

Degradation of ofloxacin by biochar synergized with oxalic acid under visible light

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Abstract: In order to investigate the degradation performance and underlying mechanism of antibiotic pollutants in an acid synergistic system composed of biochar (BC) and oxalic acid (OA) under visible light irradiation, a visible-light-driven BC-OA system (Vis-BC-OA) was established. Degradation experiments were conducted using ofloxacin (OFL) as the model contaminant. The results demonstrated that the system exhibited excellent degradation capability, achieving a high removal efficiency of 98.4% within 100 min. A marked synergistic catalytic effect was observed between BC and OA, whereas efficient degradation was scarcely achieved in single-component systems. Therefore, the Vis-BC-OA system shows promising potential for the removal of antibiotic pollutants.

1. Introduction

Intensive agricultural and industrial activities have led to the continuous discharge of refractory organic pollutants into aquatic environments. Among these, antibiotics are of particular concern due to their widespread use and persistence. Ofloxacin (OFL), a typical quinolone antibiotic, is extensively applied in medicine and animal husbandry owing to its broad-spectrum antibacterial activity [1]. However, its stable aromatic ring and fluorine substituents confer high chemical stability and poor biodegradability, resulting in long-term water persistence and food chain accumulation, which pose toxic risks to aquatic organisms and ecosystems [2]. Thus, efficient and green technologies for OFL removal are urgently needed.

At present, the treatment methods for antibiotic pollution include physical adsorption, biodegradation, chemical oxidation and others. Among them, the adsorption method is simple in operation, but only achieves phase transfer of pollutants rather than fundamental elimination of contamination [3]. Biological methods are easily inhibited by the toxicity of antibiotics and exhibit limited treatment efficiency [4]. In contrast, advanced oxidation processes can realize the deep oxidative degradation, and have attracted extensive attention in recent years [5]. In particular, visible light-driven photocatalytic systems are regarded as a green and sustainable technology for pollution remediation due to their ability to utilize solar energy [6].

Traditional photocatalytic systems mostly rely on metallic or semiconductor materials such as TiO_2 . However, these materials generally with a narrow light-response range, a high electron-hole recombination rate, and metal ion leaching, which restrict their practical application in water treatment [7]. Therefore, the development of novel, metal-free and environmentally benign photocatalytic systems has become a research hotspot. Biochar (BC) is a kind of porous carbon material, which prepared by pyrolysis of agricultural wastes under limited oxygen conditions. It possesses a large specific surface area, abundant surface functional groups and electron transport capability, exhibiting favorable application prospects in the fields of pollutant adsorption and catalytic degradation [8]. Recent studies have shown that BC can not only act as an adsorbent but also participate in electron transfer processes under light irradiation, thereby promoting the degradation of pollutants [9]. Nevertheless, due to its low separation efficiency of photogenerated electron-hole pairs, the catalytic activity remains limited when used alone [10]. As a small-molecule organic acid widely present in nature, oxalic acid (OA) exhibits excellent electron-donating and complexing capacities. In iron oxide systems, OA can adsorb onto the surface of iron oxides to form Fe(III)-OA complexes [11], ferrous ions (Fe(II)) and reactive oxygen species are generated in situ, which can degrade the organic pollutants [12]. However, the synergistic mechanism of OA in metal-free carbon-based photocatalytic systems has not been systematically explored up to now. Accordingly, this study established a visible

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light driven BC-OA synergistic system (Vis-BC-OA), with OFL as the target pollutant, to provide a theoretical foundation for the development of green and efficient metal-free photocatalytic technologies for antibiotic remediation.

2. Materials and Methods

2.1 The preparation of BC

The BC used in this study was prepared from rice straw collected from Kunming, Yunnan Province, China. First, the rice straw was washed by ultrapure water to remove its surface dust and then dried in an oven at 80°C to constant weight. The dried rice straw was cut into pieces, placed and compacted in a crucible, then covered to create an oxygen-limited environment. Subsequently, the crucible was transferred into a muffle furnace for pyrolysis under continuous nitrogen flow with the rate of 0.6-0.8 L/min. During pyrolysis, the temperature was raised to 500°C at a heating rate of 10°C/min and maintained at 500°C for 120 min. After the furnace cooled naturally to room temperature, the resulting black solid was taken out, ground, and sieved through a 100-mesh sieve. The obtained BC powder was stored in a desiccator for subsequent use.

2.2 Characterization of BC

2.2.1 Surface morphology and Elemental Distribution (SEM)

A scanning electron microscope (SEM, ZEISS Sigma 300, Germany) was employed to observe the surface morphology of BC. A small amount of dried BC sample was adhered to conductive adhesive, sputter-coated with gold, and then examined at an accelerating voltage of 15 kV. Meanwhile, elemental distribution on the sample surface was analyzed using an energy-dispersive X-ray spectrometer (EDS) attached to the microscope.

2.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

The types of functional groups on the BC surface were analyzed using a Fourier transform infrared spectrometer. The dried BC sample was mixed with KBr at a mass ratio of 1:100, ground, and pressed into a tablet, followed by scanning over the wavenumber range of 400-4000 cm^{-1} .

2.3 Degradation Experiments

Degradation experiments were carried out in a quartz photoreactor equipped with a circulating cooling

water system, and the reaction temperature was controlled at $25 \pm 1^\circ\text{C}$. A 300 W xenon lamp was used as the light source to simulate visible light. A total of 100 mL of OFL solution with a concentration of 17.14 $\mu\text{mol/L}$ was added to the reactor, followed by the optimal dosages of BC and oxalic acid. The light source was then turned on to initiate the reaction, and the reaction time was recorded immediately. At predetermined time intervals (0, 5, 10, 15, 20, 40, 60, 80 and 100 min), 0.8 mL of the reaction solution was collected, filtered through a 0.22 μm aqueous filter membrane into a brown sampling vial containing an equal volume of methanol to quench the reaction. All experiments were performed in duplicate. The concentration of OFL in the samples was determined by high performance liquid chromatography (HPLC), and the degradation efficiency was calculated accordingly.

3. Results and discussion

3.1 Effect of BC and OA Dosages on OFL Degradation

To determine the optimal reaction conditions for OFL degradation in the Vis-BC-OA system, the effects of BC dosage and OA concentration on OFL degradation efficiency were investigated separately, and the experimental results are shown in Figure 1. In a 100 mL reaction system with fixed OA concentration, varying the BC dosage from 0mg to 70 mg showed that the blank control group that without BC only achieved a degradation efficiency of 24.12%, which could be attributed to the acid effect of OA itself. As the BC dosage gradually increased to 0.3 g/L and 0.4 g/L, the degradation efficiency of OFL rose to 85.9% and 89.3%, respectively. The degradation efficiency peaked at 98.4% within 100 min at the BC dosage of 50 mg. Further increasing the dosage to 60 mg and 70 mg, the degradation efficiency slightly decreased to 95.5% and 97.6%, respectively. This phenomenon can be explained by excessive BC enhancing light scattering and causing overlapping active sites, thereby reducing light utilization efficiency.

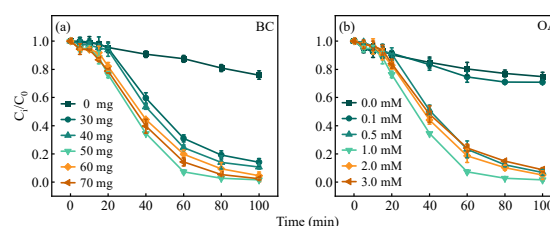


Figure 1. Effects of BC (a) and OA (b) dosage on ofloxacin degradation.

In summary, BC and OA exhibit a significant synergistic catalytic effect during the degradation of OFL. Neither BC alone nor OA alone can achieve efficient degradation of OFL, rapid degradation can only be realized when the two components coexist.

3.2 Characterization of BC

EDS elemental mapping images (Figures 2 a-e) demonstrate that the BC surface mainly contains C, O, and a small amount of Si. Notably, metal elements (such as Fe, Al, etc.) that play key roles in common metal-chelated BC photocatalytic systems were either not detected or present at extremely low contents in this material (Figure 2a). These results confirm that the BC used in this study is a metal-free carbon material. Its photocatalytic activity should be mainly attributed to the carbon skeleton and surface oxygen-containing functional groups, excluding the possibility of metal oxides acting as catalytic active sites.

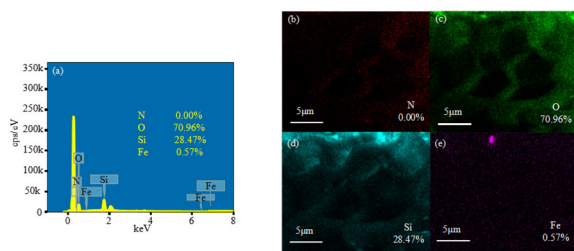


Figure 2. X-ray energy dispersive spectroscopy (EDS) spectra of BC, (a) overall spectrum; (b) N-BC; (c) O-BC; (d) Si-BC; (e) Fe-BC.

Fourier transform infrared spectroscopy (FTIR) was employed to analyze the functional group structures on the BC surface, and the results are presented in Figure 3.

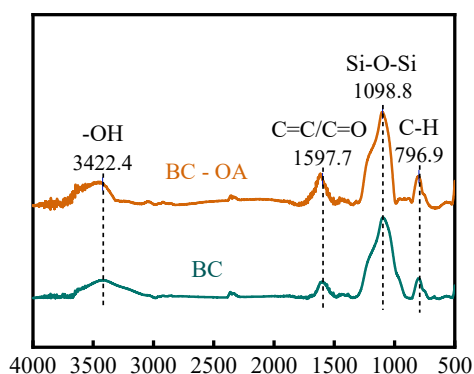


Figure 3. Comparative analysis of FTIR spectra before and after the addition of OA

According to the FTIR comparison spectra of BC before and after the reaction (Figure 3), the BC shows a broad and strong absorption peak at approximately 3422 cm^{-1} , which is assigned to the

stretching vibration of -OH groups[13], indicating abundant hydroxyl functional groups on the BC surface. The absorption peak at around 1598 cm^{-1} can be attributed to the stretching vibration of aromatic C=C or carbonyl C=O bonds [14]. The broad and intense peak at approximately 1099 cm^{-1} is likely associated with the stretching vibration of Si-O-Si bonds [15]. However, no obvious changes in these peaks were observed before and after the reaction, suggesting that Si-O bonds were not involved in the subsequent catalytic process.

Oxygen-containing functional groups exert multiple promoting effects on the degradation of OFL. Firstly, in terms of enhancing visible-light absorption and electron transfer, polar functional groups such as hydroxyl and carbonyl groups can act as trapping sites for photogenerated electrons, suppressing electron-hole recombination and thus prolonging the lifetime of reactive species. Meanwhile, the graphitic-like structure of BC exhibits favorable electrical conductivity. Secondly, these functional groups participate in synergistic reactions as active sites. Hydroxyl groups on the BC surface can form hydrogen bonds or surface complexes with OA, analogous to the role of Fe(III)-OA complexes in iron oxide systems, thereby achieving photoactivation of OA under metal-free conditions and generating reactive oxygen species. This is highly consistent with the observation in degradation efficiency of single BC or single OA systems were both below 25%, while the efficiency increased to 98.4% when both coexisted, confirming that surface functional groups of BC serve as crucial mediators for synergistic catalysis. In addition, BC can enhance pollutant enrichment cause its porous structure and oxygen-containing functional groups can adsorb OFL via π - π interactions and hydrogen bonding, increasing the local concentration and accelerating the degradation reaction, which is also agrees with the 25.14% removal efficiency in the single BC system shown in Figure 1. In summary, the metal-free nature of BC and its abundant surface oxygen-containing functional groups (hydroxyl, carbonyl, etc.) enable it to synergize with OA under visible light for efficient degradation of OFL. These structural features provide direct evidence for understanding the catalytic mechanism of Vis-BC-OA system.

4. Conclusions

This study investigated the photocatalytic degradation mechanism of OFL in the Vis-BC-OA system. The prepared BC is a metal-free carbon material and rich in oxygen-containing functional groups such as hydroxyl groups and aromatic

C=C/C=O bonds on its surface. These structural features may serve as active sites and electron transfer mediators for photocatalytic reactions. Under optimal reaction conditions, the system achieves a degradation efficiency of 98.4% for OFL within 100 min. A significant synergistic effect exists between BC and OA, and efficient degradation is difficult to realize in single-component systems, confirming that metal-free carbon-based photocatalytic systems can effectively remove antibiotic pollutants from water.

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