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Analysis of the Application of Sludge BC in the Removal of Organic Dyes from Wastewater

Yifan Xiang[1, *]

[1]College of Environmental and Chemical Engineering, University of Electric Power, Shanghai, 201306, China

*Corresponding author: 20220531@mail.shiep.edu.cn

Abstract:

With industry development, wastewater discharge has triggered serious environmental pollution problems, especially the most prominent in the dye industry. Biochar(BC) adsorption is a cost-effective means of wastewater treatment and can achieve sludge resourcing, which has become a hot research topic. This paper summarizes the adsorption mechanism of BC. It focuses on various factors affecting the adsorption performance of BC, covering the performance characteristics of BC itself, such as pore size and specific surface area, as well as the dosage of adsorbent and adsorption time during the operation process, and also the effects of the initial pollutant concentration and pH value. In addition, the optimal preparation process of sludge BC and its applicable conditions are summarized. The paper also describes the performance deficiencies of sludge BC in practical applications and the pollution problems caused by it and summarizes the current modification methods for sludge BC. This review provides a reference for the application of sludge BC and its improvement for further enhancement in the field of environmental protection.

Keywords: Dye, adsorption method, sludge BC, mechanism, performance.

1. Introduction

Water is one of the indispensable resources for human survival, however, only 0.02% of water resources are available for direct human use [1]. With the continuous development of industry, the discharge of inorganic or organic pollutants has caused serious damage to water bodies, making the already scarce water resources more and more tense [2]. Further, good or bad water quality can have direct or indirect effects on life activities, as evidenced by habitat destruction and decreased biodiversity [3]. Among the various water pollutants, dye pollution is particularly prominent, especially in the textile, printing, and other dyeing industries. Some data show that the textile industry produces 10% of global wastewater discharges annually, about 92 million tonnes, and the main pollutants in wastewater are dyes [4]. However, dyes have three major characteristics: difficult to degrade, easy to enrich, and high color, which not only pose a threat to the organisms in the water but also pose a hidden danger to human health [4]. Taken together, the removal of dyes from wastewater is important.

Common treatment methods include advanced oxidation, and ion exchanges, photochemistry, and electrochemical methods are also used in some specific cases [3]. However, these methods are costly and prone to secondary pollution. Adsorption, with its advantages of low cost, high efficiency, and ease of operation, is now widely regarded as a superior treatment method [5]. Common raw materials for biochar(BC) preparation include forestry waste, municipal solid waste, and the organic fraction of agricultural waste [5,6]. However, these virgin BC have many shortcomings, such as limited ability to adsorb high concentrations of pollutants, difficulty in separating the product from water during the preparation process, and adsorption capacity affected by the raw material and pyrolysis method [2]. In order to overcome these shortcomings, BC modification techniques have emerged. In recent years, common methods include activation treatment by acid and alkali to increase the specific surface area of BC, addition of specific substances to change the functional groups of BC to enhance its adsorption capacity for specific substances, or combining it with some metals to form composite materials [2]. All these modification methods are effective ways to enhance the performance of BC.

In the process of wastewater treatment, a large amount of sludge is generated [7], and by preparing sludge BC, the sludge's value can be made, as well as effectively alleviate the environmental pollution problems caused by sludge. In addition, sludge BC also performs well in the adsorption application of dyes in wastewater, which creates economic benefits and further promotes environmental protection. In this paper, the preparation process of sludge BC and its characteristics are reviewed, the influencing factors of its adsorption effect on dyes are analyzed, and the current modification technology of sludge BC is discussed.BC preparation and removal mechanism.

2. BC Preparation and Removal Mechanism

2.1 BC preparation

The main method of preparing BC is pyrolysis, which can be classified according to the speed as slow pyrolysis, high-speed pyrolysis, and flash pyrolysis, in addition to the common methods of hydrothermal carbonization and gasification [2]. During the reaction process, the raw material is decomposed into liquid, gas, and solid (BC). The choice of preparation method has a direct impact on the yield of BC. In one study, the usage of hydrothermal carbonization and flash pyrolysis ensured a yield of more than 50%, whereas the other methods yielded less than 40% [2].

2.2 Removal mechanism

Adsorption is a physicochemical process in which physical and chemical forces are generated, and the functional groups of BC determine the adsorption capacity [7]. -OH and C-H are typical functional groups that affect the adsorption capacity, and -OH produces a stretching effect in the adsorption of organic pollutants, combining with hydrogen atoms on the pollutant to form a hydrogen bond and the bending vibration of C-H proves the presence of benzene ring, which also enhances the adsorption capacity, and is also a manifestation of π-π adsorption [7]. It has been shown that functional groups on chicken manure BC can be modified to enhance the adsorption of dimethyl sulfide by adding HNO_3/NH_3 [6]. Pore size refers to the average width of the voids of BC,[7] and according to the size of the BC pore size, it can be divided into microporous (<2 nm), mesoporous (2-50 nm) and macroporous (>50 nm), the larger the pore size, which contributes to the water passability, the faster the adsorption rate will be, and the shorter the contact time will be[8]. During the process of adsorption of organic matter, the micro- and mesopore structure, and the large specific surface area significantly enhance the pore-filling effect, which allows the organic matter to be firmly anchored in the voids and achieves efficient organic matter removal [8]. The attraction of electrons and protons is also affected by BC, which usually has a negative charge on its surface, making it suitable for the adsorption of cations [6]. In one study, Pb2+, Cd2+, and Cu2+ were readily adsorbed by BC due to electrostatic forces, with maximum capacities of 56.9 mg/g and 26.1 mg/g for Cd2+ and Zn2+, respectively [8]. BC can also be modified to make it adsorb anions, and some experiments have improved the positive polarity of corn cob BC by adding magnesium salts, resulting in enhanced phosphate adsorption [6].

In general, the adsorption mechanisms of BC are mainly stretching and π-π electrostatic interactions caused by surface functional groups, pore filling, and electrostatic adsorption.

3. Analysis of factors affecting adsorption performance

3.1 BC pyrolysis conditions

The pore structure formed by BC varies greatly under dif-

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ferent preparation conditions, which is determined by the pyrolysis temperature of the BC [3], and it has been pointed out in the adsorption mechanism that the pore structure has an important role in the process of adsorption of organic matter, so it is very important to understand the operating conditions.

Table 1 is a summary of the physical properties of sludge BC at different pyrolysis temperatures. At the same pyrolysis time (50 min), with the gradual increase of the pyrolysis temperature from 500°C to 900°C, the specific surface area of the BC was enhanced from 25.42 m²/g to 67.5 m²/g, which is a significant increase, while the pore volume and pore diameter were also slightly enhanced. The adsorption capacity can judge the superiority of the adsorption performance of BC, Fig. 1 shows the uptake of an organic compound by sludge BC at different pyrolysis times. The adsorption capacity of BC after 2 h of pyrolysis was significantly higher than that after 1 h of pyrolysis at 400 °C and 700 °C, whereas the results were reversed at 500 °C and 600 °C.Such a phenomenon is a result of the joint action of temperature and time, the violent reaction caused by high temperature will lead to the damage of the pore structure, so that the adsorption performance will be reduced, in addition, the heat treatment time is too long will lead to the collapse of the pore structure of the BC, while the heat treatment time is too short will lead to the moisture and volatile components in the sludge can not be sufficiently reacted, which is not conducive to the generation of pore space [9]. Therefore, the choice of operating conditions directly affects the physical structure of BC, and appropriate reaction conditions can ensure the use of the effect.

Table 1 Summary of specific surface, pore size and pore volume of sludge BC at different pyrolysis temperatures

Pyrolysis temperature (°C)	Pyrolysis Time (min)	Surface area (m2/g)	Diameter of hole (nm)	Pore volume (cm3/g)	Reference
500	50	25.42	3.743	0.0561	[7]
600	50	20.27	3.758	0.0537	[7]
700	50	32.18	3.745	0.0684	[7]
800	50	48.49	3.771	0.0899	[7]
900	50	67.60	3.840	0.0986	[7]

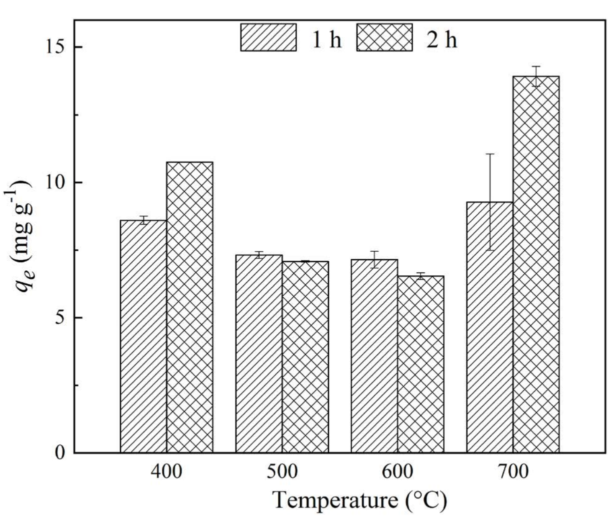

Fig .1 Tetracycline uptake by sludge BC at different pyrolysis temperatures and times [9]

3.2 BC dosage and adsorption time

The adsorbent dosage is closely related to the adsorption capacity, which ultimately affects the adsorption efficiency, but its adsorption performance tends to saturate after the adsorbent reaches a certain critical concentration, i.e., the enhancement of the removal rate by continuing to increase the adsorbent dosage will become limited. [6]. Fig.2(a) shows the relationship between the sludge BC dosage and the removal rate of methylene blue, when the initial concentration of methylene blue in an aqueous solution is the same, increasing the dosage of BC can improve the removal rate. When the concentration of BC reaches 12g/L, the removal rate reaches 98% and does not increase with the increase in the dosage of the adsorbent, and at the same time, with the increase in the concentration of the adsorbent, the unit adsorption capacity of the adsorbent decreased. These phenomena can be explained by the active adsorption sites [6], where the increase in adsorption sites favors the adsorption process. The decrease in the unit adsorption capacity may be related to the saturation of the adsorption sites with methylene blue molecules [5].

Reaction time is also an important factor affecting the removal of methylene blue [5].Fig.2(b) shows the relationship between the reaction time and the removal rate. When the adsorbent dosage is the same and the initial concentration of methylene blue in the aqueous solution is the same, the removal rate rises with the increase of the adsorption time and reaches 98% after 10 hours of adsorption, and tends to be stabilized after that, finally reaching 100% after about 25 hours of adsorption The removal rate increased with the increase of adsorption time.

Based on the above two influencing factors, the selection of the appropriate amount of sludge BC and the adsorption time are the key factors to ensure the removal efficiency and operating cost.

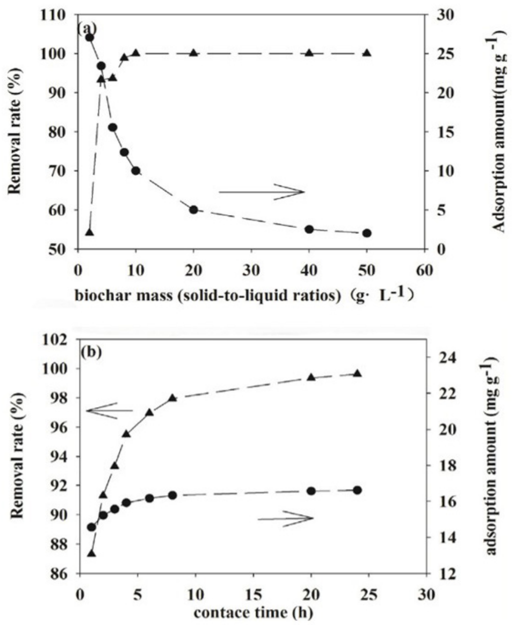

Fig.2 BC mass(a) and contact time(b)[5]

3.3 Starting concentration of solution

The gradual increase in the starting concentration of pollutants in the solution helps the adsorption process in the initial stage, but as the concentration continues to rise, the concentration effect increases the mass transfer resistance between the aqueous and solid phases, leading to poorer removal [3].In the adsorption of tetracycline using sludge BC, it was shown that when the starting concentration of tetracycline increased from 10 mg/L to 20 mg/L, the change in concentration provided the driving force to enable rapid diffusion of tetracycline molecules into the adsorption sites, but as the starting concentration continued to increase (from 20 mg/L to 100 mg/L), the limited number of adsorption sites instead inhibited adsorption from proceeding, resulting in a rate of adsorption that slowing down [9]. In another study, the decolorization rate of BC for methylene blue decreased from 96.6% to 58.7% as the concentration of methylene blue dye increased (10 mg/L-50 mg/L), while at the same time, the equilibrium capacity reached a maximum value (195.8 mg/g), indicating that the adsorption sites were saturated and there was a lack of active sites that could bind to methylene blue [10]. Therefore, BC has a good removal effect when adsorbing pollutants of lower concentration, but the adsorption effect decreases significantly for high-concentration pollutants due to the shortage of adsorption sites.

3.4 PH

It has been reported that the KOH-modified BC becomes less charged at solution pH <5, and at solution pH <3, the ζ-potential on the surface of the BC is close to 0. The adsorption performance of the BC on methylene blue dye (positively charged) decreases drastically with the decrease of pH, which is due to the repulsive effect caused by the same charge of the BC and methylene blue [4]. Fig.3 also reflects the effect of PH value on adsorption performance, with the gradual increase of PH value, the adsorption rate of methylene blue by BC and the equilibrium capacity of BC also increased. The pH value of the solution is a key factor affecting the adsorption, and the PH value affects the electronegativity of the BC, and the sharp increase in the H+ concentration will combine with the functional groups on the surface of the BC when the pH value of the solution is low, which will ultimately make the electronegativity of the surface of the BC weakened [4].

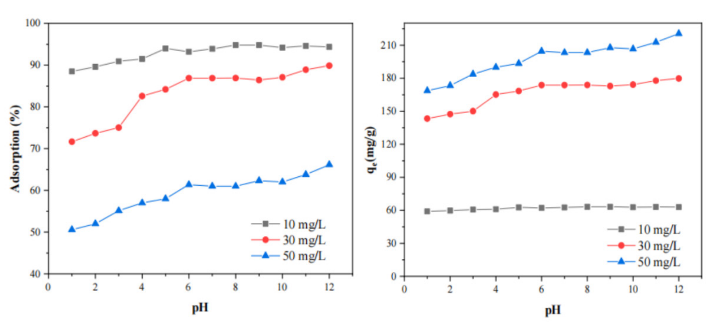

Fig.3 Uptake and adsorption capacity of methylene blue by sludge BC at different pH values [10]

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4. Challenges and prospects

Currently, the main challenges faced by sludge BC in organic dye adsorption include its limited adsorption capacity and the contamination generated during the preparation process. Compared with other types of BC, raw sludge BC has limited adsorption sites in the carbon matrix and low adsorption capacity, usually less than 379.9 mg/L, which is ineffective for dye removal. In addition, sludge BC produces serious heavy metal pollution, such as Zn, Cu, and Pb, during pyrolysis [8]. The small adsorption capacity can be overcome by modifying the original sludge BC, such as increasing the pore size, enriching the pore structure, and improving the specific surface area, which can be improved by chemical activation and metal loading. For example, in lanthanum-modified hydrothermal sludge BC, the adsorption capacity of phosphorus in wastewater was improved to realize the feasibility of sludge-based BC for the treatment of low-concentration domestic wastewater [11]. Sludge BC after acid activation has a great specific surface area of 365 m^2/g, which can absorb sulfamethoxazole and lincomycin well [12]. Therefore, BC modification can improve the adsorption capacity of a substance, so the adsorption capacity of dyes can also be improved by new preparation methods. As for the problem of heavy metal contamination of sludge BC, sludge can be pretreated (e.g., acid enrichment, advanced oxidation, Fenton oxidation) [8] to reduce its internal metal content, so that the metal residue after evaporation of sludge during pyrolysis can be reduced.

5. Conclusion

Sludge BC has a wide range of applications and great potential for adsorption of pollutants. This review summarises the adsorption mechanism of BC (surface functional groups, pore-filling effect, electrostatic effect) and, in conjunction with a number of studies, the key factors affecting the adsorption performance, as well as the suitable preparation process and conditions for the use of sludge BC. The current problems of sludge BC and the corresponding solutions are summarised, however, there is no method that can comprehensively improve the performance of sludge BC, but only improve its absorption of specific substances. The research on the modification of sludge BC should be deepened in order to make the preparation method universal and to make the sludge BC show excellent results in the adsorption of all kinds of pollutants.

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