Research Progress of Biomass-based Adsorption Materials

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Abstract. Pollution control has always been the core of research in the field of environmental engineering. Adsorption is an important means to remove pollutants. Choosing a suitable adsorbent is of great significance to environmental protection. This article discussed the research of biomass adsorption materials in recent years including the preparation, utilization and regeneration of biomass adsorption materials. The details of the influencing factors, the modification methods during the preparation of adsorption materials and the suggestions for future research were provided.

1. Introduction
With rapid economic development and the continuous improvement of productivity, the pollutants arising from the production and life process are also increasing over time. Looking for environment-friendly, economical and effective treatment technologies to remove pollutants has become the focus of academic research. Biomass refers to various organisms formed through photosynthesis, including all animals, plants and microorganisms. It has the advantages of abundance, low pollution and renewability, and is an important biological resource on the earth. Common biomass includes tobacco stems[1], bagasse[2], wood chips[3], fruit shells[4], tree trunks[5], shrimp shells[6], algae[7], and fungi[8]. They have a good effect in medicine, composite materials, waste water and waste gas treatment[9]. These varieties of biomass contain a large amount of carbon, which provides a natural carbon source. Besides, they have huge specific surface area and porous structure. The surface has active groups such as carboxy and hydroxy groups. Therefore, it is a good material for making adsorbents. China is a large agricultural country with the largest food output around the world. It is also the world's largest producer of fruits, vegetables and aquatic products. According to the implementation opinions issued by the Ministry of Agriculture on the deployment of key agricultural and rural tasks in 2021, it is necessary to strengthen the recycling of agricultural waste. The utilization of agricultural waste as biomass resources to make adsorption materials not only meets the needs of clean production, but also plays an important role in the rational allocation of resources.

The conventional methods of removing pollutants from the gas and liquid phases include biological treatment, flocculation, membrane separation, chemical precipitation, ion exchange and adsorption[10]. The adsorption method relies on adsorbents to remove pollutants. Compared with other treatment methods, the adsorption method consumes fewest cost, has a more stable effect, beyond that, the adsorption materials can be regenerated for use. It has been widely used in pollution control in domestic and abroad. Adsorption is divided into two categories, physical adsorption and chemical adsorption. Physical adsorption is caused by intermolecular force, which has a small effect and is easy to desorb. Chemical adsorption is caused by chemical bonds, and the adsorption energy is larger and firmer. Physical adsorption and chemical adsorption often occur at the same time. Using biomass as a
precursor to prepare adsorption materials requires carbonization, which is the process of turning biomass into biochar. Biomass undergoes high temperature and pressure, then the main components (lignin, cellulose and hemicellulose) are converted into carbon and ash. The ratio of carbon and ash determines the efficiency in biomass adsorption of pollutants. Wan[11] et al. studied the relationship between the content of various components and the adsorption performance, which showed that the higher the lignin content, the better the biomass adsorption effect. In order to improve the adsorption capacity or make the adsorption process more targeted, the biochar will be modified. Li[12] and others modified the biomass by microwave and hydrogen peroxide impregnation. The specific surface area and the number of surface functional groups of biochar were increased, and the adsorption capacity of mercury was enhanced to a certain extent. Understanding the preparation, utilization and regeneration of biomass adsorption materials will play an important role in our in-depth research in the future.

2. Preparation of adsorption materials

2.1. Laboratory preparation of adsorbent materials

2.1.1. Carbonization

In general, the preparation of bio-based adsorption materials in the laboratory goes through three steps: pretreatment, pyrolysis and carbonization, and activation treatment. Pretreatment is the process of removing surface impurities from biomass. The biomass is washed with deionized water, dried and crushed to a suitable particle size, then weighed for later use. The conversion of biomass into pyrolysis charcoal at a certain temperature is called carbonization. The purpose of carbonization is to increase the pore size of biochar, expand the pore volume, increase the specific surface area, and form a preliminary carbon skeleton. The pyrolysis of lignin, cellulose and hemicellulose in biomass produces three components: charcoal, tar and gas. Smith[13] et al. studied the effect of pyrolysis temperature on the surface morphology characteristics of the formed char. The pyrolysis of the three components occurs at a temperature between 300 and 700℃, besides, lignin contains polyaromatic structures. When the pyrolysis temperature fell below than 400℃, the polyaromatic structure is made denser. The pyrolysis of cellulose and hemicellulose started at 300℃. When heated to 500℃, the reduction of cellulose and hemicellulose tends to be gentle. Experiments showed that the more lignin, the higher the carbon yield. Therefore, obtaining high content of lignin by controlling the temperature is significant to improving the carbon yield.

2.1.2. Activation

Activation is divided into physical activation and chemical activation. The physical activation method is to pass gas (such as water vapor, oxygen, carbon dioxide, etc.) into the pyrolysis carbon, which can dredge the blockage caused by the impurities in the carbonization process and increase the number of holes. In general, the method of chemical impregnation is adopted for chemical activation. The purpose of chemical impregnation is to change the physical and chemical properties of the biomass surface and to increase the trees and types of active functional groups. Common activators include KOH, H2SO4, ZnCl2 and so on. Oginni[14] et al. activated the three raw materials of longleaf pine, red oak, and hard maple with MgO activator, and then compared the microstructure before and after activation with an electron microscope. Due to the removal of volatile substances in the carbonization stage, the pore structure after carbonization showed visible pores. The surface of the activated biochar is similar to the molten state, which is because MgO covers the surface of the biochar and generates MgCl2 solution during the pyrolysis process, while the position of the MgO particles forms the middle hole of the biochar.

2.2. Influencing factors

In addition to the differences in the raw materials themselves, different experimental conditions also have a great impact on the adsorption performance of biomass. We usually express the adsorption
performance as saturated adsorption capacity (mg/g) or removal rate (%). Zhang[15] et al. used polyethyleneimine to make Fe₃O₄/straw composite adsorbents to adsorb chromium in wastewater. By changing the pH of the solution, the adsorption time, the amount of adsorbent and the initial concentration of chromium ions, the optimal adsorption conditions were determined. The pH of the solution determines the surface properties of the adsorbent, thereby affecting the redox reaction between the ions to be removed and the adsorbent materials, which in turn affects the removal rate. The adsorption capacity increases with the adsorption time, but it is not without cut-off. After a period of adsorption, the adsorption capacity of biochar reaches saturation, after which the concentration of pollutants in the solution will no longer decrease. If the adsorption is stopped before this, the removal will be affected. rate. When the initial concentration of pollutants is unchanged, increasing the amount of adsorbent can provide more adsorption sites, so as to maximize the removal rate. In the case of a certain amount of adsorbent, the number of adsorption sites is also certain. Compared with the high-concentrated initial pollutant, the initial pollutant with lower concentration can more effectively use the active sites, so the removal rate of lower concentrated initial pollution is higher. Different experimental conditions have different influencing factors on the adsorption performance of biomass. For example, Saravanan[16] and others also studied the influence of temperature on the removal rate of zinc ions. The results showed that in this experiment, as the temperature increases, the adsorption performance of the agent on zinc decreases. This is because the force between the adsorbate and the adsorbent is weak, and the valence bond is broken by increasing the temperature.

2.3. Adsorption performance analysis

The adsorption of pollutants by adsorbents needs to be analyzed by thermodynamics and kinetics. The adsorption results are required to conform to thermodynamic equations and kinetic equations. Commonly used thermodynamic equations include Freundlich equation (formula 1) and Langmuir equation (formula 2). The former means that the biochar has good adsorption performance for specific pollutants and is easy to adsorb, while the latter has a good fitting effect shows that the adsorption is dominated by single-layer adsorption. Kinetic equations include first-order kinetic equations and second-order kinetic equations (formulas 3 and 4).

$$ Q_e = K_F C_e^{1/n} $$  \hspace{1cm} (1)  

$$ C_e/Q_e = 1/(K_L Q_m) + C_e/Q_m $$ \hspace{1cm} (2)  

$$ \ln(Q_e - Q_t) = \ln Q_e - K_1 t $$ \hspace{1cm} (3)  

$$ t/Q_t = 1/(K_2 Q_0^2) + t/Q_e $$ \hspace{1cm} (4)

Zhang Shilin[17] et al. studied the adsorption performance of perilla straw, wheat straw and peanut shell on Cu²⁺, and used isotherm equation and kinetic equation to fit the adsorption equilibrium data. The results showed that the first-order kinetic equation fits the data better \((R^2>0.97)\), and the Langmuir equation \((R^2>0.96)\) fits better than the Freundlich equation \((R^2<0.93)\).

3. Adsorption of pollutants

The use of biomass-based adsorption materials can be traced back to the last century. As early as 1993, Seifritz[18] proposed the idea of converting biomass into charcoal. After more than 30 years of research and practice, biochar has been widely used, and it has a good adsorption effect on the pollutants in the gas, liquid and solid phases.

3.1. Adsorption of gas

The pollutants released in the air often have the characteristics of low concentration, difficult to capture, and easy to diffuse. Generally, photocatalysis and adsorption methods are used. The catalytic method has high reaction costs, complex device design, and the catalyst may cause certain toxicity. The adsorption method is considered to be the most promising way to remove gaseous pollutants. Choosing a suitable activator to adsorb gaseous pollutants can increase the saturated adsorption
capacity and prolong the adsorption time. If the air contains two or more pollutants at the same time, a modification step can be added after activation to obtain more active sites. Gebreegziabher[19] et al. used corn cob as raw material to make biochar, used KOH as the activator, and introduced copper ions to modify the biochar, and the adsorption capacity of H2S, NH3 and TMA reached 164.54mg/g, 190.68mg/g, and 323.56mg/g. The removal of TMA in the first 30 minutes is almost twice that before modification. Zeng Fan[20] et al. used municipal sludge and corn stalks as raw materials to prepare activated carbon to adsorb H2S gas, He selected KOH as the activator. When the material-alkali ratio is 5:1, the maximum saturated sulfur capacity can reach 7mg/g. When the ratio of material to alkali is 1:1, the saturated sulfur capacity is relatively reduced by 25%. Vikrant[21] et al. studied the adsorption of gaseous VOCs (benzene and methyl ethyl ketone) by 12 types of biochar. The maximum adsorption capacity of cork granular biochar and rice husk biochar to toluene is 2.9mg/g, and the maximum adsorption of methyl ethyl ketone is 43mg/g.

3.2. Adsorption of wastewater

According to different sources, wastewater can be divided into printing and dyeing wastewater, medical wastewater, papermaking wastewater, tannery wastewater, etc. Each type of wastewater has its own characteristics and treatment difficulties. The use of biomass adsorption can effectively reduce treatment costs. Taking printing and dyeing wastewater as an example, the dyeing wastewater has high chromaticity, high organic content, strong persistence, partial toxicity, that causes it to become one difficult-to-treat wastewater. Angelova[22] et al. used sargassum as a substrate and modified iron oxide nanoparticles and microparticles synthesized by microwave to study its removal rate of acridine orange, crystal violet, malachite green, methylene blue and safranine. The adsorbent had the highest removal rate of methylene blue and low adsorption rate of malachite green, and the time to reach adsorption equilibrium was between 30-50 minutes. In addition, Bello[23] et al. did related experiments on H3PO4 activated coconut shell charcoal, and the adsorption capacity of ibuprofen in water can reach 76.92mg/g. Zhao[24] et al. studied the adsorption of chromium on pine, pine charcoal, and TiO2-modified pine. They found that pine charcoal had the largest adsorption capacity for Cr(III), which can reach 12.4mg/g. TiO2-modified pine had the highest adsorption capacity for Cr(IV), which was 12.8mg/g.

3.3. Adsorption of pollutants in the soil

Biomass-based adsorption materials play an important role in the adsorption of pollutants in the soil, especially for the adsorption of radioactive elements. Shen[25] et al. produced a magnesium oxide coated corncob activated carbon to adsorb lead in the soil. BET analysis showed that the surface area of the modified biochar increased from 0.07m2/g to 26.56m2/g. The adsorption mechanism is that the ions on the surface of the biochar interact with lead, and the lead is adsorbed to the surface of the biochar, forming Pb(OH)2 and Pb3(CO3)2(OH)2 precipitation with the coated MgO. This process is further enhanced fixation of lead by biochar. Due to the many interference factors in the soil and the complex structure, the method of synergistically repairing the soil with biochar and other composite materials is generally used.

4. Regeneration of adsorbent

Biomass as an adsorption material not only has a wide range of sources, but also can be recycled and reused by desorption. The process of recovering saturated biochar to its original structure through a series of means is called adsorbent regeneration. Due to incomplete desorption, small pores becoming larger pores, or other reasons, the adsorption performance of the regenerated activated carbon for pollutants will be lost. To desorb activated carbon and open the clogged pores, it is necessary to break the adsorption balance. Commonly used methods include heating, microbial degradation, solvent extraction, electrochemical and microwave radiation. Gong[26] studied the desorption efficiency of different desorbents on lead, and the results showed that the desorption rate of HNO3 on biochar was the highest, reaching more than 90%, and the desorption effect of citric acid was the worst, only about
80%. Gebreegziabher[19] used an method of using inert gas to protect heating and blowing off. On the one hand, the inert gas can protect the stripping device, on the other hand, it can replace the gas pollutants in the activated carbon pores. Take NH\textsubscript{3} as an example, set the initial concentration of NH\textsubscript{3} is 400ppm. After five consecutive regeneration cycles, the removal rate of NH\textsubscript{3} by biochar has dropped from 100% to 70%.

5. Conclusion
The rapid development of social economy has made environmental problems more and more exposed. In order to balance the relationship between development and environmental protection, choosing clean and efficient methods to remove pollutants is the key direction of modern scholars research. The low-cost and recyclable characteristics of biomass-based adsorption materials just meet the requirements of sustainable development. The commonly used methods for making biochar have low yields, so a large amount of raw materials are required. If you want to extend it to engineering practice, the quality relationship between biochar materials and raw materials should be considered. Further exploration of modification and regeneration methods is still a future research trend.

Acknowledgments
This study was supported by the key project of Jilin provincial science and technology department of China (No.20180201073SF) and by the project of Jilin education department (No.JJKH20180577KJ).

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