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Removal of PFAS from Water by Surface-Engineered Biochar: Differential Adsorption Mechanisms of Short- and Long-Chain Compounds and Challenges in Practical Water Treatment

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Abstract. PFAS have been widely concerned because of their persistence and potential risks, and short-chain PFAS are more difficult to remove due to their low hydrophobicity. Surface-engineered biochar has great potential for PFAS adsorption because of its wide availability, ease of modification, and strong adsorption performance. This paper analyses the research progress of removing PFAS from water by surface-engineered biochar, mainly compares the differential adsorption mechanisms of short- and long-chain PFAS, and also analyses the application limitations in real water environments. Existing studies show that long-chain PFAS are adsorbed mainly through hydrophobic interactions. Short-chain PFAS, however, usually rely more on other mechanisms, such as surface charge effects, electrostatic attraction, and active sites. To improve short-chain PFAS adsorption, researchers often modify biochar through surface engineering, including pore structure regulation, surface chemistry modification, and composite or loading methods. However, problems such as DOM interference, high costs, and reduced regeneration performance of the material in real water environments still limit the practical application of surface-engineered biochar.

Keywords: PFAS, surface-engineered biochar, adsorption, DOM, regeneration

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) have become one of the major pollutants of concern in water treatment because of their high environmental persistence, high mobility, and difficulty in removal. Among various removal methods, adsorption has been widely applied to PFAS removal due to its simple operation and wide applicability. Studies have shown that PFAS with different chain lengths differ clearly in removal efficiency: long-chain PFAS are generally easier to adsorb, whereas traditional methods are less effective for short-chain PFAS because they are less hydrophobic [1]. For this reason, short-chain PFAS often depend more on compensatory mechanisms, such as surface charge effects, active sites, and electrostatic forces [2]. This means that improving short-chain PFAS removal and understanding PFAS adsorption behaviour from a chain-length perspective have become important research topics. Theoretically, this helps deepen

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understanding of the interactions among pore structure, surface functional groups, and surface charge. In practice, it can also guide the design and use of biochar materials for removing short-chain PFAS. In recent years, biochar has attracted attention because it is widely available, easy to modify, and has inherent adsorption capacity. Surface-engineering methods, including pore structure modification, surface chemistry and charge regulation, and composite/loading modification, can improve the adsorption of PFAS by biochar, especially short-chain PFAS [3]. However, most existing studies examine modification methods and adsorption effects separately. Surface engineering strategies that affect the different adsorption behaviours of long- and short-chain PFAS have not been systematically summarised. The reasons why short-chain PFAS depend more on surface property regulation are still unclear. In addition, problems such as DOM interference, reduced regeneration performance, and high costs remain. This means that the high adsorption performance observed under laboratory conditions still needs further evaluation for engineering application [4,5]. This review focuses on the adsorption of PFAS by surface-engineered biochar. It examines different modification strategies and their adsorption mechanisms. It pays particular attention to the adsorption differences between long- and short-chain PFAS. It also discusses the limits of applying these materials in practical water treatment.

2. PFAS and short-/long-chain differences

PFAS can be divided based on chain length and terminal group type. Based on carbon chain length, PFAS with 4–6 carbon atoms (C4–C6) are usually defined as short-chain PFAS, while those with 7 or more carbon atoms (C7+) are defined as long-chain PFAS. However, the exact definition may vary slightly among different studies [6]. Based on terminal functional groups, PFAS with a carboxyl group (-COOH) are called perfluorocarboxylic acids (PFCAs), while those with a sulfonic acid group (–SO_3H) are called perfluoroalkyl sulfonic acids (PFSAs) [7]. These classification methods provide the basis for the following discussion of adsorption differences among different PFAS types.

3. Surface-engineered biochar

Surface engineering is an important way to improve PFAS uptake by biochar. Its main goal is to strengthen the ability of biochar to adsorb PFAS, especially short-chain PFAS, by changing pore structure, surface chemistry and charge, and composite/loading properties [8-10].

3.1. Pore structure engineering

Pore structure strongly affects PFAS adsorption. Pore size distribution and pore openness affect whether PFAS can enter the biochar and be adsorbed efficiently. Thermal treatment is a common method for pore structure engineering. Factors such as pyrolysis temperature, residence time, and heating rate can change the properties of biochar and affect its applications in different fields [3]. However, compared with thermal treatment, activation usually improves pore development more directly. It can increase the specific surface area and pore volume, and thus enhance the adsorption capacity of biochar for PFAS. Taking PFOA as an example, Hu et al. activated biochar using $KHCO_3$, which improved the material's porous structure; the specific surface area reached 1471.6 m^2/g, far exceeding that of the unmodified biochar of the same type, and the adsorption capacity was also significantly increased. Hu et al. further pointed out that this enhancement in adsorption is

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closely related to enhanced pore filling [8]. This indicates that activation, by improving the pore structure, creates favourable conditions for PFAS to enter and be adsorbed.

3.2. Surface chemistry and charge engineering

Surface chemistry and charge engineering primarily enhance the adsorption of PFAS by modulating the surface functional groups and charge state of biochar; in particular, they provide the additional driving force required for short-chain PFAS with weaker hydrophobicity. Specifically, the regulation of oxygen-containing surface functional groups is a common and effective method. Acid oxidation can introduce oxygen-containing functional groups, such as carboxylic acids and hydroxyl groups, onto the biochar surface. Alkaline modification can also alter the surface properties of the material. These changes affect the polarity and surface charge of biochar. They further influence its hydrophilicity or hydrophobicity, and thus its adsorption behaviour towards PFAS of different chain lengths. Wei et al. used $ZnCl_2$-modified banana peel biochar and found that the number of oxygen-containing functional groups on the surface increased. However, after PFAS adsorption, the number of these groups decreased. This indicates that these groups were involved in the adsorption process. Wei et al. also found that the surface potential of the modified material changed with the pH of the solution. This suggests that oxygen-containing functional groups on the surface can also affect PFAS adsorption by influencing the surface potential [9].

3.3. Composite and loading engineering

Composite/loading engineering prepares new biochar-based composites with additional properties by combining or loading a second phase, such as minerals, metal oxides, or other nanomaterials [5,10]. Metal-based loading is a common composite/loading strategy. It loads metal species such as zero-valent iron onto the surface of biochar and provides additional active sites. Wang et al. used Fe-loaded bone charcoal (BM-Fe) and found that an active iron oxide phase formed on its surface. This improved the removal efficiency of various PFAS. They further confirmed that the main reason for the increased removal efficiency was the enhanced electrostatic interaction between iron oxides and PFAS. This suggests that loading metal-based components can introduce additional positive surface sites and active metal phases. These changes provide extra adsorption driving force, especially for short-chain PFAS, which are more difficult to remove [10].

In addition to metal-based components, biochar can also be combined with functional materials. This can introduce new surface functional groups and charge properties to the biochar. Deng et al. incorporated sulfobetaine polymer and acrylamide onto the biochar surface. This introduced N- and S-containing functional groups and increased the specific surface area of the biochar. The study suggested that PFAS adsorption by this composite involved electrostatic interactions, hydrophobic interactions, pore diffusion, and complexation. In particular, quaternary ammonium enhanced the electrostatic attraction between biochar and PFAS, while amide groups could interact with the carboxyl or sulphonic acid groups of PFAS. Compared with the original biochar, the composite showed a clear improvement in the removal of short-chain PFAS. However, the adsorption order still showed that long-chain PFAS were more easily adsorbed than short-chain PFAS. This indicates that although polymer composites improved the removal of short-chain PFAS, they did not change the general trend that long-chain PFAS are adsorbed more easily.

The significance of composite/loading engineering lies not only in enhancing adsorption capacity; some materials also possess a certain capacity for regeneration and reuse. However, in

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practical applications, their performance may be affected by coexisting components in real water systems [5].

4. Differences in the adsorption mechanisms of short- and long-chain PFAS

PFAS with different chain lengths differ in hydrophobicity and interfacial interactions, and therefore show different adsorption behaviours on surface-engineered biochar. Long-chain PFAS are usually easier to adsorb through hydrophobic interactions and pore-filling mechanisms, whereas short-chain PFAS rely more on compensatory mechanisms such as electrostatic attraction and active sites [1,2].

4.1. Hydrophobic interactions and pore filling (long-chain advantage)

Due to their longer perfluorocarbon chains, long-chain PFAS are often more easily adsorbed than short-chain PFAS, and hydrophobic interactions and pore-filling effects are generally considered to play dominant roles in the adsorption process. Fabregat-Palau et al. compared the adsorption behaviour of seven PFAS compounds with different chain lengths on carbon-rich materials. The results indicated that the adsorption capacity increased with increasing perfluorocarbon chain length, which was related to hydrophobic interactions. At the same time, the organic carbon/oxygen ratio (C/O) and specific surface area (SSA) are considered to be the main influencing factors [1]. Meservey et al. compared the adsorption capacities of biochar produced at 600 °C and 900 °C and found that, although the two samples had similar specific surface areas (SSA) and porosity, their adsorption performance differed greatly. They further pointed out that an appropriate pore size distribution (PSD), especially a higher proportion of mesopores, was also important for improving PFAS adsorption rates [11]. Overall, traditional hydrophobic surfaces and pore-filling effects favour the adsorption of long-chain PFAS, but their adsorption capacity for short-chain PFAS is still limited. Therefore, compensatory mechanisms such as electrostatic attraction and cation-related interactions are still needed to improve short-chain PFAS adsorption through surface engineering.

4.2. Electrostatic interactions and surface active sites

Due to their weaker hydrophobicity, short-chain PFAS are generally more difficult to adsorb than long-chain PFAS. Therefore, they rely more on surface engineering to regulate the surface properties of biochar. For example, this can be achieved by introducing surface-active sites and functional groups, or by changing the surface charge state and chemical environment of the material. Taking perfluorocarboxylic acids (PFCAs) as an example, Imran et al. adjusted the pH of the solution to change the degree of amino protonation and the charge state of the material. They then measured the adsorption of negatively charged PFCAs. The results showed that electrostatic interactions played a key role in PFCA adsorption, especially for short-chain PFCAs [2].

Such electrostatic enhancement often depends on the specific surface properties of biochar. These include positively charged sites formed under low pH conditions, metal species, oxygen-containing functional groups, and their ion-exchange capacity. Hassan et al. prepared modified biochar by loading red mud containing metal oxides onto the biochar surface. Although the material had a lower specific surface area, it showed better adsorption capacity under acidic conditions. This suggests that surface charge and functional groups can also improve adsorption under certain conditions. However, this study also showed that PFOS adsorption still resulted from the combined effects of hydrophobic interactions and electrostatic interactions [12].

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Electrostatic interactions do not typically determine adsorption efficiency alone, but instead act together with factors such as hydrogen bonding, pore structure, and hydrophobic interactions. Wu et al. used PFOA as a model and employed principal component analysis (PCA) to investigate the intrinsic relationship between the structural characteristics of biochar and its PFOA adsorption performance. The results indicated that metal content, pore structure and surface functional groups are all closely related to the adsorption capacity for PFOA, suggesting that electrostatic interactions are not an isolated factor, but act together with hydrogen bonding, pore structure, and hydrophobic interactions to influence PFAS removal. However, in this study, electrostatic interactions were still considered to be the dominant mechanism [13].

In terms of adsorption mechanisms, the reason why short-chain PFAS depend more on the regulation of surface charge states, functional groups, and other active sites is not that electrostatic interactions alone determine the adsorption performance. Rather, due to their higher solubility and weaker hydrophobicity, short-chain PFAS usually cannot obtain sufficient driving force from hydrophobic interactions alone. Therefore, compensatory mechanisms such as electrostatic attraction are more important. This was also supported by the study of Imran et al. on PFCAs. The study found that the adsorption of short-chain PFCAs was strongly affected by surface charge. This indicates that electrostatic interactions are important in the removal of short-chain PFAS, especially short-chain PFCAs [2].

However, electrostatic attraction can also be affected by co-existing substances such as pH, ionic strength, and DOM. Therefore, although these surface-active sites can improve the removal of short-chain PFAS, the performance of the material is still limited under complex real water conditions and depends on its resistance to interference [2].

5. Practical application challenges in water treatment

Surface-engineered biochar can improve PFAS adsorption by regulating pore structure, surface chemistry, and composite/loading modification. It can also help address the difficulty of removing short-chain PFAS. However, under real water conditions, its performance may be limited by factors such as dissolved organic matter (DOM) and regeneration ability.

In real water systems, DOM may occupy the high-energy pores in biochar and block the adsorption sites for PFAS. Some organic matter may also change the surface charge of biochar and weaken the electrostatic attraction between PFAS and biochar [4]. As a result, the high adsorption performance observed under ideal laboratory conditions may not be directly achieved in real water treatment systems. In addition, short-chain PFAS are less hydrophobic. So it is difficult for them to rely only on hydrophobic interactions for enough adsorption driving force. Therefore, DOM interference in real water may further reduce the adsorption of short-chain PFAS.

Besides DOM interference, regeneration performance is also an important factor in judging whether a material is suitable for practical water treatment. Adsorption only transfers PFAS from water and still requires further treatment afterwards. Repeated regeneration may also reduce the adsorption performance of biochar. Therefore, in practical water treatment, adsorption materials cannot be evaluated only by adsorption efficiency. Their regeneration performance, material lifespan, and operating costs should also be considered [5]. Surface-engineered biochar has shown potential for PFAS removal, especially for short-chain PFAS. However, its practical use in real water systems still faces several challenges. Factors such as DOM interference, regeneration performance, and operating costs need to be carefully considered.

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6. Conclusions

This review analyses the adsorption mechanisms and application potential of surface-engineered biochar for PFAS with different chain lengths, especially short-chain PFAS. Existing research indicates that short-chain PFAS are generally harder to adsorb due to their weaker hydrophobicity. Surface engineering methods, including pore structure engineering, surface chemistry/charge regulation, and composite/loading modification, can all improve the adsorption performance of biochar to different extents and affect its adsorption behaviour toward PFAS with different chain lengths. This suggests that the adsorption of short-chain PFAS no longer relies solely on hydrophobic interactions, but rather on compensatory mechanisms such as surface charge regulation, the introduction of active sites, and electrostatic attraction.

However, existing studies are still mainly conducted under laboratory conditions, and issues such as DOM interference in real water systems, insufficient regeneration capacity, and high operational costs continue to limit the practical application of surface-engineered biochar. Future efforts should focus on further research into targeted regulation of biochar properties for short-chain PFAS. It should also deepen understanding of the intrinsic relationship between material structure and adsorption mechanisms. Practical factors, including cost, regeneration capacity and safety in real water systems, also need to be considered. This will help promote the engineering applications in PFAS pollution control.

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