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Modification and application of biochar on heavy metal and organic pollutants removal

DOCTORAL THESIS

Doctor of Philosophy:

YANG Ye

Doctoral Supervisor:

Assoc. Prof. Dr. Habil. BELDEAN-GALEA Mihail Simion

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Acknowledgment

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Contents

Abstract

In recent years, aquatic environments have been threatened by emerging pollutants such as pharmaceuticals and heavy metals. These pollutants are frequently detected in surface water, groundwater, and even drinking water. Traditional wastewater treatment processes often fail to completely remove these persistent and trace pollutants. These pollutants threaten ecological risks, human health, and the habitats of aquatic plants and animals. Therefore, there is an urgent need to develop efficient, low-cost, and environmentally friendly technologies to treat complex, multi-component wastewater.

This study summarizes recent research progress on typical emerging organic pollutants and heavy metals in water and, based on this, develops a biochar-based photocatalyst. First, an S-type heterojunction BC/$CoFe_2O_4$/Fe_2O_3 photocatalyst was developed. This catalyst can activate peroxymonosulfate (PMS) under visible light and can more effectively remove tetracycline (TC) and hexavalent chromium (Cr(VI)). DFT and UPS analyses confirmed the S-type band arrangement, which can effectively separate photogenerated carriers and has strong redox capabilities. LC-MS and Fukui index calculations elucidated the degradation pathway and toxicity evolution of TC. Secondly, the heterogeneous nano-zero-valent iron (nZVI) Fenton process was used to simultaneously degrade four nonsteroidal anti-inflammatory drugs (NSAIDs): ketoprofen, naproxen, diclofenac, and ibuprofen. Response surface methodology determined that pH, H_2O_2 dosage, and NaCl concentration were the key parameters. Under optimized conditions, the removal rates of all four NSAIDs exceeded 90% within 30 minutes. Based on this, a biochar-supported Schottky photocatalyst BC/$CoFe_2O_4$/nZVI was constructed, which can also activate PMS under visible light. This system can simultaneously remove ibuprofen (IBU), TC, and Cr(VI), with removal efficiencies exceeding 90%. In addition, the catalyst demonstrates strong stability and can be easily recovered by magnetic separation. Radical scavenging experiments, electron spin resonance, density functional theory, and machine learning models collectively showed that $SO_4\bullet^-$, $\bullet OH$, and $\bullet O_2^-$ radicals dominated the degradation of IBU and TC, while Cr(VI) was primarily reduced electronically.

Overall, these findings point out very promising opportunities for a biochar-based photocatalyst in the remediation of complex matrices with organic and heavy metal pollutants. Coupling renewable biochar supports with tailored heterojunctions does not only enhance their light capture, charge separation, and radical generation but also confers magnetic recoveries, structural stabilities, and economic advantages. Furthermore, analysis of degradation products and post-treatment ion detection further demonstrate the system's environmental friendliness. Real-world testing in aquatic environments demonstrates the system's broad adaptability. These findings are crucial for practical applications, providing a scalable, energy-efficient, and environmentally sustainable solution for wastewater treatment.

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Chapter 1 General Introduction

Water pollution is one of the most pressing environmental challenges of our time, driven by rapid industrialization, urban growth, and rising population pressures(Strokal & Kroeze, 2020; Nishmitha et al., 2025). Contamination comes from agricultural runoff, industrial discharge, and improper disposal of household and medical waste(Nishmitha et al., 2025). Climate change compounds the problem by worsening water scarcity, while untreated wastewater routinely introduces hazardous substances into natural water systems(Nishmitha et al., 2025; Rueda-Marquez et al., 2020; Sousa et al., 2018). The consequences stretch across public health, aquatic ecosystems, and agricultural productivity, with waterborne diseases remaining a major concern especially in developing countries(Grădinariu et al., 2025; Brandão et al., 2013).

Key Pollutants of Concern

The chapter focuses on three categories of water pollutants. The first is antibiotics, particularly tetracycline (TC), one of the most widely used broad-spectrum antibiotics globally(Anderson et al., 2022). Tetracycline is applied extensively in human medicine and animal husbandry(Zama et al., 2018; Nie et al., 2024; Sarmah et al., 2006; Yang et al., 2018; Nishmitha et al., 2025), and because it cannot be fully metabolized, it is excreted and enters water systems through urine and feces(Xu et al., 2021; Yang et al., 2020). Its persistence in the environment and resistance to conventional treatment makes it a serious concern, not least because it promotes the development of antibiotic-resistant microorganisms(Shokoohi et al., 2020; Peiris et al., 2017; Wang et al., 2017; Xu et al., 2021).

The second category is non-steroidal anti-inflammatory drugs (NSAIDs), with ibuprofen (IBU) highlighted as a representative compound. NSAIDs are among the most consumed pharmaceuticals worldwide and are only partially metabolized in the body(Wojcieszyńska & Guzik, 2020; Placova et al., 2023; Huynh et al., 2023). They enter wastewater systems through excretion and pharmaceutical effluents, and conventional treatment plants are poorly equipped to remove them(Huynh et al., 2023;

Mussa et al., 2022; Rastogi et al., 2021). Even at low concentrations, ibuprofen has been shown to cause oxidative stress, growth inhibition, and reproductive problems in aquatic organisms(Sehonova et al., 2018; Przedpełska et al., 2025).

The third category is heavy metals, specifically hexavalent chromium (Cr(VI)), which originates from industries such as electroplating, dyeing, and leather tanning(Zhang et al., 2023; Saravanan et al., 2024; Jamil Emon et al., 2023). Unlike its trivalent counterpart, Cr(VI) is highly toxic and mobile, capable of crossing cell membranes and causing DNA damage and oxidative stress(Zhigalenok et al., 2025; Sharma et al., 2022; Zhitkovich, 2011). It accumulates in fish tissue and frequently co-occurs with other pollutants, making it particularly difficult to manage(Fu et al., 2013; Liu et al., 2024; Di et al., 2017).

Limitations of Current Treatment Technologies

Conventional physicochemical and biological treatment processes, while effective for standard contaminants, fall short when it comes to emerging pollutants(Fernandes et al., 2024; Abdel-Hady et al., 2025; Letsoalo et al., 2023; Rodriguez-Narvaez et al., 2017). Activated sludge systems and sand filtration cannot reliably remove pharmaceuticals or antibiotic-resistant compounds(Hernández-Tenorio, 2023). Advanced oxidation processes (AOPs), though more powerful, can generate toxic byproducts and are expensive to operate, limiting their feasibility in lower-income regions(Adeoye et al., 2024; Han et al., 2022; Ahmed et al., 2025; Gopalakrishnan et al., 2023; Misdan et al., 2012; Shabib et al., 2025). Chemical precipitation and ion exchange address heavy metals but struggle with incomplete removal, especially at trace concentrations, and often produce problematic secondary waste in the form of sludge(Qasem et al., 2021; Fu & Wang, 2011; Kacprzak et al., 2025; Salva et al., 2025). A further weakness is that most systems operate in isolation, treating specific pollutants without accounting for the complex mixture of contaminants found in real water bodies(Falås et al., 2016; Grandclément et al., 2017).

Research Objectives and Significance

To address these gaps, this dissertation develops and evaluates biochar-based photocatalytic and Fenton-like systems for the simultaneous removal of TC, IBU, and Cr(VI) from water. The research aims to construct biochar-supported catalysts, investigate the mechanisms behind pollutant removal through radical quenching experiments and simulation analyses, and assess the long-term stability, reusability, and environmental safety of these materials.

The broader significance lies in offering a cost-effective, eco-friendly alternative to conventional methods, derived from waste biomass and capable of tackling multiple co-existing contaminants. By clarifying degradation pathways and evaluating intermediate toxicity, the research also contributes to more rigorous risk assessment, and points toward more integrated, resource-efficient water treatment strategies.

Chapter 2 Advanced Methods for Removing Emerging Pollutants from Water

Because conventional water treatment processes fail to adequately remove emerging pollutants such as pharmaceuticals, pesticides, and endocrine-disrupting compounds, a range of advanced treatment technologies has been investigated(Morin-Crini et al., 2022; Grandclément et al., 2017; Rout et al., 2021; Rodriguez-Narvaez et al., 2017). These include engineered sorbents, high-pressure membrane systems, advanced oxidation processes (AOPs), and enhanced biological systems like membrane bioreactors(Rout et al., 2021; Rodriguez-Narvaez et al., 2017). This chapter focuses particularly on two of these approaches: Fenton-based oxidation and biochar-supported photocatalysis.

Fenton and Fenton-like Processes

The Fenton process is a well-established AOP in which ferrous ions (Fe^{2+}) react with hydrogen peroxide (H_2O_2) under acidic conditions to produce highly reactive hydroxyl radicals (•OH)(Mukherjee et al., 2016; Mahtab et al., 2021; Pignatello et al., 2006). These radicals are powerful enough to break down a wide range of organic pollutants into harmless small molecules(Mahtab et al., 2021; Pignatello et al., 2006; Deng et al., 2023; Parvulescu & Granger, 2013). The underlying mechanism, described by the Haber-Weiss theory, involves a self-sustaining catalytic cycle in which Fe^{2+} is continuously regenerated, allowing radical production to continue throughout the reaction(Haber & Weiss, 1997; Hussain et al., 2021; Deng et al., 2023; Parvulescu & Granger, 2013).

While the homogeneous Fenton process is fast and effective, it has significant practical drawbacks: it requires a narrow acidic pH range, produces large quantities of iron sludge, and leaves residual metal ions that can cause secondary pollution(Ziembowicz & Kida, 2022; Bello et al., 2019; Babuponnusami & Muthukumar, 2014). To address these limitations, heterogeneous Fenton-like systems have been developed, where the active iron species are embedded within a solid-phase catalyst(Thomas et al., 2021; Zhang et al., 2021; Zhang et al., 2023; Huang et al., 2023; Hussain et al., 2021; Thomas et al., 2021; Pei et al., 2024; Wu et al., 2025; Lu et al., 2021; Biswas et al., 2020). This broadens the usable pH range, simplifies catalyst recovery, and reduces secondary contamination. These catalysts can be metal or metal oxide-based, or supported systems where active components are loaded onto porous carriers such as activated carbon, zeolites, or metal-organic frameworks. Fenton and Fenton-like processes have been shown to degrade antibiotics, ibuprofen, and other pharmaceuticals at removal efficiencies typically exceeding 80-90%, with photo-Fenton systems achieving even faster reaction kinetics(Li et al., 2022; Mirzaei et al., 2017; Gou et al., 2021; Befenzi et al., 2025; Jiang et al., 2023; Trovó et al., 2009).

Biochar and Biochar-Based Catalysts

Biochar is a carbon-rich material produced by heating biomass, such as forestry waste, under oxygen-limited conditions through pyrolysis or hydrothermal carbonization(Yuan et al., 2021; Boraah et al., 2022; Bożym et al., 2021; Wieruszewski et al., 2022). Pyrolysis, carried out at temperatures between 300 and 900°C, is the more common method and yields a porous solid with a large surface area and oxygen-containing functional groups(Pahnila et al., 2023; Wang et al., 2022). Slow pyrolysis generally produces higher biochar yields than fast pyrolysis, and the process is simpler and cheaper than producing conventional carbon materials like graphene(Brassard et al., 2017; Yaashikaa et al., 2020). Hydrothermal carbonization, in contrast, uses water as the reaction medium at lower temperatures and can process wet or unconventional feedstocks without energy-intensive pre-drying(González-Arias et al., 2021; Sharma et al., 2020; Maniscalco et al., 2020).

These properties make biochar an effective adsorbent for a broad range of contaminants, including heavy metals, organic pollutants, and polycyclic aromatic hydrocarbons (PAHs)(Yuan et al., 2021; Boraah et al., 2022; Qiu et al., 2021). Studies have demonstrated, for instance, that rice straw-derived biochar can achieve cadmium adsorption capacities of up to 93 mg g^{-1}, while swine-manure biochar has shown 97% removal of lead(Yang et al., 2018; Zhang et al., 2018). Biochar can also be combined with metals or metal oxides to form composite materials with enhanced catalytic activity(Wang et al., 2020; Jha et al., 2023; Bartoli et al., 2023).

Photocatalytic Heterojunctions

Photocatalysts generate reactive charge carriers (electrons and holes) when exposed to light, driving oxidation and reduction reactions that degrade pollutants(Gaya, 2014; Muñoz-Batista & Luque, 2021; Herrmann, 1999; Sahu et al., 2025; Kudo & Miseki, 2009). While promising, single-component photocatalysts are limited by poor visible-light absorption and rapid recombination of charge carriers(Yang et al., 2021). Heterojunction photocatalysts, formed by coupling two or more semiconductor materials, overcome these weaknesses by improving charge separation, broadening light absorption, and sustaining higher redox activity(Zu et al., 2024; Amin et al., 2025; Cai et al., 2023; Hosseini et al., 2023).

Several heterojunction types have been explored. P-n heterojunctions use an internal electric field to direct charge flow(Goktas & Goktas, 2021; Chi et al., 2021). S-scheme heterojunctions selectively transfer carriers between components while preserving high redox potentials(Wang et al., 2022; Yang et al., 2023; Alzahrani & Ismail, 2023; Wen et al., 2022). Z-scheme heterojunctions mimic natural photosynthesis by keeping electrons and holes in separate semiconductors, maintaining strong oxidizing and reducing capabilities simultaneously(Pan et al., 2021; Zou et al., 2023; Yan et al., 2023; Askari et al., 2021). Most of these systems achieve degradation rates above 90% for target antibiotics and can treat multiple pollutants at once(He et al., 2022; Shao et al., 2022; Pan et al., 2021).

When biochar is used as a support for heterojunction photocatalysts, the material benefits further: the porous structure increases pollutant concentration near active sites, surface functional groups facilitate electron transfer, and the overall stability and reusability of the composite improve(Qiu et al., 2022; Jha et al., 2023; Bartoli et al., 2023). Despite these advantages, most studies remain limited to controlled laboratory conditions with simplified water matrices, and questions around long-term stability, metal leaching, and the toxicity of degradation products remain underexplored. These gaps point to the need for more systematic investigation under realistic conditions.

Chapter 3 Construction of $CoFe_2O_4/Fe_2O_3$ S-type Heterojunctions on Biochar for Activating Peroxymonosulfate towards Simultaneous Removal of TC and Cr(VI)

The construction of S-type heterojunctions for restraining the rapid recombination of photogenerated charges is considered an efficient approach to boost redox capacity. Herein, the growth of $CoFe_2O_4/Fe_2O_3$ S-type heterojunctions on biochar (BC) was accomplished by thermal polymerization-hydrothermal. $BC/CoFe_2O_4/Fe_2O_3$ displayed a wide range of light absorption from 200 to 800 nm and enhanced photocurrent (0.41 $\mu A\ cm^{-2}$). Furthermore, $BC/CoFe_2O_4/Fe_2O_3$ can remove tetracycline (TC) (98.84%) and Cr(VI) (88.43%) more efficiently compared to the $CoFe_2O_4$ (40.32% of TC, 68.52% of Cr(VI)) and Fe_2O_3 (29.81% of TC, 53.67% of Cr(VI)) single counterparts upon 45 min visible light irradiation in the presence of peroxymonosulfate (PMS). Free radical capture experiments revealed that $^{\bullet}OH$, $^{\bullet}O_2^-$, and $SO_4^{-}\bullet$ are the primary activated species for the removal of TC and e^- is the major activated species for the removal of Cr(VI). Meanwhile, the degradation pathway of TC was monitored via LC-MS and Fukui index calculations. Combining density functional calculations (DFT) with UPS and radical capture tests, the possible mechanism of photocatalytic degradation was proposed. The findings demonstrated the remarkable photocatalytic activity and stability of the photocatalyst, evidencing the potential of $BC/CoFe_2O_4/Fe_2O_3$ for practical wastewater treatment.

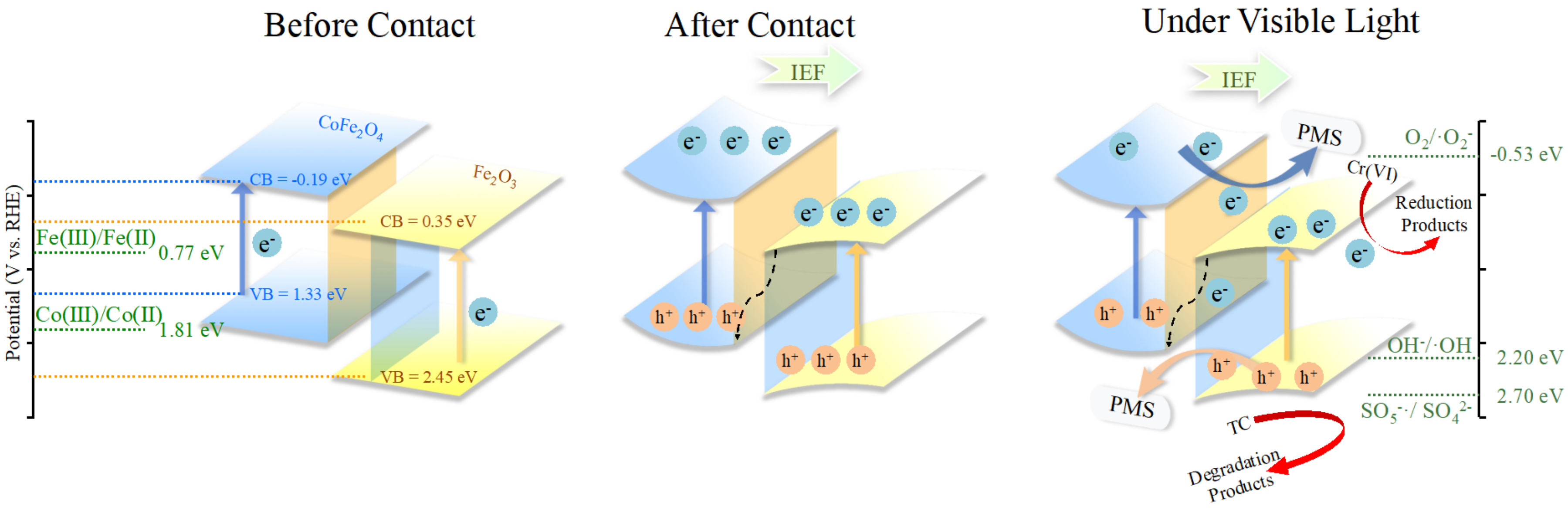

Fig. 3.3.46. The proposed reaction mechanism for the photocatalysis combined with advanced oxidation system.

Based on the band gap of $CoFe_2O_4$ and Fe_2O_3, the reaction mechanism of BC/$CoFe_2O_4/Fe_2O_3$ with PMS is depicted in Fig. 3.3.46, and the reaction procedure was explained by Equations (1)–(11) (Wei et al., 2021; Li et al., 2018; Li et al., 2021; Liu et al., 2021; Deng et al., 2017). The energy level of CB of $CoFe_2O_4$ is -0.62 eV, and its VB energy level is 1.76 eV. The CB of Fe_2O_3 is 0.35 eV, while its VB energy level is 2.45 eV. Therefore, a typical S-type heterojunction was formed between $CoFe_2O_4$ and Fe_2O_3. Under visible light irradiation, $CoFe_2O_4$ and Fe_2O_3 were activated to form e^- and h^+. The generated electrons reduced Cr(VI) to Cr(III) or Cr(II). The e^- migrated from the CB of $CoFe_2O_4$ to the VB of Fe_2O_3, and the h^+ remained on VB. The CB energy level of $CoFe_2O_4/Fe_2O_3$ is more negative compared to the reduction potential of $O_2/^{\bullet}O_2^-$ (-0.53 eV), and the electrons participated in the reduction of O_2 to produce superoxide radicals ($^{\bullet}O_2^-$), resulting in the removal of TC. Furthermore, the existence of PMS in the solution is activated by electrons and holes, contributing to the formation of strong oxidizing species ($SO_4^{-}\bullet$ and $^{\bullet}OH$) via transfer of electrons between surfaces involving Co(II) and Fe(II) complexes. The standard reduction potential of Co(III)/Co(II) and Fe(III)/Fe(II) is 1.81 and 0.77 eV, respectively (Zhuang et al., 2024; Wei et al., 2015), which are lower than the VB energy level of Fe_2O_3. This suggests the feasibility of the redox cycles of Fe(III)/Fe(II) and Co(III)/Co(II). In summary, the experimental results demonstrate the efficient degradation of TC with BC/$CoFe_2O_4/Fe_2O_3$ in present of PMS, which is explained by the generation of electron-hole pair and reactive species ($^{\bullet}O_2^-$, $SO_4^{-}\bullet$, and $^{\bullet}OH$), the reduction principle of Cr(VI) is realized through e^-.

$$\equiv Co^{2+} + O_2 \rightarrow \equiv Co^{3+} + \cdot O_2^- \tag{1}$$

$$\equiv Co^{2+} + HSO_5^- \rightarrow \equiv Co^{3+} + SO_4^{2-} + \cdot OH \tag{2}$$

$$\equiv Co^{3+} + HSO_5^- \rightarrow \equiv Co^{2+} + SO_5^- \cdot + H^+ \tag{3}$$

$$\equiv Co^{2+} + H_2O \rightarrow \equiv Co^{2+}\text{-}OH + H^+ \tag{4}$$

$$\equiv Co^{2+}\text{-}OH + HSO_5^- \rightarrow \equiv Co^{3+}\text{-}OH + SO_4^{2-} + OH^- \tag{5}$$

$$\equiv Fe^{3+} + HSO_5^- \rightarrow \equiv Fe^{2+} + SO_5^- \cdot + H^+ \tag{6}$$

$$SO_5^- \cdot + O^{2-} \rightarrow SO_4^- \cdot + O_2 \tag{7}$$

$$SO_4^- \cdot + OH^- \rightarrow SO_4^{2-} + \cdot OH \tag{8}$$

$$\equiv Co^{3+} + \equiv Fe^{2+} \rightarrow \equiv Co^{2+} + \equiv Fe^{3+} + e^- \quad (9)$$

$$SO_4^{-}\cdot / \cdot OH / \cdot O_2^{-} + TC \rightarrow \text{Degradation Products} \quad (10)$$

$$Cr(VI) + e^- \rightarrow Cr(II) + Cr(III) \quad (11)$$

$$Cr(VI) + Fe(II) \rightarrow Cr(II)/Cr(III) + Fe(III) \quad (12)$$

Conclusion

In this study, S-type heterojunctions $BC/CoFe_2O_4/Fe_2O_3$ was synthesized via the thermal polymerization-hydrothermal two-step method, which owns strong spectral absorption and high specific surface area. Furthermore, $BC/CoFe_2O_4/Fe_2O_3$ exhibits improved separation efficiency of photogenerated carriers and redox ability. In the present of PMS, $BC/CoFe_2O_4/Fe_2O_3$ has outstanding photocatalytic activity with compound contaminant containing TC and Cr(VI) as target pollutant. Meanwhile, $BC/CoFe_2O_4/Fe_2O_3$ can be recycled by magnetic fields to avoid secondary pollution. This study not only offers a fresh perspective for the synthesis of efficient and recyclable photocatalysts but also lays a foundation for the reutilization of waste biomass. However, this study only discussed the removal of TC and Cr(VI) pollutants, and it is necessary to evaluate the removal efficiency of composites for more pollutants and their applicability in different environmental contexts in the future, thereby enhancing their potential for practical implementation.

Chapter 4 Efficiency of Heterogeneous Nano Zero-valent Iron Fenton Process for Removal of Non-steroidal Anti-inflammatory Drugs from Water

Non-steroidal anti-inflammatory drugs are a major contributor to the pollution of pharmaceutical products in aquatic habitats and for this reason it is crucial to find fast, efficient and ecological techniques for their elimination. The purpose of this study is to examine the feasibility of a nano-zero-valent iron Fenton process to simultaneously remove ketoprofen, naproxen, diclofenac and ibuprofen from water. Since the effectiveness of the Fenton process is influenced by some parameters such as pH, H_2O_2 and NaCl concentration, the response surface methodology was used to analyze the effects of these parameters on the experimental results. The novelty of this work consists in the use of NaCl to increase the production of iron ions and thus increase the efficiency of the Fenton process. The experimental results show that the process has a good effect on the four pollutants. Under optimal experimental conditions, the degradation rate can exceed 90%. Simultaneously, the analysis of the response surface approach provides assistance in understanding the relationship between the factors affecting the process and the optimization of the experimental settings. In addition, it provides valuable information for addressing similar organic water pollution problems.

Conclusion

This study provides valuable information on the degradation behavior of four NSAIDs in the nZVI Fenton process. The results of the study showed that:

1) Single-factor tests demonstrate that the Fenton reaction exhibits optimal efficacy when the pH is set to 2, the H_2O_2 concentration is 10 mg L^{-1}, and the concentration of NaCl is 3 mg L^{-1}. Under these conditions, the degradation rates of substances ketoprofen, naproxen, diclofenac, and ibuprofen are 92.63%, 96.48%, 97.78%, and 93.38%.

2) Based on the response surface study, has could be established that the pH has the greatest impact on nZVI Fenton process, followed by H_2O_2, while NaCl has the least significant influence.

In this study, NSAIDs were simultaneously degraded by the nZVI Fenton process. Under the optimal conditions, the degradation efficiency was maintained above 90% within 30 minutes. compounds. At the same time, the response surface was used to systematically analyze the various conditions that limited the reaction. The data obtained can be a starting point for the development of nZVI Fenton industrial processes for the effective removal of these pharmaceutical products from wastewater. Although this study demonstrated the effectiveness of the nZVI-Fenton system in the simultaneous removal of four nonsteroidal anti-inflammatory drug (NSAID) contaminants under controlled conditions, there are still some limitations, such as the impact of different ions and actual water bodies on the system and the leakage of iron ions after the reaction. The next step will be to conduct in-depth research on these aspects to translate laboratory-scale findings into practical applications in actual wastewater treatment scenarios.

Chapter 5 Interfacial Schottky Junction-enhanced Charge Separation in BC/$CoFe_2O_4$/nZVI for Photocatalytic Removal of Complex Pollutants via Peroxymonosulfate Activation

Constructing heterojunctions to facilitate charge separation and suppress the recombination of photogenerated carrier is a pivotal strategy for improving photocatalytic removal of complex pollutants. Herein, a biochar-supported composite (BC/$CoFe_2O_4$/nZVI) was synthesized via a hydrothermal process followed by reduction treatment. The close contact between $CoFe_2O_4$ and nanoscale zero-valent iron (nZVI) formed a Schottky interface, effectively preventing nZVI aggregation and facilitating electron transfer, thereby improving charge separation and photocatalytic performance. BC/$CoFe_2O_4$/nZVI achieved splendid removal of ibuprofen (IBU) (100%), tetracycline (TC) (93.46%), and hexavalent chromium (Cr(VI)) (90.80%) in the presence of a peroxymonosulfate (PMS) system, outperforming $CoFe_2O_4$ (10.70% of IBU, 39.93% of TC and 48.38% of Cr(VI)) or nZVI (52.40% of IBU, 26.26% of TC and 51.39% of Cr(VI)). More importantly, BC/$CoFe_2O_4$/nZVI demonstrated excellent synergistic degradation efficiency for complex pollutants (100% of IBU, 93.28% of TC and 90.27% of Cr(VI)). Radical scavenging tests indicated that •OH, $•O_2^-$, and $SO_4•^-$ dominated TC and IBU degradation, whereas e^- species mainly contributed to Cr(VI) reduction. Machine learning models (random forest and partial least squares regression) further clarified the key reaction variables, indicating competitive interactions between TC and IBU degradation and an independent pathway for Cr(VI) reduction. Electron spin resonance and density functional theory analyses confirmed the fabrication of a Schottky-type junction and elucidated the direction of charge migration. Overall, BC/$CoFe_2O_4$/nZVI demonstrated excellent stability, reusability, and adaptability toward composite pollutants, demonstrating great potential for practical wastewater treatment.

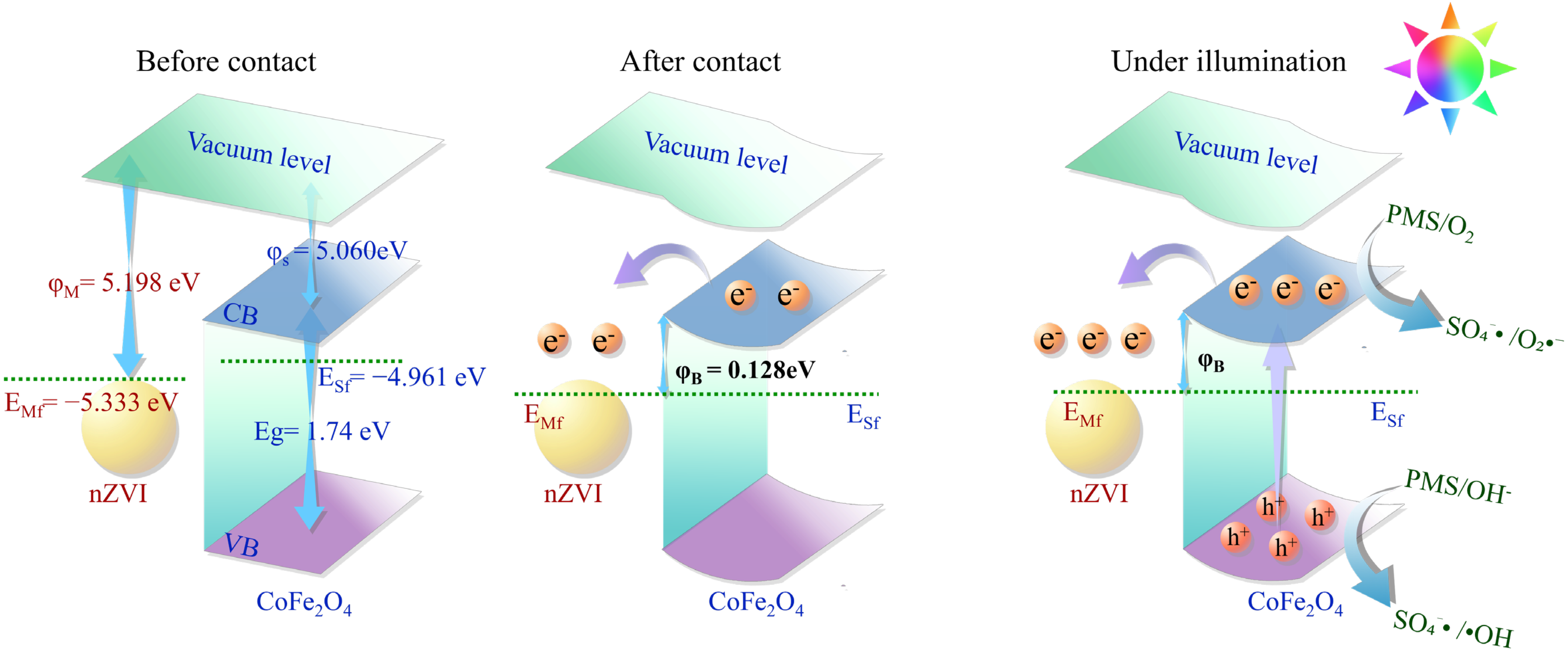

Fig. 5.3.36. The proposed reaction mechanism for the photocatalysis BC/$CoFe_2O_4$/nZVI combined with PMS system.

Based on the above findings, a photocatalytic mechanism is proposed (Fig. 5.3.36). Given that the Fermi level of nZVI is lower than that of $CoFe_2O_4$-corresponding to a higher work function-a Schottky junction is formed at their interface. When n-type $CoFe_2O_4$ and nZVI come into contact, electrons flow from the conduction band (CB) of $CoFe_2O_4$ to the nZVI surface until their Fermi levels align. This charge transfer leads to band bending and the formation of an electron depletion layer at the $CoFe_2O_4$ side, creating a built-in electric field and a Schottky barrier (φB). Under visible light irradiation, $CoFe_2O_4$ absorbs photons and generates electron-hole pairs. The internal electric field at the junction drives photogenerated electrons from the CB of $CoFe_2O_4$ toward the nZVI, while holes remain in the valence band (VB) of $CoFe_2O_4$. This spatial separation of charge carriers significantly inhibits recombination. The transferred electrons on nZVI can reduce molecular oxygen to generate reactive superoxide radicals ($\bullet O_2^-$), while holes in the VB of $CoFe_2O_4$ oxidize water or hydroxide ions to form hydroxyl radicals (•OH). In addition, these holes can activate peroxymonosulfate (PMS), producing sulfate radicals ($SO_4\bullet^-$), which further contribute to the degradation of complex organic pollutants such as TC and IBU. Moreover, the strong reducing power of the electrons enables the conversion of toxic Cr(VI) to less harmful Cr(III) or Cr(II), demonstrating the system’s potential for heavy metal remediation alongside organic pollutant degradation.

Conclusion

This study successfully developed a multifunctional Schottky junction photocatalyst, BC/$CoFe_2O_4$/nZVI, which exhibits enhanced visible-light absorption and efficient charge transport. The BC/$CoFe_2O_4$/nZVI excellent photocatalytic performance with PMS for the simultaneous removal of organic pollutants TC and IBU and the heavy metal Cr(VI), along with high stability and reusability. Its magnetic separability and environmentally benign synthesis further highlight its potential for practical environmental applications. To optimize operational performance, a RF model was employed to fine-tune reaction parameters, while PLSR identified the most influential variables affecting pollutant removal efficiency. Mechanistic insights were gained through DFT calculations, which elucidated the charge migration behavior and interfacial electron transfer dynamics across the Schottky junction. Additionally, HPLC-MS analysis and T.E.S.T. evaluation confirmed a substantial reduction in the toxicity of intermediate degradation products, ensuring environmental safety. Overall, this work contributes to the advancement of multifunctional photocatalysts and offers valuable guidance for designing integrated semiconductor systems for efficient pollutant remediation.

Chapter 6 General Concluding Insights and Future Directions

6.1. Research summary

This study, focusing on the overall goal of "synergistic removal of typical emerging organic pollutants and heavy metals by biochar-based photocatalysis and Fenton-like systems," has conducted three sequential and progressive research projects. These three papers demonstrate from different perspectives that, using biochar-supported iron-based heterojunction composite materials in advanced oxidation systems with activated peroxymonosulfate, the synergistic removal of multiple pollutants, including antibiotics, non-steroidal anti-inflammatory drugs, and Cr(VI), can be efficiently achieved.

6.1.1. Overview and methodology

First, a BC/$CoFe_2O_4$/Fe_2O_3 S-scheme photocatalytic-PMS system was established, focusing on the simultaneous removal of TC and Cr(VI). $CoFe_2O_4$ and Fe_2O_3 were grown in situ on biochar using a two-step thermal polymerization-hydrothermal method, constructing an S-scheme heterojunction with a wide visible light response range (200–800 nm), high photocurrent, and low impedance. Under PMS and visible light conditions, this material achieved a TC removal rate of approximately 99% and a Cr(VI) removal rate of approximately 88% within 45 min, significantly outperforming single $CoFe_2O_4$ or Fe_2O_3. The reaction mechanism was investigated using free radical quenching experiments and ESR tests. The results showed that $SO_4{\bullet}^-$, $\bullet OH$, and $\bullet O_2^-$ are the dominant reactive species in TC degradation, with electron-dominant reduction of Cr(VI). UPS and DFT calculations confirmed the S-type bandgap between $CoFe_2O_4$ and Fe_2O_3 and the efficient carrier separation pathway. Furthermore, combined with LC–MS and Fukui index analysis, a stepwise oxidation, ring-opening, and mineralization pathway of TC was constructed, and the changes in intermediate reactivity and potential toxicity were analyzed, demonstrating that the material exhibits excellent stability, low risk of secondary pollution, and significantly reduced environmental toxicity.

The second study examines the concurrent elimination of four common NSAIDs (ketoprofen, naproxen, diclofenac, and ibuprofen) through the nZVI heterogeneous Fenton process. The results show that the nZVI–H_2O_2 system can break down all four NSAIDs by more than 90% in 30 minutes when the conditions are right. This shows that the nZVI system could be a quick and effective way to clean up a wide range of pharmaceutical pollutants. A Box-Behnken response surface methodology (RSM) was developed to conduct a more in-depth examination of the impacts of pH, H_2O_2, and NaCl concentrations on degradation efficiency and their interrelations. The findings demonstrate that acidic conditions and suitable oxidant dosage can facilitate the reaction, while also highlighting the dual function of Cl^- in enhancing Fe(0) dissolution and potentially competing for free radicals. This study offers a significant reference for developing a "photocatalytic-advanced oxidation" system from the standpoint of process optimisation.

Finally, based on this, BC/$CoFe_2O_4$/nZVI Schottky junction photocatalytic-PMS system was constructed and systematically performance of its was investigated in simultaneously removing IBU, TC, and Cr(VI) under visible light. The results show that, compared to single $CoFe_2O_4$ or nZVI, this ternary composite material can achieve nearly 100% removal of IBU, approximately 93% of TC, and approximately 90% of Cr(VI) in the presence of PMS, while maintaining high efficiency in multi-pollutant coexisting systems. Free radical quenching experiments and DFT calculations revealed that $SO_4^{\bullet -}$, •OH, and $\bullet O_2^-$ dominate the degradation of organic matter, while electrons are mainly responsible for Cr(VI) reduction. The Schottky heterojunction formed by $CoFe_2O_4$/nZVI significantly promotes the separation and directional migration of photogenerated electrons and holes. In addition, RF, PLSR, and SHAP analyses quantified the effects of factors such as pH, initial concentration, and PMS dosage on the removal of multiple pollutants, providing theoretical support for optimizing conditions in complex systems. Cyclic experiments, metal precipitation, actual water body experiments, and intermediate product toxicity assessments demonstrated the material's high stability, low risk of secondary pollution, and environmental friendliness.

6.1.2. Materials design and construction

This research focuses on the combination of "iron-based active components and advanced oxidants," using biochar as a support to load semiconductor heterojunctions onto its porous carbon framework, thus constructing a visible-light-responsive photocatalyst. Biochar provides a high specific surface area and a conductive framework, which is beneficial for pollutant enrichment and electron transport. Iron and iron-based oxides provide a visible-light-responsive heterojunction framework, capable of absorbing light and generating charge carriers in the 200–800 nm range. In the Fenton-like system, the valence state changes of iron and cobalt act as activation centers and electron pools for PMS, participating in free radical generation and providing electrons for heavy metal reduction. All materials possess a certain degree of magnetism, facilitating rapid recovery after the reaction via an external magnetic field.

In summary, this research demonstrates a clear approach at the materials level: achieving efficient removal of multiple pollutants in a low-cost iron-based system through "biochar support and heterojunction structure and photocatalysis," while simultaneously considering visible light utilization, magnetic separation, and recyclability.

6.1.3. Pollutant removal mechanism

Mechanistically, the research mainly focuses on the free radical oxidation of organic pollutants and the electron reduction of heavy metal pollutants. In the biochar-supported photocatalytic activation PMS system, the catalytic activity of Schottky and S-type heterojunctions is utilized to generate $SO_4^{\bullet -}$, $\bullet OH$, and $\bullet O_2^-$ free radicals in the presence of visible light, attacking TC and IBU, thereby achieving the degradation and mineralization of organic pollutants. For heavy metal pollutants, the generated electrons mainly reduce the high-valence, highly toxic hexavalent chromium to the low-toxicity trivalent chromium.

Work function calculations and charge density difference results explain the electron transfer within the material, thus explaining the material's excellent treatment effect. This provides theoretical support for subsequent material design.

Notably, the research did not stop at the level of "qualitative mechanism diagrams" but introduced machine learning for modeling. Random forest, PLSR, and SHAP analyses identified key factors such as initial concentration and PMS dosage. Furthermore, the optimal experimental conditions were explored under the guidance of the model, providing strong support for subsequent large-scale experiments. Overall, the study constructed a multi-scale mechanistic framework that extends from experiment to theory and back to experiment.

6.1.4. Environmental safety and application potential

6.1.4.1. Catalyst stability and metal leaching

During over six cycles of experiments, the photocatalytic system witnessed only minor degradation of efficiency for the removal of pollution. Pre- and post-reaction analyses also revealed that there were no changes in the crystal phase and morphology of the material. Along with this, the leaching of Fe and Co was found to be below the emission standards.

6.1.4.2. Intermediate product toxicity and antibiotic activity reduction

Intermediates in the degradation of organic pollutants were identified using LC-MS and simulation calculations. Combined with T.E.S.T. calculations of the toxicity of various products, the results showed that the toxicity of most intermediates was significantly lower than that of the TC and IBU. The toxicity of the final products was also lower than that of the TC and IBU. Antibacterial activity experiments were also conducted, showing a significant reduction in pollutant toxicity.

6.1.4.3. Applicability to real-world water bodies

At the application level, the research did not remain confined to the laboratory but was applied to treat pollutants in real-world water bodies such as lakes, dyeing and printing wastewater, and pharmaceutical wastewater. The system can still maintain a removal efficiency of over 60-80% in real water samples, indicating that it has a certain tolerance to interference from inorganic anions and cations and natural organic matter.

6.2. Future research

Based on the current research, future research will be deepened in areas such as material design, mechanism refinement, environmental safety, and scale-up applications.

6.2.1. Deepening of materials design and system integration

This work clearly elucidates the benefits of using biochar-based heterojunction photocatalytic systems for the concurrent degradation of various pollutant species. For optimizing these systems, material synthesis can play a crucial role. Adding a metal oxide or carbon material will help create a multi-interface composite material that can provide the benefits of photocatalytic reactions (referred to as Fenton-like reactions) and adsorption. Nevertheless, optimizing the structure and surface properties of the biochar material along with the easy synthesis of the material will also help achieve the goals of efficient use of energy and environmental conservation.

6.2.2. Deepening of mechanistic understanding and data-driven design

The refinement of mechanistic studies allows for more comprehensive material characterization, such as enhanced in-situ XPS, XAFS, ESR, or in-situ infrared spectroscopy. Such characterization methods allow for the direct observation of changes that take place in the Fe and Co valence states during the photoinduced reaction, thereby providing insight into PMS activation and the absorption, degradation, and reduction processes that take place for the intermediates. This provides support for the predicted band structure and charge transfer routes that take place using the DFT model. Additionally, the use of machine learning helps with reversing the design of material compositions.

6.2.3. Further improvement of environmental safety and toxicological assessment

Currently, the main focus is on toxicity simulation calculations and antibacterial experiments on bacteria. Further in-depth research is planned for the next stage. This includes incorporating multi-trophic-level biological experiments with algae, invertebrates, and mammalian cells to assess chronic toxicity, endocrine disruption, and genotoxicity. Simultaneously, long-term cycling and immersion experiments, combined with speciation analysis, will be used to track the distribution of Fe, Co, and Cr in the solid-liquid phase, clarifying the risks of metal migration and accumulation under long-term operation.

6.2.4. Engineering scale-up and practical application expansion

The next step could be to design fixed-bed or fluidized-bed photoreactors, magnetic separation-recirculation systems, etc., to achieve continuous treatment of pollutants in wastewater. The range of pollutants could also be expanded by adding more types of mixed antibiotics and drugs, as well as organic pollutants such as dyes. Simultaneously, other heavy metals could be added to evaluate the system's applicability under more complex pollution profiles.

Overall, this study systematically constructed a multifunctional catalytic system using biochar as a carrier, combining iron-based heterojunctions and Fenton-like reactions. The photocatalytic system achieved highly efficient synergistic removal of typical emerging organic pollutants (TC, IBU) and heavy metal Cr(VI). Furthermore, the synergistic pathway of free radical oxidation and electron reduction was clearly revealed mechanistically. Simultaneously, the environmental safety and engineering application potential of the system were verified through cycle stability, metal leaching, and intermediate product toxicity assessments, providing a solid theoretical and experimental foundation for subsequent scale-up to complex water body treatment and further material optimization.

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Abbreviations

ACN	Acetonitrile
AOPs	Advanced Oxidation Processes
BC	Biochar
BET	Brunauer – Emmett – Teller
B-nZVI	Bentonite-supported nanoscale zero-valent iron
CB	Conduction Band
CFX	Cephalexin
CIP	Ciprofloxacin
CTC-HCl	Aureomycin hydrochloride
Cr(VI)	Hexavalent Chromium
DIC	Diclofenac
DFT	Density Functional Theory
DO	Doxycycline
DO-HCl	Doxycycline hydrochloride
EDD	Electron Density Difference
EDS	Energy-Dispersive X-ray Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
ENR	Enrofloxacin
ESR	Electron Spin Resonance

FTIR	Fourier Transform Infrared Spectroscopy
FQs	Fluoroquinolones
HPLC	High-Performance Liquid Chromatography
HPLC-MS	High-Performance Liquid Chromatography – Mass Spectrometry
HRTEM	High-Resolution Transmission Electron Microscopy
IBU	Ibuprofen
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IRA	Interdisciplinary Research Academy
KET	Ketoprofen
LC	Liquid Chromatography
LEF	Levofloxacin hydrochloride
LEV	Levofloxacin
LOD	Limit of Detection
LOQ	Limit of Quantification
LOM	Lomefloxacin
MTZ	Metronidazole
NIR	Near-Infrared
NAP	Naproxen
NOR	Norfloxacin
NSAIDs	Non-Steroidal Anti-Inflammatory Drugs

nZVI	Nanoscale Zero-Valent Iron
OFL	Ofloxacin
OTC	Oxytetracycline
PEG	Polyethylene Glycol
PDOS	Partial (or Projected) Density of States
PMS	Peroxymonosulfate
PL	Photoluminescence
PLSR	Partial Least Squares Regression
RF	Random Forest
RhB	Rhodamine B
RR2	Reactive red 2
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SHAP	SHapley Additive exPlanations
SIZ	Sulfisoxazole
SMX	Sulfamethoxazole
SRM	Surface Response Methodology
T.E.S.T.	Toxicity Estimation Software Tool
TC	Tetracycline
TCH	Tetracycline hydrochloride

TDOS	Total Density of States
TEM	Transmission Electron Microscopy
TOC	Total Organic Carbon
UPS	Ultraviolet Photoelectron Spectroscopy
UV	Ultraviolet
UV – Vis	Ultraviolet – Visible
UV-vis DRS	Ultraviolet–Visible Diffuse Reflectance Spectroscopy
VB	Valence Band
WWTPs	Wastewater Treatment Plants
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

List of Publication

Y. Yang, Z. Yu, S. Yang, W. Liu, M.-S. Beldean-Galea, G. Pei Sean, S. Shan, X. Shen, Q. Xue, Construction of $CoFe_2O_4/Fe_2O_3$ S-type heterojunctions on biochar for activating peroxymonosulfate towards simultaneous removal of TC and Cr(VI), *Separation and Purification Technology* 354 (2025) 129157. (IF=9.0) https://doi.org/10.1016/j.seppur.2024.129157.

Y. Yang, X. Shen, S. Shan, J. Vial, M.C. Bruzzoniti, M.S. Beldean-Galea, Efficiency of heterogeneous nano zero-valent iron Fenton process for removal of non-steroidal anti-inflammatory drugs from water, *Toxicological & Environmental Chemistry* 107 (2025) 1489–1508. (IF=1.1) https://doi.org/10.1080/02772248.2025.2532743.

Y. Yang, S. Liu, M. Li, J. Li, M.-S. Beldean-Galea, H. Pan, Q. Xue, S. Shan, X. Shen, Interfacial Schottky junction-enhanced charge separation in BC/$CoFe_2O_4$/nZVI for photocatalytic removal of complex pollutants via peroxymonosulfate activation, *Chemical Engineering Journal* 526 (2025) 171561. (IF=13.2) https://doi.org/10.1016/j.cej.2025.171561.

List of Conference

International Symposium on Separation Science 2023 (ISSS 2023)

24–27 September 2023, Cluj-Napoca, Romania

Poster: The degradation of several non-steroidal anti-inflammatory drugs under the action of nanoscale zero-valent iron.

Symposium Environment & Progress

13–15 June 2024, Cluj-Napoca, Romania

Poster: S-scheme BC/$CoFe_2O_4$/Fe_2O_3 photocatalyst for activation of peroxymonosulfate towards degradation of tetracycline.

International Symposium on Separation Science 2024 (ISSS 2024)

22–25 September 2024, Messina, Italy

Poster: S-type BC/$CoFe_2O_4$/Fe_2O_3 photocatalyst for activation of peroxymonosulfate to treat TC and Cr(VI) together.

Euroanalysis 2025 (European Conference on Analytical Chemistry)

31 August–4 September 2025, Barcelona, Spain

Poster: Visible light driven biochar based $CoFe_2O_4$/nZVI heterojunction activating peroxymonosulfate for simultaneous ibuprofen, tetracycline oxidation and Cr(VI) reduction.

Simpozionul ENVIRONMENT & PROGRESS

14 November 2025, Cluj-Napoca, Romania

Presentation: Multi-pollutant treatment by biochar-based heterojunctions.