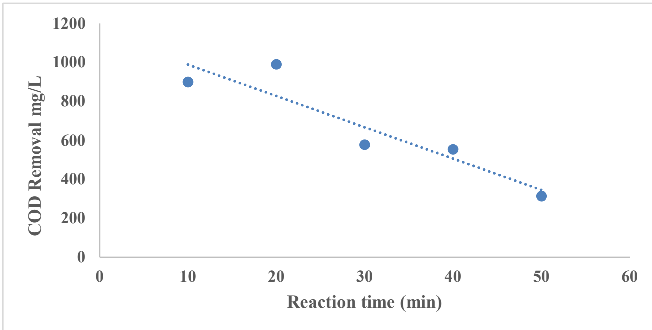
Additionally, high Fe^{2+} concentrations may exceed the desired levels. Excessive application of Fe^{2+} ions can also increase the amount of sludge produced and associated sludge disposal costs. It can be inferred that increasing the relative concentration of Fe^{2+} in relation to the organic substrate enhances 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 $^{\bullet}OH$ 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 $^{\bullet}OH$.

$$Fe^{2+} + OH \rightarrow Fe^{3+} + OH^{\bullet} \quad \ldots(10)$$

Effect of H_2O_2 on COD Removal

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 to 0.5 M, was investigated. It is crucial to determine the optimal H_2O_2

(a)



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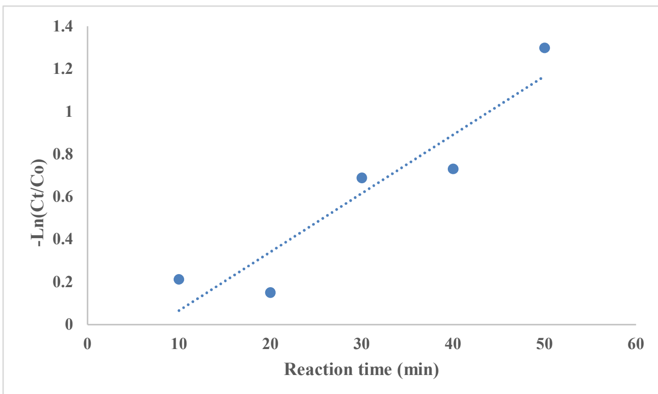

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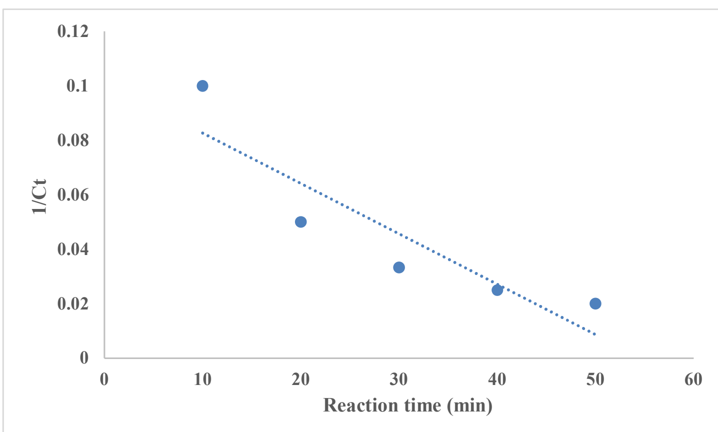

Fig. 4: Kinetics for COD removal in electroplating effluent (a) Zero order Kinetics, (b) First order Kinetics, (c) Second order Kinetics.

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, the 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^{-1}. 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, H_2O_2 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.

$$\ln (Co/ C) = -k_1 t \quad \ldots(11)$$

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

Where k_1 (min^{-1}) and K_2 (mg.L^{-1}.min^{-1}) are the apparent first and second-order rate constants, respectively. Also, C (mg.L^{-1}), Co (mg.L^{-1}), 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 R^2 value of 0.9068. This finding is compared to the relationship between 1/C - 1/Co and time, which had an R^2 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 favorable, 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).

Table 6: Kinetics for COD removal in electroplating effluent.

Kinetics	Rate constants	Precision (R^2)
Zero order	K = -16.08 [mg.L^{-1}]	0.8508
First order	k_1 = 0.027 [min^{-1}]	0.9068
Second Order	K_2 = -0.001[mg.L^{-1}.min^{-1}]	0.8132

CONCLUSIONS

In the present study, the performance EF process for the removal of COD in the electroplating wastewater using stainless steel electrodes was analyzed, and the effects of pH, Fe^{2+}, and H_2O_2 were investigated. The cathode and anode, made up of stainless steel, were used. The observations of these investigations 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, Fe^{2+} concentration of 0.005 M, H_2O_2 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 a 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.

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