Modified Biochar for Antibiotics Removal in Aqueous Environments: A Mini Review

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Modified biochar for antibiotics removal in aqueous environments: A Mini Review

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Abstract: *The excessive utilization of antibiotics has led to heavy ecological pollution. Biochar has become one of the primary approaches for treatment of water pollution as its high specific surface area, stable structure, environmental friendliness, low cost and other unique advantages. However, biochar has limited adsorption capacity and is difficult to recycle. Therefore, recent researches have concentrated on biochar's surface modification to improve adsorption performance and environmental benefits. Biochar can be modified by alkali, acid, oxide, and metal salt. A suitable method of modification should be chosen based on the properties of various antibiotics and environmental conditions. This review summarizes the mainstream methods of chemical modification of biochar. The ability of antibiotic adsorption and surface chemistry of biochar were summarized and compared according to different chemical modification techniques and biomass type. The mechanism of antibiotic removal by modified biochar was clarified. This review presents many examples of antibiotic removal from water by biochar. In conclusion, chemical modification improves the antibiotic removal efficiency of biochar, which has a promising prospect in environmental remediation.*

Keywords: Antibiotic; Biochar; Chemical activation; Surface modification.

1. INTRODUCTION

The serious water pollution not only causes a decline in the function of water usage, but also a worsening problem of water scarcity, which threatens the safety and health of human beings. Water pollution caused by antibiotics is becoming a critical environmental problems affecting the survival of mankind [1]. Due to the persistence of antibiotics, the potential for inducing antibiotic resistance，antibiotics are used extensively in medical treatment, animal husbandry, agricultural production and many other fields [2]. With the increasing use of antibiotics, a large number of wastewater with antibiotic is flowed into the water. It has been found that 94 antibiotics have been detected in 25 aquatic environments including groundwater, tap water, surface water and seawater in China [3]. Most of these antibiotics are difficult to degrade and are usually released directly into the water bodies as undecomposed drugs, causing potential risks to the ecological environment.

It is difficult to remove antibiotics completely by conventional wastewater treatment techniques, so developing an effective and sustainable remediation technique is necessary. Many studies have reported methods to remove antibiotics from water. The common ones are adsorption [4], oxidation [5], membrane separation [6] and biodegradation [7]. Adsorption is widely used in antibiotic treatment due to its low cost, high efficiency and simple operation. Although other adsorbents such as zeolites, metal-organic framework materials (MOFs), and resins have different advantages, biochar is special due to its abundance of raw materials, low price, and ease of synthesis [8]. Biochar is a solid material obtained by high-temperature pyrolysis of different kinds of biomass under an inert environment. Biochar has a large specific surface area, porosity and a large number of functional groups on surface (e.g., -OH, -COOH, -C=O, etc.) that can effectively adsorb organic pollutants in water. Recently, it has been shown that biochar can effectively adsorb a wide range of antibiotics, including tetracyclines, sulphonamides and quinolones, highlighting its potential as a low-cost and efficient adsorbent [9,10] . Biomass can be made from a lot of sources. There are already reports in the literatures on using various agricultural wastes (wheat straw, coconut husk, rice straw) [11], plants [12], industrial wastes (sludge) [13], algal biomass, and animal manure [12] for biochar preparation.

It is crucial to understand the mechanisms of antibiotic adsorption on biochar in order to optimise its performance and application. The interaction of biochar with antibiotics is usually through van der Waals forces and hydrogen bonding. Since the adsorption is a surface phenomenon, the adsorbents tend to saturate easily with time. To improve the adsorption efficiency, surface modification technologies are important to improve the adsorption efficiency of specific pollutants. The surface modification generally improves the adsorption capacity and selectivity by altering the functional groups, charge density, specific surface area and pore properties of the adsorbent [14]. Currently, common modification methods for biochar include physical, chemical and biological modification. Physical modification can improve the pore quantity and specific surface area of the biochar. Generally, modification involves high-temperature treatment and mechanical milling, which may damage the structure and stability. Chemical modification method is one of the common methods used by researchers. A chemical modification refers to the addition of acid, alkali or redox reagents to change the physicochemical properties, which will improve the ability to remove pollutants [15]. Biological modification requires microorganisms or enzymes, and the long reaction time and difficult to control conditions are one of the main drawbacks. Many studies have confirmed the

excellent pollutant removal effect of biochar as an adsorbent after surface modification.

Due to the increasingly serious problem of water pollution, biochar will surely be applied on a large scale with its renewable advantages. This review focuses on using chemical modification methods to obtain the carbon-based adsorbents from biomass for antibiotic removal from water. In this review, the main objective is to summarise the different chemical modification techniques and to compare the sorption capacity of various modified biochars. Besides, it provides a summary of the mechanism for antibiotic removal. Finally, it presents the prospects for the development and future challenges of modified biochar, which is intended to guide the development of more effective biochar-based materials for environmental remediation.

2. MODIFICATION OF BIOCHAR

Biochar is produced by thermochemical conversion of pyrolysed/gasified biomass. Pyrolysis can reduce the content of volatile substances (e.g. moisture, organic matter) in biochar, increase the content and crystallinity of solid carbon, and it also enhances the thermal and chemical stability and sorption properties of the biochar [16]. However, the obtained biochar has limited adsorption capacity and requires modification to increase its specific surface area and pore volume. The chemical modification methods are generally divided into: acid modification, alkali modification and other modifications. Different agents play different roles and have variable adsorption effects after modification. Therefore, it is important to choose suitable modifiers for high-performance activated carbon preparation.

2.1 Acid-modified biochar

Acid modification can eliminate other impurities and introduce more acidic functional groups on the biochar surface. Furthermore, acidic functional groups may with positive charges and exchange ions with antibiotic molecules that are negatively charged. Such an interaction is efficient to remove antibiotics by adsorbing them onto the biochar surface [17]. Some common acids include H_3PO_4, H_3BO_3, HNO_3, and HCl [18]. **Table 1** summarises the use of acids in chemical modification. It can be seen that H_3PO_4 is most commonly used chemical modifiers. Phosphoric acid has a milder acidity and does not cause as much violent corrosion and damage as H_2SO_4 or HCl, which can better maintain the structural integrity of the biochar. Moreover, phosphoric acid modification can also introduce phosphate groups on the surface of biochar, which can enhance the adsorption capacity of biochar for organic pollutants. Usually, acid modification changes the specific surface area, and both the type and concentration of the acid will influence the adsorption effect. For example, the specific surface area (SSA) of reed biochar increased from 58.75 to 88.35 m^2/g after modification with 1 mol/L HCl [26]. However, the SSA of rice straw biochar decreased from 71.35 to 56.9 m^2/g after treatment with 2% H_2SO_4 treatment [27]. It was shown that the SSA and pore volume of the majority of biochars usually increased with increasing acid concentration. This result is related to the formation of new pores through the gradual degradation of biopolymers (cellulose, hemicellulose and mainly lignin) by chemical treatment [28]. However, some biochar showed the opposite trend. Anuar [29] found that the SSA and pore volume of biochar obtained by modification of H_3PO_4 concentration at 1 M (421 m^2/g, 0.06 cm^3/g) were higher than those obtained at 5 M (354 m^2/g, 0.04 cm^3/g). It is assumed that the ultimate collapse of the pore shell in the central portion of the biochar led to this result [30]. As can be seen, the type and concentration of acid, raw materials and preparation methods influence the sorbent surface area. Therefore, optimal conditions need to be explored to achieve maximum removal.

Table 1. Acid-modified biochar for antibiotic removal.

biomass	Chemical agent	Surface area (m^2/g)	Antibiotic	Maximum sorption capacity (mg/g)	Adsorbent dose (g/L)	Ref.
Wood sawdust	H_3BO_3	305.5	Tetracycline	173.9	1.5	[19]
Cherry kernel	H_3PO_4	657.1	Sulfamethoxazole	19.181	4	[20]
Rice straw	$C_{76}H_{52}O_{46}$	61.1	Tetracycline	308	1.2	[21]
Prosopis juliflora wood	H_3PO_4	946.06	Ciprofloxacin	250	1	[22]
Walnut shell	HNO_3	/	Sulphonamide	46	0.4	[23]
Cotton shell	H_3PO_4	1225.58	Sulfadiazine	86.98	1	[24]
Sugarcane bagasse	HCl	9.3	Tetracycline	68.2	1	[25]

2.2 Alkaline-modified biochar

The alkali modification not only increases the number of oxygen-containing functional groups (e.g., hydroxyl and carboxyl groups) but also improves the surface alkalinity of the biochar. Popular alkali modifiers involve KOH, NaOH, Na_2CO_3, $KHCO_3$ and $Mg(OH)_2$. **Table 2** lists examples of common alkali-modified biochars used for antibiotic adsorption. The physical properties of biochar such as adsorption capacity and pore size are closely related to the activation temperature and time, and the amount of alkali. Yang [36] modified willow-based biochar with KOH when the addition of KOH was fixed to four times as much biochar and the activation temperature was varied (750, 800 and 850 °C, respectively). The test results showed that the modification effectively increased the specific surface

Table 2. Alkaline-modified biochar for antibiotic removal.

biomass	Chemical agent	Modification condition	Surface area (m^2/g)	Antibiotic	Maximum sorption capacity (mg/g)	Ref.
Spent coffee ground	NaOH	Chemical ratio: 15:32 Impregnation time: 2 h Impregnation temperature: 25 °C Activation temperature: 500 °C, 2 h (100 cc/min N_2 gas)	116.59	Tetracycline	113.64	[31]
Enteromorpha prolifera (algae)	KOH	Carbonization temperature: 500 °C, 5 h (400 ml/min N_2 gas) Chemical ratio: 0, 0.5, 1,2,3 Activation temperature: 800 °C, 2 h (200 ml/min N_2 gas)	2172.08	Sulfamethoxazole	744.32	[32]
Tea waste	$KHCO_3$	Hydrothermal temperature: 200 °C, 10 h (N_2 gas)	1350.11	Tetracycline	451.49	[33]
Conocarpus wastes	$Mg(OH)_2$	Chemical ratio: 1M $MgCl_2$, NaOH solution adjust pH=11 Activation temperature: 600 °C, 30 min	154.9	Ciprofloxacin	84.6-99.8%	[34]
Sewage sludge	Na_2CO_3	Chemical ratio: 45 mL 5% Na_2CO_3 and 5 g sewage sludge Impregnation time: 24 h Activation temperature: 700 °C, 1 h	519	Sulfamethoxazole	139.8	[35]

area and improved the porosity of the biochar. As the specific surface area of the three samples (2906, 3212 and 3342 m^2/g) increased, the adsorption capacity increased accordingly (987, 1026 and 1182 mg/g), respectively. The adsorption ability of modified biochar is directly dependent on the specific surface area. However, excessive addition of alkali may will cause the carbon skeleton structure to collapse, thus reducing the adsorption capacity [37]. Actually, the use of KOH in the process of pyrolysis of biochar at high temperatures can generate many micropores and mesopores, which is helpful for the enhancement of adsorption capacity. The KOH modified seaweed (algae)-based carbon adsorbent displayed a promisingly high specific surface area of 2172.08 m^2/g at a mass ratio of 0.5:1, but when the mass ratio was increased from 1:1 to 2:1 and 3:1, the surface area abruptly decreased to 930.85 m^2/g, 1161.75 m^2/g and 1832.98 m^2/g [38]. In summary, KOH can effectively improve the biochar's specific surface area. However, the amount of addition should be reasonably controlled, and excess KOH will destroy the original pore structure [37].

2.3 Oxidate-modified biochar

Oxidate-modified biochar can increase the amount of oxygen-containing functional groups on surface. $KMnO_4$ modification has been reported to increase the acidic functional groups (e.g. carbonyl, carboxyl, lactonised and phenolic groups) to improve its removal efficiency of antibiotics [39]. The modified biochar's surface was coated with ultrafine MnO_x using banana peels as raw material treated with $KMnO_4$. Due to the amount of oxygen functional groups increase, the removal efficiency of tetracycline through the modified biochar was more than 95% [40]. In addition, Mn mainly existed as Mn-O and Mn-OH in the $KMnO_4$-modified biochar. As a strong oxidant, H_2O_2 can increase the amount of carboxyl groups on biochar and give additional active adsorption sites for the surface complexation of heavy metal ions [41]. Xue [42] reported that peanut shell-based biocarbon modified with H_2O_2 exhibited excellent Pb^{2+} adsorption capacity (22.82 mg/g), which was over 20 times than original activated carbon (0.88 mg/g). The low cost of H_2O_2, and its final decomposition into H_2O and O_2 , makes it a green and sustainable adsorbent [43].

2.4 Metal salts or metal oxides modified biochar

Two methods are commonly used to modify biochar with metal salts or metal oxides: (1) mixing metal salts or metal oxides with biomass and subsequently pyrolysing it to produce biochar; (2) pyrolysing the biomass first, and then impregnating it with metal salts or metal oxides solution. Common metals are aluminium, iron, magnesium and manganese [44]. Iron doping improves the magnetic qualities of biochar, which can be easily recycled through external magnetic sources. The specific surface area of the biochar (Fe-N-RSBC) produced by the co-pyrolysis of $FeCl_3 \cdot 6H_2O$ and urea with rice straw increased 3.4-fold compared to the primary biochar, and the maximum adsorption capacity of TC was 156 mg/g. Iron oxide nanoparticles including γ-Fe_2O_3, Fe_3O_4, and Fe_3C were detected in Fe-N-RSBC, suggesting that the modified biochar is magnetic [45]. Iron doping in biochar

significantly promotes the formation of oxygen-rich functional groups, and can effectively increase the degree of carbonisation for providing more adsorption sites to improve antibiotic removal [46]. Recently, nano zero-valent iron (nZVI) has great potential for treating organic pollutants in water because of its specific surface area, reduction reaction ability and other unique advantages [47]. It is noteworthy that biochar-loaded nZVI can combine the advantages of both nZVI and biochar compared to their separate use. Biochar composites made of hazelnut shells loaded with nZVI showed removal efficiencies of up to 95% towards hygromycin and chlortetracycline in wastewater, which has opened up a potential application for antibiotic removal [48].

In conclusion, there are many methods of biochar modification, and each has its own advantages and disadvantages. Acid or alkali modification increases the active sites on biochar surface by introducing functional groups. However, modified biochar requires post-treatment, which increases the complexity of the preparation process. Future research could consider subsequent modification by alkali and acids. Oxidant modification will add oxygenated functional groups, but cost and oxidant handling are major limitations. Consideration of how to recycle the oxidants could reduce costs. Metal or metal oxide modification is usually applied to increase the sorption and catalytic activity sites, but the metal ion leakage will cause secondary pollution of the water body, which will cause a severe harm to the environment. Therefore, cost, environment, and removal efficiency must be considered comprehensively.

Table 3. Other types of chemical agent-modified biochar for antibiotic removal.

biomass	Chemical agent	Modification condition	Surface area (m^2/g)	Antibiotic	Maximum sorption capacity (mg/g)	Ref.
Banana peel	$KMnO_4$	Chemical ratio: 1:100 (0.2M $KMnO_4$) Impregnation time: 24 h Impregnation temperature: room temperature Activation temperature: oven dried	112.57	Tetracycline	148	[49]
Rape stalk	H_2O_2	Impregnation temperature: 25 ℃ Impregnation time: 24 h	117.05	Tetracycline	55.11	[50]
Sawdust	$FeCl_3 \cdot 6H_2O$	Chemical ratio: 1 g : 50 ml 30% H_2O_2 Impregnation time: 24 h Impregnation temperature: 100 °C Activation temperature: 600 °C, 2 h	N/A	Tetracycline	0.052	[51]
Willow wood	Fe_3O_4	Chemical ratio: 3:1 ball mill at a speed of 960 rpm for 30 min Impregnation time: 24 h	662.07	Daptomycin	217.77	[52]
Granular sludge	$ZnCl_2$	Impregnation temperature: room temperature Activation temperature: 700 °C, 2 h (N2 gas)	852.41	Tetracycline	93.44	[53]
Wheat stalk	K_2FeO_4	Impregnation time: 4 h Impregnation temperature: 80 °C Activation temperature: 400-700 °C, 2 h	155.43	Sulfadiazine	44.16	[54]

3. MECHANISM OF ANTIBIOTIC REMOVAL

Biochar adsorption of antibiotics relies on several interactions, primarily including electrostatic forces, π-π interactions, hydrogen bonding, van der Waals forces, hydrophobicity, cation exchange and pore filling (**Fig. 1**). Examining the adsorption mechanism will offer deeper understanding into the antibiotic removal process.

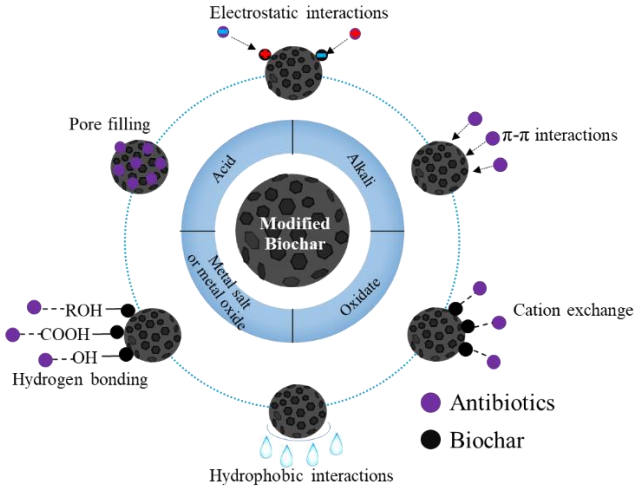

Fig. 1. Mechanism of contaminant adsorption in water using modified biochar.

The π-π interactions is one of the most important mechanisms of antibiotic adsorption on modified biochar. Functional groups like carboxyl and nitro groups on biochar surfaces can serve as electron acceptors, thus increasing the aromatic pollutants adsorption. In addition, the various amine and hydroxyl groups of the modified biochar will serve as effective π electron donors [55]. The adsorption mechanism between sugarcane bagasse biochar and tetracycline(TC) is mainly π-π interaction. The pyrolysed sugarcane biochar with a graphitised surface, functions as a π-electron donor, while the negatively charged TC also serves effectively as a π-electron donor [56]. Various thermochemical conditions markedly influenced the oxygen containing functional groups and the extent of graphitization on the biochar surface. Xie [57] discovered that the adsorption affinity of biochar for sulfonamides was significantly influenced by its degree of graphitization. The primary adsorption mechanism was identified as the π-π interaction between the graphite surfaces of biochar and sulfonamide molecules. Actually, the π-π interactions between them are realised through electronic interactions between aromatic rings or conjugated systems.

Another potential mechanism is electrostatic interactions between antibiotic molecules and biochar. The electrostatic interaction between them is dependent on the charge characteristics of both and is significantly affected by the solution environment. Geng [58]reported the adsorption mechanism of sulfonamides on nitrate-modified walnut shell-based biochar (NBC). The surface of NBC was negatively charged through zeta potential analysis, which could attract the ionised sulfonamide molecules. Therefore, electrostatic interactions can work effectively. Optimizing surface functional groups and pH adjustments can enhance electrostatic interactions, thereby improving biochar's adsorption efficiency of antibiotics [59]. Inconsistent with other studies, the removal of TC onto H_3PO_4-modified biochar showed enhancement as pH levels increased from 5 to 9. This phenomenon can be attributed to the reinforced electrostatic attraction between the positively charged biochar surface and the negatively charged TC [60].

Hydrogen bonding interaction plays an important role between biochar and antibiotic molecules, especially in the presence of abundant oxygen functional groups on biochar surfaces, enabling the formation of stable hydrogen bonds with antibiotics. The very strong bonding energy between them makes the antibiotic and biochar not easy to separate. Ahmad et al. [61]used nZVI to modify biochar prepared for adsorption of chrysomycin (CTC). The nano zero-valent iron modified biochar adsorbed CTC more efficiently under hydrogen bonding, particle diffusion and π-π bonding interactions. Heo et al. [62]prepared composites of novel biochar loaded with magnetic $CuZnFe_2O_4$ biochar using a simple hydrothermal way for the removal of BPA and SMX wastewater. The primary adsorption mechanisms identified encompassed hydrogen bonding, hydrophobic interactions, and π-π bonding.

Hydrophobic interactions between hydrophobic groups of antibiotic molecules and hydrophobic groups of biochar molecules (e.g., C-H) lead to adsorption, a common occurrence in biochar adsorption processes. Guo et al. [63] reported that a new magnetite biochar composite material exhibited rapid and efficient adsorption of tylosin (Tyl) in water. The adsorption mechanism includes electrostatic, hydrogen bonding, hydrophobicity, cation exchange and π-π bonding interactions. In the study of wastewater containing sulfonamide antibiotics, biochar was prepared from pine wood chips and magnetically modified to adsorb sulfamethazine. The adsorption mechanism of sulfamethizole was found to be driven by hydrophobic interactions and π-π bonding interactions under varying conditions of pH, ionic strength, natural organic matter and 17α-ethynylestradiol conditions [64].

Pore filling and intra-particle diffusion significantly influence antibiotic removal on biochars. Biochar's adsorption capacity is positively correlated with its pore volume and specific surface area. Jang [65]synthesized biochar for the removal of TC from water by activating alfalfa hay with NaOH. Their results indicated that the activated biochar exhibited a higher adsorption capacity of TC (302.37 mg/g) compared to the original biochar. Adsorption isotherms and kinetic studies indicated a powerful chemisorption reaction exists on TC with biochar, and intra-particle diffusion is the dominant principle mechanism for the adsorption of TC on biochar.

Ion exchange is a reversible reaction occurring in the solid phase and liquid phase ions. When specific ions within the liquid phase are attracted to an ion-exchange solid, the solid will release an equal amount of ions into suspension, so that the electro neutrality of the aqueous solution is maintained. It is difficult to convert antibiotics to the ionic form because they are organic compounds. Therefore, very little ion exchange occurs when antibiotics are adsorbed on biochar. However, ion exchange also plays a significant role in the sorption of antibiotics on biochar. Lu [66] prepared Fe/S biochar from sludge and chitosan as feedstock for TC removal from water. Besides π-π bonding, electrostatic attraction, pore-filling, and hydrogen-bonding, ion exchange was a major mechanism for TC removal by biochar.

Many studies have demonstrated that modified biochar adsorbs antibiotics through multiple mechanisms. However, the dominant mechanism, and the degree of action of each mechanism is unknown. Therefore, further studies are required to improve the ability of modified biochar to remove antibiotics in water.

4. CONCLUSION

This review primarily examines various biochar modification techniques and their applications in antibiotic removal from water, along with the underlying removal mechanisms. The main mechanisms by which biochar adsorbs antibiotics encompass π-π interaction, electrostatic attraction, hydrogen bonding, hydrophobic interaction, pore filling, and cation exchange. At present, the modification techniques are mainly concentrated on the co-mingling of biochar with chemical reagents. Therefore, it is necessary to consider the potential impacts that the modified materials may produce on the water body as much as possible.

The characteristics of the biochar are dependent on the type of raw material, the pyrolysis procedure and the post-treatment of the biochar. The sorption performance of biochar with modification can be strengthened through improving the porosity structure and specific surface area, increasing the amount of functional groups and active sites on the surface. The prospective application of modified biochar for the antibiotic removal from aqueous environments through adsorption has been well demonstrated, but its application in engineering needs further study.

Moreover, many studies have indicated that the degradation of antibiotics in water with biochar is a combination of multiple mechanisms. Therefore, it is crucial to explore in depth which mechanism is dominant and the extent of its influence. As the research on biochar and its modified materials in the degradation of antibiotic wastewater and even the whole organic pollutant wastewater system continues to deepen and improve, it has a broader application prospect in the future water treatment.

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