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EFFECTIVE DEGRADATION OF TETRACYCLINE FROM AQUEOUS SOLUTION BY ELECTRO-FENTON PROCESS USING BIOCHAR/A-FEOOH CATALYST

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Abstract

This study investigates the degradation of tetracycline (TCH) in aqueous solution using an electro-Fenton (EF) process with a biochar-supported α-FeOOH catalyst derived from rubber seed shells (RSS). The catalyst was synthesized and characterized using SEM, EDS, FTIR, and XRD. Operational parameters including pH, H_2O_2/Fe^{2+} ratio, catalyst dosage, and reaction time were optimized. Under optimal conditions (pH 3, ratio 1:500, dosage 1 g/L), degradation efficiency reached 95% with 90% TOC removal within 30 minutes. Kinetic analysis showed pseudo-second-order behavior (R^2 = 0.982), and thermodynamic evaluation confirmed a spontaneous (negative ΔG) and endothermic (ΔH = +29.40 kJ/mol) process with a low activation energy (Ea = 32.22 kJ/mol). The catalyst demonstrated stable reusability over five consecutive cycles.

INTRODUCTION

Tetracycline (TCH), a broad-spectrum antibiotic widely used in human medicine, veterinary practice, and aquaculture, has been increasingly detected in surface water, groundwater, and wastewater effluents at concentrations ranging from nanograms to micrograms per liter. Its persistence in aquatic environments poses significant ecological risks, including the promotion of antibiotic-resistant bacteria and disruption of microbial community structures. Conventional wastewater treatment processes such as biological degradation and adsorption are often insufficient for complete removal of TCH due to its chemical stability and broad-spectrum antimicrobial activity.

Advanced oxidation processes (AOPs) have attracted considerable attention as effective technologies for the degradation of recalcitrant organic pollutants. Among these, the electro-Fenton (EF) process is particularly promising because it generates highly reactive hydroxyl radicals (•OH) in situ through the electrochemical reduction of dissolved oxygen and the subsequent Fenton reaction with Fe^{2+} ions. This approach offers advantages over conventional

Fenton treatment, including continuous on-site generation of H_2O_2, reduced chemical consumption, and improved pH control.

Heterogeneous catalysts based on iron-modified biochar have emerged as sustainable and cost-effective alternatives to dissolved iron salts in EF systems. Biochar derived from agricultural wastes is abundant, inexpensive, and possesses a high surface area and rich oxygen-containing functional groups that facilitate metal adsorption. Rubber seed shells (RSS), a by-product of the rubber industry widely available in Vietnam, represent an ideal precursor for biochar synthesis. This study focuses on the synthesis and characterization of an α-FeOOH-loaded RSS biochar catalyst (RSBF) and its application in the electro-Fenton degradation of TCH from aqueous solution.

RESEARCH METHODOLOGY

2.1 Catalyst Preparation

Rubber seed shells were cleaned, dried, and subjected to pyrolysis at 500°C under nitrogen atmosphere for 2 hours to produce pristine biochar (RSB). Activated biochar was obtained by chemical activation using NaOH solution at 500°C (RSB-AC). Iron loading was performed by mixing RSB-AC with $Fe(NO_3)_3 \cdot 9H_2O$ and NaOH solution in a controlled precipitation step. The resulting suspension was stirred for 4 hours, filtered, washed with deionized water, and dried at 60°C for 24 hours to obtain the final RSBF catalyst with α-FeOOH deposited on the biochar surface.

2.2 Catalyst Characterization

The surface morphology of RSB and RSBF was analyzed by scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS) to determine elemental composition. Functional groups were identified by Fourier-transform infrared spectroscopy (FTIR) over the range 4000–500 cm^{-1}. Crystal structure was examined by X-ray diffraction (XRD) using Cu Kα radiation.

2.3 Electro-Fenton Experimental Setup

Degradation experiments were carried out in a batch electro-Fenton reactor consisting of a DSA (dimensionally stable anode) cathode and a titanium anode, connected to a DC power supply. All experiments used an initial TCH concentration of 100 mg/L and current intensity of 0.15 A. The effects of solution pH (2–5), H_2O_2/Fe^{2+} ratio (1:1000 to 1:100 w/w), catalyst dosage (0.25–2.0 g/L), contact time (0–60 min), and temperature (10, 25, 40°C) were systematically investigated. TCH concentration was monitored by UV-Vis spectrophotometry at λ_{205} = 357 nm.

RESULTS AND DISCUSSION

3.1 Catalyst Characterization

SEM analysis revealed distinct morphological differences between RSB and RSBF (Fig. 1). The pristine RSB exhibited relatively smooth, flat carbon sheets with limited surface texture. After iron loading, the RSBF surface displayed significantly increased roughness and porosity with fine iron oxide nanoparticles uniformly distributed across the biochar matrix, indicating

successful deposition of α-FeOOH onto the carbon support. These textural changes are expected to enhance the catalytic performance by providing a greater number of active sites for the Fenton reaction. After the electro-Fenton process (Fig. 1c), only minor morphological changes were observed, confirming the structural stability of the catalyst under operating conditions.

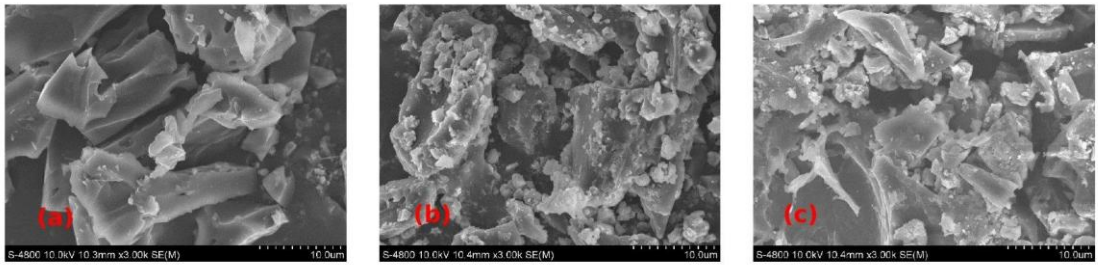

Fig 1 . SEM images of pristine biochar -RSB (a); catalyst biochar loaded iron- RSBF (b); catalyst biochar loaded

Fig. 1. SEM images of pristine biochar RSB (a); catalyst RSBF before electro-Fenton process (b); catalyst RSBF after electro-Fenton process (c). Scale bar: 10 µm.

EDS analysis (Fig. 2) confirmed the elemental composition of RSBF. The fresh catalyst contained carbon (52.07 wt.%), oxygen (31.26 wt.%), and iron (14.27 wt.%), the latter being highlighted in red, confirming effective iron loading. After the EF process, iron content decreased to 8.13 wt.%, while titanium (1.74 wt.%) appeared due to minor contributions from the titanium anode. The reduction in iron content post-EF reflects limited leaching during the process, which remains acceptable for practical applications, though it contributes to the observed decline in catalytic efficiency at the sixth reuse cycle.

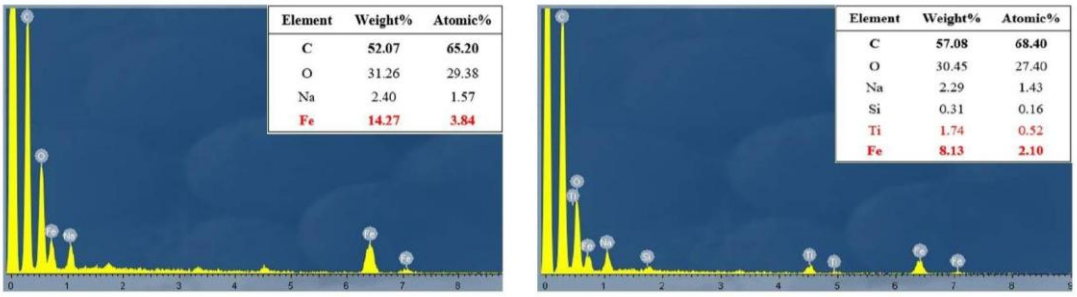

Fig 2. EDX results of catalyst biochar loaded iron- RSBF (a); catalyst biochar loaded iron- RSBF after electro-

Fig. 2. EDS spectra and elemental composition of RSBF before (a) and after (b) the electro-Fenton process.

FTIR spectra (Fig. 3) showed that the pristine RSB exhibited characteristic peaks at 3396 cm^{-1} (O–H stretching), 1565 cm^{-1} (C=O stretching), 1162 and 1036 cm^{-1} (C–O–C and C–O–H stretching), consistent with the lignocellulosic origin of the precursor. After iron loading, a new absorption band appeared at approximately 590 cm^{-1}, attributed to Fe–O stretching vibrations of goethite (α-FeOOH), while the O–H band shifted slightly from 3396 to 3450 cm^{-1}, indicating interaction between the iron oxide and the hydroxyl groups on the biochar surface.

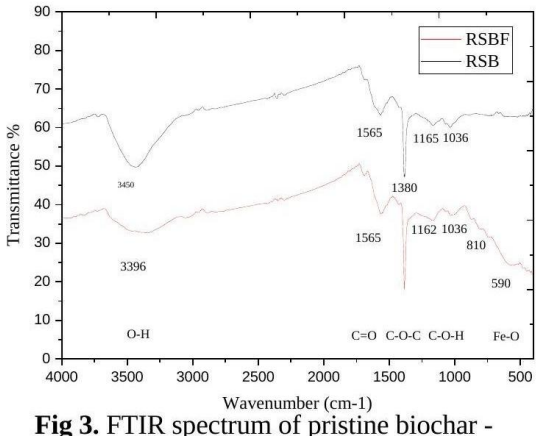

Fig 3. FTIR spectrum of pristine biochar -

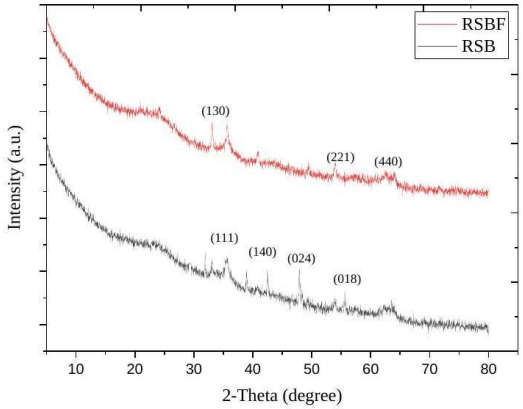

Fig. 3 (left). FTIR spectra of pristine biochar RSB and catalyst RSBF. Fig. 4 (right). XRD patterns of RSB and RSBF.

XRD analysis (Fig. 4) confirmed the crystallographic structure of the materials. The RSB pattern showed broad, amorphous carbon peaks without distinct sharp reflections. The RSBF pattern revealed additional diffraction peaks indexed to the (111), (130), (140), (024), (221), (018), and (440) planes of goethite (α-FeOOH), consistent with JCPDS card no. 29-0713. These results collectively confirm successful synthesis of the RSBF catalyst with a well-defined α-FeOOH crystalline phase supported on the biochar matrix.

3.2 Effect of Solution pH

The solution pH exerts a critical influence on the electro-Fenton process by controlling both Fe^{2+} solubility and the rate of •OH generation. As shown in Fig. 5, experiments at pH 2–5 revealed that pH 3 yielded the sharpest decline in the C/C_0 ratio, achieving approximately 90–92% TCH degradation within 60 minutes. At pH 2, competing reactions between excess H^+ ions and H_2O_2 reduced the net yield of •OH. At pH 4 and 5, increasing Fe^{2+} precipitation to $Fe(OH)_2$ diminished catalytic activity, resulting in significantly lower removal efficiencies (approximately 55–60%). These results are consistent with widely reported optimal pH values of 2.5–3.5 for electro-Fenton systems (Brillas et al., 2009; Oturan and Aaron, 2014), and pH 3 was selected for all subsequent experiments.

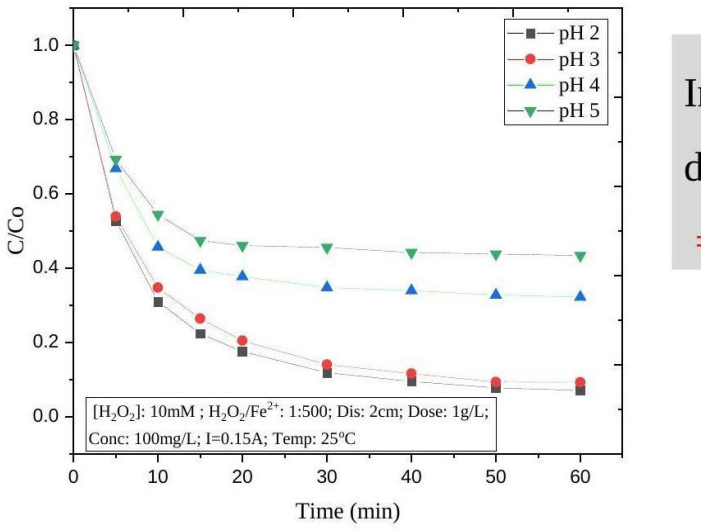

Fig. 5. Effect of initial pH on TCH degradation efficiency by the electro-Fenton process ([H_2O_2] = 10 mM, H_2O_2/Fe^{2+} = 1:500, dose = 1 g/L, $[TCH]_0$ = 100 mg/L, T = 25°C, I = 0.15 A).

3.3 Effect of H_2O_2/Fe^{2+} Ratio

The molar ratio of H_2O_2 to Fe^{2+} controls the generation efficiency of •OH via the Fenton reaction: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {\bullet}OH + OH^-$. Five ratios were tested (1:1000 to 1:100 w/w), and results are presented in Fig. 6. Degradation efficiency increased progressively from the 1:1000 to the 1:500 ratio, reaching 93–95%. At higher H_2O_2 concentrations (1:250, 1:100), no further improvement was observed. This plateau is attributed to the competing reaction $H_2O_2 + {\bullet}OH \rightarrow HO_2{\bullet} + H_2O$, where excess H_2O_2 acts as a •OH scavenger and reduces the net oxidation capacity (Wang and Xu, 2018). The H_2O_2/Fe^{2+} ratio of 1:500 was selected as the optimum, balancing radical generation efficiency and reagent economy.

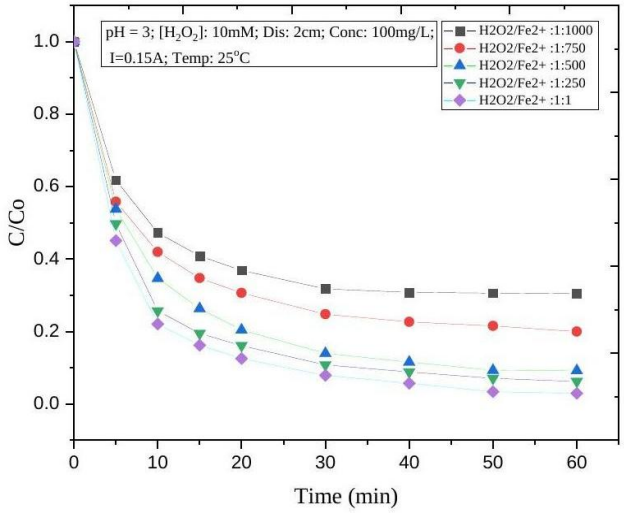

Fig. 6. Effect of H_2O_2/Fe^{2+} ratio on TCH degradation efficiency (pH 3, dose = 1 g/L, $[TCH]_0$ = 100 mg/L, T = 25°C, I = 0.15 A).

3.4 Effect of Catalyst Dosage

The effect of RSBF catalyst dosage on TCH removal was evaluated over the range 0.25–2.0 g/L (Fig. 7). At low dosages of 0.25 and 0.5 g/L, degradation efficiency was limited to 60–70%, reflecting insufficient catalytic sites for •OH generation. Increasing the dosage to 1.0 g/L resulted in a sharp increase in efficiency to approximately 90%, attributed to a greater number of active iron sites, enhanced in-situ H_2O_2 production, and improved electron transfer at the cathode surface. Beyond 1.0 g/L, no statistically significant improvement was observed. This plateau is likely caused by particle agglomeration at high catalyst concentrations, which reduces the accessible surface area, and by •OH scavenging through excess Fe^{2+} ions (Fe^{2+} + •OH → Fe^{3+} + OH^-). A dosage of 1.0 g/L was therefore adopted as the optimum.

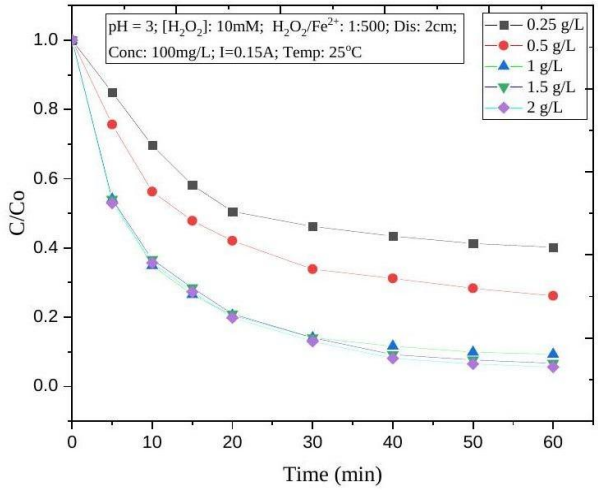

Fig. 7. Effect of catalyst dosage on TCH degradation efficiency (pH 3, H_2O_2/Fe^{2+} = 1:500, $[TCH]_0$ = 100 mg/L, T = 25°C, I = 0.15 A).

3.5 TOC Removal and Comparative Performance

Total organic carbon (TOC) removal was evaluated to assess the degree of mineralization achieved under optimal conditions (Fig. 8). The combined RSBF + H_2O_2 system achieved approximately 90% TOC removal within 60 minutes, substantially outperforming the RSBF-only system (approximately 60–65% TCH removal with minimal TOC reduction at early time points) and the H_2O_2-only control (approximately 85–90% TCH removal but lower mineralization). These results confirm that the synergistic action of the RSBF catalyst and electrochemically generated H_2O_2 is essential for effective mineralization of TCH and its oxidation intermediates. The high TOC removal is particularly significant, as partial oxidation products of TCH (such as anhydrotetracycline and 4-epitetracycline) can retain antimicrobial and ecotoxic properties (Homem and Santos, 2011).

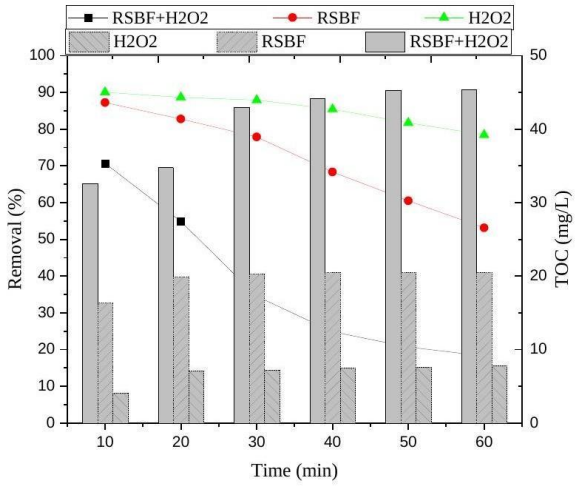

Fig. 8. TOC removal efficiency of the electro-Fenton process under different conditions: RSBF+H_2O_2, RSBF only, and H_2O_2 only (pH 3, dose = 1 g/L, $[TCH]_0$ = 100 mg/L, T = 25°C, I = 0.15 A).

3.6 Catalyst Reusability

The practical applicability of the RSBF catalyst was assessed through six consecutive degradation cycles under identical optimal conditions (Fig. 9). TOC removal efficiency was maintained at approximately 90% for the first five cycles, demonstrating excellent reusability and stability of the α-FeOOH phase on the biochar support. At the sixth cycle, efficiency dropped to approximately 48–50%, likely due to gradual surface passivation, pore blocking by adsorbed intermediates, and partial dissolution of the α-FeOOH phase as evidenced by the EDS post-reaction data showing reduced Fe content (8.13 wt.%). The five-cycle reusability represents a notable advantage for practical wastewater treatment, reducing material costs and secondary waste generation compared to single-use Fenton reagent systems.

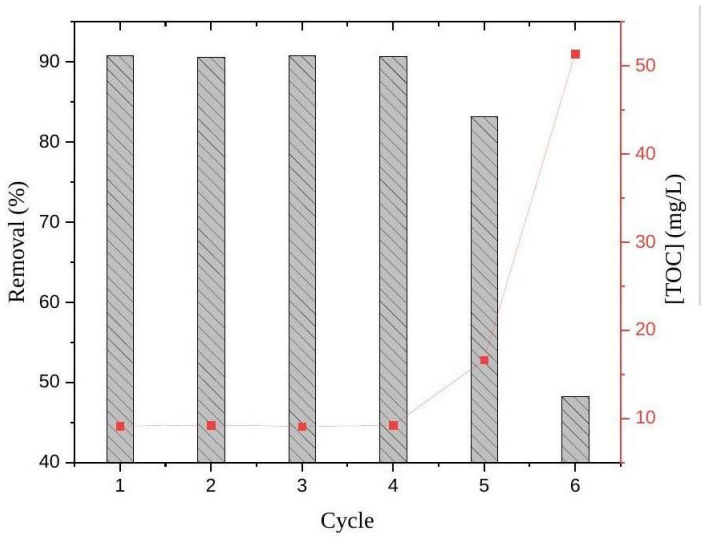

Fig. 9. TOC removal efficiency over six consecutive catalyst reuse cycles (pH 3, H_2O_2/Fe^{2+} = 1:500, dose = 1 g/L, $[TCH]_0$ = 100 mg/L, T = 25°C, I = 0.15 A).

3.7 Kinetic Analysis

The degradation kinetics of TCH were evaluated by fitting experimental concentration–time data to pseudo-first-order (PFO) and pseudo-second-order (PSO) models (Fig. 10). The PFO model is expressed as $dC/dt = -k_1C$, yielding the integrated form $C = C_0 \exp(-k_1t)$, while the PSO model is expressed as $dC/dt = -k_2C^2$, yielding $C = C_0/(1 + k_2C_0t)$. Regression analysis indicated that the PSO model provided a significantly better fit to the experimental data ($R^2 = 0.982$; $k_2 = 1.14 \times 10^{-4}$ L·mg^{-1}·min^{-1}) compared to the PFO model ($R^2 = 0.854$). This suggests that the rate of TCH degradation depends on both the TCH concentration and the concentration of reactive oxidizing species (•OH) generated in the system, consistent with a bimolecular mechanism for •OH-mediated pollutant oxidation (Qiang et al., 2002).

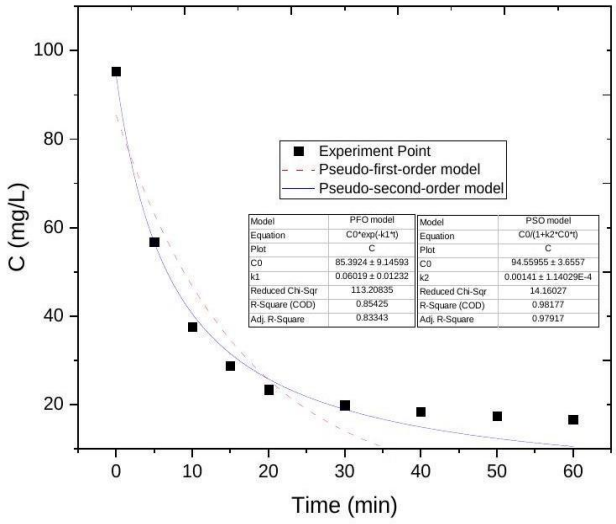

Fig. 10. Kinetic plots for TCH degradation: pseudo-first-order (dashed) and pseudo-second-order (solid) model fitting under optimal electro-Fenton conditions.

3.8 Thermodynamic Analysis

Thermodynamic parameters of the EF degradation process were calculated from experiments at three temperatures (283 K, 298 K, and 313 K) using the Arrhenius equation and van't Hoff relation. The calculated values are summarized in Table 1. The activation energy (Ea) of 32.22 kJ/mol indicates that the TCH oxidation reaction proceeds with a relatively low energy barrier, consistent with the high catalytic activity of the RSBF/EF system and the non-selective reactivity of •OH radicals (Luo et al., 2015). For reference, conventional Fenton-based systems typically exhibit Ea values in the range 25–40 kJ/mol (Zhang et al., 2019).

The positive enthalpy change ($\Delta H = +29.40$ kJ/mol) confirms that the degradation reaction is endothermic, consistent with the observed enhancement of efficiency with increasing temperature. The negative Gibbs free energy values ($\Delta G = -24.95$, -27.83, and -30.71 kJ/mol at 283, 298, and 313 K, respectively) demonstrate that the oxidative degradation of TCH is thermodynamically spontaneous under all tested conditions, with spontaneity increasing at higher temperatures.

Table 1. Thermodynamic parameters for TCH degradation by the electro-Fenton process.

T (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol·K)	Ea (kJ/mol)
283	-24.95	29.40	0.19	32.22
298	-27.83			
313	-30.71			

The positive entropy change (ΔS = +0.19 kJ/mol·K) reflects increased disorder in the system during the degradation process, as TCH molecules are broken down into smaller, more mobile fragments. These thermodynamic findings collectively confirm that the RSBF-catalyzed electro-Fenton process is energetically favorable and practically applicable for tetracycline wastewater treatment.

CONCLUSIONS AND SUGGESTIONS

A biochar-supported α-FeOOH catalyst (RSBF) was successfully synthesized from rubber seed shells via a two-step pyrolysis and iron precipitation method. SEM, EDS, FTIR, and XRD characterization confirmed the successful deposition of α-FeOOH onto the biochar support, with approximately 14 wt.% iron content and a well-defined goethite crystal structure. Under optimized electro-Fenton conditions (pH 3, H_2O_2/Fe^{2+} = 1:500, catalyst dose = 1 g/L, I = 0.15 A), TCH degradation and TOC removal efficiencies reached 95% and 90%, respectively, within 60 minutes. Kinetic analysis confirmed pseudo-second-order behavior (R^2 = 0.982), and thermodynamic evaluation revealed a spontaneous, endothermic process with low activation energy (Ea = 32.22 kJ/mol). The catalyst maintained stable performance over five reuse cycles. These results demonstrate that the RSBF/EF system is a promising, sustainable, and cost-effective approach for the remediation of antibiotic-contaminated wastewater, utilizing low-cost agricultural waste as the catalyst precursor.

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