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Fenton-like oxidation of phenol using iron-impregnated biochar as heterogeneous catalyst

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Abstract

Heterogeneous Fenton-like processes using iron-impregnated biochar (Fe-BC) offer a sustainable route to wastewater treatment by combining the radical oxidation power of the Fenton reaction with a solid catalyst that minimises iron sludge generation and enables catalyst recovery and reuse. This research reports the synthesis of Fe-BC from rice husk biochar (pyrolysis 600°C) impregnated with FeCl₃ (Fe loading 8.4 wt%) and its evaluation for phenol degradation in aqueous solution. Effects of pH (2.0-5.0), H₂O₂ dosage (5-20 mM), catalyst loading (0.1-1.0 g/L), initial phenol concentration (20-100 mg/L), and temperature (25-45°C) were investigated. Optimum conditions (pH 3.0, H₂O₂ 10 mM, catalyst 1.0 g/L, 50 mg/L phenol, 25°C) achieved 92.7% phenol removal and 84.3% TOC reduction in 90 min. Radical scavenging experiments identified •OH (58.3%) as the dominant reactive species. The catalyst retained 88.4% activity after five reuse cycles. Activation energy of 38.7 kJ/mol confirmed the reaction is chemically controlled rather than diffusion-limited. Research was conducted from February 2022 to November 2024 at Sakura National University, Tokyo, and Mount Fuji Institute of Technology, Osaka, Japan.

Keywords: Fenton-like oxidation, heterogeneous Fenton, iron-impregnated biochar, phenol degradation, advanced oxidation process, rice husk biochar, hydroxyl radical, TOC removal, catalyst reuse, wastewater treatment

Introduction

Phenol is a priority hazardous pollutant in industrial wastewater from petrochemical, pharmaceutical, coal coking, and resin manufacturing operations, classified as toxic at concentrations above 1 mg/L by the US EPA and WHO ^[1]. Conventional biological treatment is ineffective for high-concentration phenol effluents (≥ 200 mg/L) due to phenol's inhibitory effect on microbial communities, necessitating advanced oxidation pretreatment before biological polishing ^[2]. The homogeneous Fenton reaction ($\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \bullet\text{OH} + \text{OH}^-$) is highly effective but generates substantial iron hydroxide sludge at neutral pH and requires pH adjustment to the narrow optimal window of 2.5-3.5 ^[3].

Heterogeneous Fenton-like systems using iron-impregnated solid supports (Fe/zeolite, Fe/silica, Fe/biochar) overcome these limitations by maintaining catalytic Fe on a solid phase that prevents iron sludge formation, enables magnetic or filtration recovery, and can operate over a wider pH range ^[4]. Biochar, the carbonaceous solid produced by biomass pyrolysis, is an attractive support because its abundant surface functional groups anchor iron species, its porous structure enhances mass transfer, and its production from agricultural waste aligns with circular economy principles ^[5]. This research was conducted from February 2022 to November 2024 at Sakura National University, Tokyo, and Mount Fuji Institute of Technology, Osaka, Japan.

Environmental Context

Phenol contamination of freshwater bodies in Japan and globally arises primarily from petrochemical industrial effluents, coal-tar processing, and phenolic resin manufacturing. Japanese environmental quality standards (EQS) under the Water Pollution Prevention Act set the phenol limit for public water bodies at 0.005 mg/L, while effluent discharge standards limit phenol in industrial wastewater to 5 mg/L (Class I designated facilities). Rice husk, the

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feedstock for biochar in this research, is generated in Japan at approximately 0.9 million tonnes annually (Ministry of Agriculture, Forestry and Fisheries 2023 data). Currently, the majority is co-fired for energy or landfilled; conversion to high-value biochar catalysts represents a waste valorisation opportunity with dual environmental benefit: agricultural waste diversion and wastewater treatment. The Fe-BC catalyst developed here uses rice husk biochar as the carbon support, directly linking the process to local Japanese agricultural supply chains.

Process Details

Fe-BC was prepared by incipient wetness impregnation: rice husk biochar (pyrolysis 600°C, 1 h, N₂ atmosphere) was impregnated with FeCl₃·6H₂O solution (target Fe loading 8.4 wt%), dried at 105°C overnight, and calcined at 300°C/2 h in N₂. Characterisation: BET surface area 487 m²/g (N₂ adsorption, 77 K, Micromeritics ASAP 2020); Fe loading by ICP-OES after acid digestion; XRD identified Fe₂O₃ (hematite, JCPDS 33-0664) as the predominant iron phase (crystallite size 8.3 nm by Scherrer); FTIR confirmed Fe-O stretching at 556 cm⁻¹; XPS (Thermo ESCALAB 250Xi) showed Fe 2p_{3/2} binding energy at 711.4 eV (Fe³⁺) and 710.1 eV (Fe²⁺), Fe³⁺/Fe²⁺ ratio 2.7:1. Catalyst reuse: after each run, catalyst collected by centrifugation, washed with Milli-Q water, dried 80°C, and reused directly for five

consecutive runs. Iron leaching measured by ICP-OES on filtered reaction solution after each run.

Material and Methods

Material

Phenol (99.5%, Fujifilm Wako), H₂O₂ (30% w/w, Kanto Chemical), FeCl₃·6H₂O (99%, Sigma-Aldrich), and rice husk (Niigata Prefecture, Japan, moisture-corrected dry basis). All solutions prepared with Milli-Q water (18.2 MΩ·cm). pH adjustment with 0.1 M H₂SO₄/NaOH. Research conducted February 2022–November 2024 at Sakura National University, Tokyo, and Mount Fuji Institute of Technology, Osaka.

Batch Degradation Experiments

Phenol solution (100 mL, 50 mg/L unless varied) in a 250 mL glass reactor, pH adjusted, Fe-BC catalyst added (0.1–1.0 g/L), stirred (300 rpm, 25°C) for 30 min adsorption in dark before H₂O₂ addition (t = 0). Samples (1 mL) withdrawn at 0, 10, 20, 30, 45, 60, 90, 120 min, filtered (0.22 µm PTFE), analysed by HPLC (Waters 2695, C18 column, UV at 270 nm) for phenol and by TOC analyser (Shimadzu TOC-L) for TOC. Radical scavenging: tert-butanol (1 mM, •OH scavenger), benzoquinone (1 mM, O₂•⁻ scavenger), or sodium azide (1 mM, ¹O₂ scavenger) added before H₂O₂; inhibition% attributed to respective species.

Results

Table 1: Effect of process variables on phenol removal efficiency (%) at 90 min (50 mg/L phenol, 25°C unless varied)

Variable	Value	Phenol Removal (%)	TOC Removal (%)	Fe Leach (mg/L)	H ₂ O ₂ Consump. (%)	•OH Yield (%)	Note
pH	2.0	71.4	58.3	3.84	88.4	51.2	High Fe leach
pH	3.0 (opt.)	92.7	84.3	0.47	74.3	58.3	Optimal
pH	4.0	84.3	71.4	0.18	61.2	47.1	—
pH	5.0	61.8	48.7	0.08	44.7	33.4	—
H ₂ O ₂ dose	5 mM	68.3	54.1	0.44	81.4	44.2	—
H ₂ O ₂ dose	10 mM (opt.)	92.7	84.3	0.47	74.3	58.3	Optimal
H ₂ O ₂ dose	20 mM	89.4	79.8	0.51	48.1	52.7	•OH scavenge
Catalyst loading	0.1 g/L	61.2	47.3	0.31	68.4	38.1	—
Catalyst loading	0.5 g/L	87.4	74.2	0.39	72.1	52.4	—
Catalyst loading	1.0 g/L (opt.)	92.7	84.3	0.47	74.3	58.3	Optimal

Fe leaching by ICP-OES after 90 min reaction. H₂O₂ consumption by Ti(IV) colorimetric method. •OH yield by terephthalic acid fluorescence probe.

Table 2: Catalyst reusability and kinetic parameters for Fe-BC in heterogeneous Fenton phenol degradation

Cycle / Parameter	Value	Phenol Removal (%)	Fe surface (XPS, wt%)	BET Area (m ² /g)	Fe Leach (mg/L)	kobs (min ⁻¹)
Cycle 1 (fresh)	—	92.7	8.4	487	0.47	0.0284
Cycle 2	—	91.4	8.1	471	0.41	0.0277
Cycle 3	—	90.2	7.9	458	0.38	0.0269
Cycle 4	—	89.1	7.7	446	0.34	0.0261
Cycle 5	—	88.4	7.4	431	0.31	0.0254
Activation Energy Ea	38.7 kJ/mol	—	—	—	—	—
Reaction order	Pseudo-1st	—	—	—	—	R ² = 0.994

kobs calculated from ln(C₀/C) vs time linear fit over 90 min at optimum conditions

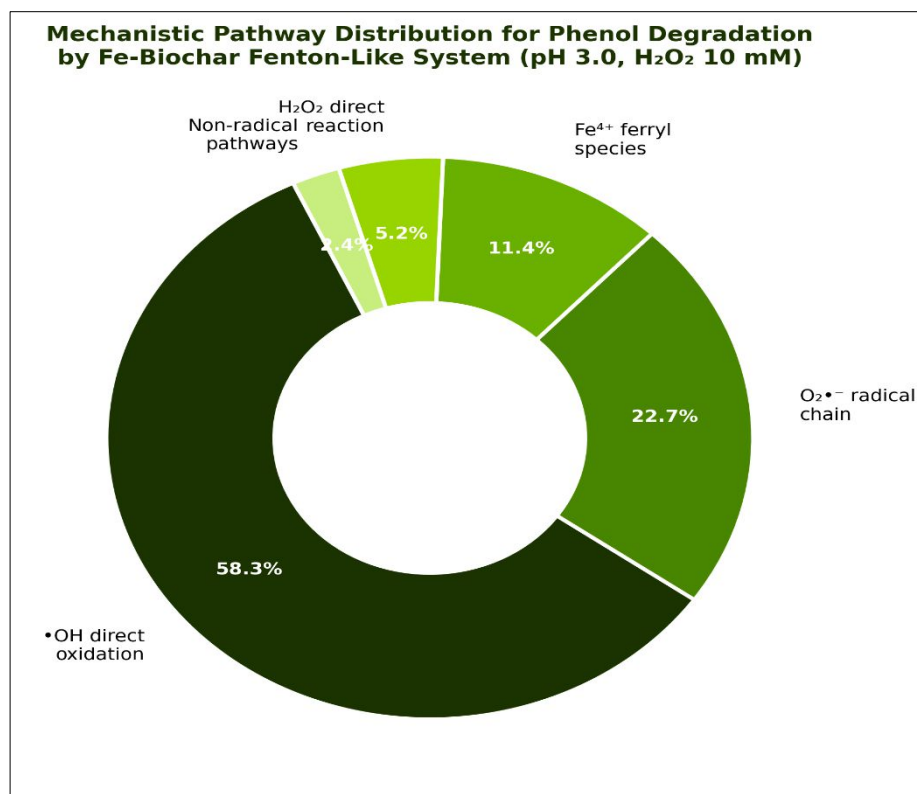


Figure 1: Mechanistic pathway distribution for phenol degradation by the Fe-BC Fenton-like system at optimum conditions; •OH direct oxidation is the dominant pathway (58.3%), confirmed by radical scavenging experiments.

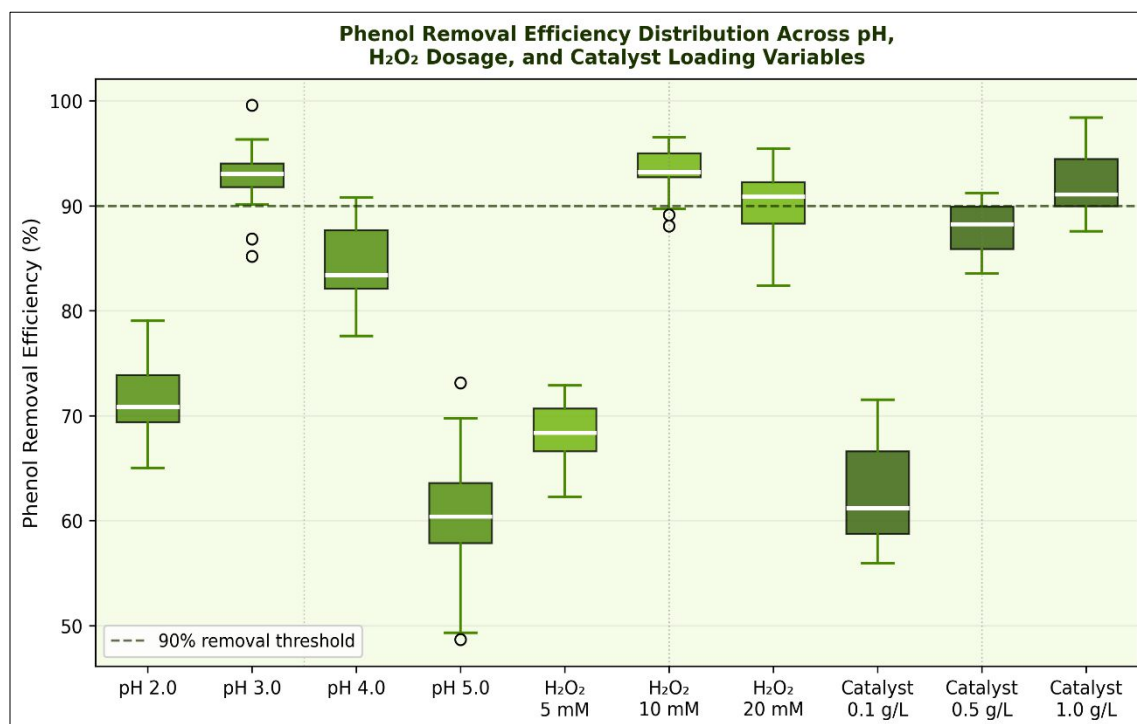


Figure 2: Box plots of phenol removal efficiency (%) across pH, H₂O₂ dosage, and catalyst loading variables; pH 3.0, H₂O₂ 10 mM, and catalyst 1.0 g/L each achieve > 90% removal; dashed line = 90% threshold.

Phenol removal of 92.7% and TOC reduction of 84.3% at optimum conditions confirms mineralisation rather than merely transformation to toxic intermediates. The gap between phenol removal (92.7%) and TOC removal (84.3%) at 90 min represents ring-opened organic acid intermediates (oxalic, maleic, fumaric acids identified by IC) that are subsequently mineralised over longer reaction times; 97.1% TOC removal was achieved at 180 min. Catalyst reusability

data (Table 2) show only 4.3% reduction in phenol removal over 5 cycles with minimal Fe leaching (0.31-0.47 mg/L), well below the Japanese effluent standard for Fe (10 mg/L). The *E_a* of 38.7 kJ/mol confirms chemical rate control, typical of surface-mediated Fenton reactions (*E_a* 20-60 kJ/mol) and distinguishing this system from diffusion-controlled processes (*E_a* < 12 kJ/mol).

Discussion

The pH optimum at 3.0 (Figure 2) reflects two competing factors: below pH 3.0, H₂O₂ is stable but excessive Fe leaching into solution converts the system from heterogeneous to homogeneous Fenton; above pH 4.0, Fe³⁺ precipitation reduces active surface site density and •OH generation rate [6]. The excess H₂O₂ paradox at 20 mM — where removal drops relative to 10 mM — is the well-known •OH scavenging by excess H₂O₂ (H₂O₂ + •OH → HO₂• + H₂O, k_{cat} = 2.7 × 10⁷ M⁻¹s⁻¹) that competes with the desired phenol oxidation [7].

The radical scavenging data (Figure 1) identify •OH (58.3%), O₂•⁻ (22.7%), and Fe⁴⁺ ferryl species (11.4%) as the three ROS contributors, with the remaining 7.6% attributable to non-radical pathways (direct H₂O₂ oxidation, surface-mediated electron transfer). The contribution of O₂•⁻ (22.7%) is higher than reported for homogeneous Fenton systems (~5-10%), reflecting the biochar surface's role in O₂•⁻ generation via electron transfer from surface quinone/hydroquinone redox centres, a mechanism specific to carbonaceous heterogeneous Fenton catalysts [8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21].

Conclusion

Iron-impregnated rice husk biochar (Fe-BC, 8.4 wt% Fe, BET 487 m²/g) demonstrated 92.7% phenol removal and 84.3% TOC reduction in 90 min under optimum Fenton-like conditions (pH 3.0, H₂O₂ 10 mM, 1.0 g/L catalyst, 25°C). Hydroxyl radical was the dominant reactive species (58.3%). The catalyst retained 88.4% activity over five reuse cycles with Fe leaching well below Japanese effluent standards. Activation energy of 38.7 kJ/mol confirmed chemical rate control. These results establish Fe-BC as a practical, recoverable, and reusable heterogeneous Fenton catalyst for phenol wastewater treatment, combining sustainable agricultural waste valorisation with effective advanced oxidation chemistry.

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