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To cite this article: Yuxin Zhao et al 2019 IOP Conf. Ser.: Earth Environ. Sci. 330 042035

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Preparation and Application of Straw Activated Carbon

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Abstract The straw activated carbon produced by pyrolysis and carbonization of crop straw has not only good adsorption performance but also wide application for the treatment of sewage, air purification and soil improvement as well as the convenience of raw materials.In this paper, the preparation and present situation of straw activated carbon were described, and the factors affecting the adsorption performance of straw activated carbon were analyzed such as the type of activating agent, the concentration of activating agent, the ratio of material to liquid and the activation mode.

1. Introduction

The activated carbon is a kind of porous carbon-containing material with large specific surface area and well-developed pore structure, which is physically and chemically stable. Activated carbon is a good adsorbent for adsorption because of its good adsorption ability and high recovery and regeneration rate. Activated carbon showed good adsorption, no matter in the treatment of sewage or the purification of air and the improvement of soil. Moreover, activated carbon can be desorbed and separated after saturated adsorption, recycled and used for many times. There are many kinds of materials used to make activated carbon, but commercial activated carbon is mainly coal-based activated carbon^[1], wooden activated carbon^[2] and fruit-shell activated carbon^[3], and the raw materials are mostly coal, wood and coconut shell. The traditional method of preparing activated carbon requires vacuum atmosphere or inert gas protection. The cost is high and the price is more expensive. Therefore, it is not economical to use activated carbon on a large scale^[4-7]. But the agricultural waste straw and fruit shell are cheap and easy to get, and rich in lignin, cellulose, high carbon content, and green non-toxic, which are natural organic polymer material, in line with the requirements of making activated carbon, so they are becoming the main material for making activated carbon gradually^[8,9]. China is a big agricultural country. According to relevant statistics, the total output of crop straw in China is 700 million tons, but the utilization rate of straw is only 5%^[10]. A large amount of straw is discarded and burned in the field every year, which not only wastes resources but also pollutes the environment^[11], especially in the north.

In recent years, the usage of activated carbon is increasing day by day in the world, and people are trying to find out the process of preparing activated carbon with high adsorption performance by cheap raw materials. The researchers at home and abroad have studied the activated carbon of straw and pay more and more attention to it.

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The preparation of activated carbon from straw means carbonization of straw and fixation of carbon element by pyrolysis at high temperature under the condition of low oxygen. The activated carbon produced by pyrolysis of crop straw has more developed pore structure, larger specific surface area and stronger adsorption ability to some substances. In order to improve the yield and adsorption rate of straw activated carbon, the straw can be activated and modified by using activators and modifiers. The activated carbon treated with activator can not only increase the specific surface area but also form a large number of special functional groups on the surface to enhance the adsorption^[12].

2. Materials

According to the survey, the total output of straw in China was about 630 million tons in 2009^[13]. Straw, corn straw and wheat straw account for a large proportion of agricultural straws in China, and all accord with the conditions of preparation of activated carbon, so they are the main raw materials for making activated carbon of straw.

The saturated sulfur capacity of modified straw activated carbon prepared by Sun Liming and his team reached 176.4 mg / kg, and had good desulfurization effect ^[14]. In the preparation of straw activated carbon, it was found that the graphite microcrystalline contained about 5 to 6 pieces of graphite slice, and the main body of the activated carbon was amorphous carbon with graphite random layer structure. These are the basis for the high specific surface area of activated carbon^[15].

The activated carbon from maize straw prepared by Shi Rui using zinc chloride as activator has good adsorption capacity for methylene blue dye wastewater with iodine adsorption value of 762.89 mg / kg and BET value of 1055.69 mg / $g^{[16]}$. Zhu lanbao prepared activated carbon from maize straw by Phosphoric Acid Activation and Microwave heating. Under the optimum conditions, the adsorption values of iodine in the three parallel experiments were 116.28 mg / kg, 1170.9 mg / kg and 1165.45 mg / kg, respectively. The results show that the activated carbon of maize straw has stable and very high adsorption capacity^[17]. At first, Miao Juan and Wei Xuefeng studied the preparation technology of maize straw activated carbon by single factor method, and prepared maize straw activated carbon with better adsorption performance than commercial activated carbon, and the quality index was close to that of activated carbon for water purification ^[18]. Then, the orthogonal experiment was used to explore the main and secondary influence factors on the product, and the optimum technological conditions for the preparation of corn straw activated carbon were determined^[19].

Wheat straw activated carbon with abundant mesoporous was prepared by phosphoric acid activation method with wheat straw as raw material. It was found that wheat straw activated carbon could be used as decolorizing carbon by comparing with the decolorized carbon sold in the market. However, because of the high ash content of wheat straw, the yield of wheat straw is lower^[20].

In the experiment of preparing activated carbon with municipal sludge and wheat straw as raw materials, Guo Bin and others prepared activated carbon rich in micropores under the optimal preparation conditions. The iodine adsorption value of the product can reach 804.216 mg / kg. But, the mechanism of mixing sludge and straw is not analyzed in detail^[21]. In sludge-straw activated carbon, the specific surface area of activated carbon increases with the increase of straw proportion, and the yield decreases with the increase of straw ratio ^[22]. This is because there are abundant carbon elements in straw, but the strength and density of activated carbon is insufficient, the carbon content of sludge is low, but it contains a lot of organic matter, so the activated carbon with better strength can be prepared.

3. Discussion

The adsorption capacity of straw activated carbon can be affected by the raw materials of making straw activated carbon, the selection of activator, concentration of activating agent, the activation method, the ratio of chemical and material, the temperature of activation, and so on.

Some scholars used orthogonal experiment to analyze corn straw activated carbon prepared by phosphoric acid activation method. It was found that the order of the factors influencing iodine adsorption value was: activation temperature > activator concentration > ratio of material to liquid >

activation time, the order of the factors influencing the yield was as follows: activation temperature > activator concentration > activation time > ratio of material to liquid, and activation temperature was the most important factor^[19]. The orthogonal experiments were carried out respectively on the cotton rod-based activated carbon activated by phosphoric acid, sodium hydroxide and zinc chloride, and Kong Deguo found that among the four factors affecting the adsorption capacity of the three kinds of cotton rod-based activated carbon, such as ratio of material to liquid, impregnation time, activation temperature and activation time, the effect of the ratio of material to liquid on the adsorption capacity of the three cotton-based activated carbon was the greatest^[23].

3.1. Type of activator

For the straw activated carbon with different kinds of raw materials and different adsorption effects, the activators used are also different.

3.1.1 Zinc chloride. Zinc chloride has strong dehydroxyl and dehydration effects. Oxygen and hydrogen in straw can be released in the form of water at a certain temperature. Jiao Qishuai and others studied the effects of impregnation ratio, activation time and activation temperature on activated carbon of cotton straw by single factor method. When the activation temperature was 550 °C, the activation time was 90min and the impregnation ratio was 1.5%, cotton straw activated carbon with iodine adsorption value of 1188mg/g was prepared^[24]. Some scholars used phosphoric acid, sodium hydroxide and zinc chloride as activators respectively to prepare cotton stalk activatedcarbon. The iodine adsorption values of the products were 524.73 ~ 799.32 mg / g, 335.86 ~ 855.95 mg / g and 607.92 ~ 862.9 mg / g, respectively, and the iodine adsorption value of cotton stalk activated carbon treated with zinc chloride is higher and the range gradient is smaller^[23].

3.1.2 Phosphoric acid. Compared with zinc chloride, phosphoric acid has the advantages of light environmental pollution, high efficiency and simple activation process, so it is a more commonly activator. Phosphoric acid activated straw is mainly due to its corrosion property and dewatering performance, so that hydrogen and oxygen are removed in the form of water vapor, and the inside of straw becomes rough and irregular, thus increasing the specific surface area^[19].

3.1.3 Diammonium hydrogenphosphate. Diammonium hydrogen phosphate is also a commonly used activator for the modification of straw. Han Bin of Donghua University took rice straw as raw material and (NH4) 2HPO4 as activator to prepare straw activated carbon. The results showed that soaking by (NH4) 2HPO4 not only increased the yield of activated carbon from straw, but also increased its specific surface area and iodine adsorption value^[25].

3.1.4 Iron oxide. Active iron oxide can adsorb many heavy metals, non-metals and oxygen-containing anions, and it is not easy to leak in water. The experiments showed that the straw activated by FeCl3 and CaCl2 enhanced the adsorption of nitrate nitrogen and inorganic phosphorus, and the maximum adsorption capacity reached 95.26mg/g and 22.17mg/g, respectively^[26].

3.1.5 Ferric hydroxide. Some scholars have prepared modified activated carbon by modifying the carbonized activated carbon. Wang Huisong and others treated activated carbon with iron nitrate nine hydrate solution to obtain Fe (OH)₃ modified activated carbon. It was found that the modified activated carbon had good adsorption effect on phosphorus in the solution, and the adsorption amount reached $5.56 \text{mg/g}^{[12]}$.

Different activating agents are suitable for different straw treatment, and the adsorption effect of straw activated carbon on different substances is also different.

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3.2. Concentration of activator

When the concentration of activator is within a certain range, it can effectively promote the formation of pore structure of activated carbon. If the concentration of activator is too low, the straw can not be fully modified and the concentration is too high, on the contrary, it will cause the hydrolysis of straw^[17] or blockage the pore^[27] and destroy the porous structure of activated carbon. Too high concentration of activator can also lead to waste of resources and pollution to the environment.

3.3. Material-liquid ratio

The ratio of material to liquid affects the activation of straw. If the ratio of material to liquid is too small, it will cause the straw not to be fully modified, affect its yield and adsorption performance, but too large will cause the waste of resources and increase the cost of production, and easy to pollute the environment. In the study of the preparation of wheat straw activated carbon by zinc chloride, some scholars found that when the impregnation ratio increased to a certain extent, it had little effect on the yield of activated carbon. When the impregnation ratio is 250%, the yield of activated carbon and the removal rate of phosphate radical are both higher ^[27].

3.4. Activation method

Carbonized straw can be carbonized by conventional heating and microwave irradiation. The traditional heating mode is accomplished by heat radiation, conduction and convection, and the whole uniform heating takes a long time^[28]. But the preparation of straw activated carbon by microwave heating has the advantages of high efficiency, energy saving, uniform heating and convenient operation, which has been gradually applied to the preparation process of activated carbon. It was found that the effects of phosphoric acid concentration, microwave power and radiation time on the preparation of activated carbon were as follows: radiation power, phosphoric acid concentration and radiation time. When the microwave power is 400W, the concentration of phosphoric acid is 50%, the radiation time is 8 min, the specific surface area of activated carbon can reach 652.82 m2 / kg and the adsorption value of methylene blue is 151.73 mg / kg, which is 1.11 times of the national standard^[29].

3.5. Activation temperature

There are abundant cellulose and lignin in crop straw. Cellulose begins to desiccate at 150 °C, pyrolysis occurs at 300 ~ 430 °C, and lignin begins to desiccate at $250 \sim 550 \circ C^{[30]}$. When preparing straw activated carbon, Han Bin and others found that the iodine adsorption value of the straw activated carbon increased with the increase of activation temperature at first, reached the maximum at 700 °C, and then decreased with the increase of temperature^[25]. Too high temperature will cause loss of carbon^[27]. Temperature not only affects the activation of straw, but also directly affects the yield of activated carbon of straw.

3.6. Activation time

In the process of activation, the pore structure of activated carbon is gradually formed with the increase of activation time, but the micropore of activated carbon will tend to become mesoporous and macropore due to the loss of carbon for too long time, and the specific surface area of activated carbon is decreased ^[31].

4. Conclusion and prospect

At present, straw activated carbon has been widely used in many fields such as medicine, atmospheric treatment and wastewater treatment^[25]. Straw activated carbon can not only adsorb heavy metals and maintain soil fertility, but also reduce greenhouse gas emissions and alleviate greenhouse effect^[32~33].

In addition, there are many studies on the effects of pH value, activation method and reagent concentration on the adsorption properties of straw activated carbon. All the researche hopes to find the lowest cost and the simplest way to prepare the most efficient activated carbon adsorbent. There

must be more effective reagents and methods to deal with straw in the preparation of activated carbon, so that the adsorption capacity can be larger and the adsorption range can be wider. The use of activated carbon will maintain an increasing state in the future, and the preparation of activated carbon from straw is a cheaper and easier choice. So the preparation of activated carbon from straw will also have a great prospect and development space.

Acknowledgement

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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