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CATALYTIC OXIDATION OF GALLIC: MECHANISMS, KINETICS, AND BYPRODUCT ANALYSIS

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Abstract. *This paper investigates the catalytic oxidation of gallic acid utilizing Fenton and Fenton/UV reactions, focusing on elucidating the mechanisms, kinetics, and byproducts of the oxidation processes. Gallic acid, a naturally occurring phenolic compound, presents both health benefits and environmental challenges due to its persistence and potential toxicity. The Fenton and Fenton/UV reactions generate highly reactive hydroxyl radicals, initiating the oxidation of GA. The study explores the pseudo-first-order kinetics of GA degradation ($1.47 \cdot 10^{-4}$ M), examining variables such as [Fe^{2+}], [H_2O_2], pH, and temperature. Results indicate 50% degradation and 30% mineralization after 5 min, with improved COD removal over 60 min. Optimal conditions were identified as [H_2O_2] = $5 \cdot 10^{-4}$ M, [Fe^{2+}] = $1 \cdot 10^{-5}$ M, pH=3.0. The average rate constant ($k_{av}g$) was $5.7 \cdot 10^{-3}$ s^{-1}. Intermediate byproducts include hydroxylated derivatives and carboxylic acids. These findings highlight the relevance of advanced oxidation for environmental biotechnology.*

Keywords: Fenton, gallic acid, kinetics, oxidation, wastewater treatment.

INTRODUCTION

Gallic acid (GA), a trihydroxybenzoic acid prevalent in various plant materials and industrial effluents, is widely utilized in pharmaceutical, cosmetic, and food industries due to its antioxidant, antimicrobial, and anti-inflammatory properties [1]. However, its release into aquatic systems contributes to environmental contamination and necessitates effective treatment technologies [2].

Traditional wastewater treatment methods often fail to degrade such recalcitrant phenolic compounds effectively. Advanced oxidation processes (AOPs), particularly the Fenton and photo-Fenton reactions, have emerged as promising alternatives. These methods rely on the in situ generation of hydroxyl radicals (•OH), which are highly reactive and capable of mineralizing a wide spectrum of organic pollutants [3].

This study aims to investigate the kinetics, efficiency, and degradation mechanisms of GA oxidation via Fenton and Fenton/UV processes, with an emphasis on intermediate byproduct formation and potential integration with microbiological

treatments.

MATERIALS AND METHODS

Reagents and Reaction Conditions

Gallic acid ($C_7H_6O_5$) degradation was studied using Fenton (Fe^{2+}/H_2O_2) and photo-Fenton ($Fe^{2+}/H_2O_2/UV$) systems. Gallic acid (GA) solutions at an initial concentration of $1.47 \cdot 10^{-4}$ M were prepared using deionized water. Hydrogen peroxide (H_2O_2) served as the oxidizing agent, and ammonium iron(II) sulfate ($(NH_4)_2SO_4 \cdot Fe(SO_4) \cdot 6H_2O$) provided the ferrous ions. Hydroxyl radicals were generated through the classical Fenton reaction:

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

Experiments were conducted at room temperature (25 ± 1 °C) in a batch reactor. The solution pH was adjusted to 3.0 using sulfuric acid (H_2SO_4), based on the optimal acidic condition for Fenton and Fenton/UV reactions (Bautista et al., 2008). For the Fenton/UV process, a UV lamp emitting at 254 nm was used to irradiatethe reaction mixture to enhance •OH radical generation. Samples were withdrawn at fixed time intervals for analysis.

The concentration of gallic acid was monitored by UV-Vis spectrophotometry at 265 nm. Chemical oxygen demand (COD) was measured according to standard methods to assess the mineralization degree.

Analytical Methods

The degradation of GA was monitored via UV–Vis spectrophotometry at 265 nm. Mineralization was evaluated by chemical oxygen demand (COD) analysis, and byproduct identification was performed using high-performance liquid chromatography (HPLC), following methods reported in prior studies [4].

Kinetic Modeling

The degradation of gallic acid was modeled by pseudo-first-order kinetics, with the rate equation:

$$d[C]/dt = -k_{obs}\,[C]$$

where:

[C] is the concentration of gallic acid at time t

k_{obs} is the observed pseudo-first-order rate constant (s^{-1})

Integration between $t = 0$ and $t = t$ yields:

$$ln([C_0]/[C_t]) = k_{obs} \cdot t$$

where:

$[C_0]$ and $[C_t]$ are the initial and time-dependent concentrations of GA, respectively.

The half-life $\tau_{1/2}$ of GA under these conditions is given by:

$$\tau_{1/2} = ln(2) / k_{obs}$$

The average reaction rate during the half-life was calculated as:
$r_{avg} = \Delta C / \Delta t = ([C_0] - [C\tau_{1/2}]) / \tau_{1/2}$

Average reaction rates were derived from concentration versus time data, enabling assessment of overall degradation efficiency.

RESULTS AND DISCUSSIONS

Gallic Acid Degradation Kinetics

The oxidation of gallic acid (GA) by Fenton and Fenton/UV processes resulted in rapid degradation. Under optimized conditions, approximately 50% of GA was degraded and 30% mineralized within the first 300 s. After 60 min, the chemical oxygen demand (COD) removal increased slightly, indicating prolonged oxidation of intermediates The average reaction rate was calculated as $6.7 \cdot 10^{-7}$ $M \cdot s^{-1}$, and the pseudo-first-order rate constant was determined to be $5.7 \cdot 10^{-3}$ s^{-1}, with a corresponding half-life ($\tau_{1/2}$) of 118 s.

These results are consistent with earlier studies reporting that optimal Fenton oxidation occurs at low pH values (around 3.0) due to the maximum stability of Fe^{2+} ions and effective generation of •OH radicals [3]. UV irradiation in the photo-Fenton process further enhanced the oxidation efficiency by photoreducing Fe^{3+} back to Fe^{2+} and generating additional •OH radicals through photolysis of H_2O_2 [5].

The intermediates detected included hydroxylated compounds and low molecular weight acids such as oxalic acid, formic acid, and acetic acid. These findings suggest both hydroxylation and ring cleavage mechanisms are active. The table below summarizes the kinetic parameters, which were obtained by plotting $\ln([C_0]/[C_t])$ versus time and fitting a linear regression to experimental data.

Table 1. Kinetic parameters and experimental conditions

Parameter	Value	Units	Notes
Initial GA concentration (C_0)	$1.47 \cdot 10^{-4}$	M	Set experimentally
$[H_2O_2]$	$5 \cdot 10^{-4}$	M	Optimal oxidant dose
$[Fe^{2+}]$	$1 \cdot 10^{-5}$	M	Catalyst
pH	3.0	-	Optimal acidic condition
Rate constant ($k_{av}g$)	$5.7 \cdot 10^{-3}$	s^{-1}	Pseudo-first-order
Half-life ($\tau_{1/2}$)	118	s	Calculated via ln(2)/k
Average reaction rate ($\Delta c/\Delta t$)	$6.7 \cdot 10^{-7}$	$M \cdot s^{-1}$	Degradation velocity
Degradation at 5 min	50%	%	Spectrophotometric analysis
Mineralization at 5 min	30%	%	COD analysis
COD removal at 60 min	~55%	%	Final removal efficiency

Byproduct Formation and Oxidation Mechanism

Analysis of the reaction intermediates revealed the formation of hydroxylated aromatic compounds and short-chain aliphatic acids, including oxalic, formic, and acetic acids. These findings indicate a sequential degradation pathway involving initial hydroxylation of the aromatic ring, followed by oxidative ring cleavage and

mineralization to CO_2 and H_2O [4].

The regeneration of Fe^{2+} ions by GA and its oxidized products, such as quinones and semiquinone radicals, suggests a self-sustaining mechanism where GA acts both as a substrate and a reducing agent. This process not only sustains the catalytic cycle but also enhances pollutant degradation efficiency [4,5]. Figure 1 illustrates the proposed mechanism of GA oxidation under Fenton conditions, highlighting the formation of hydroxylated intermediates, ring-opening reactions, and mineralization steps. This mechanism aligns with prior research on phenolic compound degradation via Fenton chemistry [5].

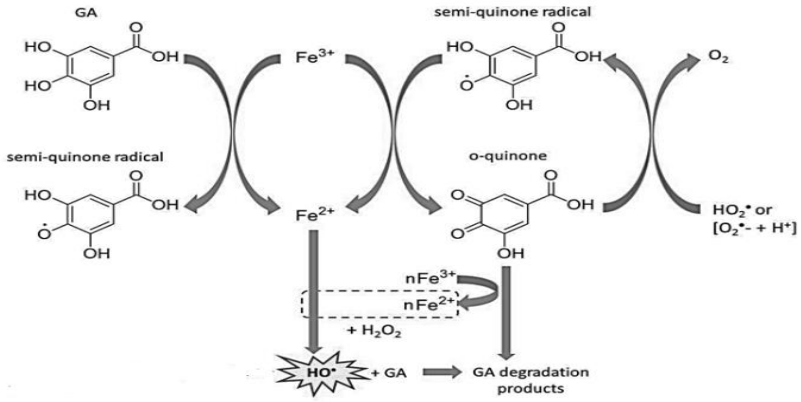

Figure 1. Oxidation mechanism of gallic acid under Fenton conditions

The mechanism behind involves initial hydroxylation of the aromatic ring, followed by ring opening and formation of short-chain organic acids. Complete mineralization results in the production of CO_2 and H_2O.

MICROBIOLOGICAL ASPECTS AND FUTURE PERSPECTIVES

While Fenton-based processes provide rapid and efficient chemical degradation, they may not achieve complete mineralization of all byproducts. Consequently, integrating biological post-treatment can significantly enhance the overall treatment performance. Microorganisms such as Pseudomonas putida, Aspergillus niger, and Bacillus subtilis are known to degrade GA and its oxidation products through enzymatic systems involving laccases, tannases, and dioxygenases [6,7]. Studies have shown that low-molecular-weight acids, such as those formed during Fenton oxidation, are readily biodegradable under aerobic conditions by heterotrophic bacteria commonly found in activated sludge systems [7,8]. In this context, hybrid chemical-biological systems emerge as sustainable solutions for industrial wastewater treatment.

The integration of advanced oxidation processes with biological treatment has already been successfully applied in various studies, demonstrating improved

mineralization rates and reduced toxicity of effluents [7]. Future work should focus on optimizing operational parameters, selecting robust microbial consortia, and evaluating potential toxicity of intermediates to ensure safe and effective full-scale application.

CONCLUSIONS

This study demonstrated that Fenton and photo-Fenton processes are effective for the degradation of gallic acid in aqueous systems. The oxidation followed pseudo-first-order kinetics, with rapid initial degradation and significant mineralization observed under optimal conditions. Identified intermediates included hydroxylated aromatic compounds and short-chain acids, which can serve as substrates for subsequent microbial degradation.

The findings highlight the potential for integrating chemical oxidation with biological treatment in wastewater remediation strategies. Such hybrid systems can maximize removal efficiency while aligning with principles of environmental sustainability and green chemistry.

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REFERENCES

1. MOCANU, L., GRIGORAS, C., GONTA, M. Gallic acid degradation in aqueous solution by Fenton's reagent. In: *International Symposium "The Environment and The Industry", SIMI 2024, Book of Abstracts, section Sustainable Environmental Technologies*, 2024, pp. 55-56.
2. GAO, J., HU, J., HU, D., & YANG, X. A. Role of Gallic Acid in Oxidative Damage Diseases: A Comprehensive Review. In: *Natural Product Communications, 2019, 14(8), 1934578X1987417*. http://10.1177/1934578x19874174
3. GONTA, M., MOCANU, L., DUCA, Gh. Redox technologies in wastewater treatment for removal of pharmaceutical (Cephalexin) contaminants. In: *Fundamental and Biomedical Aspects of Redox Processes.* Hershey: 2023, pp. 400-416. ISBN 978-166847200-2, 978-166847198-2. DOMINGUEZ, C. M., et al. Catalytic degradation of gallic acid by Fenton-like processes: A mechanistic insight. In: *Environmental Technology*, 2018, 39(7), pp.877–885.
4. TABELINI, C. H. B., LIMA, J. P. P., & AGUIAR, A. Gallic acid influence on azo dyes oxidation by Fenton processes. In: *Environmental Technology*, 2021, 43(22), 3390–3400.
5. FUCHS, G., BOLL, M. ȘI HEIDER, J. Microbial degradation of aromatic compounds—from one strategy to four. In: *Nature Reviews Microbiology*, 2011, 9(11), pp.803–816.
6. ZHANG, L., LIU, Y. & YANG, M. Recent advances in integration of advanced oxidation processes with biological treatment for wastewater treatment. In: *Chemical Engineering Journal*, 2019, 376, 120910. https://doi.org/10.1016/j.cej.2018.12.079
7. RAMAKRISHNAN, A. & SHANMUGAM, S. Biodegradation of phenolic compounds. In: *International Journal of Environmental Science and Technology*, 2014, 11(5), pp.1421–1430.