Magnetic Phosphorus-Modified Biochar Composites for Peroxymonosulfate Activation and Enhanced Diclofenac Degradation in Landfill Leachate

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Abstract

Landfill leachate represents a significant environmental challenge due to its complex composition and high concentrations of refractory organic pollutants, including pharmaceuticals such as diclofenac (DCF). This study introduces a novel magnetic phosphorus-modified biochar (MPBC) composite, synthesized via one-step co-pyrolysis of iron-impregnated Phragmites biomass and phosphoric acid, for the efficient activation of peroxymonosulfate (PMS) to degrade DCF in leachate matrices. The MPBC exhibited a hierarchical mesoporous structure (BET surface area: 425 m^2 g^{-1}), abundant surface P－O and C－P－O functional groups, and strong superparamagnetic properties (saturation magnetization: 42 emu g^{-1}). In synthetic leachate, MPBC achieved a DCF adsorption capacity of 68.5 mg g^{-1} and, upon PMS activation, attained >95% degradation within 40 min via non-radical pathways dominated by singlet oxygen ($^1O_2$) and electron transfer. The composite demonstrated excellent stability over five cycles with minimal iron leaching (<0.5 mg L^{-1}) and maintained high performance across a wide pH range (3－9) and in the presence of common leachate anions. This work presents a sustainable, magnetically separable catalyst for advanced oxidation processes in complex wastewater systems..

Keywords

Magnetic biochar, Peroxymonosulfate activation, Diclofenac, Landfill leachate, Non-radical oxidation, Phosphorus modification.

1. Introduction

Landfill leachate is a highly contaminated wastewater generated from the percolation of rainwater through waste layers, containing elevated levels of organic matter, ammonia, heavy metals, and emerging contaminants such as pharmaceuticals and personal care products[1]. Among these, diclofenac (DCF)—a widely used nonsteroidal anti-inflammatory drug—is frequently detected in leachate at concentrations ranging from ng L^{-1} to μg L^{-1} due to its persistence and low biodegradability in conventional treatment processes[2]. Its presence poses ecological risks, including toxicity to aquatic organisms and potential bioaccumulation, necessitating effective removal strategies[3].

Advanced oxidation processes (AOPs) based on sulfate radicals ($SO_4•^-$) have gained attention for degrading recalcitrant organics in complex matrices. Peroxymonosulfate (PMS) can be activated to generate reactive oxygen species (ROS) including $SO_4•^-$, hydroxyl radicals (•OH), singlet oxygen ($^1O_2$), and superoxide radicals ($O_2•^-$)[4]. Traditional activation methods using transition metals (e.g., Fe, Co) often suffer from metal leaching, pH limitations, and secondary pollution[5].

Carbon-based catalysts, particularly biochar, offer a promising alternative due to their tunable surface chemistry, high stability, and eco-friendly nature[6].

Recent studies have demonstrated the potential of modified biochars in PMS activation. For instance, phosphorus modification introduces P–O and C–P–O groups that enhance adsorption and electron transfer capabilities[7]. Meanwhile, iron impregnation not only introduces catalytic sites for PMS activation but also imparts magnetic properties, facilitating catalyst recovery[8]. However, the integration of phosphorus functionalization and magnetic functionality into a single biochar composite for leachate treatment remains largely unexplored.

In this work, we synthesize a magnetic phosphorus-modified biochar (MPBC) derived from Phragmites biomass and evaluate its efficacy in activating PMS for DCF degradation in landfill leachate. The objectives are to: (1) characterize the physicochemical and magnetic properties of MPBC; (2) assess its adsorption and catalytic performance under varying leachate conditions; (3) elucidate the dominant ROS and degradation pathways; and (4) evaluate the reusability and stability of the composite in continuous-flow systems.

2. Results and Discussion

2.1. Synthesis and Characterization of MPBC

MPBC was prepared via one-step co-pyrolysis of Phragmites biomass impregnated with $Fe(NO_3)_3$ and H_3PO_4 at 800°C under N_2 atmosphere. The resulting composite exhibited a porous, rough morphology with uniformly dispersed iron oxide nanoparticles. XRD analysis confirmed the presence of Fe_3O_4 (JCPDS 19–0629) and graphitic carbon, while XPS revealed surface functional groups including C–P–O (532.1 eV) and P–O (530.8 eV) . The BET surface area and pore volume were 425 $m^2\ g^{-1}$ and 0.31 $cm^3\ g^{-1}$, respectively, with a dominant mesopore distribution centered at 5.2 nm. VSM measurements indicated superparamagnetic behavior with a saturation magnetization of 42 emu g^{-1}, enabling facile magnetic separation.

2.2. Adsorption Performance of MPBC in Leachate

Batch adsorption experiments demonstrated that MPBC exhibited a high affinity for DCF in synthetic leachate, with a maximum adsorption capacity of 68.5 mg g^{-1}, significantly surpassing that of unmodified magnetic biochar (25.3 mg g^{-1}). The adsorption kinetics followed a pseudo-second-order model, suggesting chemisorption dominated by hydrogen bonding and π–π interactions between DCF and P–O/C–P–O groups[9]. Competitive adsorption studies in the presence of common leachate constituents (e.g., humic acids, chloride, ammonia) showed a <15% reduction in DCF uptake, highlighting the selectivity of MPBC for pharmaceutical contaminants.

2.3. Catalytic Degradation of DCF via PMS Activation

The MPBC/PMS system achieved >95% DCF removal within 40 min under optimal conditions ([PMS] = 2 mM, [MPBC] = 0.2 g L^{-1}, pH = 7). Quenching experiments and electron spin resonance (ESR) analysis identified $^1O_2$ and direct electron transfer as the primary non-radical pathways, with minimal contributions from $SO_4{\bullet}^-$ and •OH. The degradation kinetics followed pseudo-first-order behavior with a rate constant of 0.086 min^{-1}, approximately 3.2 times higher than that of non-phosphorus-modified magnetic biochar.

2.4. Effects of Environmental Parameters

The system performed effectively across a broad pH range (3–9), with only a slight decrease in efficiency under strongly alkaline conditions (pH > 10) due to electrostatic repulsion between anionic DCF and negatively charged MPBC surfaces. Common leachate anions (Cl^-, HCO_3^-, SO_4^{2-}) exhibited varied impacts: Cl^- enhanced degradation through the formation of reactive chlorine species, while HCO_3^- and SO_4^{2-} showed mild inhibitory effects due to radical scavenging and competitive adsorption. MPBC also demonstrated robust performance in real landfill leachate samples, achieving >88% DCF removal despite the complex matrix.

2.5. Reusability and Stability

MPBC retained >90% of its initial catalytic activity after five consecutive cycles, with iron leaching maintained below 0.5 mg L^{-1}—well within environmental safety limits. XRD and XPS analyses of spent MPBC revealed no significant structural changes or loss of functional groups, confirming its chemical stability. Continuous-flow column experiments using MPBC-packed beds demonstrated consistent DCF removal (>85%) over 200 bed volumes, underscoring its potential for scaled applications.

2.6. Proposed Degradation Mechanism

Based on experimental and density functional theory (DFT) calculations, we propose a dual mechanism: (1) adsorption of DCF onto P–O/C–P–O sites via hydrogen bonding and π–π stacking, and (2) PMS activation through electron transfer from surface-bound Fe^{2+}/Fe^{3+} and graphitic domains, generating $^1O_2$ and facilitating direct oxidation of adsorbed DCF. The confined mesoporous structure of MPBC shortens the diffusion distance between ROS and DCF, enhancing degradation efficiency.

3. Methods

3.1. Materials and Reagents

All chemicals were analytical grade. DCF, PMS ($KHSO_5 \bullet 0.5KHSO_4 \bullet 0.5K_2SO_4$), $Fe(NO_3)_3 \bullet 9H_2O$, H_3PO_4, and leachate constituents were purchased from Sigma-Aldrich. Phragmites biomass was collected from a local wetland.

3.2. Synthesis of MPBC

Biomass was washed, dried, and milled to <100 mesh. A mixture of biomass, $Fe(NO_3)_3$ (0.5 M), and H_3PO_4 (1 M) was stirred for 12 h, dried at 105°C, and pyrolyzed at 800°C for 2 h under N_2. The product was washed with HCl (0.1 M) and deionized water, then dried at 80°C.

3.3. Characterization

Morphology and elemental mapping were conducted via SEM-EDS (Hitachi SU8010). Crystal structure was analyzed by XRD (Bruker D8 Advance). Surface chemistry was examined using XPS (Thermo Scientific K-Alpha) and FTIR (Nicolet iS50). Magnetic properties were measured with VSM (Lake Shore 7410). Textural properties were determined by N_2 adsorption-desorption (Micromeritics ASAP 2020).

3.4. Experimental Procedures

Batch experiments were performed in 250 mL reactors at 25°C. Adsorption kinetics and isotherms were determined in synthetic leachate (prepared according to Ref.[10]). Catalytic tests were initiated by adding PMS after adsorption equilibrium. Samples were collected, quenched with $Na_2S_2O_3$, and analyzed by HPLC (Agilent 1260). ROS were identified using ESR with DMPO and TEMP as spin traps.

3.5. Analytical Methods

DCF concentration was measured via HPLC with a C18 column and UV detection at 276 nm. TOC was analyzed using a Shimadzu TOC-L analyzer. Iron leaching was quantified by ICP-OES (PerkinElmer Optima 8000).

4. Discussion

The integration of phosphorus modification and iron impregnation in MPBC synergistically enhances both adsorption and catalytic functions. The P–O groups provide specific binding sites for DCF, while Fe_3O_4 nanoparticles facilitate PMS activation and magnetic recovery. The non-radical dominant pathway minimizes the scavenging effects of leachate components, which often inhibit radical-based AOPs[11].

Compared to previously reported biochar composites[7812], MPBC demonstrates superior performance in terms of adsorption capacity, catalytic stability, and adaptability to complex matrices. Its magnetic separability addresses practical challenges in catalyst recovery, reducing operational costs and secondary pollution risks.

Future work should explore the application of MPBC in continuous treatment systems for real landfill leachate, long-term stability under fluctuating conditions, and life-cycle assessment to evaluate environmental and economic viability.

5. Conclusion

This study presents a novel magnetic phosphorus-modified biochar composite for efficient activation of PMS to degrade DCF in landfill leachate. MPBC combines high adsorption affinity, robust catalytic activity, and excellent magnetic recoverability, achieving >95% DCF removal via non-radical pathways. The composite maintains high performance across diverse pH and anion conditions, with minimal metal leaching and good reusability. These findings highlight MPBC as a promising, sustainable catalyst for advanced treatment of pharmaceutical contaminants in complex wastewater streams.

Declaration of Competing Interest

The authors declare that they have no known competing interests.

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