Modification of Straw-based Biochar and Its Application in Wastewater Treatment

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Abstract: Biochar has attracted much attention in the field of pollution control because of its cheap and easily available raw materials and high adsorption efficiency. The pyrolysis conditions and composition of raw materials should be taken into account when preparing biochar for specific use. Straw, as a common and typical agricultural waste, has been paid more attention to the preparation of biochar. In this paper, the preparation, properties, modified methods, removal of pollutants in water environment and application prospect of straw-based biochar were reviewed. Through physical, chemical and composite material modification, the specific surface area and surface functional groups of biochar can be increased, and its adsorption capacity can be effectively enhanced. However, in practical application, the potential ecological risk of biochar to the environment, application stability and large-scale production should also be considered. This paper can provide a reference for resource utilization of agricultural wastes, and application of straw biochar in wastewater treatment.

1 INTRODUCTION

Adsorption method has been considered as a suitable way for removing pollutants such as heavy metals and organics in wastewater for its simple and effective operation (Khan 2021). Traditional activated carbon material has limited adsorption efficiency, low reproducibility and high economic cost, which confines its practical application. In recent years, biochar derived from the by-products or wastes in industrial and agricultural production, such as straw, rice husk, livestock manure and sewage sludge, gradually become a research hotspot for its wide sources, low cost, efficient adsorption and high environmental stability (Xing 2021, Li 2014) (Zhang 2013) (Liu 2012).

Many studies have focused on the preparation of different type and of biochar, as well as its properties and removal of contaminants (Xing 2021, Li 2014, Zhang 2013, Liu 2012). Nevertheless, researches on the characterization, optimization, mechanism, application and prospects of straw-based biochar are still lack of comprehensive research. In this study, the preparation, physical and chemical properties and different modified methods of straw-based biochar (SBC) were summarized. Then, the removal and mechanism of pollutants after biochar applied in water environment were explored. Finally, the existing problems and application prospects of straw-based biochar were also proposed, aiming to provide a reference for resource utilization and pollutant adsorption of agricultural wastes.

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2 DEFINITION AND PREPARATION OF SBC

Biochar is a kind of porous carbon material with high specific surface area and stable structure, which is formed by pyrolysis of biomass such as agricultural wastes, trees, sludge or animal manure under oxygen-limited conditions at high temperature (400 ºC-700 ºC) (Khan 2021). The unique properties enable it to be widely used in many fields such as carbon fixation, soil remediation, water treatment (Xing 2021, Li 2014). Owing to simple pyrolysis process, low cost and easily available feedstock, researches on the preparation, modification and application of biochar receive much attention (Cobbina 2018).

Pyrolysis can be further divided into two categories according to temperature control: fast pyrolysis and slow pyrolysis (Cobbina 2018, Uchimiya 2015). Fast pyrolysis generally refers to the addition of biomass to a reactor after the reactor has reached the desired temperature, with a faster temperature rise and generally shorter residence time.

Slow pyrolysis refers to the process that at the beginning of pyrolysis, biomass is added to the reactor, while the temperature rise rate is slower compared to fast pyrolysis, and with a longer residence time to get biochar product. Fast pyrolysis could facilitate the decomposition of organic matters, resulting in a relatively low production yield of biochar (Bridgwater, 2012), while it tends to produce more gaseous products and oil. Slow pyrolysis not only produces more biochar, but also produces more carbon than fast pyrolysis. In addition, biochar produced by fast pyrolysis and slow pyrolysis has significantly different physical chemistry properties (Bruun et Al., 2012), which in turn affects the performance of biochar in practical applications of biochar (Cobbina 2018, Kong 2014).

Straw is one of the most traditional feedstocks, which is mainly composed of lignin, cellulose and hemicellulose. Compared with other biochar (e.g. sludge biochar), straw-based biochar has the advantage in carbon sequestration, heavy metal retention and pollutants removal, and less potential toxic elements, which could be widely and safely used in wastewater treatment (Zhang 2013). Researchers found that pyrolysis process and the properties of biochar were mainly affected by the pyrolysis conditions (temperature, retention time, heating rate) and components of the raw materials (Liu 2012).

3 PHYSICAL AND CHEMICAL PROPERTIES OF SBC

In the process of biomass pyrolysis, a variety of comprehensive reactions occur, including physical and chemical reactions, and these reactions were mainly affected by both pyrolysis conditions (e.g. pyrolysis temperature, pyrolysis residence time, heating rate, etc.) and biomass raw material composition (Lian et 2017, Lehmann 2015, Sun 2014, Wallace 2019). Because of the different components of biomass, the physical and chemical reactions will change during pyrolysis, which will affect the formation and properties of biochar. The composition of the raw material could have a more significant effect on the physical and chemical properties and function of the biochar than the pyrolysis conditions (Hossain 2010). Therefore, when preparing biochar for a specific use, for example, watewater treatment or soil remediation, the control of pyrolysis conditions and the selection of biomass raw materials should be considered carefully.

The main physical and chemical properties of SBC and analysis methods were shown in Table 1. The properties include pH, particle distribution and porosity, specific surface area, morphology, elemental composition, components such as volatile matter and ash, as well as functional groups. Organic components in raw materials can be decomposed and recombined at high temperature to form C=C, C-O, C-N, aromatic hydrocarbon and other functional groups during pyrolysis, which can increase the adsorption capacity and improve the fertility of biochar (Liu 2012).

Table 1. The main properties and analysis technology of SBC.

Physico-chemical properties	Analysis technology
morphology	SEM, SEM-EDX
ash contents	Gravimetric method
volatile matter	Gravimetric method
particle distribution and surface area	BET
structure or morphology of atoms	XRD
element composition and formula	XPS

C, H, O, N, S ratios	Elemental analysis
Heavy metals	ICP-MS
Functional groups	FTIR/FTIS
Surface potential	Zeta potential analyzer
Acidic and basic functional groups	Boehm titration

4 MODIFICATION OF BIOCHAR

Aiming to solve the problem of biochar properties and limited adsorption, different modification methods were adopted to adjust and control biochar in order to enhance its structure and function and reach the expected effect. It often include three modification methods of biochar: physical modified method, chemical modification and composite modification.

4.1 Physical Modification

The common methods of biochar modification mainly include physical, chemical and composite ways. The preparation, effect and mechanism of modified biochar were shown in Table 2. The physical modification mainly adopts heat or gasification treatment such as steam, nitrogen, oxygen, ammonia, carbon dioxide, or some other gas during biomass pyrolysis process. Physical modification can optimize the pore structure and improve the hydrophilicity of biochar by promoting the formation of crystalline carbon (Li 2014, Zhang 2013).

4.2 Chemical Modification

Chemical modification methods include acid-base modification, oxidant modification and metal modification (adding metal salt or metal oxidant). Acid-base modification can optimize the properties of biochar by increasing the number and variety of functional groups and increasing the specific surface area on the surface of biochar (Cazetta 2011, Feng 2018, Li 2014, Liu 2012, Jin 2014, Peng 2016). Oxidants modified biochar by increasing the number and type of oxygen-containing functional groups (Huff 2016). The modification of biochar by oxidant depends on the type and amount of oxygen-containing functional groups in biochar. Besides, metal modification can improve biochar adsorption and endow biochar with magnetism, which is beneficial for its recovery (Fang 2015, Tan 2016, Wang 2018, Yang 2014).

4.3 Composite Modification

The modification methods mainly change the physical properties and structural characteristics of biological carbon. At present, some researches adopt different modification methods by adding another carbon-containing material as modifier in the preparation of biochar during pyrolysis. Biochar can be modified by adding different carbon-containing composite materials as modifying agent during co-pyrolysis. This modification method often choose some biomass as substrate, then find another carbon containing materials as additives, thus modified biochar was obtained (Ghaffar 2014, Inyang 2014, Jing 2014, Wang 2019). Carbon containing materials can be materials such as carbon nanotubes, organic solvents, MgAl hydrotalcite, bentonite, sludge, sawdust and other organic wastes (Lyu 2020, An 2020). Carbon nanotubes is expensive and the preparation process is pretty complex, while biochar modified with organic wastes is more applicable, while wastes can be utilized as resources at the same time (Lyu 2020).

Table 2. Preparation, effect and mechanism of modified biochar.

Method	Material	Effect	Mechanism
physical modification			
heat	bamboo	remove furfural from water	improve the pore structure and the hydrophilicity of biochar
NH_3/CO_2	cotton stalk	CO_2 capture	improve specific surface area and physical/chemical adsorption capacity
chemical modification			
HCl/HNO_3, NaOH	rice husk	remove tetracycline from aqueous solution	increase surface area, oxygen-containing functional groups, and π-π bond interactions
load Ca/Mg	corn straw	recover phosphorus from biogas fermentation wastewater	add functional groups and nano MgO particles
amino	sawdust	enhance adsorption of copper ions	enhance amino functional groups combine

		from synthetic wastewater	more stable with Cu^{2+}
composite modification			
MgAl hydrotalcite composite	ramie	remove crystal violet from wastewater	increase pore volume and functional groups
wood /bamboo polyethylene	pine sawdust	improve the tensile and strength of material	enhance the thermal barrier and delay thermal reaction of wood fiber
bentonite	cotton stalk	improve sustained-release nutrients	bentonite can be used as a slow-release phosphorus source and improve nutrients of biochar

5 APPLICATION OF SBC IN WASTEWATER TREATMENT

Biochar has important effects on the removals of heavy metal ions, organic and inorganic pollutants in wastewater treatment in recent years. Yang studied that sawdust biochar prepared at high temperature (800 ºC) enhanced amino functional groups and had good adsorption effect on Cd^{2+} (Yang 2014). The biochar prepared from wheat straw and peanut shell could adsorb more than 30 mg/g of Pentachlorophenol (PCP) in water (Khan 2021). Deng found that the adsorption capacity of modified straw biochar with phosphoric acid was significantly higher than that of original biochar, the removal rates of phenol and dimethyl disulfide could reach above 80%, which had great potential in black and odorous water treatment (Deng 2021).

The adsorption capacity of biochar can be affected by its surface functional groups. For example, biochar containing amino groups can enhance the adsorption of Cu^{2+} through complexation. Oxygen-containing groups on the surface of ball milled biochar improved the adsorption of Methylene blue by electrostatic attraction and ion exchange. Lyu considered that the adsorption mechanism of Fe-loaded biochar mainly included pore filling, electrostatic attraction, precipitation, surface complexation, ion exchange and oxidation-reduction (Khan 2021, Lyu 2020, An 2020).

6 CONCLUSION AND PROSPECT

Biochar is a carbon-rich material with low cost and wide sources, which could be widely used in water treatment. Through physical, chemical and composite material modification, the adsorption ability of biochar can be improved, which is due to its high functional groups, large specific surface area and strong ion exchange ability. When biochar is applied in wastewater treatment, attention should also be paid to its potential risk to the environment, and following aspects need to be studied deeply in future: (i) identify the potential impact of biochar on ecological environment and reduce its toxicity; (ii) explore the mechanism of biochar for emerging organic pollutants (e.g, PPCPs, EDCs) in wastewater; (iii) consider the batch production, large-scale application and recycling of biochar.

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