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ADVANCED ELECTROCHEMICAL OXIDATION OF PARACETAMOL IN WASTEWATER USING AN ELECTRO-FENTON SYSTEM: EXPERIMENTAL STUDY AND PROCESS OPTIMIZATION

The widespread occurrence of pharmaceutical residues, especially paracetamol (PCT), a non-opioid analgesic and antipyretic that exhibits weaker anti-inflammatory effects compared to ibuprofen and other Nonsteroidal anti-inflammatory drugs NSAIDs, in aquatic environments presents serious ecological and human health challenges due to their persistence, potential for bioaccumulation, and insufficient removal by conventional wastewater treatment methods. This study evaluates the effectiveness of the electro-Fenton (EF) process for advanced oxidation and degradation of PCT in aqueous media. A cylindrical batch reactor using a stainless steel felt cathode and platinum anode was utilized, and key operational parameters (ferrous ion concentration (Fe^{2+}), hydrogen peroxide (H_2O_2) dosage, and current density) were optimized using the Box–Behnken response surface methodology. Results showed that the EF process achieved up to 95% PCT removal, with a maximum degradation rate constant of 0.018 $m^3/(mol \cdot min)$ under optimal conditions ([Fe^{2+}] = 0.075 mol/m^3, [H_2O_2] = 18 mol/m^3, current density = 150 A/m^2). Statistical analysis identified Fe^{2+} concentration and current density as significant factors, while H_2O_2 dosage had a lesser effect. Despite demonstrating high efficiency, limitations remain regarding batch-scale operation, energy demand, and by-product toxicity.

1. INTRODUCTION

The increasing presence of pharmaceutical compounds in aquatic environments has become a major environmental concern due to their persistence, bioaccumulation potential, and adverse ecological effects. Among these, paracetamol (PCT, $C_8H_9NO_2$, also known

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as acetaminophen) is one of the most widely consumed non-opioid analgesics and antipyretics, and it exhibits weaker anti-inflammatory effects compared to ibuprofen and other non-steroidal anti-inflammatory drugs (NSAIDs). The widespread occurrence of PCT residues in aquatic environments presents serious ecological and human health challenges due to their persistence, potential for bioaccumulation, and insufficient removal by conventional wastewater treatment methods.

The occurrence of PCT in aquatic environments has raised growing concerns regarding its potential impacts on both ecosystem health and human safety. Although paracetamol is generally considered to be of low acute toxicity in humans when used thera-peutically, its chronic presence in the environment, especially in mixtures with other pharmaceuticals, can lead to significant ecotoxicological risks. In aquatic ecosystems, PCT has been shown to affect non-target organisms, particularly fish, algae, and invertebrates. Sub-lethal effects, including oxidative stress, enzyme inhibition, reproductive disruption, and beha- vioral changes, have been reported even at environmentally relevant concentrations in the ng/dm^3 to low μg/dm^3 range [1].

Several laboratory studies have demonstrated that PCT exposure can alter antioxidant enzyme activity and increase lipid peroxidation in fish, indicating cellular-level oxidative damage. For example, Ferrari et al. [2] observed inhibited catalase and glutathione-S--transferase activities in *Cyprinus carpio* exposed to low concentrations of PCT. Similarly, Nunes et al. [3] found that chronic exposure to environmentally realistic levels of PCT impaired embryonic development and induced DNA damage in zebrafish (*Danio rerio*). These findings are concerning, given the compound's widespread presence in natural water bodies, particularly near urban and industrial effluent discharge points.

Beyond ecotoxicity, concerns have also been raised about the potential for PCT and its transformation products to pose risks to human health, particularly through drinking water contamination and reuse of treated wastewater. Although conventional drinking water treatment can remove much of the parent compound, trace levels have still been detected in finished drinking water in several countries [4]. Moreover, advanced oxidation processes used to degrade PCT can lead to the formation of toxic by-products, such as hydroquinone and benzoquinone, which may have greater cytotoxicity and mutagenic potential than the parent drug [5, 6]. Among the most commonly reported transformation products of PCT are hydroquinone, 1,418-benzoquinone, 4-aminophenol, and acetamide. Hydroquinone and benzoquinone are frequently detected in surface water, wastewater, and drinking water, typically at concentrations ranging from low ng/dm^3 to several μg/dm^3 [7]. Acetamide has been classified by the International Agency for Research on Cancer (IARC) as possibly carcinogenic to humans (Group 2B) [8]. Although these concentrations are generally lower than those of the parent compound, their higher toxicity and carcinogenic potential raise concerns for both ecological and human health.

From a public health perspective, chronic exposure of vulnerable populations (pregnant women, infants, and immunocompromised individuals) to low levels of pharmaceuticals in drinking water raises concerns about poorly understood long-term cumulative

effects. The World Health Organization (WHO) has noted that although current levels in drinking water are generally low and unlikely to pose immediate risks, the absence of comprehensive toxicological data on long-term exposure to pharmaceutical mixtures remains a critical knowledge gap [9]. PCT, due to partial human metabolism and limited removal in conventional wastewater treatment plants (WWTPs), is routinely detected in surface water, groundwater, and even finished drinking water. Reported concentrations range from nanograms to several micrograms per liter, depending on region and treatment efficiency [4, 10].

Contamination reflects rapid urbanization, high consumption, and insufficient treatment infrastructure. In China, the PCT concentration levels up to 17 μg/dm^3 have been detected in rivers near hospitals and industries, particularly in the Yangtze and Pearl River basins [11]. In Vietnam, hospital effluents and rivers contained 0.01–5 μg/dm^3 [12]. Globally, PCT remains one of the most frequently detected pharmaceuticals. In Europe, levels up to 6 μg/dm^3 have been measured in hospital effluents and 0.1–2 μg/dm^3 in rivers [10]; in the United States, PCT was found in over 20% of streams sampled nationwide [13].

Despite its relatively high biodegradability compared to other pharmaceuticals, PCT's continuous input into aquatic systems results in its persistent presence. Moreover, its transformation products can exhibit greater toxicity than the parent compound, posing risks to aquatic life and complicating environmental risk assessments. The global occurrence of PCT in water sources underscores the urgent need for improved wastewater treatment technologies, stronger regulatory frameworks, and expanded monitoring programs, particularly in developing and emerging economies.

The removal of pharmaceutical contaminants such as PCT from water sources has become a significant challenge for environmental engineers due to their persistence and potential ecological impacts. Traditional wastewater treatment plants (WWTPs), particularly those employing conventional activated sludge (CAS) processes, often demonstrate limited efficiency in fully eliminating PCT and its metabolites. Studies have shown that while PCT is more biodegradable than many pharmaceuticals, its removal efficiency in CAS systems varies widely, ranging from 50 to over 90%, depending on factors such as microbial community composition, hydraulic retention time, and influent concentration [10]. This variability underscores the need for more advanced treatment solutions to ensure consistent and effective removal.

The adsorption techniques using activated carbon or emerging nanomaterials have been employed to remove PCT from aqueous solutions. Powdered activated carbon (PAC) and granular activated carbon (GAC) are widely used due to their high surface area and strong affinity for aromatic compounds like PCT. However, adsorption does not degrade the pollutant but merely transfers it from the aqueous to the solid phase, raising concerns about subsequent handling and regeneration of spent adsorbents [14]. Recent developments in carbon nanotubes, biochars, and metal-organic frameworks (MOFs) offer enhanced adsorption capacities and potential for regeneration, but their high cost and uncertain environmental impact limit large-scale applications at present [15].

Another emerging approach is the use of membrane bioreactors (MBRs), which combine biological degradation with membrane filtration to achieve higher contaminant removal and effluent quality. MBRs have been shown to achieve PCT removal efficiencies of over 95%, particularly when operated under optimal conditions of solid retention time and membrane flux [16]. The external loop airlift membrane bioreactor (ELAMBR), a variation of the MBR, has also demonstrated superior performance in treating pharmaceutical wastewater, with complete removal of PCT within 24 hours in semi-batch configurations [17].

In addition to activated carbon or emerging nanomaterials technologies, among the most promising technologies are advanced oxidation processes (AOPs), which rely on the generation of highly reactive hydroxyl radicals (•OH) to degrade organic pollutants. AOPs such as ozonation, UV/H_2O_2, Fenton and photo-Fenton reactions, and electrochemical oxidation have demonstrated high efficiency in degrading PCT in both water and wastewater matrices. For example, Andreozzi et al. [5] reported efficient mineralization of paracetamol using solar-driven photo-Fenton processes. Despite these advantages, the electro-Fenton (EF) processes also present operational constraints that merit consideration. Reported energy consumption for EF systems spans from as low as approximately 0.37 kWh/m^3 under optimized low-current conditions [18] to ca. 9.6 kWh/m^3 in more energy-intensive configurations, supporting a typical range of 0.5–2.5 kWh/m^3 for many practical setups. Additionally, electrode fouling remains a common challenge: Pt electrodes can develop polymeric fouling layers that drastically reduce active surface area [19], while carbonaceous cathodes in microfluidic systems are susceptible to clogging and fouling due to material buildup. These limitations underscore the need for careful optimization and system design to enhance EF's long-term applicability in wastewater treatment. Similarly, EFsystems have gained increasing attention due to their ability to degrade synthetic organic dyes rapidly under mild conditions, with mineralization efficiencies exceeding 90% under optimized parameters [20]. These techniques are particularly advantageous because they can be integrated into existing treatment systems and adapted to on-site pharmaceutical wastewater sources.

In summary, a wide range of physical, chemical, and biological treatment technologies are available or under development to address PCT contamination in water systems. While AOPs and MBRs represent the most effective current solutions in terms of removal efficiency and operational scalability, their energy demands, chemical consumption, and cost considerations must be balanced.

Among available AOPs, ozonation and UV/H_2O_2 systems have shown promising results; however, they often involve high-pressure equipment, complex operation, and significant capital costs. In contrast, EF was selected in this study due to its lower capital investment, simpler operation, and greater feasibility in resource-limited settings, particularly in developing countries [21]. While EF has been extensively applied to synthetic dyes and other organic pollutants, limited studies have focused on its optimized

application to PCT degradation, particularly using Box–Behnken response surface methodology. Addressing this gap, the applicability of EF processes in the treatment of PCT-containing wastewater was investigated in this study. The primary aim of this study is to evaluate the efficiency of an EF oxidation process for the degradation of PCT in aqueous solutions, and to optimize its operational parameters using response surface methodology (RSM) with a Box–Behnken design. This research addresses a critical environmental challenge by systematically assessing the influence of key factors – such as ferrous ion concentration, hydrogen peroxide dosage, and current density – on the degradation efficiency of PCT. The significance of this work lies in its contribution to the growing body of knowledge on advanced oxidation processes, particularly the EF system, as a promising and scalable solution for treating pharmaceutical-contaminated water. By integrating experimental design with kinetic modeling, the study not only demonstrates high removal and mineralization efficiencies under optimized conditions but also provides insights for real-world applications in wastewater management, especially in regions facing high pharmaceutical loads and inadequate treatment infrastructure.

Furthermore, this study advances sustainable pharmaceutical wastewater treatment by presenting a low-cost, high-efficiency EFoxidation method that is particularly adaptable to developing country contexts. Our findings align with recent reports demonstrating EF's effectiveness in pharmaceutical pollutant removal, such as the magnetically enhanced electrode system achieving rapid degradation, while also reflecting the cost benefits observed in industrial wastewater pretreatment, where EF proved more economical than conventional Fenton processes ($2.06 vs. $3.12 per unit volume) [22]. Moreover, the eco-friendly nature, automation potential, and promising scalability of EF technology reinforce its suitability for low-resource settings aiming to implement advanced wastewater treatment [23]. Taken together, this work underscores EF's promise as a viable, efficient, and cost-conscious approach for addressing pharmaceutical contaminants in wastewater across developing regions.

2. MATERIALS AND METHODS

Chemicals and analytical methods. All chemical reagents were used as received without any further purification or modification to maintain consistency across all experimental runs. The main organic contaminant studied was PCT, which was obtained from Merck with a purity greater than 99%. The oxidative agent employed in the EF process was hydrogen peroxide (H_2O_2) at a concentration of 35%, likewise sourced from Merck. To provide the ferrous ions necessary for catalyzing Fenton reactions, ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), also supplied by Merck, was added to the reaction mixture.

Quantitative determination of the PCT concentration during the degradation process was carried out using high-performance liquid chromatography (HPLC). The system used

was manufactured by Waters, equipped with a C18 reversed-phase column measuring 25 cm in length and 4.6 mm in internal diameter, which is well-suited for separating small organic molecules. Detection was performed with a UV1000 detector set at a wavelength of 254 nm, which corresponds to the maximum absorbance of PCT, ensuring sensitive and accurate detection. The chromatographic conditions were carefully optimized to achieve clear resolution and reproducibility. The column was maintained at a constant temperature of 25 °C. The mobile phase consisted of a binary mixture of 65% methanol and 35% deionized water, selected to balance polarity and elution strength. The flow rate of the mobile phase was kept at 1 cm^3/min, providing efficient separation within a short retention time.

To systematically evaluate the effects of key operational parameters and optimize the degradation efficiency of PCT, the experimental design and statistical analysis were conducted using the Design Expert software, version 13. This software facilitated the implementation of a structured optimization approach – likely through response surface methodology (RSM) – to determine the combination of variables that would yield the highest PCT removal efficiency.

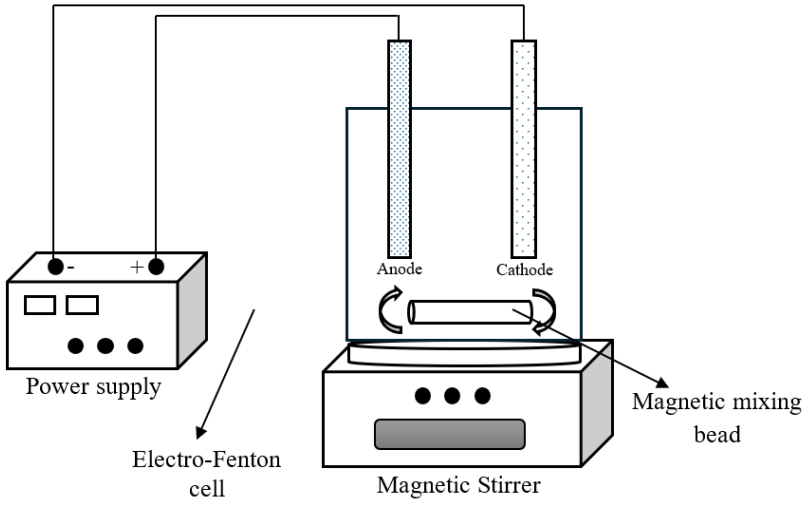

Fig. 1. The simulation diagram for the electro-Fenton set-up

Experimental setup. A custom-designed cylindrical glass reactor with a diameter of 10 cm and a height of 15 cm was utilized to perform the EF oxidation process, as depicted in Fig. 1. This reactor configuration was specifically selected to ensure adequate mixing and mass transfer during the degradation of PCT. A total volume of 800 cm^3 of aqueous PCT solution was introduced into the reactor chamber. For the electrochemical setup, a stainless steel felt cathode was employed, providing an effective surface area of 45 cm^2, paired with a platinum sheet anode (dimensions: 5 cm × 5 cm). The electrodes were placed

at a fixed inter-electrode distance of 5.0 cm, which was dictated by the geometric constraints of the reactor system. To supply electrical energy to the electrochemical cell, a digital DC power source (Alexan brand), operating range: 10–30 V, 5 A) was used. The electrodes were connected via alligator clips to allow for easy adjustment and stable application of the desired voltage and current. This arrangement ensured precise and reproducible control of electrochemical parameters during each experimental run. All experiments were conducted under ambient room temperature conditions. Experiments were conducted at ambient laboratory temperature (25±2 °C). Temperature was monitored with a digital thermometer throughout each run, and no external heating or cooling was applied, as EF reactions are not highly temperature-sensitive under the tested conditions. This study adopted an initial PCT concentration of 1000 mg/dm^3 (ca. 6.62 mol/m^3) to evaluate the reaction performance. Before the start of electrolysis, a known quantity of ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) was introduced into the reactor solution to provide the necessary Fe^{2+} catalyst for Fenton reactions. The pH of the solution was carefully adjusted to pH 3, which is considered optimal for hydroxyl radical production via Fenton chemistry. To establish baseline conditions, samples were collected before the addition of H_2O_2. The reaction time was considered to begin immediately upon the addition of H_2O_2. Each EF experiment was conducted for a total reaction time of 120 min. These samples were promptly mixed with NaOH to neutralize the acidic environment and quench the reaction. Each sample was filtered through a 0.2 μm membrane filter to remove any precipitates, ensuring clarity for subsequent analytical measurements.

EF is regarded as a highly promising advanced oxidation process (AOP) for the treatment of wastewater containing recalcitrant organic pollutants. It promotes the degradation of organic compounds primarily through the generation of hydroxyl radicals ($^{\bullet}OH$), one of the most powerful oxidizing species, via the classical Fenton reaction (Eq. (1)). These radicals are capable of non-selectively attacking and mineralizing a wide variety of organic pollutants into harmless end-products such as carbon dioxide and water.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \tag{1}$$

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

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{3}$$

A key advantage of the EF process is its ability to continuously generate hydrogen peroxide in situ through the two-electron reduction of oxygen at the cathode, as illustrated in Eq. (2). This eliminates the need for external addition of H_2O_2, making the process more sustainable and cost-effective.

Simultaneously, ferrous ions (Fe^{2+}), which are essential catalysts in the Fenton reaction, can be regenerated electrochemically from ferric ions (Fe^{3+}) through reduction at the cathode surface (Eq. (3)). This regeneration mechanism maintains a continuous supply of Fe^{2+} in the system, thereby sustaining the Fenton cycle and enhancing the overall efficiency of the process. The success of these electrochemical steps is largely dependent on the choice of electrode materials. For instance, the use of a suitable cathode material such as carbon-felt has been widely reported to facilitate both the electrogeneration of H_2O_2 and the reduction of Fe^{3+}, thereby supporting the sustained catalytic cycle of the EF system [24].

Box–Behnken experimental design (BBD). The BBD statistical experimental approach is recognized a powerful tool for the optimization of analytical methods, offering an efficient strategy for systematically evaluating the influence of multiple factors and their interactions on a given response [25]. In the present study, BBD was employed specifically to investigate the effects of key operational parameters on the degradation of PCT and to optimize the overall performance of the treatment system. As a subset of response surface methodology (RSM), BBD is characterized by its use of three-level incomplete factorial designs, which enable the modeling of quadratic responses without requiring a full factorial design. One of the significant advantages of BBD over other RSM designs is that it necessitates fewer experimental runs, thereby making the optimization process more economical and less time-consuming while maintaining reliable statistical accuracy.

For the experimental design and data analysis, the Design-Expert software version 13 was utilized. This software facilitated the determination of optimum operating conditions for PCT degradation by fitting the experimental data to a suitable response surface model. The optimization procedure involved generating statistically designed combinations of independent variables, estimating the coefficients of the response functions, and subsequently predicting the response behavior at various factor levels. The parameters under investigation included initial concentrations of Fe^{2+}, H_2O_2, and the applied current density, each varied within specified lower and upper limits determined from preliminary studies. Specifically, the initial Fe^{2+} concentration ranged from 0.01 to 0.1 mol/m^3, the initial H_2O_2 concentration from 10 to 30 mol/m^3, and the current density from 50 to 150 A/m^2. These ranges were chosen based on prior experimental work to capture the relevant operational window. Within the BBD framework, these factors were coded at three levels: high (+1), middle (0), and low (−1), enabling the exploration of nonlinear relationships.

The primary response variable for the optimization was the degradation efficiency of PCT, assessed by both the removal percentage and the rate constant of degradation for each experimental run. To describe the kinetics of PCT degradation, various kinetic models, including zero-order, first-order, and second-order reaction models, were applied to the experimental data. Among these, the second-order kinetic model was found to provide the best fit, as evidenced by the highest coefficient of determination (R^2) values. Consequently, the second-order model was selected for calculating the reaction rate constants, ensuring a more precise representation of the degradation kinetics under the studied conditions.

3. RESULTS AND DISCUSSION

3.1. EMPIRICAL CORRELATION

To evaluate the interactive effects of key operational parameters on PCT degradation, a Box–Behnken experimental design was applied, and the resulting removal efficiencies and kinetic constants are summarized in Table 1.

Table 1

Box–Behnken design experiment conditions, results of PCT removal and reaction rate constant

RUN	[Fe^{2+}] [mol/m^3]	[H_2O_2] [mol/m^3]	Current density [A/m^2]	PCT remaining concentration [mg/dm^3]	PCT removal [%]	Reaction rate constant [m^3/(mol·min)]
1	0.02	10	100	650	65	0.0045
2	0.1	10	100	850	85	0.0135
3	0.02	30	100	700	70	0.006
4	0.1	30	100	880	88	0.014
5	0.06	10	50	760	76	0.0078
6	0.06	30	50	830	83	0.011
7	0.06	20	100	920	92	0.015
8	0.02	20	50	680	68	0.0055
9	0.1	20	50	840	84	0.012
10	0.06	20	150	950	95	0.018
11	0.06	20	100	890	89	0.0165
12	0.06	10	150	930	93	0.0175
13	0.02	20	150	720	72	0.007
14	0.1	20	150	870	87	0.015
15	0.06	30	150	900	90	0.016

The experimental results presented in Table 1 demonstrate the influence of Fe^{2+} concentration, H_2O_2 dosage, and current density on the EF degradation efficiency of PCT in aqueous solution. Overall, PCT removal efficiency ranged from 65 to 95%, with the corresponding degradation rate constants increasing from 0.0045 to 0.018 m^3/(mol·min), indicating that higher removal percentages are closely associated with faster reaction kinetics. Runs with moderate Fe^{2+} concentration (0.06 mol/m^3), intermediate to high H_2O_2 dosages (20–30 mol/m^3), and elevated current densities (100–150 A/m^2) consistently exhibited higher removal efficiencies (≥ 89%) and reaction rate constants (≥ 0.015 m^3/(mol·min)), particularly in runs 10, 11, 12, and 15. For instance, run 10, which employed a current density of 150 A/m^2 and 20 mol/m^3 of H_2O_2, achieved the highest removal (95%) and reaction rate constant (0.018 m^3/(mol·min)), highlighting the strong positive effect of increased current on $^{\bullet}OH$ radical generation. Conversely, lower Fe^{2+} concentrations (0.02 mol/m^3) and lower current densities (50 A/m^2) led to reduced degradation performance, as observed in runs 1, 3, and 8. These trends suggest that an

optimal balance of reagent concentrations and sufficient current input are critical to maximizing PCT degradation efficiency via the EF process.

Table 2

ANOVA for PCT removal

Source	Sum of squares	*df*	Mean square	*F*-value	*p*-value	Remarks
Model	1285.72	9	142.86	13.22	0.0055	significant
A	595.13	1	595.13	55.09	0.0007	
B_2	18.00	1	18.00	1.67	0.2532	
C	148.30	1	148.30	13.73	0.0139	
AB	1.0000	1	1.0000	0.0926	0.7732	
AC	0.2500	1	0.2500	0.0231	0.8850	
BC	25.00	1	25.00	2.31	0.1887	
A^2	418.83	1	418.83	38.77	0.0016	
B^2	36.30	1	36.30	3.36	0.1262	
C^2	12.98	1	12.98	1.20	0.3229	
Residual	54.01	5	10.80			
Lack of fit	49.51	4	12.38	2.75	0.4209	not significant

A represents Fe^{2+}, B – H_2O_2, C – current density.

The analysis of variance (ANOVA) results (Table 2) reveals that the regression model is statistically significant, with an *F*-value of 13.22 and a *p*-value of 0.0055, indicating that the selected factors collectively have a meaningful influence on the response variable. Among the individual terms, Fe^{2+} concentration (A) shows the strongest effect on the system, with a highly significant *p*-value of 0.0007 and the highest *F*-value (55.09), suggesting its dominant role in the EF degradation process. Current density (C) is also significant ($p = 0.0139$), highlighting its important contribution to hydroxyl radical generation and pollutant removal. In contrast, H_2O_2 concentration (B) is not statistically significant ($p = 0.2532$), implying that variations within the tested range did not substantially affect the response. Interaction terms (AB, AC, and BC) and quadratic terms for H_2O_2 and current density (B^2 and C^2) were all non-significant, while the quadratic term for Fe^{2+} (A^2) was significant ($p = 0.0016$), suggesting a non-linear relationship between Fe^{2+} concentration and the response. The lack-of-fit test was not significant ($p = 0.4209$), confirming that the model adequately fits the experimental data without systematic error. These findings indicate that optimization efforts should primarily focus on Fe^{2+} concentration and current density to enhance process efficiency.

The ANOVA results for the reaction rate constant model (Table 3) indicate that the overall regression is statistically significant, with an *F*-value of 10.29 and a *p*-value of 0.0097, confirming that the model effectively explains the variation in the rate constant of the EF process. Among the individual factors, Fe^{2+} concentration (A) exhibits the most significant influence ($p = 0.0015$, $F = 39.71$), followed by current density (C), which is also significant ($p = 0.0088$, $F = 17.35$). These results underscore the critical role of both

Fe^{2+} dosage and applied current in enhancing the generation of hydroxyl radicals and, consequently, the degradation kinetics. In contrast, the effect of H_2O_2 concentration (B) is not statistically significant ($p = 0.4925$), suggesting that within the tested range, changes in H_2O_2 levels did not meaningfully affect the reaction rate. All interaction terms (AB, AC, BC) and the quadratic terms for H_2O_2 and current density (B^2 and C^2) were also non-significant ($p > 0.05$), while the quadratic term for Fe^{2+} (A^2) was highly significant ($p = 0.0037$), indicating a non-linear effect of Fe^{2+} on the reaction rate constant. The non-significant lack-of-fit ($p = 0.3929$) suggests that the model fits the data well without unexplained variability. Overall, these results highlight Fe^{2+} concentration and current density as the primary factors driving the rate of PCT degradation in the EF process.

Table 3

ANOVA for the reaction rate constant

Source	Sum of squares	*df*	Mean square	*F*-value	*p*-value	Remarks
Model	0.0003	9	0.0000	10.29	0.0097	significant
A	0.0001	1	0.0001	39.71	0.0015	
B_2	1.711×10^{-6}	1	1.711×10^{-6}	0.5478	0.4925	
C	0.0001	1	0.0001	17.35	0.0088	
AB	2.500×10^{-7}	1	2.500×10^{-7}	0.0800	0.7886	
AC	5.625×10^{-7}	1	5.625×10^{-7}	0.1801	0.6889	
BC	5.523×10^{-6}	1	5.523×10^{-6}	1.77	0.2411	
A^2	0.0001	1	0.0001	26.20	0.0037	
B^2	9.514×10^{-6}	1	9.514×10^{-6}	3.05	0.1414	
C^2	3.952×10^{-6}	1	3.952×10^{-6}	1.27	0.3117	
Residual	0.0000	5	3.124×10^{-6}			
Lack of fit	0.0000	4	3.623×10^{-6}	3.22	0.3929	not significant

A represents Fe^{2+}, B – H_2O_2, C – current density.

Empirical correlations between the PCT degradation efficiency (PCT_{rem}), the reaction rate constant (k), and the three factors were obtained using the Box–Behnken experimental design for both processes. A reduced cubic model was fitted for both processes, having an R^2 value of 0.96.

$$\mathrm{PCT_{rem}} = 90.98 + 8.63A + 1.50B + 4.11C - 0.50AB - 0.25AC - 2.50BC - 10.98A^2 - 3.23B^2 + 2.01C^2 \quad (4)$$

$$k = 0.0159 + 0.039A + 0.0005B + 0.0025C - 0.0002AB + 0.0004AC - 0.0012BC - 0.0049A^2 - 0.0017B^2 + 0.0011C^2 \quad (5)$$

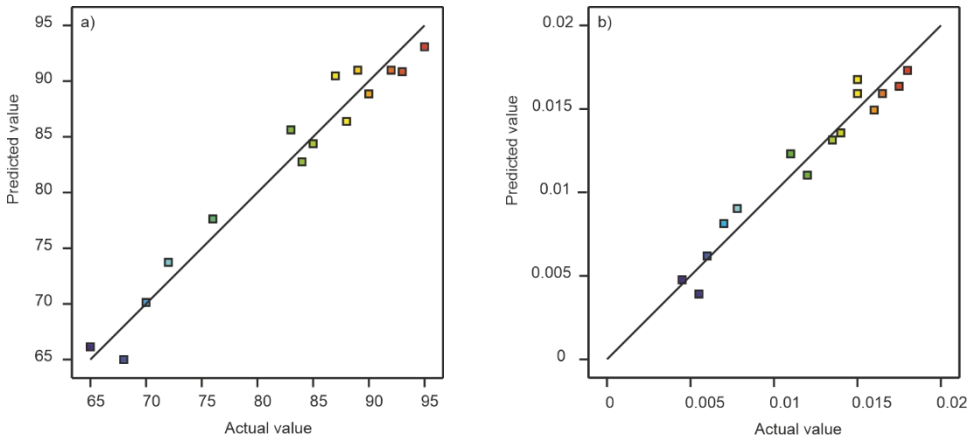

Fig. 2. Experimental and model-predicted results: a) PCT removal, b) reaction rate constant

Figure 2 presents the correlation between the actual experimental values and model-predicted results for (a) PCT removal efficiency and (b) the reaction rate constant, serving as a diagnostic for model accuracy. In both plots, the data points closely align along the 45-degree reference line, indicating a strong agreement between predicted and actual outcomes. This alignment suggests that the developed cubic models effectively capture the underlying relationships between the operating parameters and both response variables. The minimal deviation of points from the line reflects low prediction error, supporting the statistical significance and goodness of fit demonstrated in the ANOVA analyses. Additionally, the color gradient – ranging from blue (low values) to red (high values) – visually affirms the model's ability to accurately track changes across the entire range of observed values. These results confirm that the response surface methodology (RSM) models are robust and reliable tools for predicting PCT removal and reaction rate constant performance in the EF process.

3.2. THE OPTIMUM CONDITION FOR PCT REMOVAL

Figure 3 illustrates the individual effects of Fe^{2+} concentration, H_2O_2 dosage, and current density on PCT removal efficiency in the EF process. PCT removal increases with Fe^{2+} concentration up to approximately 0.06 mol/m^3, beyond which it plateaus or slightly declines, suggesting that excessive Fe^{2+} may lead to scavenging of hydroxyl radicals or formation of iron sludge, thereby reducing efficiency. Figure 3b shows a relatively flat response to increasing H_2O_2 concentration, indicating that within the tested range (10–30 mol/m^3), H_2O_2 does not significantly affect the removal efficiency. This aligns with ANOVA results showing its statistical insignificance. In Figure 3c, an increase in current density from 50 to 150 A/m^2 results in a steady improvement in PCT removal, likely due to enhanced regeneration of Fe^{2+} and production of reactive oxygen species. The trends in

all three plots fall within the 95% confidence interval bands, supporting the model's reliability. These results highlight Fe^{2+} concentration and current density as the most influential parameters for optimizing PCT degradation, while the effect of H_2O_2 appears less pronounced under the studied conditions.

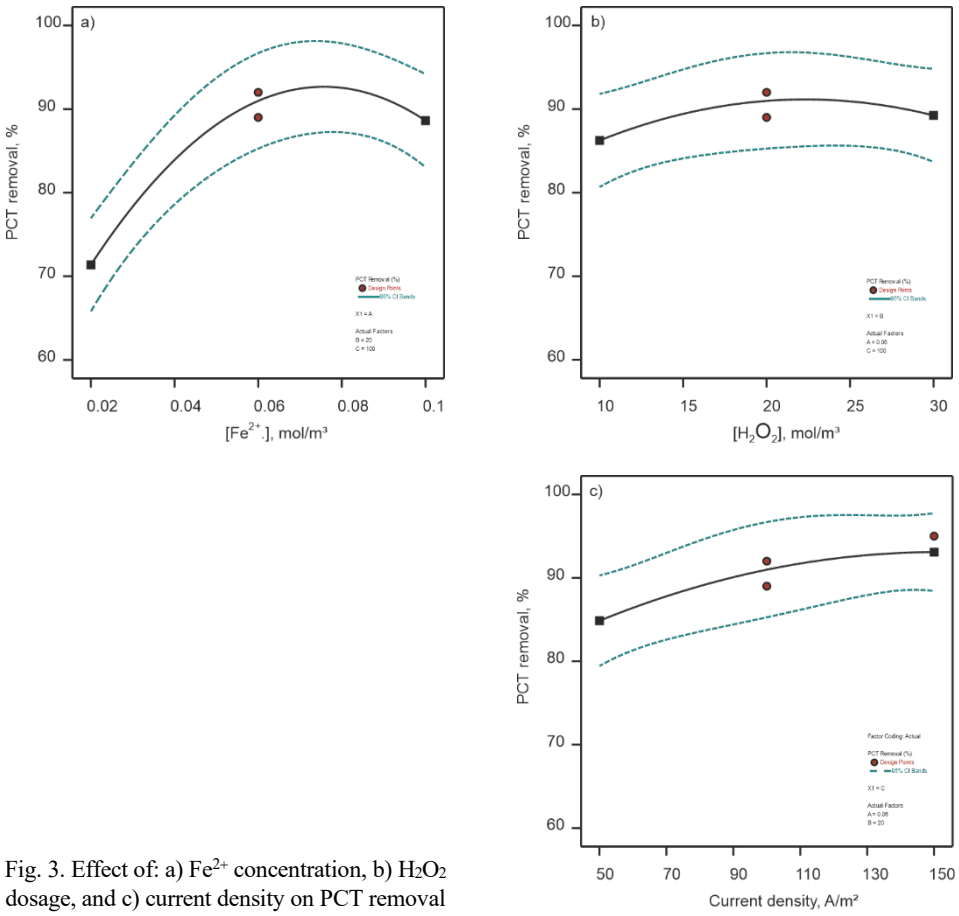

Fig. 3. Effect of: a) Fe^{2+} concentration, b) H_2O_2 dosage, and c) current density on PCT removal

Figure 4 shows 3D surface plots depicting the interaction effects of key operational parameters on the removal of PCT. As shown in Fig. 4a, the synergistic effect of Fe^{2+} and H_2O_2 indicates a pronounced increase in PCT removal efficiency with increasing concentrations of both reagents, reaching an optimal zone around 0.06 mol/m^3 Fe^{2+} and 20 mol/m^3 H_2O_2. This trend suggests enhanced generation of hydroxyl radicals through Fenton-like reactions. In Figure 4b, the interaction between Fe^{2+} concentration and current density show a similar enhancement, with removal efficiency improving as current density increases, likely due to improved coagulant generation and radical production via electrochemical processes. PCT removal exceeds 90% at higher current densities (> 120 A/m^2)

and Fe^{2+} concentrations (> 0.06 mol/m^3). Figure 4c illustrates the interaction between H_2O_2 dosage and current density, which also positively influences removal efficiency, although the effect appears to plateau at higher H_2O_2 dosage levels. Overall, these results demonstrate that optimal combinations of Fe^{2+} concentration, H_2O_2 dosage, and current density significantly enhance the EF process for efficient PCT removal.

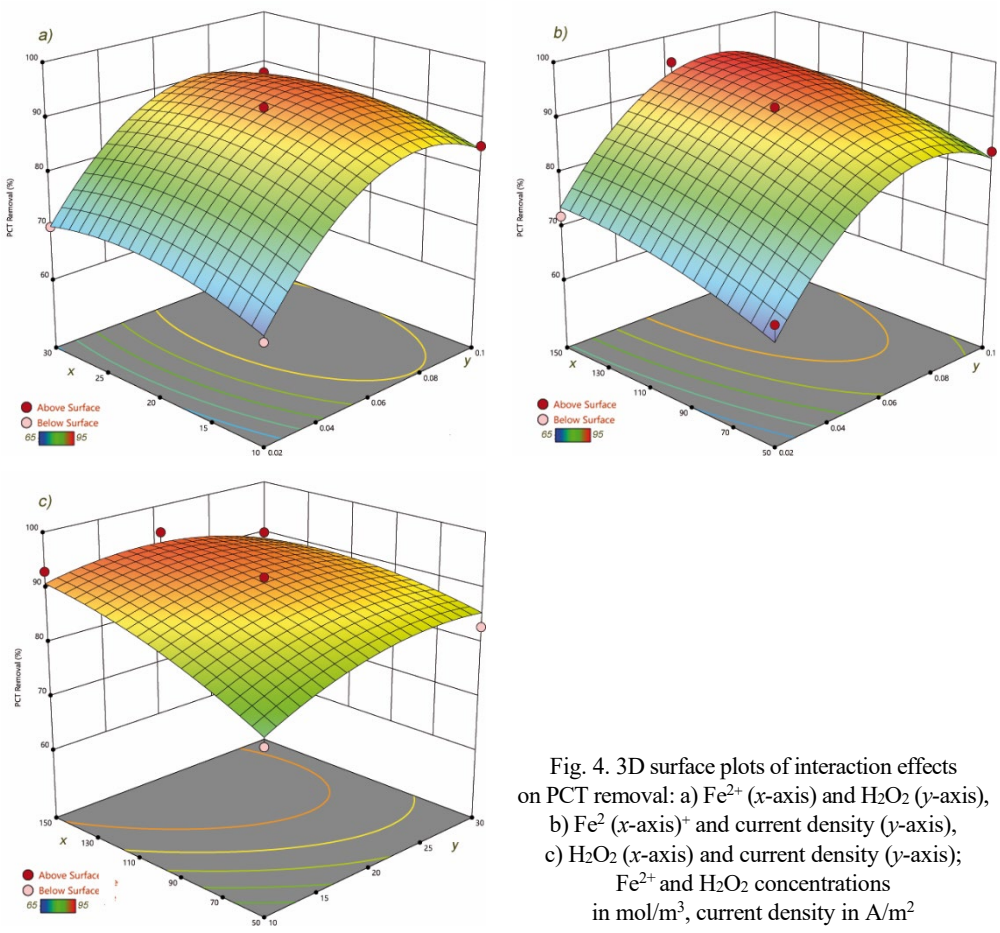

Fig. 4. 3D surface plots of interaction effects on PCT removal: a) Fe^{2+} (*x*-axis) and H_2O_2 (*y*-axis), b) Fe^2 (*x*-axis)$^+$ and current density (*y*-axis), c) H_2O_2 (*x*-axis) and current density (*y*-axis); Fe^{2+} and H_2O_2 concentrations in mol/m^3, current density in A/m^2

The optimization results derived from the Box–Behnken experimental design identified the ideal operational conditions for maximizing PCT removal from wastewater via the EF process. The optimum parameter values were determined to be 0.075 mol/m^3 of Fe^{2+}, 18 mol/m^3 of H_2O_2, and a current density of 150 A/m^2. Under these conditions, the actual PCT removal efficiency achieved was 93.45%, closely aligning with the model's predicted value of 94.78%, with a minimal deviation of only 1.33% (Table 4). This small difference between actual and predicted values confirms the reliability and accuracy of the statistical model in predicting treatment performance.

Table 4

The optimum condition for PCT removal

Values of optimum parameters	Fe^{2+}, mol/m^3	0.075
	H_2O_2, mol/m^3	18
	current density, A/m^2)	150
Values of PCT removal, %	actual	93.45
	predicted	94.78
	difference	1.33

The high removal efficiency at these optimum conditions further demonstrates the strong synergistic effect between Fe^{2+} concentration, H_2O_2 dosage, and current density, validating the effectiveness of the optimized EFsystem for PCT-contaminated wastewater treatment. Conventional wastewater treatment plants often exhibit limited and variable removals of pharmaceuticals, with examples showing only around 51% removal of PCT in fluidized aerobic bioreactors [26]. By contrast, our optimized EF setup achieved over 95% PCT removal, demonstrating a significant performance enhancement.

3.3. THE OPTIMUM CONDITION FOR REACTION RATE CONSTANT

Figure 5 presents the individual effects of Fe^{2+} concentration, H_2O_2 dosage, and current density on the reaction rate constant (k) of the EF process for PCT degradation. As shown in Fig. 5a, the reaction rate constant increases notably with Fe^{2+} concentration increase, particularly between 0.02 and 0.075 mol/m^3, after which the trend begins to plateau. This behavior reflects the enhanced generation of hydroxyl radicals due to the availability of Fe^{2+} ions that catalyze H_2O_2 decomposition, accelerating the degradation kinetics. In Fig. 5b, the influence of H_2O_2 dosage shows a mild rise in the reaction rate constant as the concentration increases from 10 to 20 mol/m^3, followed by a slight decline, indicating that excessive H_2O_2 may act as a scavenger of hydroxyl radicals, thereby reducing the effective degradation rate. Figure 5c illustrates that increasing the current density leads to a progressive enhancement of the reaction rate constant, highlighting the role of current in generating coagulants and promoting the Fenton reaction. The upward trend suggests improved reaction kinetics at higher current densities due to more efficient electron transfer and reactive species generation. These results collectively confirm that Fe^{2+} concentration and current density are critical drivers of reaction kinetics, while optimal dosing of H_2O_2 is essential to avoid self-quenching effects.

Figure 6 illustrates the 3D surface plots of the interaction effects of Fe^{2+} concentration, H_2O_2 dosage, and current density on the rate constant (k) of PCT degradation during the EF process. In Figure 6a, the combined effect of Fe^{2+} and H_2O_2 reveals a significant synergistic interaction, where increasing both parameters leads to a marked rise in the reaction rate constant, with an optimal zone observed around 0.075 mol/m^3 Fe^{2+} and 18 mol/m^3 to 20 mol/m^3 H_2O_2. This suggests enhanced generation of hydroxyl radicals via Fenton's

reaction, accelerating the degradation kinetics. Figure 6b demonstrates that the reaction rate constant increases notably with both Fe^{2+} concentration and current density, particularly at higher levels, reflecting the crucial role of current density in facilitating electron transfer and activating the Fenton process through electrochemical generation of coagulants and oxidants. Similarly, Fig. 6c shows that the interaction between H_2O_2 and current density positively influences the reaction rate constant, although the increase becomes less steep at higher H_2O_2 levels, potentially due to scavenging effects. Collectively, these interaction plots underscore that optimizing the simultaneous input of Fe^{2+} concentration, H_2O_2 dosage, and current density significantly enhances the kinetics of PCT removal, demonstrating their critical influence on the degradation efficiency in the EFsystem.

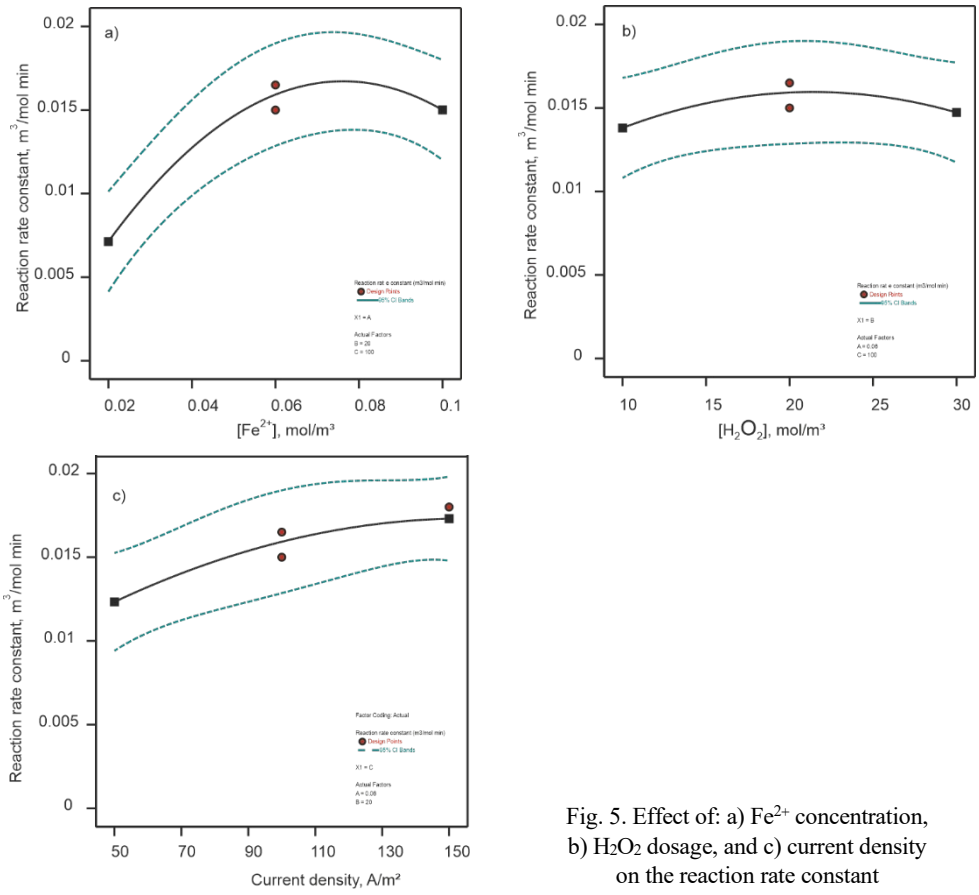

Fig. 5. Effect of: a) Fe^{2+} concentration, b) H_2O_2 dosage, and c) current density on the reaction rate constant

The optimization results obtained from the Box–Behnken experimental design identified the most favorable conditions for maximizing the reaction rate constant of PCT degradation in the electrocoagulation-Fenton process. The optimal parameters were determined to be 0.068 mol/m^3 of Fe^{2+}, 18 mol/m^3 of H_2O_2, and a current density of 145 A/m^2. Under

these conditions, the actual experimental reaction rate constant achieved was 0.017 $m^3/(mol \cdot min)$, aligning with the model's predicted value of 0.018 $m^3/(mol \cdot min)$, with a minimal deviation of only 0.001 $m^3/(mol \cdot min)$.

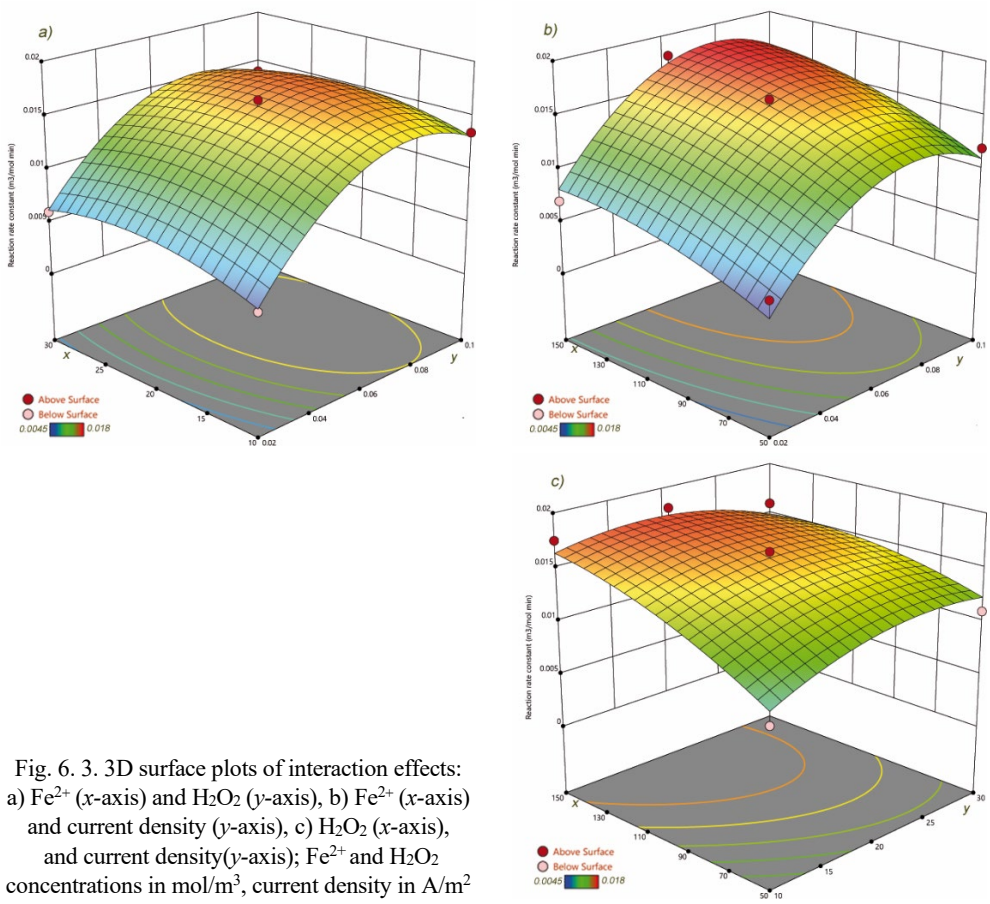

Fig. 6. 3. 3D surface plots of interaction effects: a) Fe^{2+} (*x*-axis) and H_2O_2 (*y*-axis), b) Fe^{2+} (*x*-axis) and current density (*y*-axis), c) H_2O_2 (*x*-axis), and current density(*y*-axis); Fe^{2+} and H_2O_2 concentrations in mol/m^3, current density in A/m^2

Table 5

The optimum condition for reaction rate constant

Values of optimum conditions	Fe^{2+}, mol/m^3	0.068
	H_2O_2, mol/m^3	18
	current density, A/m^2	145
Reaction rate constant, *k*, $m^3/(mol \cdot min)$	actual	0.017
	predicted	0.018
	difference	0.001

This close agreement confirms the reliability and predictive accuracy of the Box–Behnken design in modeling the reaction kinetics. The high reaction rate constant under

optimized conditions highlights the strong kinetic response of the system, driven by efficient radical generation and enhanced mass transfer. These findings reinforce the significance of carefully tuning operational parameters to accelerate the degradation process and improve the treatment efficiency of PCT-contaminated wastewater. When compared with alternative treatment technologies, EF generally offers higher degradation rates for recalcitrant pharmaceuticals with a relatively lower footprint, but it incurs higher energy consumption than membrane bioreactors (MBRs) (e.g., EF-based systems may require ca. 20.9 kWh/m^3, whereas MBRs typically consume 0.5–1 kWh/m^3) [27].

4. CONCLUSIONS

In this study, the degradation efficiency of PCT from aqueous solutions was investigated using an optimised EF process. Through a Box–Behnken response surface methodology, the effects of three critical operational parameters (ferrous ion concentration, hydrogen peroxide dosage, and current density) were systematically evaluated to maximize both degradation efficiency and reaction kinetics. The results demonstrated that ferrous ion concentration and current density were the most significant factors influencing the performance of the EF system, whereas hydrogen peroxide had a less pronounced effect within the studied range. Under optimal conditions ($[Fe^{2+}]$ = 0.075 mol/m^3, $[H_2O_2]$ = 18 mol/m^3, current density = 150 A/m^2), the process achieved a high PCT removal efficiency of 94.78% and a reaction rate constant of 0.018 m^3/(mol·min). The strong agreement between experimental and predicted values confirmed the validity and robustness of the developed statistical model, indicating that the EF process can serve as an effective treatment method for pharmaceutical-contaminated wastewater.

Despite the promising outcomes, several limitations should be acknowledged. First, the study was conducted under controlled laboratory-scale batch conditions, which may not fully replicate the complexities of real wastewater matrices or continuous-flow systems. Second, the analysis focused primarily on the degradation efficiency of the parent compound without detailed characterization of intermediate by-products or their potential ecotoxicity. Third, while the study explored key operating parameters, it did not consider factors such as temperature, solution conductivity, or the economic and energy implications of scaling up the process. Lastly, the system's long-term stability, fouling behavior, and potential electrode degradation over repeated use were not addressed.

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