Research Progress on Biochar Adsorption of New Antibiotic Contaminants

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Abstract: Growing concern regarding emerging contaminants—driven largely by their persistent detection in water bodies—has attracted significant attention from the research community. As a specific class of emerging contaminants, antibiotics have become a focal point in aquatic environmental management due to characteristics such as continuous discharge and environmental persistence, as well as the potential risk of promoting the spread of antibiotic resistance. In recent years, the third-generation cephalosporin antibiotic cefixime (CFX) has been frequently detected in the environment; however, despite its complex environmental behavior, research specifically targeting its removal remains limited compared to studies on sulfonamides and tetracyclines. This paper provides a comprehensive review of the pollution characteristics, current contamination status, and control technologies associated with CFX. It focuses on strategies for the preparation and modification of biochar and its application in removing emerging contaminants and antibiotics, while also offering an in-depth analysis of the mechanisms and influencing factors regarding CFX adsorption by biochar. Finally, the article summarizes current challenges in using biochar to remove CFX and outlines future prospects for the design of high-performance biochar materials, synergistic multi-technology approaches, and engineering applications, aiming to advance both the theoretical understanding and practical implementation of biochar technology for antibiotic pollution remediation.

Keywords: Emerging Pollutants; Antibiotics; Cefixime; Biochar

1. Introduction

1.1 Overview of Antibiotic-Class Emerging Contaminants

Emerging contaminants (ECS) are chemicals that are not included in environmental monitoring and management [1]. However, the environment and health are in danger, which has gradually attracted the attention of the whole world in recent years. Most of these emerging pollutants are accumulated in the body and remain in the environment for a long time, which has the characteristics of toxicity. It is widely spread through water, air and soil, which brings potential dangers to the ecosystem and human health. Emergent pollutants are mainly divided into four categories: persistent organic pollutants (POPs), environmental endocrine disruptors (EDCs), antibiotics, and microplastics, among which the pollution of antibiotic has attracted much attention [2]. Because it is widely used and often appears in the environment, it may be the reason for the proliferation of antibiotic resistance genes.

Antibiotic pollution is a natural semi-synthetic organic compound, which can inhibit and kill microorganisms. It has the characteristics of affecting large organisms even if the concentration is low, and it will remain in the environment for a long time. Antibiotics are widely utilized across various sectors, including human medicine, livestock and poultry farming, aquaculture, and agricultural production. However, limited metabolic utilization of antibiotics in humans and animals results in their persistent entry into the environment via excretion from human and animal metabolism, discharge of medical wastewater, and input from aquaculture effluent. Their extensive use leads to their continuous entry into the environment through human and animal metabolism and excretion, discharge of medical wastewater, and inflow of aquaculture wastewater. Most antibiotic molecules possess complex cyclic skeletons (such as lactam rings, tetracyclic structures, or quinolone cores) as well as polar functional groups such as carboxyl, hydroxyl, and amino groups [3], which confer strong hydrophilicity and environmental mobility. Furthermore, the amide, lactone, and ether bonds in their molecular structures possess a certain degree of resistance to hydrolysis and biodegradation, making it difficult for them to be rapidly and completely mineralized. Consequently, long-term low-dose exposure may not only cause toxic effects on aquatic organisms but also induce the emergence and spread of antibiotic resistance genes (ARGs), exacerbating the global problem of antibiotic resistance. Therefore, the development of highly efficient and stable removal materials and treatment methods is of great significance for reducing the environmental risks posed by antibiotics.

1.2 Environmental Pollution Characteristics and Current Research Status of Cefixime (CFX)

Tetracycline hydrochloride is a Cefixime (Cefixime Trihydrate, CFX) is a typical third-generation cephalosporin antibiotic belonging to the β-lactam class. It exerts a bactericidal effect by inhibiting the transpeptidation reaction during peptidoglycan synthesis in the bacterial cell wall and exhibits good antibacterial activity against a variety of Gram-negative bacteria. It is widely used in the clinical treatment of respiratory and urinary tract infections. The oral bioavailability of this drug is only 40%–50%, and approximately 50% is excreted in the urine in its original form. This means that a significant proportion of CFX enters the sewer system without being fully metabolized and is discharged into receiving water bodies via wastewater treatment plant effluent. As one of the representative cephalosporin antibiotics, CFX has been included in the list of target substances covered by detection methods for antibiotic residues in aquatic environments. For example, monitoring of a wastewater treatment plant in Tehran by Mirzaei [4] and others showed that while the influent concentration ranged from 272 to 777 ng/L, the effluent concentration remained between 50 and 422 ng/L, and CFX was still detectable in the effluent. This indicates that conventional wastewater treatment processes are insufficient for the complete elimination of CFX. Despite the low concentrations observed (in the ng/L to μg/L range), the potential for long-term ecological and human health ramifications stemming from continuous discharge warrants serious consideration.

Compared with the advanced antibiotics such as sulfonamides and tetracyclines, the systematic study of cephalosporin antibiotics, especially CFX, needs further investigation, such as its distribution characteristics in the environment, its changing mechanism, its movement in water and soil, its toxic effects on the ecosystem, and its effective control technology.

2. Research Progress on Antibiotic Pollution Control Technologies

2.1 Chemical Treatment Technologies

Key chemical processes entail chlorination, photocatalytic and ozonated oxidations, which decompose antibiotic molecules by generating hydroxyl radicals or other strong oxidizing agents. For example, Umar et al [5] successfully synthesized a copper-titanium dioxide-silicoaluminate nanocomposite via a solvothermal method for the degradation of CFX. Under optimal conditions, the maximum photocatalytic degradation rate reached 89.95%. Furthermore, after three application cycles, the reusability of the prepared nanocomposite remained at 68% of its initial value. However, chemical treatment methods often runs into challenges like high energy demands, high reagent costs, and the tendency to generate potentially toxic degradation intermediates. In real-world engineering scenarios, it's a must to integrate it with additional techniques to guarantee the purity of the waste effluent.

2.2 Biological Treatment Technologies

Biological treatment technologies rely on the metabolic activities of activated sludge, biofilms, and functional microorganisms to degrade antibiotics and constitute a routine process step in wastewater treatment plants. For example, Aber [6] et al. used acclimated activated sludge in a sequencing batch reactor (SBR) to simultaneously remove the drugs ranitidine and CFX, employing MATLAB 8.1 software to statistically monitor the degradation of each drug. During the SBR biological treatment process, 71.67% of the ranitidine and 59.67% of the CFX were removed. However, antibiotics inherently possess antibacterial properties; at higher concentrations, they can inhibit or even kill the functional microorganisms involved in degradation. This limits the efficiency of biological treatment systems in removing antibiotics. Furthermore, traditional activated sludge processes struggle to effectively degrade structurally stable, highly polar antibiotic molecules. There is also a risk of inducing the accumulation and spread of resistance genes in the sludge, which is one of the most pressing issues currently facing biological wastewater treatment.

2.3 Physical Treatment Technologies

Physical treatment technologies primarily include membrane separation, coagulation-sedimentation, and adsorption methods. These techniques remove antibiotics from water mainly through retention, adsorption, or membrane separation without fundamentally altering their molecular structures. Moridi [7] et al. synthesized a nano-adsorbent (nZVI/copper slag) to remove CFX from wastewater, achieving a CFX removal rate of 98.71% under optimal conditions. Membrane separation technology can achieve highly efficient retention of antibiotics, but it faces issues such as membrane fouling, flux decline, and difficulties in the subsequent disposal of the concentrate; coagulation-sedimentation has limited effectiveness for removing highly polar antibiotics with low molecular weights. Consequently, the development of a removal technology characterized by high efficacy, economic viability, environmental benignity, and broad applicability has emerged as a pivotal research direction imperative within the domain of emerging contaminant abatement. In contrast, the adsorption method, with its advantages of simple operation, low cost, absence of secondary pollution, and broad applicability, is considered one of the most promising technological approaches for removing trace antibiotics from water.

2.4 Application of Adsorption in Antibiotic Removal

In the adsorption process, through the physical and chemical interaction, the antibiotic molecules in the solution are gathered on the solid surface to remove pollutants separately. This method has the advantages of strong adaptability, wide application range and low treatment cost. Commonly used adsorption materials are activated carbon, resins, clay minerals, metal-organic frameworks (MOFs), and biochar. In this study, researchers assessed the efficacy of an anion-exchange membrane constructed from quaternary ammonium poly (2,6-dimethyl-1,4-phenylene oxide) and polyvinyl alcohol (QPPO/PVA) for the removal of CFX from hospital effluent [8]. The experimentally determined maximum adsorption capacity qe was 7.01 mg/g, and the membrane retained its efficiency across three successive regeneration cycles without notable degradation. Compared with other adsorbents, biochar is made of many raw materials, and the manufacturing method is simple and does not need much money. Moreover, as long as we make great efforts in selecting raw materials and manufacturing steps, we can adjust the material properties of biochar at will. Therefore, in recent years, in the new field of decontamination research, biochar has become an important topic for everyone to study carefully.

3. Research Progress on Antibiotic Adsorption by Biochar

3.1 Overview of Biochar

Biochar, a porous carbonaceous material, is synthesized through the pyrolysis of diverse biomass feedstocks, including agricultural residues, animal excreta, sewage sludge, and lignocellulosic materials, within an anoxic or oxygen-deficient thermal decomposition environment. It is characterized by a wide range of feedstock sources, a simple preparation process, and a rich variety of surface functional groups. The performance of biochar is primarily influenced by preparation conditions, factors like the type of biomass, the temperature reached during pyrolysis, the speed of heat application, and the length of time it spends being heated. Studies have shown that as pyrolysis temperature increases, biochar typically experiences an upsurge in its specific surface area, micropore volume, and aromatic content. Conversely, the count of oxygen-containing functional groups on the surface diminishes, resulting in lower material polarity [9]. However, the adsorption capacity of raw biochar is often limited. To bolster the adsorption performance of biochar toward pollutants such as antibiotics, popular tweaking techniques involve acid-base treatments, lacing with metals or metal oxides, nitrogen doping, ball milling, and layered bimetallic hydroxide composites. These methods can improve the adsorption and selectivity of biochar as the goal by increasing the surface active sites, adding specific functional groups and making composite pore structures.

3.2 Applications of Biochar in the Removal of Emerging Pollutants

As a sustainable carbon-based adsorbent, biochar shows broad application prospects in the field of emerging pollutant control. With its highly developed pore architecture, extensive specific surface area, and a profusion of surface functional groups, biochar can achieve efficient adsorption of the aforementioned pollutants through multiple mechanisms, including pore filling, repelling water, forming π-π bonds, bonding with hydrogen, and attracting with static electricity [10]. Taking a typical emerging pollutant as an example, Liu [11] et al. used lychee seeds as raw material and modified the biomass with $ZnCl_2$ via a coprecipitation method, then prepared lychee seed biochar (M-L-BC) through high-temperature pyrolysis for the removal of PFAS from water. In comparison to the original biochar, M-L-BC exhibited significantly increased specific surface area and pore volume, achieving a PFOS removal rate of over 95%, along with a maximum adsorption capacity of 23.03 mg/g. To sum it up, due to its top-notch adsorption prowess and the ability to tweak its material traits, biochar has emerged as a critical sorbent for the remediation of emerging contaminants.

3.3 Current Applications of Biochar for Antibiotic Removal

In research on the adsorption of antibiotics by biochar, studies on typical antibiotics such as tetracycline, ciprofloxacin, and sulfamethoxazole are relatively abundant, whereas research on cephalosporin antibiotics is relatively scarce. The adsorption process of antibiotics by biochar is concurrently affected by the antibiotics' molecular composition, their acid-base dissociation characteristics, and the surface properties of the biochar. For antibiotics containing aromatic rings, π–π interactions and pore filling really make a difference; for antibiotics with polar groups such as (–COOH), (–OH), or ($–NH_2$), hydrogen bonding and electrostatic interactions may further enhance adsorption. Studies have shown that high-temperature biochar, due to its larger specific surface area and higher degree of aromatization, exhibits superior adsorption performance for doxycycline and ciprofloxacin. In a related study, two types of activated carbon—NAC and KAC—were produced from jujube pomace (DPC), an agricultural and industrial waste, via dry thermal activation with NaOH and KOH, respectively. Both exhibited good adsorption performance for CFX, with maximum single-layer capacities of 557.9 mg/g and 571.5 mg/g, correspondingly. Among them, KAC outperformed the others in terms of adsorption efficiency, largely due to its superior surface structure and abundant active sites [12]. The effective adsorption of CFX by date-residue-derived biochar indicates biochar's potential for antibiotic remediation; however, comprehensive research on CFX removal remains limited.

3.4 Current Status and Challenges in Biochar Adsorption of CFX

Compared with sulfonamide and tetracycline antibiotics, there are currently relatively few published studies on the adsorption of CFX by biochar. The molecular structure of CFX includes a β-lactam ring and a dihydrothiazine ring, and its side chain carries active functional groups such as an acryl group, a methoxyimino group, and a carboxyl group; these structural units confer broad-spectrum antibacterial activity and β-lactamase stability on the molecule. In terms of molecular properties, the CFX structure contains multiple ionizable functional groups, including –COOH, $–NH_2$, and –OH, endowing it with distinct acid-base response characteristics and complex charge-transfer behavior. The carboxyl and amino groups of CFX can undergo protonation or deprotonation under different pH conditions, causing it to exist in various forms in aqueous environments, which in turn affects its migration behavior in environmental media. In addition, the CFX molecule also contains aromatic heterocyclic structures and conjugated systems, along with an array of oxygen- and nitrogen-rich functional groups. Due to the complex molecular structure of CFX—which combines polar functional groups, aromatic ring structures, and variable charge characteristics—it exhibits strong mobility and complex environmental behavior in aqueous environments. Consequently, traditional wastewater treatment processes have limited effectiveness in removing antibiotic pollutants, and residual CFX may enter natural water bodies, posing potential ecological risks. Moreover, the presence of natural organic compounds within actual water sources can also play a role in modifying the adsorption process of CFX, which in turn changes its form within the aquatic ecosystem and its engagement with the biochar's surface, thereby influencing adsorption efficacy and governing mechanisms.

4. Current Challenges and Future Prospects

Overall, research on the adsorption of antibiotics by biochar still faces four major bottlenecks: First, there is insufficient understanding of the adsorption mechanisms and structure-activity relationships for antibiotics with complex structures, such as cephalosporins; second, existing experiments are mostly conducted under ideal conditions, lacking a systematic understanding of the interference effects of co-existing substances and water quality factors in actual aquatic environments; third, modified biochar requires further validation in terms of cost-effectiveness, environmental safety, and large-scale production;fourth, research on regeneration performance and waste disposal remains inadequate, hindering engineering applications. Future efforts should focus on typical antibiotics such as cefoxitin, using a combination of spectroscopic characterization and theoretical calculations to elucidate the adsorption-degradation coupling mechanism; strengthen research on adaptability to real-world water bodies; develop green, low-cost, targeted modification and regeneration technologies; and explore coupling with processes such as advanced oxidation and biological treatment to establish a multi-technology synergistic control system.

5. Conclusion

Environmental pollution caused by antibiotic-based emerging pollutants has attracted widespread attention. Among these, CFX—a representative third-generation cephalosporin antibiotic, possesses considerable research interest owing to its unique molecular structure and discharge characteristics, despite comparatively little research in the area of environmental adsorption and removal. Biochar, with its advantages of widely available raw materials, low cost, and tunable structure, has demonstrated promising prospects for the adsorption and removal of various antibiotics; however, its adsorption mechanism, influencing factors, and engineering applications for CFX still require systematic and in-depth research. In the future, a multifaceted approach combining material modification, mechanism elucidation, and process integration should be adopted to advance theoretical innovation and practical application of biochar adsorption technology in the control of cephalosporin antibiotic pollution, thereby providing more cost-effective and efficient technical support for the management of emerging pollutants.

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