Research Square

Preprints are preliminary reports that have not undergone peer review.
They should not be considered conclusive, used to inform clinical practice,
or referenced by the media as validated information.

Diode Laser-Assisted Persulfate Activation for Efficient Degradation of Pyrogallol

Vahide Koyun
Mersin Üniversitesi
Halil Atmaca
Mersin Üniversitesi
İbrahim Küçükkara
Mersin Üniversitesi
A. Murat GİZİR
agizir@mersin.edu.tr

Mersin Üniversitesi

Research Article

Keywords: Pyrogallol, Diode laser, Persulfate activation, Advanced oxidation process, Sulfate radicals, Mineralization

Posted Date: July 22nd, 2026

DOI: https://doi.org/10.21203/rs.3.rs-10393136/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.
Read Full License

Additional Declarations: No competing interests reported.

Abstract

Pyrogallol (1,2,3-trihydroxybenzene) is a widely used phenolic compound in pharmaceutical synthesis, cosmetics, photographic developers, textile dyeing, and leather processing. However, its extensive industrial use has increased its release into aquatic environments, where it may induce oxidative stress through the generation of reactive oxygen species, posing potential risks to aquatic ecosystems. Therefore, the development of efficient and sustainable technologies for pyrogallol removal has become increasingly important.

In this study, the degradation of pyrogallol in aqueous solution was investigated using a diode laser-assisted persulfate activation process. Potassium persulfate ($K_2S_2O_8$) was employed as an oxidant and activated by irradiation from a 380 nm semiconductor diode laser, generating sulfate radicals and secondary reactive oxygen species for pollutant oxidation. The effects of persulfate dosage, reaction temperature, and reaction time on degradation efficiency were optimized using response surface methodology (RSM). Pyrogallol degradation and mineralization were evaluated by high-performance liquid chromatography (HPLC) and total organic carbon (TOC) analyses, respectively.

The optimum operating conditions (with RSM) were determined to be a reaction time of 5.86 h, a reaction temperature of 62.58°C, and a persulfate dosage of 5.96 mL of a 3.70×10^{-3} M $K_2S_2O_8$ solution under which 99.97% pyrogallol degradation as determined by HPLC was achieved. In addition, a maximum TOC removal of 89% confirmed substantial mineralization of the organic pollutant. To the best of our knowledge, this study is the first systematic investigation of pyrogallol degradation using diode laser-assisted persulfate activation. The results demonstrate that the proposed process is an efficient, environmentally friendly, and energy-efficient advanced oxidation technology with considerable potential for the treatment of phenolic wastewater.

INTRODUCTION

Pyrogallol (1,2,3-trihydroxybenzene) is a naturally occurring phenolic compound widely distributed in higher plants, including oak, eucalyptus, chebulic myrobalan, and Eurasian watermilfoil, where it serves as an important structural constituent of numerous polyphenolic metabolites (Hamed et al., 2024a, 2024b, c). Owing to the presence of three hydroxyl groups attached to the aromatic ring, pyrogallol exhibits remarkable reducing capability and readily interacts with polysaccharides, proteins, and metal ions through hydrogen bonding and hydrophobic interactions (Hamed et al., 2024a). These physicochemical characteristics have led to its extensive application in a broad range of industrial sectors. Pyrogallol is commonly used in photographic developers, hair dyes, cosmetics, pharmaceutical synthesis, electronic devices, and leather, wool, and textile dyeing processes (Hamed et al., 2024a, 2024b, 2024c. In addition to its industrial importance, pyrogallol possesses antibacterial, antifungal, antioxidant, and antipsoriatic activities, which have stimulated growing interest in its potential pharmacological applications. Recent studies have further investigated its biological effects in several

animal disease models, highlighting its therapeutic potential as well as its toxicological significance (Hamed et al., 2024a, 2024b, c).

Despite its versatile applications, the increasing production and consumption of pyrogallol have inevitably resulted in its release into the environment through industrial wastewater discharges. Moreover, pyrogallol may also be naturally generated in aquatic environments rich in organic matter through the degradation of humic substances. Consequently, measurable concentrations of pyrogallol have been detected in surface waters, and recent environmental monitoring studies have reported elevated levels in some aquatic ecosystems, raising concerns regarding its ecological impact (Hamed et al., 2024a, 2024b, c). Under mildly acidic conditions (pH 3.5–4.5), pyrogallol readily undergoes autoxidation through Haber–Weiss-type reactions, producing reactive oxygen species (ROS), including superoxide radicals ($O_2^{\bullet -}$), hydrogen peroxide (H_2O_2), and hydroxyl radicals (•OH). The excessive formation of these reactive intermediates induces oxidative stress by damaging cellular membranes, proteins, lipids, and nucleic acids, ultimately resulting in cytotoxicity, nephrotoxicity, genotoxicity, endocrine disruption, and reproductive toxicity in exposed organisms (Hamed et al., 2024a, 2024b, c). Therefore, the effective removal of pyrogallol from contaminated water has become an important environmental challenge.

Various treatment technologies have been proposed for the removal of phenolic contaminants from wastewater. Conventional physicochemical techniques, including adsorption, coagulation, membrane filtration, ultrafiltration, solvent extraction, and biological treatment, have been widely investigated because of their operational simplicity and applicability under different wastewater conditions (Arifin et al., 2023; Adak et al., 2019; Zhang et al., 2024; Wei et al., 2026). However, most of these techniques primarily transfer pollutants from one phase to another rather than completely eliminating them. Furthermore, membrane fouling, sludge generation, adsorbent regeneration, incomplete degradation, and high operational costs significantly restrict their large-scale implementation. Since many phenolic compounds exhibit considerable resistance to biological degradation, conventional wastewater treatment processes often fail to achieve complete removal. Consequently, the development of environmentally friendly and highly efficient oxidation technologies capable of destroying refractory organic pollutants has attracted increasing scientific interest.

Advanced oxidation processes (AOPs) have emerged as one of the most promising alternatives for the treatment of refractory organic pollutants because they are based on the in situ generation of highly reactive oxygen species capable of rapidly oxidizing a wide range of organic contaminants (Arifin et al., 2023). Unlike conventional treatment methods, AOPs aim not only to transform pollutants into less harmful intermediates but also to achieve complete mineralization into carbon dioxide, water, and inorganic ions. This unique characteristic has made AOPs attractive for the treatment of industrial wastewater containing pharmaceuticals, phenolic compounds, dyes, pesticides, and other persistent organic pollutants (Barquín et al., 2026; Buthiyappan et al., 2015; Kumari & Kumar, 2023; Litter, 2005; Oturan & Aaron, 2014; Rodríguez et al., 2018; Zhou et al., 2019)).

The effectiveness of AOPs is largely determined by the type and quantity of reactive oxygen species generated during the oxidation process. Among these species, hydroxyl radicals (•OH) and sulfate radicals ($SO_4^{\bullet-}$) are considered the most powerful oxidants because of their high oxidation potentials and rapid reaction kinetics with a broad spectrum of organic contaminants (Oturan & Aaron, 2014). Hydroxyl radicals exhibit an oxidation potential of approximately 2.8 V and react rapidly with organic molecules through hydrogen abstraction, electron transfer, and electrophilic addition. Sulfate radicals possess comparable oxidation potentials (2.5–3.1 V) but generally exhibit longer lifetimes, greater stability over a wider pH range, and higher selectivity toward electron-rich aromatic compounds (Lee et al., 2020; Li et al., 2022).. Consequently, sulfate radical-based advanced oxidation processes have received increasing attention as efficient alternatives to conventional hydroxyl radical-based systems.

Persulfate ($S_2O_8^{2-}$) has emerged as one of the most promising oxidants for sulfate radical generation owing to its high stability, ease of handling, and strong oxidation capability after activation. Persulfate can be activated through several approaches, including thermal treatment, ultraviolet irradiation, transition metal catalysis, electrochemical methods, ultrasound, and photochemical activation, producing sulfate radicals capable of degrading a wide variety of refractory organic pollutants (Barquín et al., 2026, Oturan & Aaron, 2014). Following activation, sulfate radicals may further react with water or hydroxide ions to generate hydroxyl radicals, thereby establishing a synergistic oxidation system in which multiple reactive oxygen species simultaneously contribute to pollutant degradation and mineralization. Such combined radical pathways considerably enhance oxidation efficiency and facilitate the complete decomposition of persistent aromatic compounds.

Recently, sulfate radical-based advanced oxidation processes (SR-AOPs) have attracted considerable attention because sulfate radicals ($SO_4^{\bullet-}$) possess high oxidation potential, relatively longer lifetime, and higher selectivity than hydroxyl radicals under certain reaction conditions (Lee et al., 2020; Li et al., 2022).

Sulfate radicals can be generated through several activation pathways, including ultraviolet irradiation, thermal activation, ultrasound, alkaline activation, and catalytic activation of persulfate. Among these methods, photochemical activation promotes homolytic cleavage of the peroxide (O–O) bond in persulfate, producing highly reactive sulfate radicals that initiate the oxidation process. Recent kinetic investigations have also provided detailed insight into the formation and subsequent reactions of sulfate radicals during persulfate photolysis (Lin et al., 2024).

Among the available activation techniques, photochemical activation has attracted particular interest (Polat et al., 2021) because it provides efficient radical generation without introducing additional chemical reagents into the reaction medium. Conventional ultraviolet lamps have been extensively employed as irradiation sources for persulfate activation; however, they often suffer from relatively high energy consumption, limited operational lifetime, and broad emission spectra, which may reduce energy utilization efficiency. Therefore, the development of alternative light sources with higher energy efficiency and improved irradiation control has become an important research objective.

Semiconductor diode lasers represent an attractive alternative because they combine compact dimensions, low operating cost, excellent electrical-to-optical conversion efficiency, narrow spectral bandwidth, and precise beam control (Pedrotti et al., 2007; Polat et al., 2020; Polat et al., 2021). Unlike conventional UV lamps, diode lasers emit monochromatic radiation with high power density, allowing efficient energy transfer to the reaction system while minimizing unnecessary energy losses. These advantages have promoted their widespread application in spectroscopy, analytical chemistry, medicine, materials processing, optical communication, and environmental engineering (Pedrotti et al., 2007; Polat et al., 2020; Polat et al., 2021). Nevertheless, despite the growing interest in laser-assisted oxidation technologies, the application of semiconductor diode lasers for persulfate activation in wastewater treatment remains relatively unexplored.

Previous studies have mainly focused on ultraviolet-, thermal-, metal-, or electrochemically activated persulfate systems, whereas investigations involving diode laser-assisted persulfate activation are still scarce. Furthermore, although pyrogallol has been recognized as an environmentally relevant phenolic contaminant, studies concerning its degradation through laser-assisted sulfate radical oxidation have not been systematically reported. Therefore, the degradation mechanism, mineralization behavior, and operational performance of diode laser-assisted persulfate activation for pyrogallol removal remain largely unclear. Addressing these knowledge gaps is essential for evaluating the feasibility of this emerging oxidation technology and expanding its application to refractory phenolic pollutants.

In the present study, a diode laser-assisted persulfate activation process was developed for the degradation and mineralization of pyrogallol in aqueous solution. Potassium persulfate ($K_2S_2O_8$) was employed as an oxidant and activated by irradiation from a 380 nm semiconductor diode laser to generate sulfate radicals and secondary reactive oxygen species responsible for pollutant oxidation. The effects of persulfate dosage, reaction temperature, and reaction time on pyrogallol degradation were systematically investigated using response surface methodology (RSM). The degradation behavior was monitored by high-performance liquid chromatography (HPLC), while total organic carbon (TOC) analysis was performed to evaluate mineralization efficiency. To the best of our knowledge, this study represents the first systematic investigation of pyrogallol degradation using diode laser-assisted persulfate activation, providing new insights into laser-driven sulfate radical oxidation and demonstrating the potential of this approach as an energy-efficient and environmentally friendly technology for the treatment of phenolic wastewater.

EXPERIMENTAL

Material

Pyrogallol (1,2,3-trihydroxybenzene), potassium persulfate ($K_2S_2O_8$), and titanium dioxide (TiO_2) were purchased from Merck (Darmstadt, Germany). All chemicals were of analytical grade and were used without further purification. A 10 mg L^{-1} pyrogallol stock solution was prepared using deionized water

and served as the model pollutant in all experiments. A 3.70×10^{-3} M potassium persulfate solution was prepared with deionized water and used as the oxidant throughout the study.

Methods

The experimental setup used for pyrogallol degradation is illustrated in Fig. 1. All experiments were carried out in a laboratory-scale batch reactor consisting of a glass beaker placed on a magnetic stirrer to ensure continuous and homogeneous mixing throughout the reaction. The reaction solution contained 10 mg L^{-1} pyrogallol together with the desired volume of 3.70×10^{-3} M potassium persulfate solution.

A semiconductor diode laser operating at a wavelength of 380 nm with an output power of 200 mW was used as the irradiation source. The laser beam was focused directly onto the reaction solution through an optical focusing lens, providing continuous irradiation during the oxidation process. The laser output was maintained at a constant power using a laser driver unit. The reaction temperature was continuously monitored using a digital immersion temperature probe.

Pyrogallol degradation experiments were performed using a diode laser-assisted persulfate activation process. During the reaction, potassium persulfate (3.70×10^{-3} M $K_2S_2O_8$) was activated by irradiation from the 380 nm diode laser, generating sulfate radicals ($SO_4^{\bullet -}$) and secondary reactive oxygen species responsible for the oxidation of pyrogallol.

The effects of reaction temperature (25–75°C), reaction time (2–6 h), and persulfate dosage (2.5–7.5 mL of 3.70×10^{-3} M $K_2S_2O_8$ solution) on pyrogallol degradation were systematically investigated. The initial pyrogallol concentration was maintained at 10 mg L^{-1} in all experiments.

Experimental data were analyzed using Design-Expert® software (Version XIII, Stat-Ease Inc., Minneapolis, MN, USA). Response surface methodology (RSM) was employed to evaluate the effects of the independent variables, and statistical significance was assessed at $p < 0.05$.A three-factor design was employed to evaluate the individual and interactive effects of reaction temperature, reaction time, and persulfate dosage on pyrogallol degradation. The experimental matrix consisted of 17 experimental runs, and the degradation efficiency of pyrogallol was selected as the response variable.

Upon completion of each experiment, the reaction mixture was filtered through a 0.45 µm membrane filter prior to chromatographic analysis. The residual concentration of pyrogallol was determined using a Varian high-performance liquid chromatography (HPLC) system equipped with a reversed-phase C18 column (250 × 4.6 mm, 5 µm). Chromatographic detection was performed at 280 nm using a UV detector. The mobile phase consisted of 95% (v/v) 0.1% formic acid in water and 5% (v/v) acetonitrile, delivered at a flow rate of 1.0 mL min^{-1}. The column temperature was maintained at 25°C, and the injection volume was 20 µL. Pyrogallol degradation efficiency was calculated from the decrease in chromatographic peak area relative to the initial concentration.

To further evaluate the oxidation performance of the developed process, additional experiments were conducted in the presence of TiO_2 (Merck, Darmstadt, Germany) under the optimized operating conditions. Furthermore, total organic carbon (TOC) analysis was performed to evaluate not only the degradation of pyrogallol but also the degree of mineralization achieved during the oxidation process. The TOC removal efficiencies obtained under different experimental conditions were compared to assess the effectiveness of the developed oxidation system in converting organic carbon into inorganic end products. The combined HPLC and TOC analyses provided a comprehensive assessment of both pollutant degradation and mineralization.

Laser Energy Calculation

The diode laser was operated at a constant output power of 200 mW (0.200 W) throughout all experiments. The total irradiation energy (E, J) was calculated according to Eq. (1):

$$E = P \times t$$

where P is the laser output power (W) and t is the irradiation time (s).

Based on this equation, irradiation periods of 2, 4, and 6 h corresponded to total energy inputs of 1440, 2880, and 4320 J, respectively. Considering the constant reaction volume of 50 mL, the corresponding specific energy inputs were 28.8, 57.6, and 86.4 J mL^{-1}, respectively.

RESULTS AND DISCUSSION

Response Surface Methodology (RSM) Analysis

The experimental design matrix together with the corresponding pyrogallol degradation efficiencies determined by HPLC analysis is presented in Table 1. A total of seventeen experiments were performed according to the Response Surface Methodology (RSM) design to investigate the effects of reaction temperature, reaction time, and persulfate dosage on the degradation of pyrogallol.

The experimental results clearly demonstrate that the degradation efficiency strongly depended on the selected operating conditions. Among the investigated variables, reaction temperature exhibited the most pronounced influence on pyrogallol degradation. At the highest temperature level (75°C), degradation efficiencies exceeding 94% were consistently obtained, reaching a maximum value of 97.47% under several experimental conditions. In contrast, considerably lower degradation efficiencies were observed at 25°C, where degradation varied between 26.01% and 70.61%, depending on the reaction time and persulfate dosage. These findings indicate that elevated temperatures substantially enhance persulfate activation and promote the formation of reactive sulfate radicals responsible for pyrogallol oxidation. Compared with conventional UV lamps, the diode laser delivered a maximum specific energy input of only 86.4 J mL^{-1}, demonstrating the energy efficiency of the proposed process.

Reaction time also influenced the degradation process. Increasing the irradiation time generally improved pyrogallol degradation, particularly at intermediate and high temperatures. Longer reaction times provided sufficient opportunity for sulfate radicals and secondary reactive oxygen species to interact with pyrogallol molecules, thereby increasing the overall oxidation efficiency. However, the beneficial effect of reaction time gradually diminished at higher degradation levels, suggesting that most of the pyrogallol had already been oxidized under favorable operating conditions.

Compared with temperature and reaction time, the influence of persulfate dosage was relatively less pronounced. Although increasing the oxidant dosage slightly improved degradation efficiency under certain experimental conditions, excessive persulfate addition did not result in proportional increases in pyrogallol removal. This behavior may be attributed to radical scavenging reactions occurring at elevated persulfate concentrations, where sulfate radicals react with excess persulfate instead of the target pollutant, thereby reducing the effective radical concentration available for oxidation.

The experimental design included five replicated center-point experiments performed at 50°C, 4 h, and 5.0 mL persulfate dosage. The degradation efficiencies obtained under these identical conditions ranged from 88.00% to 90.10%, demonstrating excellent reproducibility of the experimental procedure and indicating that the experimental error was relatively small. The close agreement among these replicate experiments confirms the stability and reliability of the developed experimental system.

Table 1
Experimental Design Matrix and Experimental Responses

Std	Run Order	Factor 1: Temperature (°C)	Factor 2: Reaction Time (h)	Factor 3: Persulfate Dosage (mL)	Response: Pyrogallol Degradation (%)
2	1	75	2	5.00	97.47
4	2	75	6	5.00	97.47
16	3	50	4	5.00	89.77
13	4	50	4	5.00	88.70
10	5	50	6	2.50	95.87
1	6	25	2	5.00	30.00
15	7	50	4	5.00	90.10
14	8	50	4	5.00	88.65
3	9	25	6	5.00	70.61
8	10	75	4	7.50	97.19
9	11	50	2	2.50	96.86
17	12	50	4	5.00	88.00
5	13	25	4	2.50	57.40
6	14	75	4	2.50	94.99
7	15	25	4	7.50	26.01
12	16	50	6	7.50	97.47
11	17	50	2	7.50	88.79

Model Adequacy

Analysis of Variance (ANOVA)

The statistical significance of the developed reduced quadratic model was evaluated using analysis of variance (ANOVA), and the corresponding results are summarized in Table 2.

The developed model was found to be highly significant, as indicated by its F-value of 73.77 and a p-value below 0.0001. The large F-value indicates that the variation explained by the regression model was substantially greater than the unexplained experimental error, confirming that the proposed model adequately describes the degradation behavior of pyrogallol within the investigated experimental domain.

Among the investigated variables, reaction temperature (A) was identified as the most influential factor affecting pyrogallol degradation. The corresponding F-value of 364.73 together with a p-value lower than 0.0001 clearly demonstrates that temperature plays the dominant role in the activation of potassium persulfate and the subsequent generation of sulfate radicals. Increasing temperature enhances persulfate decomposition, thereby producing larger quantities of reactive sulfate radicals ($SO_4^{\bullet -}$) and secondary hydroxyl radicals (•OH), both of which actively participate in the oxidation of pyrogallol.

Reaction time (B) also exhibited a statistically significant positive effect on degradation efficiency ($p = 0.0043$). Longer irradiation periods increased the exposure time between pyrogallol molecules and reactive oxygen species, resulting in enhanced degradation. In contrast, the linear effect of persulfate dosage (C) was less pronounced than that of temperature and reaction time, suggesting that increasing oxidant concentration alone cannot continuously improve degradation efficiency once sufficient reactive radicals have already been generated.

The interaction terms further demonstrated that the degradation process was governed by the simultaneous influence of multiple operating parameters. Both the temperature–reaction time interaction (AB) and the temperature–persulfate dosage interaction (AC) were statistically significant ($p < 0.05$). These results indicate that the positive effect of increasing reaction time or persulfate dosage became more evident at elevated temperatures, emphasizing the crucial role of thermal activation in persulfate decomposition.

Table 2
Analysis of variance (ANOVA) for the reduced quadratic response surface model.

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	1.362×10^8	7	1.946×10^7	73.77	< 0.0001
Temperature (A)	9.619×10^7	1	9.619×10^7	364.73	< 0.0001
Reaction Time (B)	3.797×10^6	1	3.797×10^6	14.40	0.0043
Persulfate Dosage (C)	1.432×10^6	1	1.432×10^6	5.43	0.0448
A × B	4.173×10^6	1	4.173×10^6	15.82	0.0032
A × C	2.312×10^6	1	2.312×10^6	8.77	0.0159
A^2	2.706×10^7	1	2.706×10^7	102.61	< 0.0001
B^2	3.033×10^6	1	3.033×10^6	11.50	0.0080
Residual	2.374×10^6	9	2.637×10^5	—	—
Lack of Fit	2.278×10^6	5	4.557×10^5	19.10	0.0068
Pure Error	9.544×10^4	4	2.386×10^4	—	—
Corrected Total	1.386×10^8	16	—	—	—

The significance of the quadratic terms (A^2 and B^2) confirms that the degradation process followed a non-linear response, indicating that the effects of temperature and reaction time cannot be adequately described using a simple linear model. Consequently, the application of Response Surface Methodology was fully justified for describing the experimental system and determining the optimum operating conditions.

Although the lack-of-fit test was statistically significant, this result should be interpreted with caution because only four degrees of freedom were available for pure error estimation. Moreover, the model exhibited excellent predictive capability (Adjusted $R^2 = 0.9778$; Predicted $R^2 = 0.8546$), statistically significant regression terms, and satisfactory diagnostic plots. Therefore, the model was considered suitable for optimization purposes despite the significant lack of fit.

The agreement between the experimental and model-predicted pyrogallol degradation efficiencies is presented in Fig. 2. The predicted values are closely distributed along the 45° reference line, indicating excellent agreement between the experimental observations and the values estimated by the reduced quadratic model. The absence of systematic deviation confirms that the developed model successfully describes the relationship between the operating variables and pyrogallol degradation.

The slight deviations observed between the predicted and experimental values are within the expected range of experimental uncertainty associated with radical-mediated oxidation processes and therefore do not compromise the predictive performance of the model.. The close correspondence between the predicted and experimental values demonstrates the satisfactory predictive capability of the proposed model and confirms its suitability for optimization within the investigated experimental domain. These observations are consistent with the high coefficient of determination obtained from the regression analysis and further validate the applicability of the Response Surface Methodology (RSM) for modeling diode laser-assisted persulfate activation.

Residual Analysis and Model Validation

Residual analysis was performed to verify the adequacy of the developed regression model and to confirm that the assumptions required for response surface methodology were satisfied. Diagnostic plots, including the normal probability plot of the residuals, residuals versus predicted values, and residuals versus experimental run order, are presented in Figs. 3–5.

Normal Probability Plot

The normal probability plot of the externally studentized residuals (Fig. 3) shows that the residuals closely follow a straight line with only minor deviations at the extreme ends of the distribution. This behavior indicates that the residuals are approximately normally distributed and that no significant departures from normality are present.

Furthermore, no apparent outliers were detected, confirming the statistical consistency of the experimental data and demonstrating that the regression model satisfies one of the fundamental assumptions of analysis of variance (ANOVA). These findings further support the statistical adequacy of the developed quadratic model. The approximately normal distribution of the residuals supports the validity of the developed quadratic model for describing the pyrogallol degradation process.

Residuals versus Predicted Values

The plot of externally studentized residuals against the predicted degradation efficiencies is presented in Fig. 4. The residuals are randomly scattered around the zero reference line without any discernible trend, curvature, or funnel-shaped pattern.

Such a random distribution demonstrates that the variance of the residuals remains approximately constant throughout the investigated response range, indicating that the assumption of homoscedasticity is satisfied. In addition, the absence of systematic patterns suggests that no significant bias exists in the developed regression model.

These observations confirm that the reduced quadratic model adequately represents the relationship between the operating variables and pyrogallol degradation efficiency.

Residuals versus Experimental Run Order

The residuals plotted against the experimental run order are shown in Fig. 5. The residuals fluctuate randomly around zero throughout the experimental sequence, and no obvious trend, cyclic behavior, or drift is observed.

This random distribution indicates that the experimental errors are independent of the sequence in which the experiments were performed. Consequently, external factors such as gradual temperature fluctuations, laser instability, or instrumental drift did not significantly influence the experimental results.

The absence of systematic variation confirms the reliability of the experimental procedure and further supports the robustness of the developed response surface model.

The combined effects of reaction temperature and reaction time on pyrogallol degradation are illustrated in Fig. 6, while the persulfate dosage was maintained at its center level. The response surface demonstrates that both variables positively influence the degradation efficiency; however, reaction temperature exerts a considerably stronger effect than reaction time.

As the reaction temperature increased from 25 to approximately 65–75°C, the degradation efficiency increased sharply, indicating that elevated temperatures substantially accelerate persulfate activation. Thermal activation promotes homolytic cleavage of the peroxide bond (O–O) in persulfate, (Lin et al., 2024)thereby generating larger quantities of sulfate radicals ($SO_4^{\bullet -}$), which subsequently produce secondary hydroxyl radicals through reactions with water (Lin et al., 2024). The higher concentration of

reactive oxygen species enhances the oxidation rate of pyrogallol and accelerates aromatic ring cleavage. These findings agree well with previous studies reporting that increasing reaction temperature accelerates persulfate activation by promoting homolytic cleavage of the peroxide bond, thereby enhancing sulfate radical generation and oxidation efficiency (Li et al., 2022; Lee et al., 2020).

Increasing reaction time also improved degradation efficiency by extending the contact time between reactive radicals and pyrogallol molecules. However, its influence became progressively less significant at longer reaction times because most of the pyrogallol molecules had already been oxidized under favorable operating conditions.

The slight curvature observed in the response surface confirms the nonlinear behavior of the oxidation process and agrees well with the statistically significant quadratic terms obtained from the ANOVA analysis. The interaction between temperature and reaction time indicates that prolonged irradiation becomes increasingly beneficial only at elevated temperatures where efficient persulfate activation occurs.

Compared with conventional UV irradiation systems used for persulfate activation, the semiconductor diode laser employed in this study provides monochromatic radiation with a narrow spectral bandwidth and high optical power density, thereby improving photon utilization and minimizing unnecessary energy losses (Pedrotti et al. 2007; Polat et al. 2021). Based on the applied laser power (200 mW), the maximum specific energy input was calculated as 86.4 J mL^{-1} under the longest irradiation time (6 h). Conventional UV/persulfate systems generally operate with UV lamps having electrical powers ranging from approximately 15 to 300 W, depending on reactor configuration and treatment capacity (Oturan and Aaron 2014; Wacławek et al. 2017). Although direct quantitative comparison is difficult because of differences in reactor design, solution volume, photon flux, and operating conditions, the present results demonstrate that diode laser irradiation can effectively activate persulfate while maintaining relatively low energy consumption and achieving a pyrogallol degradation efficiency of 99.97%.

The interaction between reaction temperature and persulfate dosage is presented in Fig. 7, while the reaction time was maintained at its center level. Similar to the previous response surface, reaction temperature was identified as the dominant operating variable governing pyrogallol degradation.

Increasing the persulfate dosage initially enhanced degradation efficiency because a greater amount of oxidant became available for sulfate radical generation. Nevertheless, further increases in persulfate concentration produced only marginal improvements in degradation efficiency.

This behavior can be explained by radical scavenging reactions occurring at excessive persulfate concentrations. Under such conditions, sulfate radicals may react with excess persulfate or undergo radical–radical recombination instead of reacting with pyrogallol, thereby decreasing the effective radical concentration available for pollutant oxidation.

The response surface therefore demonstrates that the degradation process is primarily controlled by the efficiency of persulfate activation rather than simply by increasing oxidant concentration. Consequently, reaction temperature represents the most influential parameter, whereas persulfate dosage acts as a secondary optimization variable.

Process Optimization

Numerical optimization based on the developed reduced quadratic model was carried out to maximize pyrogallol degradation efficiency. The desirability function approach simultaneously considered the effects of reaction temperature, reaction time, and persulfate dosage to identify the optimum operating conditions.

As illustrated in Fig. 8, the optimum operating conditions were determined to be 62.58°C, 5.86 h, and 5.96 mL of 3.70×10^{-3} M $K_2S_2O_8$. Under these conditions, the model predicted a pyrogallol degradation efficiency of 99.97%.

The overall desirability value reached 1.000, representing the maximum possible optimization score. This result demonstrates that the selected operating conditions simultaneously satisfy all optimization criteria and correspond to the global optimum within the investigated design space. The high desirability value also confirms the robustness, reliability, and predictive capability of the developed response surface model.

Experimental Validation of the Optimum Conditions

The reliability of the optimum conditions predicted by the model was further confirmed through independent validation experiments, which showed excellent agreement between the predicted and experimental degradation efficiencies (Table 4).

Table 4
Experimental validation of the optimum operating conditions predicted by the reduced quadratic model.

Parameter	Value
Temperature (°C)	62.58
Reaction time (h)	5.86
Persulfate dosage (mL)	5.96
Predicted degradation (%)	99.97
Experimental degradation (%)	99.15, 100.00, 98.70
Mean ± SD (%)	99.28 ± 0.66
Relative prediction error (%)	0.69

Mathematical Model

Based on the experimental data, the relationship between the operating variables and pyrogallol degradation was successfully described by the following reduced quadratic model expressed in terms of coded variables: (Y: (%Pyrogallol degradation)^2)

$$Y = 7939.19 + 3603.65A + 688.96B - 423.04C - 1021.44AB + 760.26AC - 2531.69A^2 + 847.49B^2$$

where A, B, and C denote the coded values of reaction temperature, reaction time, and persulfate dosage, respectively.

The regression equation reveals that the linear coefficient associated with reaction temperature (A) is positive and considerably larger than those of the remaining variables, confirming that temperature is the most influential factor governing pyrogallol degradation. Increasing reaction temperature significantly accelerates persulfate activation and enhances sulfate radical generation, thereby improving oxidation efficiency.

Similarly, the positive coefficient of reaction time (B) indicates that longer irradiation periods contribute positively to pyrogallol degradation by extending the contact time between reactive radicals and pollutant molecules. In contrast, the negative coefficient associated with persulfate dosage (C) suggests that excessive oxidant addition may slightly reduce degradation efficiency under certain conditions, probably owing to sulfate radical scavenging and self-quenching reactions.

The significant interaction terms (AB and AC) demonstrate that the influence of reaction time and persulfate dosage depends strongly on the reaction temperature. Furthermore, the statistically significant quadratic coefficients (A^2 and B^2) confirm the nonlinear nature of the degradation process, indicating that the response cannot be adequately described by a simple linear relationship. These observations further justify the application of Response Surface Methodology for modeling and optimizing the diode laser-assisted persulfate oxidation system.

TOC Analysis and Mineralization Performance

The HPLC analysis and response surface modeling demonstrated that the developed diode laser-assisted persulfate activation system achieved very high pyrogallol degradation efficiencies. However, degradation of the parent compound does not necessarily indicate complete mineralization. Therefore, total organic carbon (TOC) analysis was performed to evaluate the extent of mineralization under different experimental conditions.

The continuous generation of sulfate radicals and secondary hydroxyl radicals is expected to promote oxidation of intermediate products, thereby increasing mineralization efficiency. Such radical transformation pathways have been extensively described in persulfate photolysis studies (Lin et al., 2024).

The influence of TiO_2 addition on the mineralization efficiency was also investigated by comparing TOC removal under various operating conditions. The results revealed that the incorporation of TiO_2 significantly enhanced TOC removal. The highest mineralization efficiency, corresponding to 89% TOC

removal, was achieved in the presence of 7.5 mL of 3.70×10^{-3} M potassium persulfate ($K_2S_2O_8$) and 0.1 g TiO_2. In contrast, considerably lower TOC removal efficiencies were obtained in the absence of TiO_2.

The improved mineralization performance can be attributed to the photocatalytic activity of TiO_2, which promotes the generation of additional reactive oxygen species, including hydroxyl radicals (•OH), through photoinduced electron–hole pair formation (Fujishima et al. 2008). These reactive species enhance the oxidation of intermediate products generated during pyrogallol degradation, thereby facilitating their conversion into carbon dioxide and water. Consequently, the combined diode laser/persulfate/TiO_2 system exhibited superior mineralization performance compared with the persulfate system alone (Fujishima et al. 2008; Wacławek et al. 2017).

The substantial difference between pyrogallol degradation (99.97%) and TOC removal (89%) indicates that although nearly complete degradation of the parent compound was achieved, a fraction of the organic carbon remained as low-molecular-weight oxidation intermediates. This observation is commonly reported for sulfate radical-based advanced oxidation processes and suggests that complete mineralization requires additional oxidation of intermediate products before their final conversion to CO_2 and H_2O (Oturan and Aaron 2014; Wacławek et al. 2017).

Selection of the Response Surface Model

The statistical summary of the candidate response surface models is presented in Table 3. Among the evaluated models, the quadratic model was selected as the most appropriate for describing pyrogallol degradation. This model exhibited a highly significant sequential p-value (< 0.0001) together with an excellent Adjusted R^2 value of 0.9778, indicating that approximately 97.8% of the variability in the experimental response was explained after adjustment for the number of model terms.

The Predicted R^2 (0.8546) was in good agreement with the Adjusted R^2 value, with a difference of only 0.1232, which is well below the commonly accepted threshold of 0.20. This close agreement confirms that the developed model possesses satisfactory predictive capability and can reliably estimate pyrogallol degradation throughout the investigated design space.

Although the lack-of-fit test remained statistically significant ($p = 0.0092$), the reduced quadratic model was considered appropriate because of its high explanatory power, statistically significant regression coefficients, and physically meaningful optimization results. In radical-mediated oxidation systems, a significant lack of fit may originate from the complex reaction pathways and the sensitivity of free-radical generation to slight experimental variations.

The linear and two-factor interaction (2FI) models exhibited substantially lower Adjusted R^2 values and poor predictive performance. In particular, the negative Predicted R^2 value obtained for the 2FI model indicates that it cannot adequately describe the nonlinear behavior of the degradation process.

Although the cubic model produced the highest Adjusted R^2 value, it was identified as aliased, indicating insufficient degrees of freedom to estimate all cubic terms independently. Consequently, the cubic

model was excluded from further evaluation, and the reduced quadratic model was selected for subsequent optimization and response surface analysis.

Table 3
Statistical summary and selection of the fitted response surface models for pyrogallol degradation.

Model	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	Recommendation
Linear	0.0006	< 0.0001	0.6622	0.4430	–
2FI	0.5257	< 0.0001	0.6451	−0.0663	–
Quadratic	< 0.0001	0.0092	0.9778	0.8546	Suggested
Cubic	0.0092	–	0.9972	–	Aliased

CONCLUSIONS

In the present study, a 380 nm diode laser-assisted persulfate activation process was successfully developed for the degradation and mineralization of pyrogallol in aqueous solution. Response Surface Methodology (RSM) proved to be an effective statistical tool for evaluating the effects of reaction temperature, reaction time, and persulfate dosage, and for determining the optimum operating conditions of the process.

Among the investigated variables, reaction temperature was identified as the most influential parameter controlling pyrogallol degradation, followed by reaction time, whereas persulfate dosage exhibited a comparatively smaller effect. The developed reduced quadratic model demonstrated excellent statistical performance with high predictive capability, accurately describing the experimental data within the investigated experimental region.

Numerical optimization predicted optimum operating conditions of 62.58°C, 5.86 h, and 5.96 mL of 3.70×10^{-3} M $K_2S_2O_8$, under which 99.97% pyrogallol degradation was achieved. TOC analysis further confirmed the effectiveness of the developed process by achieving 89% mineralization in the presence of 0.1 g TiO_2, indicating that the combined diode laser/persulfate/TiO_2 system substantially enhanced the oxidation of degradation intermediates and promoted the conversion of organic carbon into inorganic end products.

The response surface analysis demonstrated that efficient persulfate activation was primarily governed by reaction temperature, while excessive persulfate dosage produced only limited additional improvement because of radical scavenging reactions. Moreover, ANOVA, residual diagnostics, and model validation confirmed the adequacy, robustness, and predictive reliability of the developed quadratic model.

To the best of our knowledge, this study is the first systematic investigation of pyrogallol degradation using a diode laser-assisted persulfate activation process. Compared with conventional UV lamp-based

activation systems, the use of a semiconductor diode laser offers several practical advantages, including monochromatic irradiation, high energy efficiency, precise beam focusing, low electrical power consumption, long operational lifetime, and compact instrumentation. These characteristics make diode laser-assisted persulfate activation a promising alternative for sulfate radical-based advanced oxidation processes.

The present study demonstrates that diode laser-assisted persulfate activation is an effective approach for the degradation and mineralization of pyrogallol in aqueous solution. The developed oxidation system exhibited behavior consistent with the established mechanisms of sulfate radical-based advanced oxidation processes reported in recent studies (Lee et al., 2020; Li et al., 2022). Under the optimized operating conditions, the process achieved 99.97% pyrogallol degradation and 89% TOC removal, confirming its high oxidation efficiency and substantial mineralization capability. These findings indicate that diode laser-assisted persulfate activation represents a promising and energy-efficient alternative for the treatment of refractory phenolic contaminants in aqueous environments.

DECLARATIONS

Author Contribution

Vahide Koyun: Investigation, Methodology, Data curation, Experimental work.Halil Atmaca: Formal analysis, Response Surface Methodology (RSM) analysis, Statistical analysis.İbrahim Küçükkara: Conceptualization of the diode laser system, Experimental setup, Validation, Review & Editing.A. Murat Gizir: Conceptualization, Supervision, Data interpretation, Writing – original draft, Writing – review & editing, Final approval of the manuscript.All authors read and approved the final version of the manuscript.

REFERENCES

1. Adak A, Das I, Mondal B, Koner S, Datta P, Blaney L (2019) Degradation of 2,4-dichlorophenoxyacetic acid by UV253.7 and UV/H_2O_2: Reaction kinetics and effects of interfering substances. Curr Res Green Sustainable Chem 5:53–60. https://doi.org/10.1016/j.crgsc.2018.12.001
2. Arifin M, Jusoh R, Abdullah H, Ainirazali N, Setiabudi H (2023) Recent advances in advanced oxidation processes (AOPs) for the treatment of nitro- and alkyl-phenolic compounds. Environ Res 229:115936. https://doi.org/10.1016/j.envres.2023.115936
3. Barquín C, Gomes A, Gorito A, Ribeiro A, Silva A, Ortiz I, Rivero MJ, Vilar VJP (2026) Strategies to improve degradation kinetics of light-driven advanced oxidation processes for micropollutant removal: Catalyst, radiation, and oxidant synergies. Chem Eng Sci 321:122888. https://doi.org/10.1016/j.ces.2025.122888
4. Buthiyappan A, Aziz ARA, Daud WMAW (2015) Recent advances and prospects of catalytic advanced oxidation process in treating textile effluents. Rev Chem Eng 32(1):1–47.

https://doi.org/10.1515/revce-2015-0034

5. Fujishima A, Zhang X, Tryk DA (2008) TiO_2 photocatalysis and related surface phenomena. Surf Sci Rep 63(12):515–582. https://doi.org/10.1016/j.surfrep.2008.10.001
6. Hamed M, Said R, Soliman H, Osman A, Martyniuk CJ (2024a) Immunotoxicological, histopathological, and ultrastructural effects of waterborne pyrogallol exposure on African catfish (Clarias gariepinus). Chemosphere 349:140792. https://doi.org/10.1016/j.chemosphere.2023.140792
7. Hamed M, Soliman H, Said R, Martyniuk CJ, Osman A, Sayed AE-DH (2024b) Oxidative stress, antioxidant defense responses, and histopathology: Biomarkers for monitoring exposure to pyrogallol in Clarias gariepinus. J Environ Manage 351:1198945. https://doi.org/10.1016/j.jenvman.2023.119845
8. Hamed M, Said REM, Martyniuk CJ, Soliman HAM, Sayed AE-DH, Osman AGM (2024c) Reproductive and endocrine-disrupting toxicity of pyrogallol in catfish (Clarias gariepinus). Environ Pollut 352:124104. https://doi.org/10.1016/j.envpol.2024.124104
9. Kumari P, Kumar A (2023) Advanced oxidation process: A remediation technique for organic and non-biodegradable pollutants. Results Surf Interfaces 11:100122. https://doi.org/10.1016/j.rsurfı.2023.100122
10. Lee J, von Gunten U, Kim J-H (2020) Persulfate-based advanced oxidation: Critical assessment of opportunities and roadblocks. Environ Sci Technol 54(6):3064–3081. https://doi.org/10.1021/acs.est.9b07082
11. Li N, Wu S, Dai H, Cheng Z, Peng W, Yan B, Chen G, Wang S, Duan X (2022) Thermal activation of persulfates for organic wastewater purification: Heating modes, mechanism and influencing factors. Chem Eng J 450:137976. https://doi.org/10.1016/j.cej.2022.137976
12. Litter MI (2005) Introduction to photochemical advanced oxidation processes for water treatment. In P. Boule (Ed.), The handbook of environmental chemistry (Vol. 2, Part M, pp. 325–366). Springer. https://doi.org/10.1007/b138188
13. Oturan MA, Aaron JJ (2014) Advanced oxidation processes in water/wastewater treatment: Principles and applications. A review. Crit Rev Environ Sci Technol 44(23):2577–2641. https://doi.org/10.1080/10643389.2013.829765
14. Pedrotti FL, Pedrotti LM, Pedrotti LS (2007) Introduction to optics, 3rd edn. Pearson Prentice Hall
15. Polat B, Özay Y, Bilici Z, Küçükkara İ, Dizge N (2020) Membrane modification with semiconductor diode laser to reduce membrane biofouling for external MBR system and modelling study. Sep Purif Technol 241:116747. https://doi.org/10.1016/j.seppur.2020.116747
16. Polat B, Yabalak E, Mutlu RN, Küçükkara İ, Gizir AM (2021) New system design for photocatalytic degradation using diode laser: Mathematical modelling, thermal and flowing analysis and kinetic study. J Environ Chem Eng 9(5):106209. https://doi.org/10.1016/j.jece.2021.106209
17. Rodríguez JL, Fuentes I, Aguilar CM, Valenzuela MA, Poznyak T, Chairez I (2018) Catalytic ozonation as a promising technology for application in water treatment. In Catalytic ozonation. IntechOpen.

https://doi.org/10.5772/intechopen.76228

18. Wacławek S, Lutze HV, Grübel K, Padil VVT, Černík M, Dionysiou DD (2017) Chemistry of persulfates in water and wastewater treatment: A review. Chem Eng J 330:44–62. https://doi.org/10.1016/j.cej.2017.07.132
19. Wei X, He M, Liu B, Zheng Q, Qu R, Wang Z, Mo L (2026) From oxidation to polymerization: Unraveling the fate of mixed phenolic compounds in the zero-valent iron-activated persulfate system. Sep Purif Technol. https://doi.org/10.1016/j.seppur.2026.138220
20. Zhang Y, Li Y, Tabassum S (2024) Nanocomposites for degradation of phenolic compounds from aqueous environments by advanced oxidation processes: A review. Environ Nanatechnol Monit Manage 61:105286. https://doi.org/10.1016/j.enmm.2024.105286

Figures

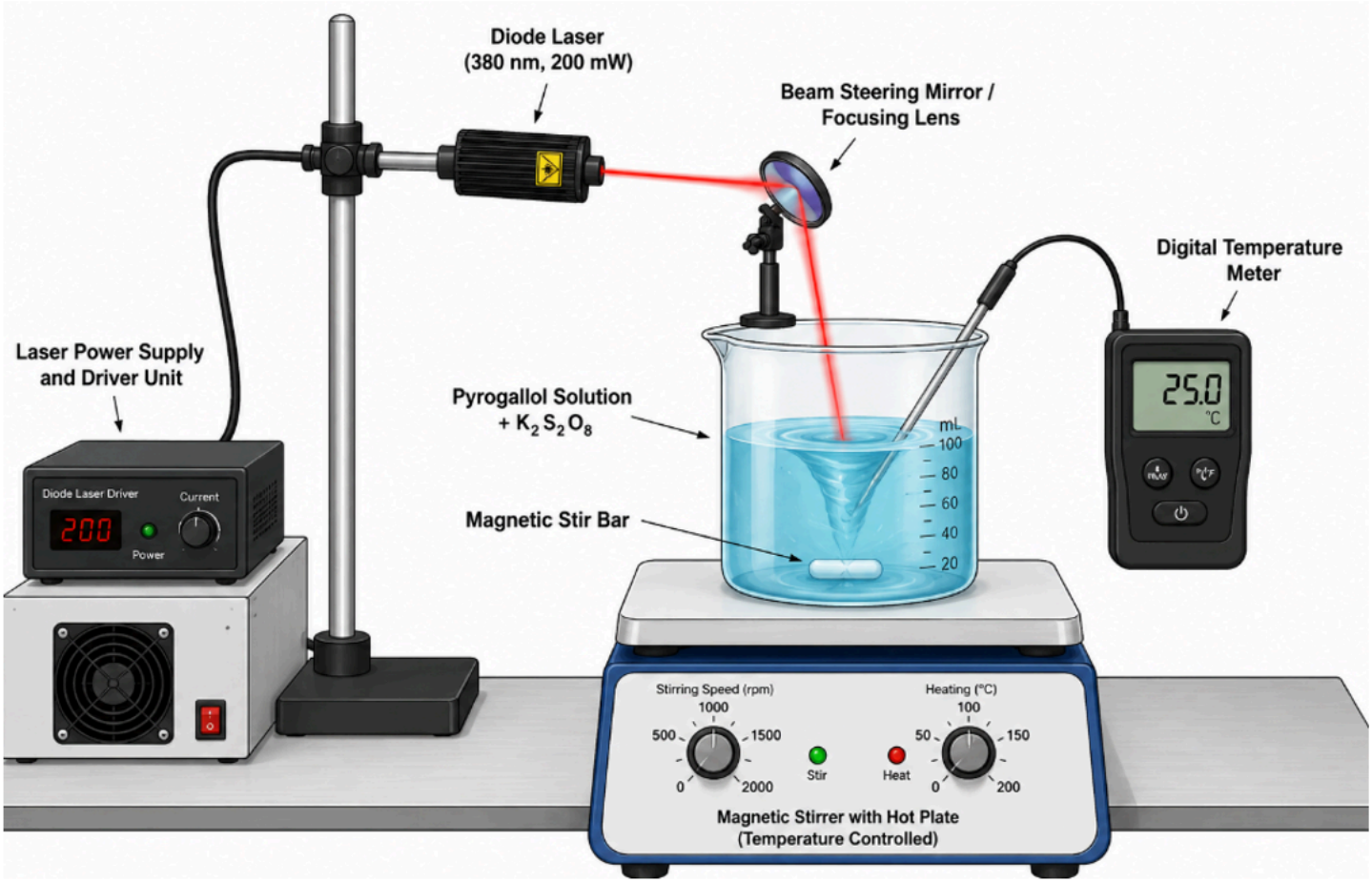


Figure 1

Schematic representation of the experimental apparatus used for the diode laser-assisted persulfate activation process.

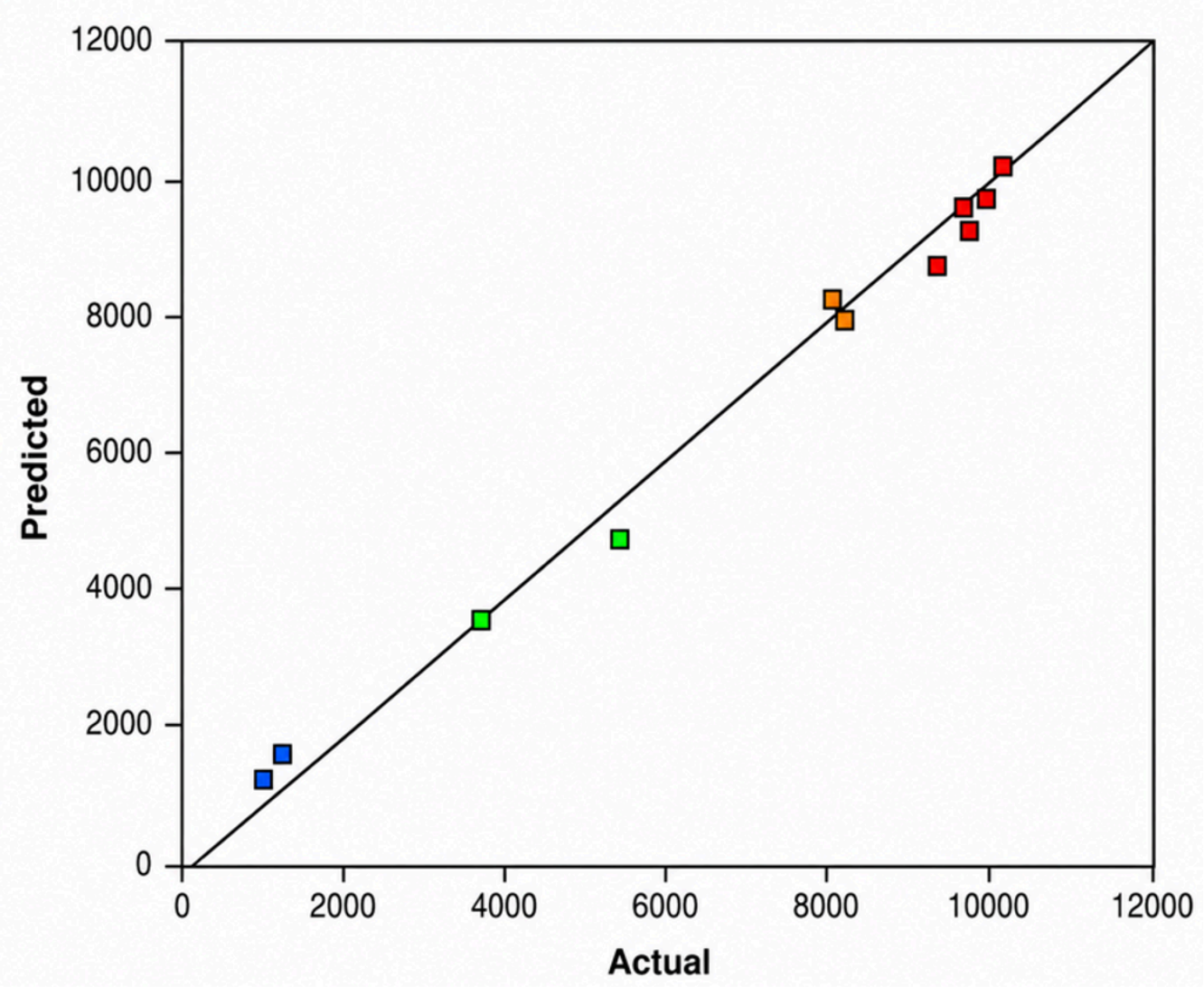


Figure 2

Correlation between the experimental and predicted pyrogallol degradation efficiencies obtained using the reduced quadratic response surface model.

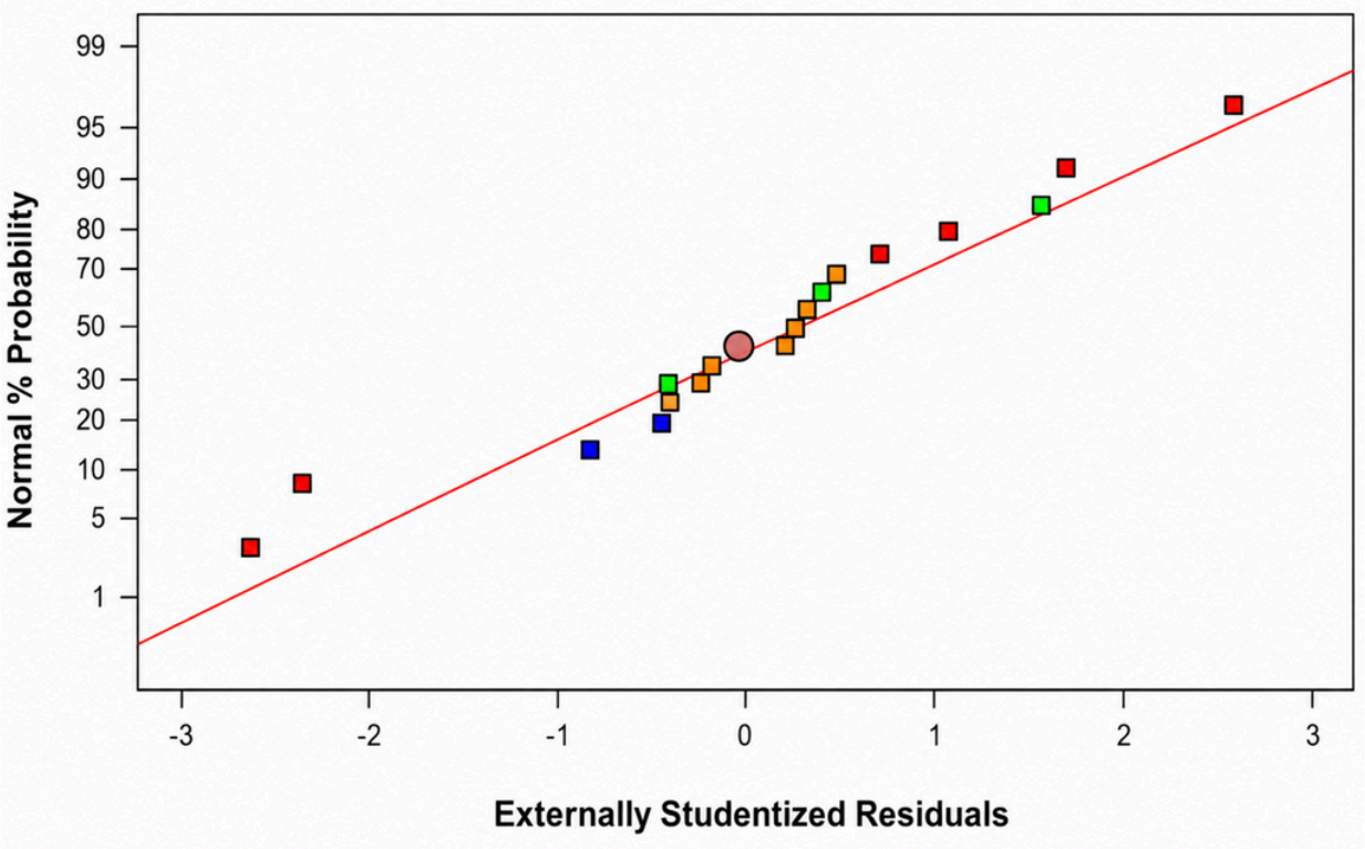


Figure 3

Normal probability plot of the externally studentized residuals, confirming the normal distribution of the residuals and the validity of the developed RSM model.

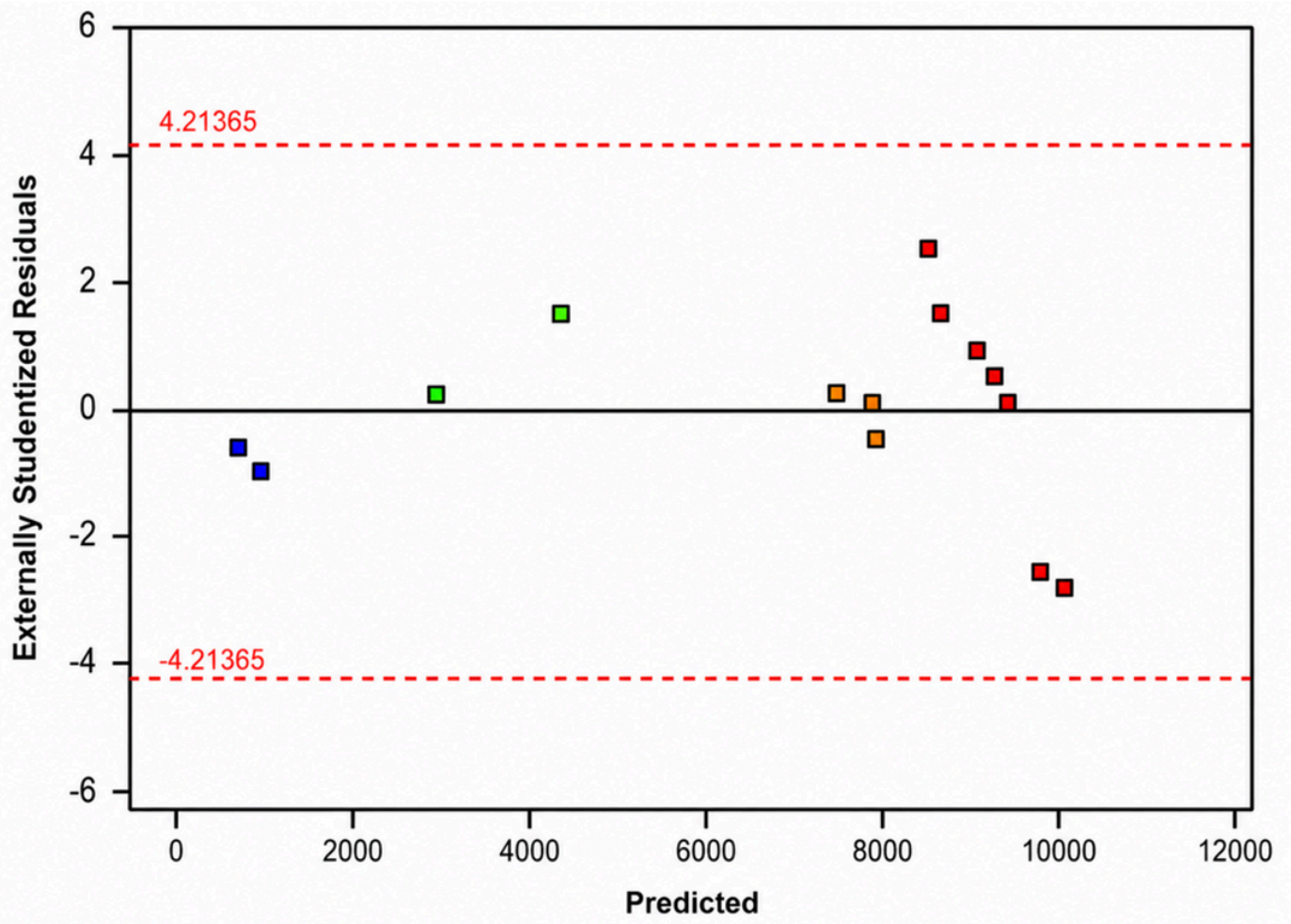


Figure 4

Residuals versus predicted values showing the random distribution of the residuals and constant variance of the developed regression model.

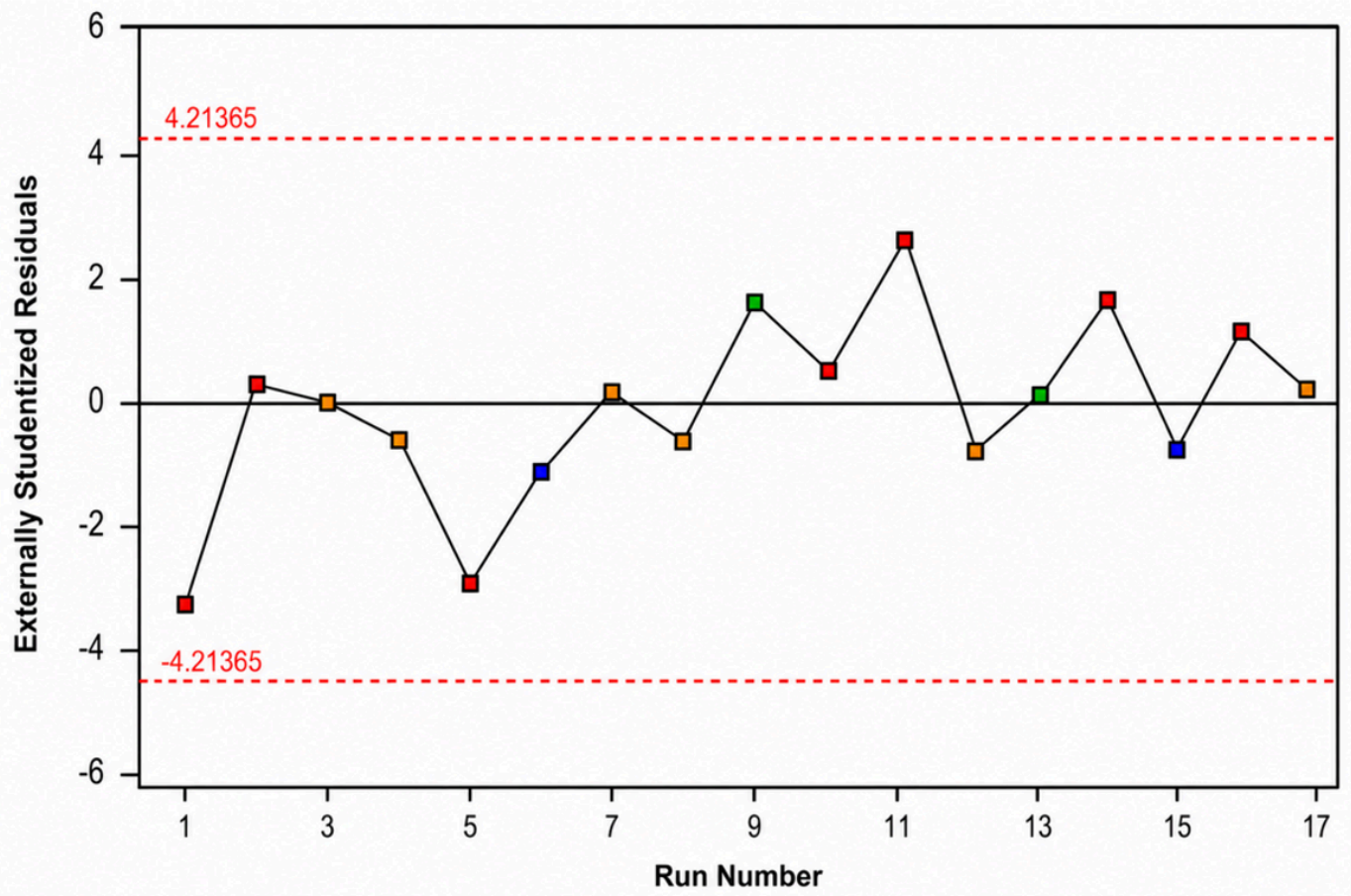


Figure 5

Residuals plotted against experimental run order demonstrating the random distribution of experimental errors and the absence of time-dependent systematic effects.

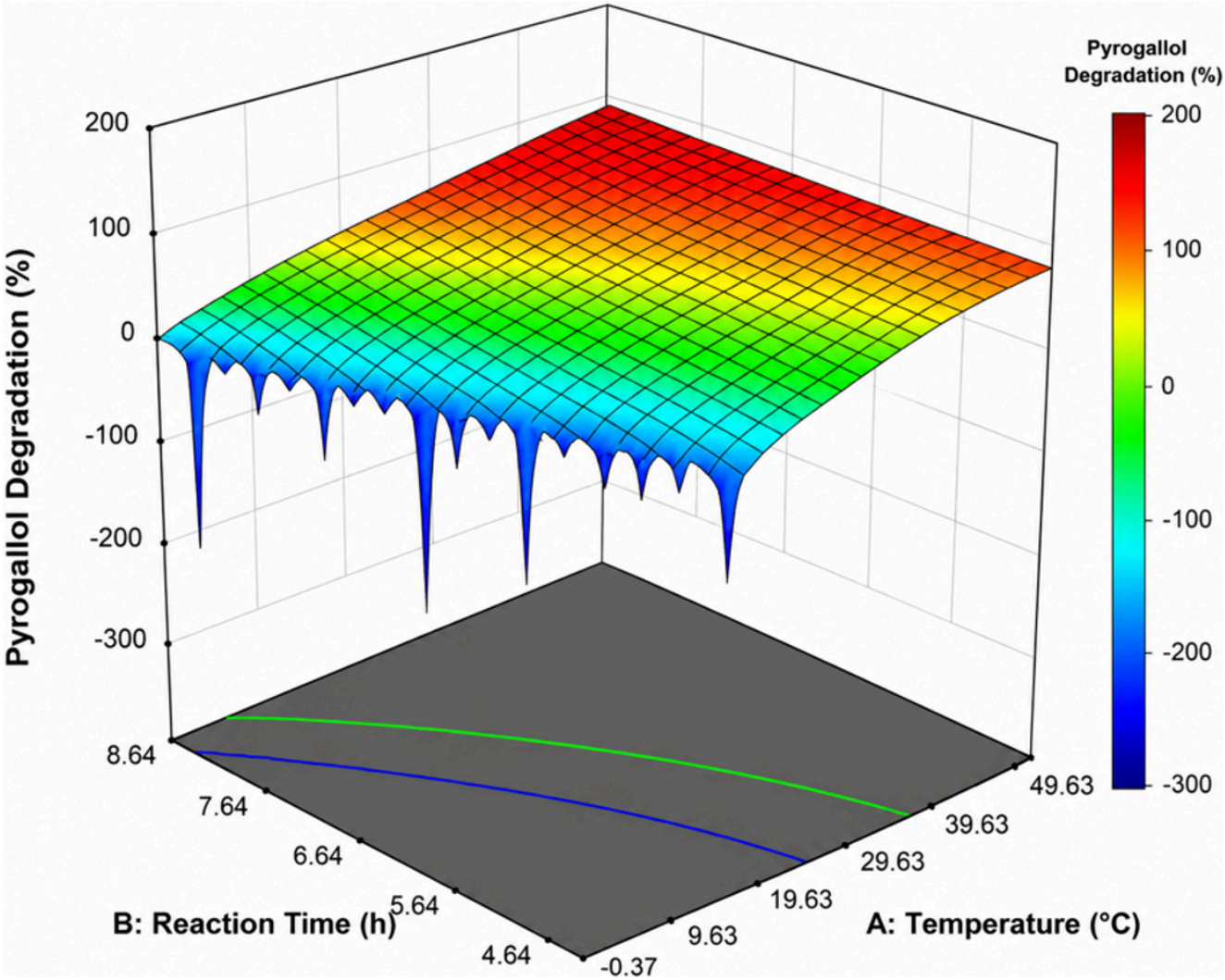


Figure 6

Response surface illustrating the combined effects of reaction temperature and reaction time on pyrogallol degradation while maintaining the persulfate dosage at its center level.

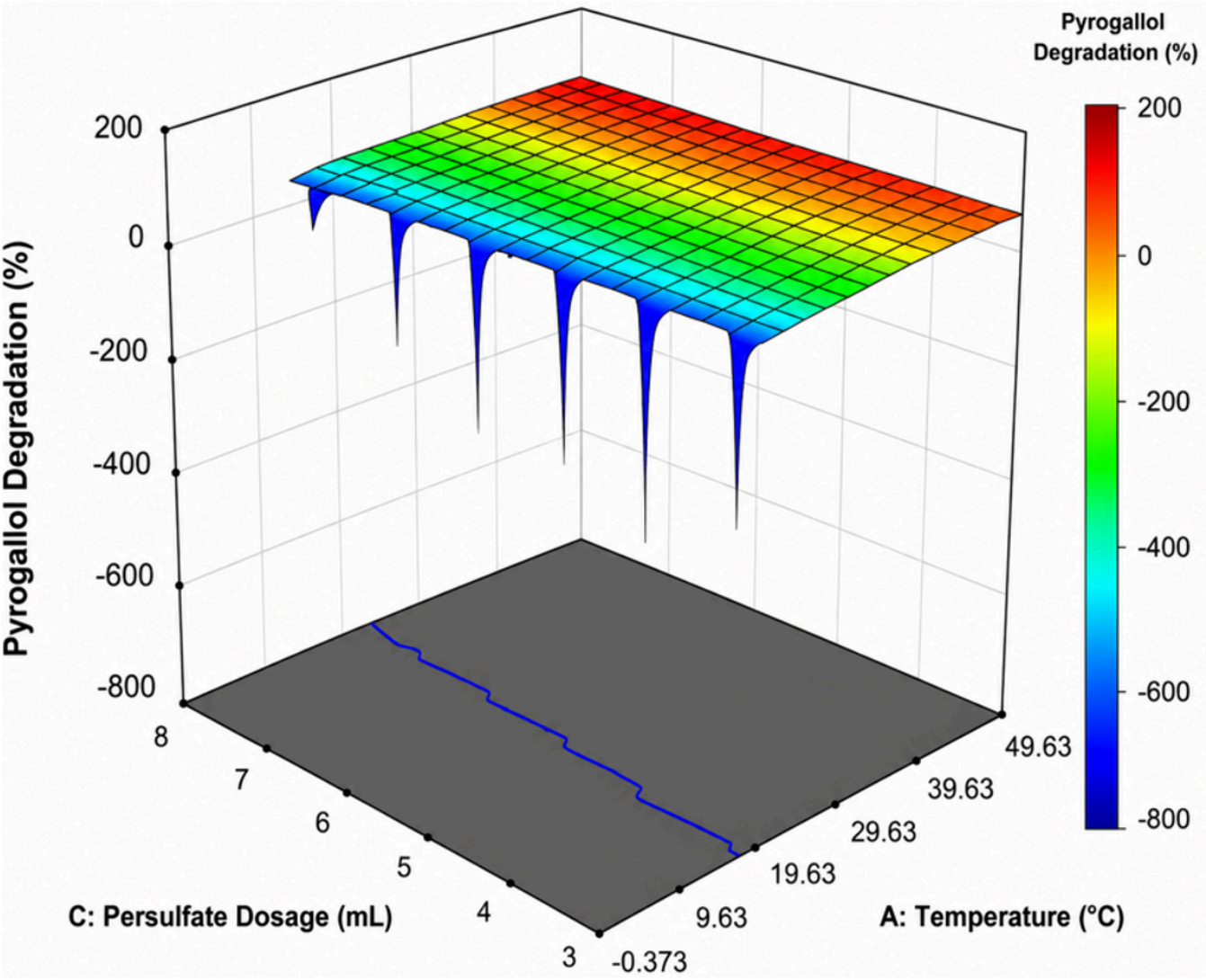


Figure 7

Three-dimensional response surface illustrating the interaction between reaction temperature and persulfate dosage on pyrogallol degradation efficiency.

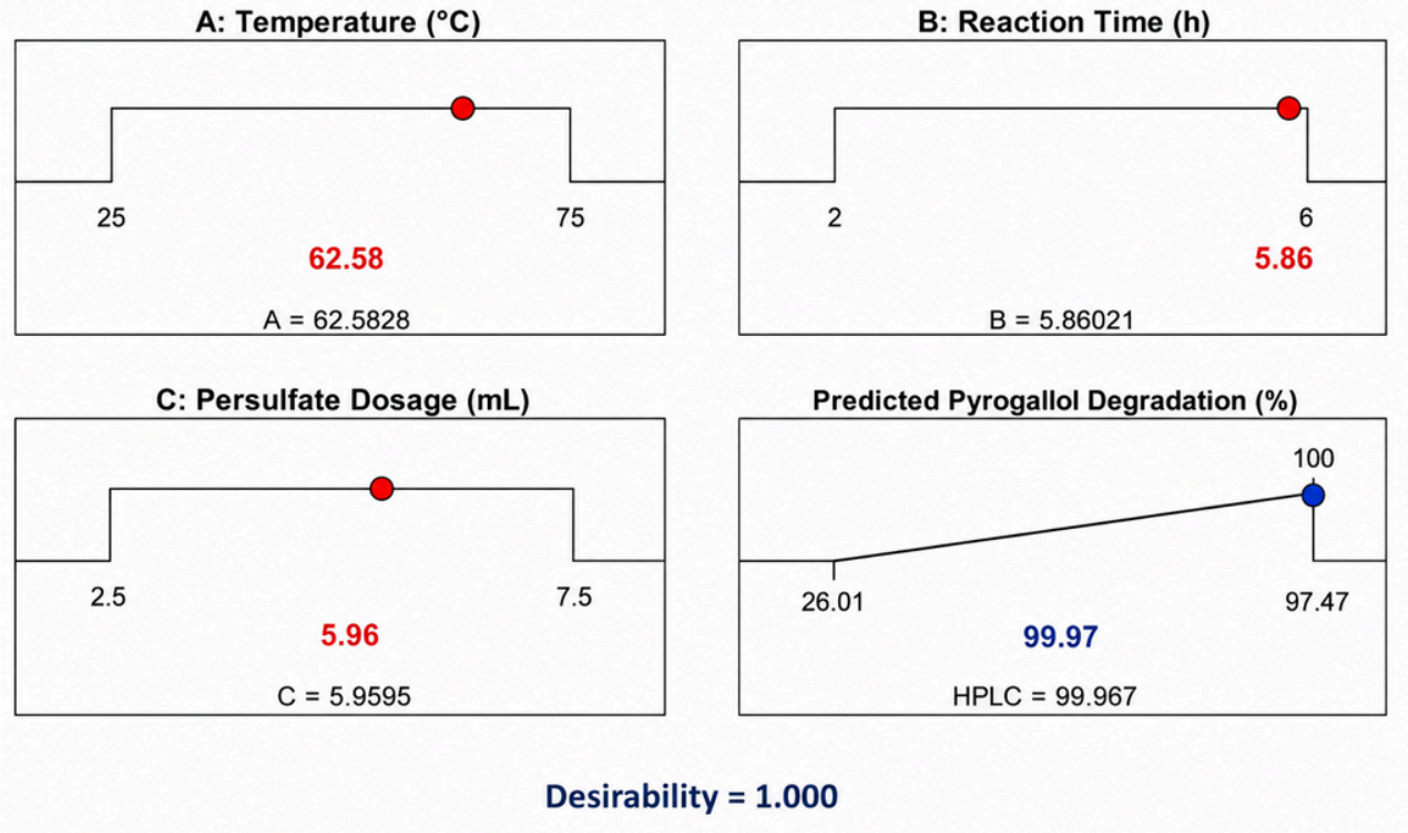


Figure 8

Desirability function plot showing the optimum operating conditions and the predicted maximum pyrogallol degradation efficiency.

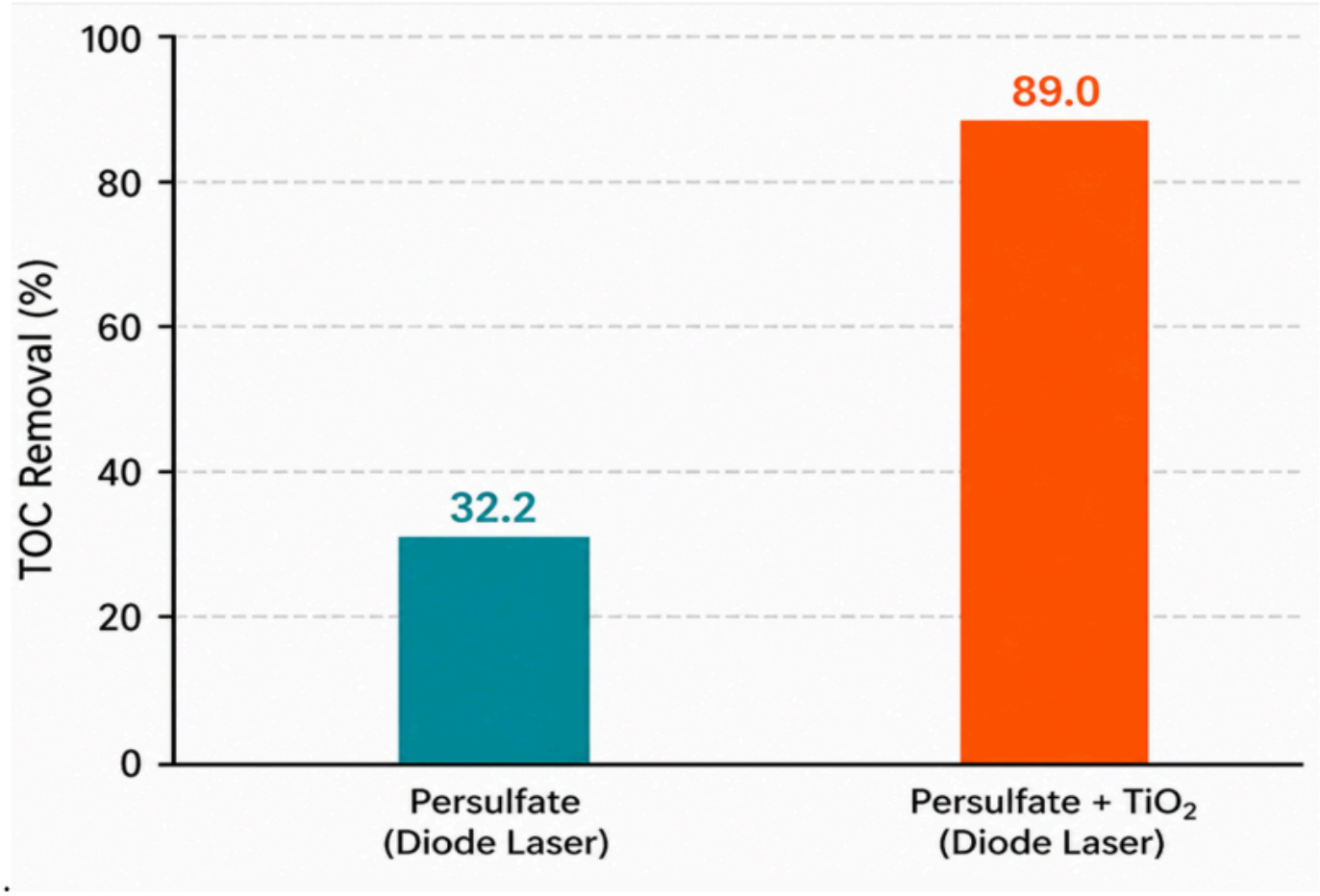


Figure 9

Effect of TiO_2 addition on TOC removal under different persulfate dosages

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- GraphicalAbstract.docx