Study on Preparation of Activated Carbon from Sludge

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Abstract. Sludge, a carbon-rich material and favourable precursor of activated carbon, has stimulated new methods for the production of activated carbons for water gas treatment. Herein, various influence factors, concluding sludge resource, pyrolysis process and the type of activators, of the preparation of sludge-based activated carbon have been compiled. Moreover, the mechanism of chemical and physical activation was analyzed. Finally, then the main research directions of preparation of activated carbons from pyrolytic sludge also were proposed.

1. Introduction
Sludge is a byproduct during the process of sewage treatment. It is difficult to handle because of its complex constituent components. Organics is an important component of sludge. In order to utilize carbon in sludge reasonably, researchers convert sludge into activated carbon with adsorption. Because the raw material of sludge-based activated carbon is cheap and easy to obtain, and its adsorption ability to some pollutants is better than that of commercial activated carbon, the application of sludge-based activated carbon prospect is appreciable [1]. Preparation of activated carbon from sludge can also achieve the goal of waste utilization. In this paper, the preparation of activated carbon from sludge is reviewed, and the development prospect of activated carbon from sludge is pointed out. The main way to prepare activated carbon from sewage sludge is pyrolysis or calcination. The adsorption capacity of activated carbon is mainly affected by factors such as sludge source, pyrolysis process and activating agent [2].

2. Influence Factors of the Preparation of Sludge-based Activated Carbon
2.1. Effect of Sludge Source
Organics content of sludge varies from sources of sludge. Organics content directly determines the surface structure and adsorption performance of sludge-based activated carbon. There are many kinds of organics in oily sludge produced by the petroleum industry, which indicates that oily sludge is a good precursor of activated carbon. The feasibility of preparing activated carbon from oily sludge was studied by Mohammad. The results showed that the activated carbon prepared from oily sludge had better adsorbability to Cd²⁺ than commercial activated carbon [3]. In addition, Deng et al. [4] had also successfully prepared activated carbon with a high surface area of more than 2000m²/g from oily sludge, which illustrates that the preparation of activated carbon from oily sludge has a promising future.

At present, most of researches are to prepare activated carbon from concentrated municipal sludge. Some studies indicate that the activated carbon prepared by concentrated municipal sludge has higher specific surface area and iodine value. However, the activated carbon synthesized by dewatering sludge will be more capable of adsorbing within shorter adsorption time [5]. Pan et al. [6] prepared
sludge-based activated carbon by digested sludge, chemically precipitated sludge and mixed sludge. The experiments adsorbed organics by the three activated carbon and commercial activated carbon from aqueous media showed that the activated carbon prepared by mixed sludge and pure chemical sludge had the strongest adsorption capacity for organics. In addition, many kinds of activated carbon are also synthesized by sludge produced during the water treatment process of leather making, paper making and textile industry. Kantarliet et al. [7] found that the equilibrium adsorption capacity to Cr$^{6+}$, methylene blue and phenol of activated carbon prepared by tannery sludge is larger than that of commercial activated carbon, which indicates that it is feasible to prepare activated carbon by sludge produced during the water treatment process of leather making. Papermaking sludge contains a large amount of cellulose and other organics, which is a good precursor for activated carbon. Vania Calisto et al. [8] used the activated carbon prepared by sludge produced during the water treatment process of papermaking to adsorb citalopram in aqueous solution. The author thinks that mixed sludge should be developed for the preparation of activated carbon in the future. We should also explore the application fields of activated carbons prepared from different sources of sludge.

2.2. Effect of Pyrolysis Process
Pyrolysis is a necessary process for the preparation of carbon. The adsorption properties of activated carbon prepared by different pyrolysis methods are quite different. Because the adsorption performance of activated carbon prepared by traditional one-step pyrolysis method is poor, the researchers separated the pyrolysis process from the activation process and form a two-step pyrolysis process. Yili Li et al. [9] prepared activated carbon by two-step pyrolysis process. The specific surface area of activated carbon prepared by two-step pyrolysis process is higher than that obtained by one-step pyrolysis process. The main reason is that part of ash in sludge can be removed by carbonization, and the activating agent can fully contact and react with the carbon in sludge during the process of activation, so that the pore of activated carbon is more abundant.

Microwave pyrolysis can produce heat both inside and outside the sludge, and thus sludge can be heated evenly. At the same time, the microwave heating rate is faster, so the preparation time of activated carbon can be shortened. Microwave pyrolysis includes three stages of drying, low temperature heating and high temperature carbonization [10]. Chunyan Yuan et al. [11] synthesized activated carbon from sludge by microwave pyrolysis under the condition that the microwave power is 500 W and the heating time is 8 min. The iodine adsorption value and specific surface area of the activated carbon obtained were satisfactory. This study indicates that microwave pyrolysis can apparently shorten the preparation time of activated carbon.

However, all the above pyrolysis methods require low moisture content of sludge. If the moisture content is high, the dewatering process of sludge will increase the cost of the preparation of activated carbon. In order to solve the high cost problem caused by high moisture content of sludge, the researchers put forward the idea of hydrothermal carbonization proposed by Bergius to the preparation process sludge-based activated carbon. Hydrothermal carbonization is a thermochemical conversion technology which can directly convert wet biomass into target carbon products in the reaction medium of subcritical water [12-13]. This method can effectively immobilize carbon elements in the precursor of activated carbon. Alatalo et al. [14] prepared activated carbon from digestive sludge and papermaking sludge by hydrothermal method, and the activated carbon obtained has better adsorption capacity for Pb$^{2+}$ in aqueous solution. In summary, the hydrothermal carbonization method can transform sludge into an effective heavy metal adsorbent.

2.3. Effect of Activators
No matter what pyrolysis method, the total pore volume and specific surface area of the product obtained by direct carbonization are small, so it is difficult to be used as adsorbent directly. Therefore, activation of activated carbon precursors should be implemented to improve the performance index of activated carbon. There are mainly three kinds of activating agent commonly used.

2.3.1. Physical Activators. Physical activating agent, also known as gas activator, was passed into the pyrolysis furnace at high temperature. Carbon compounds in sludge react with activating agent in the
pyrolysis furnace, and the gas produced by the reaction escapes from the sludge, and thus the pyrolysis products produce developed pores [15]. In the initial stage of activation, the activating gas reacts with the residual tar around the microcrystalline and between the microcrystalline, and the non-structural carbon is oxidized gradually to form a graphite-like microcrystalline surface. The reaction of microcrystals continues to expand the original pores, which forms the porous structure of activated carbon when new pores appear. The above process is that the continuous gasification of microcrystals makes the pore size of activated carbon larger. The most commonly used activating gases are water vapor, CO2 and flue gas. The mechanism of physical activation reaction is as follows:

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\begin{align*}
C + CO_2 &\rightarrow 2CO \\
C + H_2O &\rightarrow CO + H_2 \\
2CO + O_2 &\rightarrow CO_2 \\
2H_2 + O_2 &\rightarrow H_2O \\
2KOH &\rightarrow K_2O + H_2O \\
C + H_2O &\rightarrow CO + H_2 \\
CO + H_2O &\rightarrow CO_2 + H_2 \\
K_2O + CO_2 &\rightarrow K_2CO_3 \\
K_2O + H_2 &\rightarrow 2K + H_2O \\
K_2O + C &\rightarrow 2K + CO \\
4KOH + CH_2 &\rightarrow K_2CO_3 + K_2O + H_2O \\
8KOH + 2CH_2 &\rightarrow 2K_2CO_3 + 2K_2O + 5H_2 \\
K_2O + C &\rightarrow 2K + CO \\
2K_2CO_3 + 2C &\rightarrow 2K + 3CO
\end{align*}
\]

According to the above reaction, the activation process needs to absorb a lot of heat, so the physical activation is usually carried out at high temperatures of more than 800 °C. The adsorption capacity of activated carbon is related to the properties of sludge, the type of activating gas, activating temperature and activating agent flow rate. Wang et al. [16] synthesized the activated carbon through CO2 activation, the methylene blue value of activated carbon is 245mg/g, which proves the feasibility of preparation of activated carbon by physical activation.

2.3.2. Chemical Activators. Chemical activators are usually impregnated with sludge before pyrolysis, and then the impregnation products are pyrolyzed. There are many kinds of chemical activators that include ZnCl2, KOH, H2SO4 and others that facilitate the loss of H and O. In addition, some oxidizing agents are also used to be activators, such as KCr2O4 and Fenton reagent.

Taking ZnCl2 and KOH as an example, the mechanism of chemical activation is analyzed. Some scholars believe that K2O produced by the decomposition of KOH catalyze the reaction of C and H2O and the shift reaction of CO and H2O at 500 °C, which indicates that reaction (5), (6) and (7), take place at low temperature. When the activation temperature arrives around 800 °C, K2O is consumed by hydrogen or carbon, the reaction (9) and (10) take place readily. The mechanism is as follows:

However, some researchers have pointed out that KOH reacts with volatile hydrocarbons in raw materials to form K2CO3, K2CO3 plays a role in activator at high temperature.

At present, the above two kinds of reaction mechanism were relatively accepted. There are two stages during pyrolysis-carbonization process when ZnCl2 is used to be activator: catalytic dehydration and pore formation. In addition, ZnCl2 can reduce tar production during the whole process of pyrolysis, which cause that most organics convert activated carbon. The activation principle of H2SO4 and other activators is similar to that of ZnCl2, which facilitate deoxidation and hydrogen during pyrolysis. The macromolecule organics in the sludge can be oxidized into small molecule substances when oxidizing
agent, such as K$_2$Cr$_2$O$_4$, Fenton reagent, is used to be activator. And then the small molecule substances are released from the sludge during the pyrolysis process to form rich pore structure. LI et al. [17] prepared activated carbon from sludge by using ZnCl$_2$, H$_2$SO$_4$ and KOH respectively. The three kinds of activated carbons can effectively adsorb H$_2$S. After activation by ZnCl$_2$ and KOH, the saturated adsorption capacity of activated carbon on H$_2$S is greater than that of commercial activated carbon.

2.3.3. Compound Activators. Generally speaking, the compound activator is made up of two or more than two kinds of chemical activators according to certain concentration and volume ratio. In addition, some studies combine chemical and physical activators during the preparation of activated carbon. Bingkui Yin [18] synthesized carbons with strong adsorption ability towards acid red GR through the combination of chemical and physical activators. This study revealed the combination of chemical and physical activators acts important role in the preparation of activated carbon. The author thinks that the selection of activators should be determined by the nature of sludge, the process of preparation and application area of activated carbon.

3. Summary and Prospect

It is a new idea that is preparation of activated carbon from sewage sludge, which can realize the resource utilization of sludge. Compared with the preparation of traditional activated carbon, sludge-based carbon has certain economic advantages of raw materials, but large amount of activator is needed in order to obtain adsorbents with loose structure and good performance. In addition, chemical activation gives rise to serious pollution during the preparation of activated carbon. Electro thermal furnace pyrolysis and microwave heating are still caught in laboratory stage. And thus, the development of stable and efficient pyrolysis equipment, the reducing low pollution, material structure and function control will become important research directions towards the preparation of sludge-based activated carbon in the future.

4. Reference

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