CATALYTIC DEGRADATION OF NORFLOXACIN BY PERSULFATE WITH CERIUM NANOCOMPOSITE TEA BIOCHAR

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(Received 4th Feb 2025; accepted 22nd Apr 2025)

Abstract. To create cost-effective, eco-friendly, and efficient catalysts, this research effectively synthesized CeO_2/BC catalysts from waste tea biochar (BC) by modifying biochar with cerium chloride, and utilized them to initiate persulfate (PDS) for the breakdown of Norfloxacin (NOR). Results demonstrated that the CeO_2 alteration produced a porous, irregular shape on the surface of tea biochar and significantly enhanced the crystallinity of the material's surface. Secondly, FTIR spectroscopy confirmed the effective doping of Cerium onto the biochar surface, substantially increasing the concentration of surface functional groups. Thirdly, the NOR degradation trials indicated that the ideal catalyst dosage was 400 mg/L, PDS dosage was 160 mg/L, pH was 7.1, and the initial NOR concentration was 10 mg/L, resulting in a NOR removal rate of 95.19%. The functions of ·OH and $\cdot SO_4^-$ in the reduction of NOR were demonstrated by the quenching test. Both species functioned equivalently as catalysts in the CeO_2/BC system activated by PDS for NOR degradation. Finally, the NOR elimination after 8 cycles diminished to 81.75%, whereas the CeO_2/BC combination continued to exhibit substantial catalytic activity. The catalyst exhibits attributes of sustainable synthesis and high efficiency in organic matter degradation, indicating potential to scalable use.
Keywords: *free radicals, FTIR, reusability, impregnation-pyrolysis method, cerium*

Introduction

Water resources are vital natural assets essential for human survival; however, the overexploitation of marine ecosystems and the rise in anthropogenic activities have led to significant contamination of the natural aquatic environment (Argaluza et al., 2021). Pharmaceuticals and their metabolites are significant water pollutants of concern due to their environmental persistence and detrimental consequences. Research indicates that antibiotic pollutants from pharmaceutical industries, human waste, and hospital effluents can range from one nanogram per liter to several hundred milligrams per liter (Tahrani et al., 2016; Balarak et al., 2020). The presence of antibiotics in natural aquatic environments has the potential to produce harmful effects on aquatic organisms, disrupting the equilibrium of the aquatic ecosystem. Consequently, examining the remediation of antibiotic contaminants in aquatic environments is of practical importance.

Over the past few decades, researchers have employed physical, chemical, and biological strategies to eliminate antibiotic pollutants from water, including adsorption (Mangla et al., 2022), biodegradation (Oberoi et al., 2019), and improved oxidation processes (Elmolla et al., 2010). The advanced oxidation process utilizing

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/2303_56175628

Peroxydisulfuric acid (PDS) activation has garnered significant interest due to its simplicity and efficacy in the comprehensive treatment of antibiotic wastewater, attributed to its substantial free radical generation, straightforward operation, and high treatment efficiency (Honarmandrad et al., 2023; Tian et al., 2022; Pirsaheb et al., 2020). The activation techniques of PDS primarily include of thermal (Norzaee et al., 2018), UV (Pirsaheb et al., 2019), ultrasonic (Gao et al., 2022), graphene (Forouzesh et al., 2019), alkali (Kang et al., 2016) and transition metal (Li et al., 2023). While these activation methods can successfully activate PDS, they invariably present issues such as secondary contamination, elevated energy usage, and environmental repercussions. Consequently, there is an immediate necessity to establish a robust, eco-friendly, and effective activation mechanism for PDS. Biochar (BC) is an economically viable, sustainable, and aromatic solid material characterized by a rich structural composition. Researchers indicate that BC, possessing abundant functional groups, a high surface area, and a customizable porous structure, exhibits a notable ability for PDS activation (Kemmou et al., 2018). Unmodified biochar has inadequate catalytic activity owing to its instability and insufficient functional group coverage; thus, enhancing the catalytic performance of biochar is essential (Zhang et al., 2021; Shi et al., 2022). Meanwhile, biochar-based degradation catalysts have poor stability and risk of heavy metal release in real wastewater/simulated wastewater. Therefore, it is necessary to develop biochar-based antibiotic degradation catalysts with excellent stability and reusability. Recent studies have been based on the strategy of loading transition metals on the surface of biochar to enhance the active sites of the material to improve the radical generation efficiency of biochar catalysts. However, the easy leaching of transition metals makes these materials less stable (Han et al., 2022). Ce is a characteristic rare earth metal with ample availability, economical cost, and non-toxicity. Han et al. (2022) have indicated that cerium oxides proficiently store and release oxygen via the redox cycling of Ce^{3+} and Ce^{4+}, a characteristic that can result in the creation of unstable oxygen vacancies within the bulk phase of cerium oxides, significantly enhancing the electronic conversion of multi-component catalysts. Hence, the incorporation of Ce onto charcoal can mitigate issues related to metal oxide agglomeration and ion leaching, while simultaneously enhancing the catalyst's efficacy.

This study involved the preparation of CeO_2 modified tea biochar (CeO_2/BC) using impregnation pyrolysis, which was utilized for the activation of peroxydisulfate (PDS) to breakdown norfloxacin. The primary research is as follows:

(1) XRD, SEM, and FTIR were initially used to analyze the microstructure, crystal shape, and surface functional groups of CeO_2/BC.

(2) The degradation efficiencies of norfloxacin were examined according on catalyst dosage, PDS dose, pH value, and varying starting concentrations.

(3) The primary reactive oxygen species were identified using free radical burst studies, and the mechanism of NOR degradation in the CeO_2/BC/PDS system has been investigated with the goal of establishing an experimental basis for the enhanced removal of antibiotic wastewater.

Materials and methods

Reagents

The reagents utilized in the experiments, including perchloric acid, sodium persulfate, sodium nitrate, cerium sulfate, methanol, isopropanol, tert-butanol, sodium

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hydroxide, hydrochloric acid, sodium carbonate, cerium dioxide, sodium bicarbonate, potassium iodide, etc., were of superior purity and procured from Shanghai Hu Reagent Co. A standard sample of norfloxacin (100 μg/mL) was acquired from Beijing BioBW Biotechnology Co. The waste tea residue is taken from Anxi, Fujian Province, and the tea type is oolong tea.

Material preparation

The preparation of tea biochar (BC) involved the collection of discarded tea dregs prior to the experiment, which were thereafter stored in the laboratory. The tea dregs were repeatedly cleaned with deionized water and meticulously chopped into little pieces using scissors. Thereafter, the pulverized tea dregs underwent pyrolysis in a tube furnace (YHGS-120612, Shanghai Yuzhe Technology Co., Ltd.) under a nitrogen atmosphere at 600°C for 60 min to produce tea biochar (BC), which was subsequently ground and crushed using a grinder (IN~T2L, Shandong Laiyin Optoelectronics Technology Co., Ltd.) and filtered via a 100-mesh-screen.

The synthesis of CeO_2 modified tea biochar (CeO_2/BC) was conducted utilizing the impregnation-pyrolysis technique. The preparation procedure is illustrated in the *Figure 1*.

Initially, 0.5 g of tea biochar and a specified volume of 0.1 M cerium chloride solution were introduced into a beaker, establishing a mass ratio of tea powder to cerium chloride of 1:0.5. Subsequently, 5 mL of ultrapure water was incorporated, and the mixture was subjected to stirring on a stirrer (L-220, Lai Heng Science and Technology Co., Ltd.) for a duration of 12 h. Upon completion of the stirring phase, a 1 M NaOH solution was incrementally added to the mixture to elevate the pH above 11, followed by a 3-h incubation period. Subsequent to the resting period, the mixture was subjected to centrifugation using a TGL-16M centrifuge. The solution was allowed to stand for 3 h. Following this, it was centrifuged at 8000 r/min for 3 min, and the supernatant was subsequently washed three times with ethanol and ultrapure water. The centrifuged product was desiccated in a constant temperature oven at 100°C overnight and subsequently sieved through a 100-mesh screen. Subsequent to drying, the biochar precursor was positioned in a tube furnace and subjected to a temperature of 600°C at a heating rate of 5°C/min for a duration of 2 h. CeO_2-modified tea biochar was acquired following the cooling process.

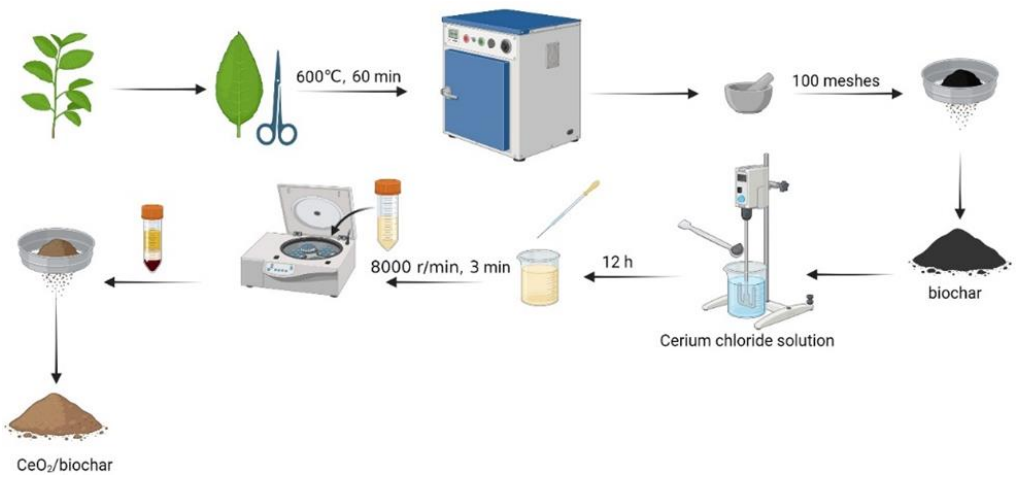

Figure 1. *Preparation procedure of CeO_2-modified tea biochar*

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Structural and performance characterization

This study analyzed the concentration of norfloxacin in degradation products using a liquid chromatograph (model LC3600, Anhui Wan Yi Technology Co., Ltd.). The pH of the solution was determined using a pH meter (model HZP-T502, Huazhi Electronic Science and Technology Co., Ltd.). The crystalline phase of the samples was examined using an XRD diffractometer (model TK-XRD-201, Beijing Taikun Industrial Equipment Co., Ltd.). Scanning was conducted under the following conditions: 40 kV, 30 mA, $\lambda = 0.154$ nm, and 0.02°/s within the 2θ range of 15 to 80°. FT-IR spectroscopy was performed using a spectrophotometer (Model MPAII, Bruker, Germany) with the KBr disc method. A field-emission scanning electron microscope (Model SEM4000Pro, National Instruments Quantum Technologies Co.) was used to create SEM pictures of the materials.

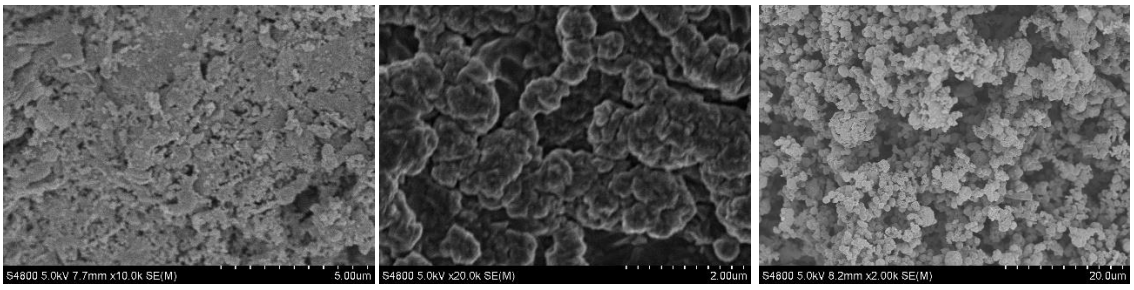
Adsorption degradation assessment

CeO_2/BC activated PDS was used to treat a 10 mg/L NOR solution at a concentration of 50 mL under the conditions of 100-400 mg/L catalyst dosing, 40-160 mg/L PDS dosing, pH range of 2.5-10.9, initial NOR concentration of 10-30 mg/L, and reaction time of 0-60 min Experiments were performed. All experiments were conducted within a thermostatic oscillator chamber and shielded from light exposure. At the sampling cycle, 2.5 mL of reaction solution was pipetted using a pipette gun, filtered through a 0.22 μm microporous filter and then 0.5 mL of 0.1 M methanol was used to terminate the reaction, after which the NOR concentration was analyzed using liquid chromatography. At the final stage of the experiment, the biochar material was retrieved through centrifugation with a centrifuge, afterwards re-centrifuged using ethanol and ultrapure water, and then dried in a thermostatic oven at 80°C for 10 h. The material was subsequently dried in a thermostatic oven for 10 h.

Results and discussion

Material structure analysis

The surface morphology of the samples was investigated using field emission scanning electron microscopy, and the findings are shown in *Figure 2a-c*. *Figure 2* illustrates that the CeO_2 sample possesses a bulk structure with a rough surface, whereas the biochar BC exhibits a smooth and non-porous morphology. Furthermore, the SEM image of CeO_2/BC reveals a porous and irregular spherical structure on the material's surface, indicating the uniform deposition of CeO_2 nanoparticles on the BC surface.



(a) CeO_2 (b) BC (c) CeO_2/BC

Figure 2. *Microscopic morphology of CeO_2, BC and CeO_2/BC*

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Figure 3 displays the experimental results of the subsequent XRD diffractometer analysis of the crystal orientation of the different samples. As presented in *Figure 3*, the peaks of the pure CeO_2 sample correspond to a face-centered cubic fluorite structure with crystal planes (100), (200), (220), (311), (222), (400), and (420). The commercial CeO_2 exhibits pronounced and sharp diffraction peaks in the XRD pattern analysis, signifying a high degree of crystallinity in these crystal planes of the material. The diffraction peaks (100), (200), and (311) associated with CeO_2 were observed in the XRD diffractograms of the CeO_2/BC material, demonstrating the presence of cerium in tea biochar as CeO_2.

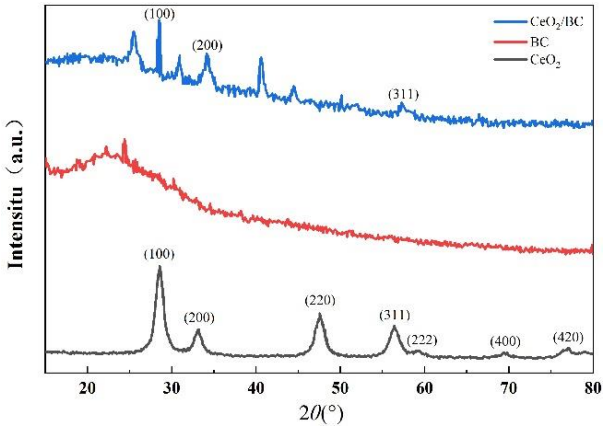

Figure 3. *XRD diffractograms of CeO_2, BC and CeO_2/BC*

The surface functional groups in the biochar BC derived from tea dregs and the cerium oxide-modified biochar CeO_2/BC were analyzed using FTIR spectroscopy. From *Figure 4*, the analyzed results reveal absorption peaks attributed to the stretching of the C = C bond and O-H stretching vibration at 1395 cm^{-1} and 3383 cm^{-1}, respectively. The peak at 1620 cm^{-1} is associated with the C = C/C = O vibration, likely due to the increased adsorption of surface oxygen by the oxygen vacancies in CeO_2, facilitating the generation of reactive oxygen species and the breakdown of contaminants. Confirmation of the successful doping of cerium onto the biochar surface is provided by the absorption peak at 564 cm^{-1}, which is attributed to the stretching vibration of the Ce-O bond.

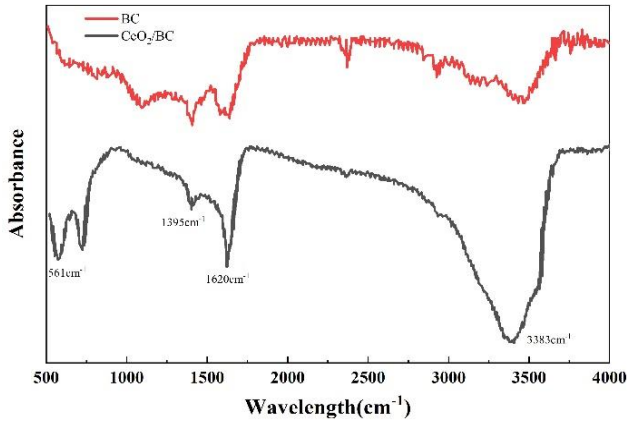

Figure 4. *FTIR spectra of BC and CeO_2/BC*

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Degradation properties of different materials

To analyze the function of each component in the NOR degradation system utilizing CeO_2/BC activated PDS, experiments were conducted to assess the degradation efficiency of various materials for NOR after 60 min of reaction under the conditions of 200 mg/L catalyst dosage, 120 mg/L PDS dosage, pH 7.1, and an initial NOR concentration of 10 mg/L. From *Figure 5*, the pairs of PDS, BC, CeO_2 and CeO_2/BC exhibited percentages of 6.47%, 18.86%, 35.35% and 61.6%, respectively, after 60 min of reaction. The elimination of NOR by PDS was minimal, suggesting that its direct oxidation of NOR was limited. The removal of NOR induced by the adsorption of PDS/BC and CeO_2/BC/PDS was 55.82% and 83.51%, respectively, indicating that the distinct functional groups in BC and CeO_2 can adsorb a portion of the NOR through π-π interactions, hydrogen bonding, and electron-pair donor or acceptor reactions. Consequently, the enhanced NOR removal by PDS/BC and CeO_2/BC/PDS may be due to the active sites enriched in BC and CeO_2/BC being less effective in oxidizing the NOR compared to their oxidation of the NOR. The enhanced active sites in BC promote the breakdown of PDS, yielding ·OH and $\cdot SO_4^-$ (Wang et al., 2023; Guan et al., 2019).

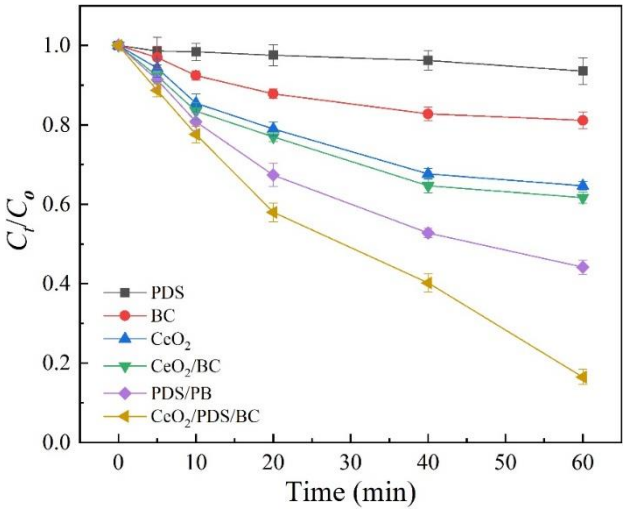

Figure 5. *Analysis of degradation efficiency of different materials*

Optimization of NOR degradation conditions

Catalyst dosage

CeO_2/BC activates PDS to generate free radicals such as ·OH and $\cdot SO_4^-$ and provides free radicals with active sites for binding NOR molecules (Han et al., 2022). Therefore, increasing the catalyst dosing is expected to have a significant effect on the degradation efficiency of NOR. The reaction conditions such as PDS dosing of 120 mg/L, pH 7.1 and initial NOR concentration of 10 mg/L were controlled to be constant in the experiments to investigate the effect of different CeO_2/BC dosages (100, 200, 300 and 400 mg/L) on the removal rate of NOR. After 60 min of reaction, the NOR removal rate of the system could reach 58.86%, 69.82%, 81.59%, and 94.50% when the CeO_2/BC dosage was 100, 200, 300, and 400 mg/L, as highlighted in *Figure 6*. Huang et al. (2020) reported the similar results that, in the system of catalyzing PDS, the high concentration of catalysts helps to promote the rate of the decomposition of PDS to

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produce radicals such as ·OH and $\cdot SO_4^-$. Accordingly, the optimum CeO_2/BC catalyst dosage in this study was 400 mg/L.

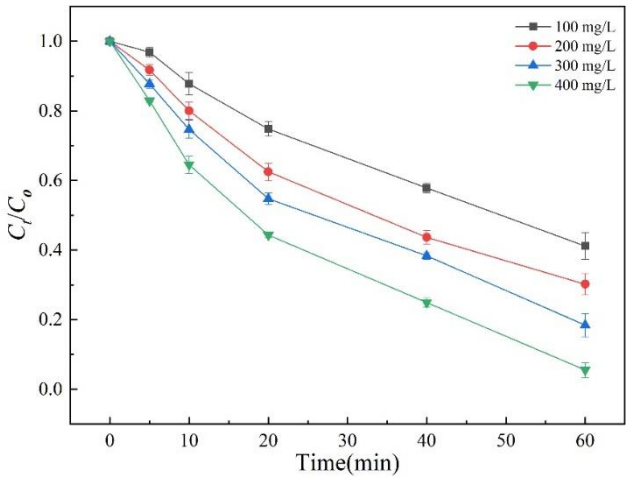

Figure 6. *Effect of catalyst dosage on NOR removal rate*

PDS dosing rate

Although the starting concentrations of pollutants and catalysts remain constant, changes in PDS concentration have a substantial impact on the target pollutants' efficiency of degradation because PDS is a precursor to free radicals (Huang et al., 2020). In this section, the catalyst dosage of 200 mg/L, pH 7.1, and the initial NOR concentration of 10 mg/L were controlled unchanged, and the effects of different PDS dosages (40, 80, 120, and 160 mg/L) on the NOR removal were investigated, and the results of the experiment are shown in *Figure 7*. From *Figure 7*, the removal rate of NOR increased rapidly with the increase of PDS dosage. The results showed that the removal rate of NOR could reach 55.72%, 72.78%, 82.12% and 95.19% after 60 min reaction time when the PDS dosage was 20, 40, 80 and 160 mg/L, respectively, which might be related to the generation rate of free radicals such as ·OH and $\cdot SO_4^-$ at high oxidant concentration. Therefore, the optimum PDS dosage in this study was 160 mg/L.

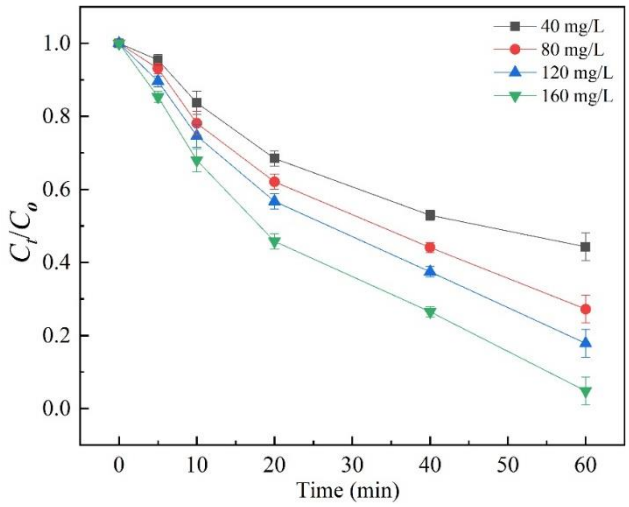

Figure 7. *Effect of PDS dosage on NOR removal rate*

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Acid-base properties

Research indicates that variations in pH influence chemical processes and redox potentials. The generation of active radicals and the surface characteristics of contaminants and nanomaterials (Qian et al., 2020). This section investigated the application scenarios of the CeO_2/BC catalyst by maintaining constant conditions: catalyst injection at 200 mg/L, PDS injection at 120 mg/L, and an initial NOR concentration of 10 mg/L. The effects of pH values of 2.5, 4.8, 7.1, 8.6, and 10.9 on the NOR removal rate were examined, with the experimental results presented in *Figure 8*. The NOR removal percentages were 48.01%, 60.23%, 84.93%, 76.12%, and 38.47% at pH values of 2.5, 4.8, 7.1, 8.6, and 10.9, respectively. The removal rate of NOR significantly diminished under both highly acidic and highly alkaline conditions. This phenomenon is attributed to the influence of extreme pH levels on the decomposition of PDS and the redox potentials of free radicals, such as ·OH and $\cdot SO_4^-$, resulting in substantial electrostatic repulsion between NOR and CeO_2/BC at pH values of 2.5 and 10.9, respectively. Furthermore, the negatively charged PDS impedes the electrostatic interaction between NOR and CeO_2/BC at a pH of 10.6, which also obstructs the surface complexation of negatively charged CeO_2/BC, ultimately leading to reduced yields of ·OH and $\cdot SO_4$- (Dey et al., 2023). The ideal pH for this study was 7.1.

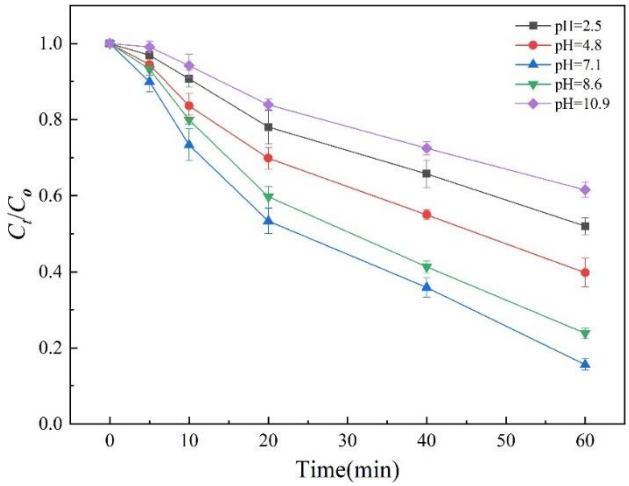

Figure 8. *Effect of different pH values on NOR removal rate*

Different initial NOR concentrations

The effects on the NOR removal rate were examined while maintaining catalyst dosing at 200 mg/L, PDS dosing at 120 mg/L, and pH at 7.1, with initial NOR concentrations set at 10, 20, and 30 mg/L. *Figure 9* displays the results of the experiments. The experimental findings show that NOR exhibits a steady drop as the initial concentration of NOR increases. The removal rate of NOR dropped from 82.59% to 58.86% as its initial concentration rose from 10 mg/L to 30 mg/L. This decline can be attributed to intensified competition for free radicals between residual NOR and intermediates, which may impede the degradation efficiency of NOR. A high concentration of NOR will not only result in rapid consumption of PDS, hindering NOR breakdown, but will also cause excessive NOR aggregation in

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CeO_2/BC, hence restricting PDS diffusion on the material's surface. The ideal initial NOR concentration was 10 mg/L.

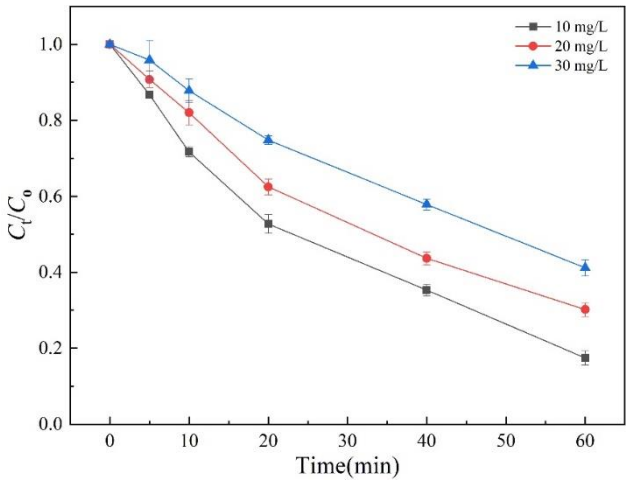

Figure 9. *Effect of different initial concentration*

Quenching test

Research indicates that isopropanol (IPA) and tert-butyl alcohol (TBA) effectively scavenge hydroxyl radicals (·OH) and sulfate radicals (·SO_4-) (Dey et al., 2023; Gao et al., 2022). Elevated concentrations of IPA and TBA exhibit superior adsorption capabilities for ·OH and ·SO_4^- compared to high concentrations of norfloxacin (NOR). Specifically, IPA reacts with -OH at a rate constant of $k_{OH/IPA}$ = 1.92×10^9 mol/L·s and with ·SO_4^- at $k_{SO4-/IPA}$ = 8.4×10^7 mol/L·s, demonstrating its efficacy as a scavenger for these radicals within the reaction system. Scavengers within the reaction system. Conversely, TBA (i.e., $k_{·OH/TBA}$ = 6.2×10^8 mol/L·s), which exhibits rapid kinetics for ·OH, was utilized only as a ·OH scavenger. To analyze the generation of free radicals in the NOR degradation reaction system utilizing the CeO_2/BC catalyst-activated persulfate, degradation experiments were conducted with 200 mg/L IPA and TBA as quenching agents, 200 mg/L catalyst dosing, 120 mg/L PDS dosing, pH 7.1, and an initial NOR concentration of 10 mg/L. The outcomes of the degradation experiments are illustrated in *Figure 10*. The experimental results indicate that the NOR removal rate declined to 22.66% and 25.21% with the application of 200 mg/L of IPA and TBA as quenching agents, respectively, demonstrating that CeO_2/BC activation during PDS breakdown of NOR generated ·OH and ·SO_4^- in the system. Both IPA and TBA exhibited nearly identical inhibitory effects, suggesting that ·OH and ·SO_4^- are significant contributors to the breakdown of NOR.

Recycling performance analysis

The recycling ability of the CeO_2/BC composite was evaluated by recycling experiments and used for subsequent catalytic runs under the same experimental conditions. As can be seen in *Figure 11*, the NOR removal rate after eight cycles decreased to 81.75%, and the CeO_2/BC composite still maintained a high catalytic activity, indicating the excellent stability of the material.

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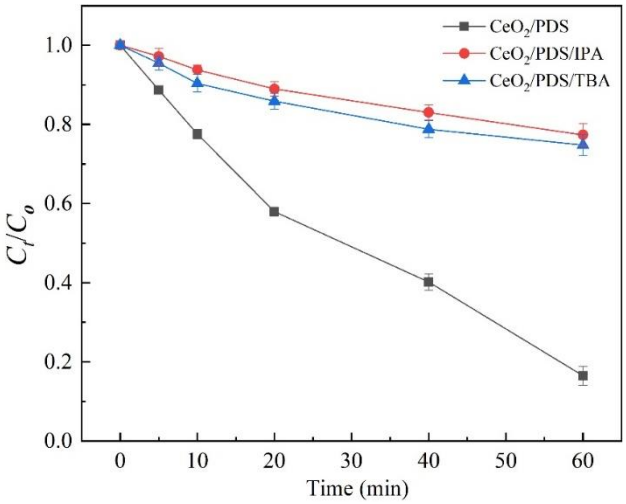

Figure 10. *Results of quenching test*

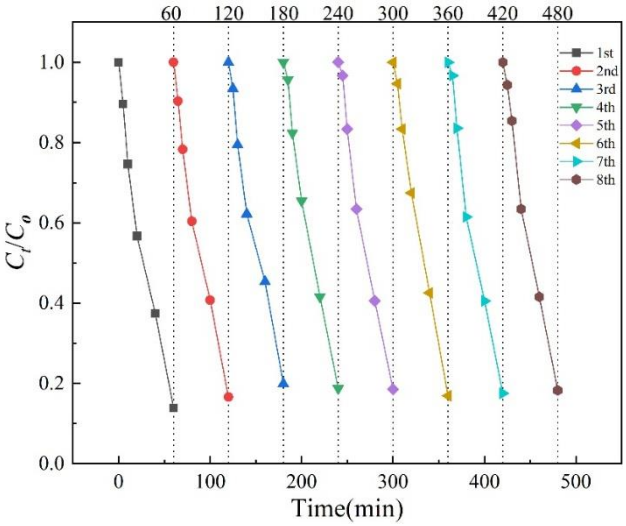

Figure 11. *Recycling performance analysis*

Conclusions

In this study, CeO_2 modified tea biochar (CeO_2/BC) was prepared by impregnation pyrolysis and used for the activation of PDS for the degradation of norfloxacin. CeO_2 modification led to a porous and irregular spherical structure on the surface of tea biochar, as well as a substantial increase in the crystallinity of the material surface, as determined by the structural analysis of the material, and secondly, Fourier infrared (FTIR) spectroscopy proved the successful doping of cerium on the surface of the biochar and significantly enriched the concentration of its surface functional groups. At the optimal catalyst dosage of 400 mg/L, PDS dose of 160 mg/L, pH 7.1, and initial NOR concentration of 10 mg/L, the NOR removal rate reached 95.19%. Subsequent quenching test proved the contribution of ·OH and $\cdot SO_4^-$ to NOR degradation and that ·OH and $\cdot SO_4^-$ freely played the same catalytic roles in the system of CeO_2/BC activated over PDS degradation of NOR. NOR removal after eight cycles decreased to 81.75% and the CeO_2/BC composite still maintained a high catalytic activity. The

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catalyst has the characteristics of sustainable synthesis and high efficiency of organic matter degradation, which makes it scalable.

This study has some limitations, including the need for further investigation of the catalyst performance under real wastewater conditions, the scalability of the synthesis method, and the potential influence of other environmental factors such as varying pollutant compositions and complex matrices in wastewater. Future studies should aim to address these aspects to enhance the practical application of the catalyst.

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