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Preparation of activated carbon from sawdust by zinc chloride activation

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Abstract A series of activated carbons were prepared from sawdust by zinc chloride activation in different operation conditions. The effects of operation parameters such as impregnation ratio, activation temperature and time on the adsorption properties of activated carbons were measured and analyzed in order to optimize these operation conditions. The experimental results show that under the experimental circumstances studied, both the yield and the adsorption for iodine and methylene blue of activated carbon can reach a relatively higher value in the chemical activation process with the impregnation ratio of 100% $ZnCl_2$/sawdust in the activation temperature of 500 °C carbonized for 60–90 minutes which are the optimum activation conditions in making wood activated carbon. The most important operation parameter in chemical activation with zinc chloride was found to be the impregnation ratio.

Keywords Activated carbon · Activation · Carbonization · Adsorption

1 Introduction

Activated carbons as porous adsorption materials with abundant micropores (0–2 nm), mesopores (2–50 nm) and macropores (>50 nm) as well as high specific surface areas are widely used in gas purification and separation, water and wastewater treatment, chemical processing, etc. Activated carbons are also used as the support of catalysts in industries such as chemical, pharmaceutical, polymerization and environmental protection. In China the production of activated carbons is estimated to exceed 200,000 tons per year in which activated carbons of 40,000 tons are wooden activated carbons manufactured by different activation methods including chemical and physical activation methods.

Most carbonaceous substances such as coal, coconut shell, wood and sawdust, etc. can be converted into activated carbons. The porous structures and final properties of activated carbons depend significantly on both the activation processes and the natures of raw materials. A lot of processes for preparing activated carbons have been developed over past century (Lua and Gua 2000; Lozano-Castello et al. 2001; Cooney 1999; Hayashi et al. 2000; Ahmadpour and Do 1996, 1997; Bernardo et al. 1997). Most processes can be divided into two different processes, the so-called physical and chemical activation. Physical activation comprises the pyrolysis (or carbonization) step followed by a stage of controlled oxidation to activate the carbon in the presence of a physical activating agent such as steam, carbon dioxide etc. Chemical activation includes that the raw material is impregnated with a given chemical agent for a given period, and pyrolyzed. The main chemical activating agents includes zinc chloride, phosphoric acid and KOH, etc.

Different requirements for the pore size distribution and properties of activated carbons exist in a variety of industrial processing. The micropore and mesopore volume is the key index of activated carbon besides its adsorption characteristics. More micropores are required for activated car-

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bon used for gas phase adsorption because diameters of most gaseous pollutant molecules are less than 1.0 nm (Lua and Gua 2000). However, activated carbon used for liquid phase adsorption should have plenty of mesopores due to larger sizes of liquid molecules (Cooney 1999).

Usually activated carbon in chemical activation has a relatively higher specific surface area and more mesopores than that in physical activation (Lozano-Castello et al. 2001). The properties of activated carbons depend significantly on the nature of raw materials and the actual activation processes. The operative parameters in activation processes play a very important role in developing the porosity of activated carbon.

The adsorption characteristics can be obtained from the adsorption values of activated carbon for different adsorbates such as iodine, methylene blue and molasses. The iodine value indicates the specific surface area which exists in pores of 1.0 nm and greater in diameter. Methylene blue has a molecule weight of 320 and an effective molecule diameter of about 1.5 nm, and thus its adsorption indicates something about the adsorption capacity of activated carbon for molecules of this size. Moreover, the molasses number is related to the amount of specific surface area at pore of 2.8 nm and greater in diameter (Cooney 1999).

The present study is to use the sawdust of local wastes in Southeastern China to prepare the activated carbons with high adsorption characteristics by zinc chloride activation. The main objectives of this work are to study the effect of various operative parameters such as agent/sawdust ratio, temperature and time of activation on the adsorption characteristics of activated carbons by different adsorption tests to optimize the preparation conditions of chemical activation process in making activated carbons. To select the adsorption of activated carbon for iodine and methylene blue is resulted from the commercial consideration needed two main indices of iodine adsorption value and methylene blue adsorption by supplier of activated carbon.

2 Experimental

Sawdust was obtained from the forest center of Southeastern China. A CE instruments (Milan, Italy) EA1110 CHNS/O elemental analyzer was used to obtain the contents of C, H, N in the sawdust. The contents of C, H, N in the sawdust are 48.6, 6.3, 0.25 wt%, respectively. Its particle size is 8 × 20 mesh. $ZnCl_2$ (purity >98%), iodine (99.5%), methylene blue were from China Shanghai Chemical Agents Co.

The raw materials were washed with water and dried in 120 °C for 24 hours, then stored for use in order to get the experimental carried in the same condition relevant to raw materials sawdust.

The chemical activation with zinc chloride was carried out using an impregnation method. 30 grams of pretreated sawdust were mixed by stirring with a solution of 23 ml contained different weight of the activation agent depending on the ratio of activating agent/sawdust used for 1 h at room temperature. The resulting impregnated sawdust was dried at 120 °C for 12 h. Then, the resulting mixture was used for carbonization.

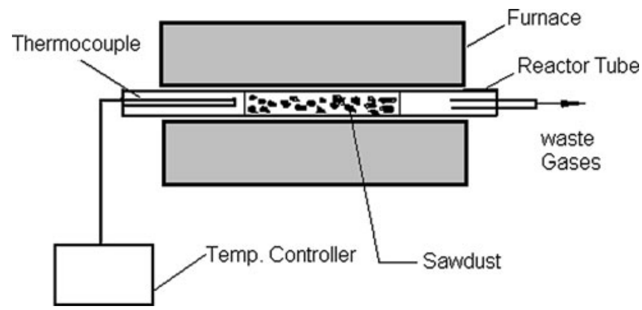

Fig. 1 The experimental apparatus for the preparation of activated carbon

The carbonization was carried out in a furnace shown in Fig. 1. The quartz reactor tube was inserted in an electricity resistance furnace (SK2-2-12H, Shanghai experimental furnace factory, China) to heat. The quartz reactor tube is 29 mm in id and 790 mm in length. The activation temperature in the reactor was controlled by a KSJ temperature controller (Shanghai experimental furnace factory, China). In order to make sure the temperature in reaction zone was kept in the same, the sawdust was put in the middle part of reactor tube. The sawdust samples were heated (10 °C/min) from room temperature to the final carbonization temperature (200 ∼ 700 °C) for different carbonization time (40 ∼ 300 min) depending on the chosen experimental conditions.

The pyrolyzed samples were put into a 0.1 M/L solution of HCl to be boiled for 20 minutes, and washed repeatedly with the 0.1 M/L solution of HCl, later with distilled water until free of chloride ions. Once the activating agent was removed, the activated carbon sample was dried at 120 °C for 12 h.

The adsorption capacity of activated carbon for iodine and methylene blue was measured according to national test standard of activated carbon (China) GB/T12496.1~22-1991 (Zhu et al. 1991).

3 Results and discussion

Both the porous texture and adsorption characteristics of the activated carbon are affected by many operation parameters in a chemical activation process even if the raw materials and the activating agent are kept constant. In the present study the effects of a variety of operation parameters in a chemical activation process such as activation temperature

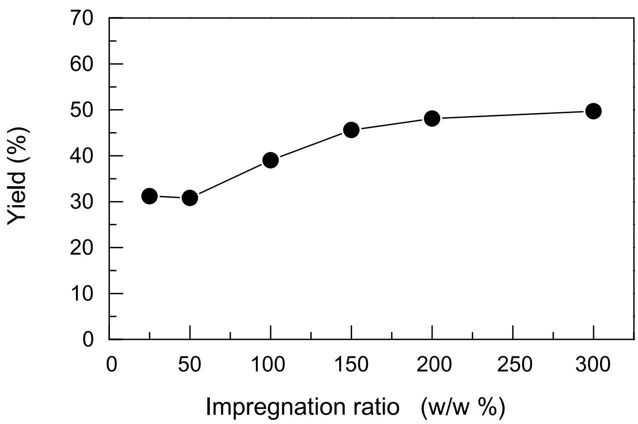

Fig. 2 The effect of impregnation ratio on yield of activated carbon

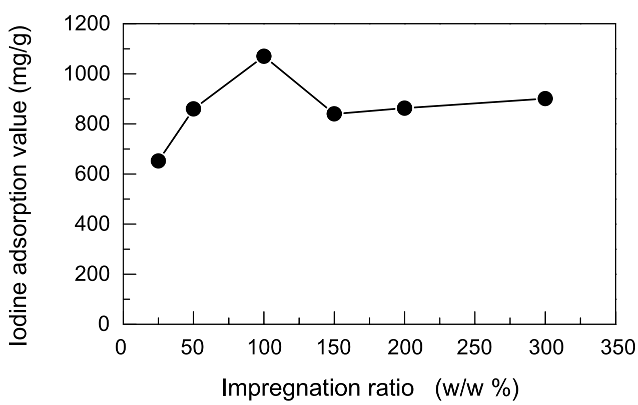

Fig. 3 The effect of impregnation ratio on iodine adsorption value of activated carbon

and time, impregnation ratio of activation agent versus sawdust on the porosity and the adsorption capacity such as iodine adsorption and methylene blue adsorption of the final activated carbon were presented.

3.1 Effect of $ZnCl_2$/sawdust

The impregnation ratio of agent/raw material has been found to be the most important parameter in a chemical activation process (Ahmadpour and Do 1996, 1997). The preparation of activated carbon was carried out using sawdust impregnated with $ZnCl_2$ in different impregnation ratio to be activated for 60 minutes by keeping the activation temperature at 500 °C. Then the adsorption capacity of the activated carbon prepared in different impregnation ratio for iodine and/or methylene blue was measured. The experimental results are shown in Fig. 2 and Fig. 3, Fig. 4, respectively.

Figure 2 shows the effect of impregnation ratio (zinc chloride/sawdust) on the yield of activated carbon. It shows that the yield of activated carbon increased with increasing the impregnation ratio, but the increase of yield is not very pronounced when the impregnation ratio is larger than

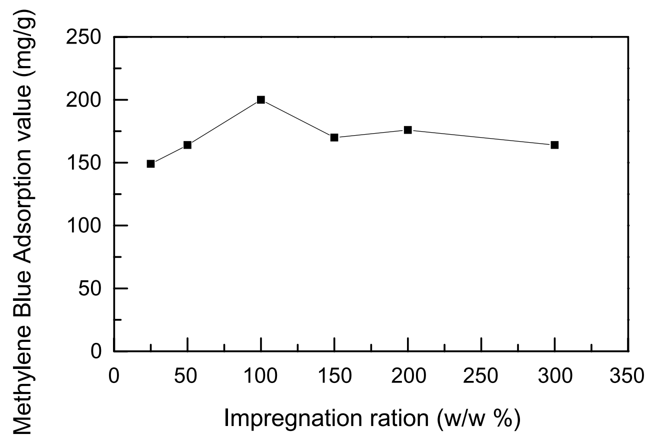

Fig. 4 The effect of impregnation ratio on methylene blue adsorption value of activated carbon

100%. This means that the weight loss of the activated carbon products in the lower impregnation ratio (<300%) almost keeps constant with increasing the impregnation ratio. The reduction of weight loss or enhancing the activated carbon yield in the zinc chloride activation process is most likely due to the effect of this chemical in which it promotes the Scholl condensation (polymerization) reactions (Ahmadpour and Do 1996, 1997). This reactions, which occur among the aromatic hydrocarbons and tar-forming compounds, result in the formation of larger molecules (polycyclic aromatics) in the activated products and increase in the carbon yield. The experimental results illustrated in Fig. 3 show the effect of impregnation ratio on the iodine adsorption value of activated carbon. It shows that the iodine adsorption value of activated carbon reach a maximum for $ZnCl_2$/sawdust ratio of 100%. The iodine adsorption value could not sharply increase with increasing the impregnation ratio when the impregnation ratio is over 100%. Figure 4 demonstrates the effect of impregnation ratio on the methylene blue adsorption value of activated carbon. The methylene blue adsorption value increases with increasing the impregnation ratio until 100%, and reach a maximum for $ZnCl_2$/sawdust ratio of 100%. The methylene blue adsorption value varies with the impregnation ratio when impregnation ratio is over 100%, but only slightly as shown in Fig. 4.

The experimental results indicate that both the yield and the adsorption characteristics of activated carbon can reach a relatively higher value if the impregnation ratio of 100% $ZnCl_2$/sawdust is chosen in the chemical activation process.

3.2 Effect of activation time

The preparation of activated carbon was carried out using sawdust impregnated with $ZnCl_2$ to be activated for different activation time by keeping the activation temperature

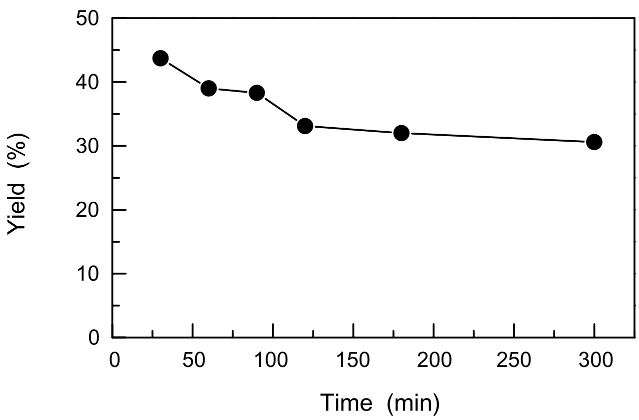

Fig. 5 The effect of activation time on yield of activated carbon

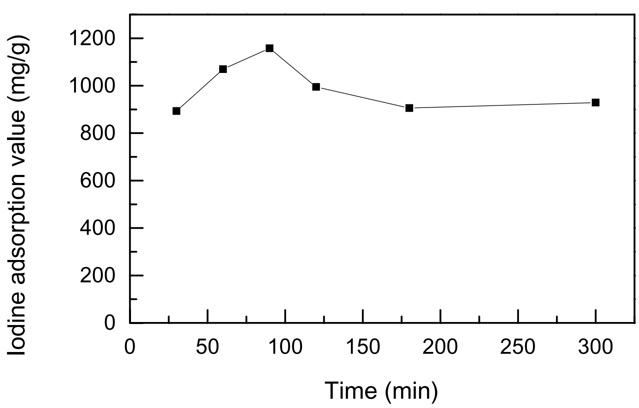

Fig. 6 The effect of activation time on iodine adsorption value of activated carbon

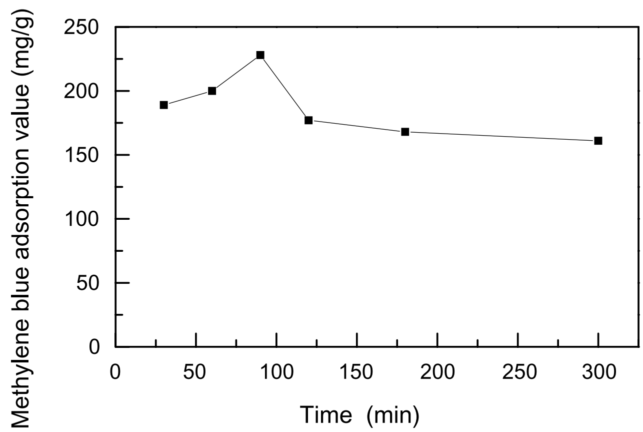

Fig. 7 The effect of activation time on methylene blue adsorption value of activated carbon

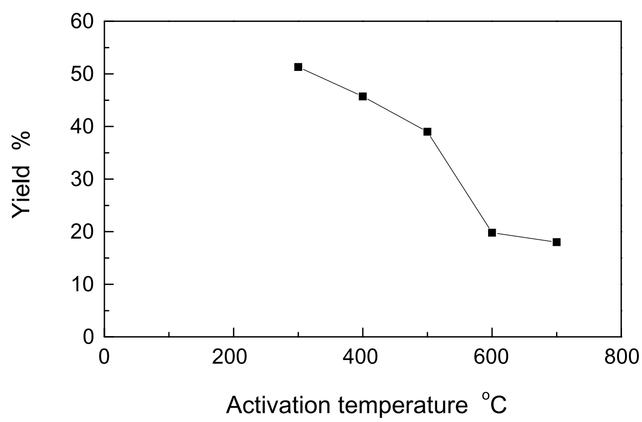

Fig. 8 The effect of activation temperature on yield of activated carbon

at 500 °C and the $ZnCl_2$/sawdust for 100%. From our investigation, the optimum impregnation ratio is 100%, and the optimum impregnation temperature is 500 °C followed below. Then the adsorption capacity of the activated carbon prepared in different activation time for iodine and/or methylene blue was measured. The effects of activation time on both the yield and the adsorption capacity of activated carbon are shown in Figs. 5–7, respectively.

The experimental results illustrated in Fig. 5 show that the yield of activated carbon decreases by increasing the activation time. This is resulted from the burn-off of carbon with increasing the activation time. Figure 6 shows that the iodine adsorption value of activated carbon sharply increase with increasing the activation time until 90 minutes and reach a maximum at the activation time of 90 minutes. Then the iodine adsorption value decreases with increasing the activation time from 90 minutes, the decrease is not very pronounced. The similar behavior has been observed for the methylene blue adsorption of activated carbon demonstrated in Fig. 7. The methylene blue adsorption value increases sharply by increasing the activation time from 30 to 90 minutes, and reach a maximum at the activation time of 90 minutes too. The methylene blue adsorption value decreases with increasing the activation time when the activation time is over 90 minutes, but only slightly as shown in Fig. 7.

The experimental results indicate that the optimum activation time is around 60–90 minutes in the zinc chloride activation process with relatively higher yield and adsorption capacity for iodine and methylene blue.

3.3 Effect of activation temperature

The effect of activation temperature was studied by using sawdust impregnated with $ZnCl_2$ to be activated in different activation temperature for 60 minutes by keeping the $ZnCl_2$/sawdust for 100% to prepare the activated carbon, then the adsorption capacity of the activated carbon prepared in different activation temperature for iodine and/or methylene blue was measured. The experimental results are shown in Figs. 8–10, respectively.

Figure 8 shows that the yield of activated carbon decreases sharply with increasing the activation temperature

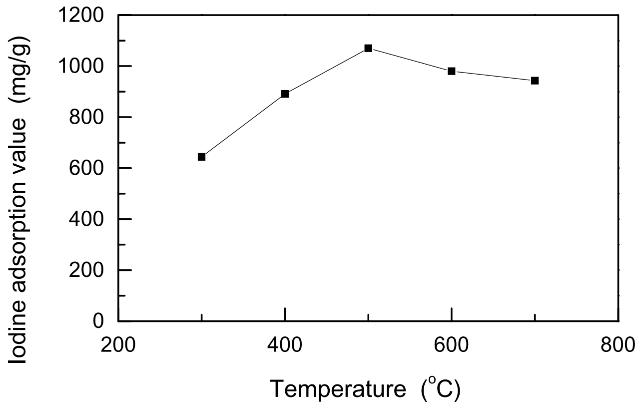

Fig. 9 The effect of activation temperature on iodine adsorption value of activated carbon

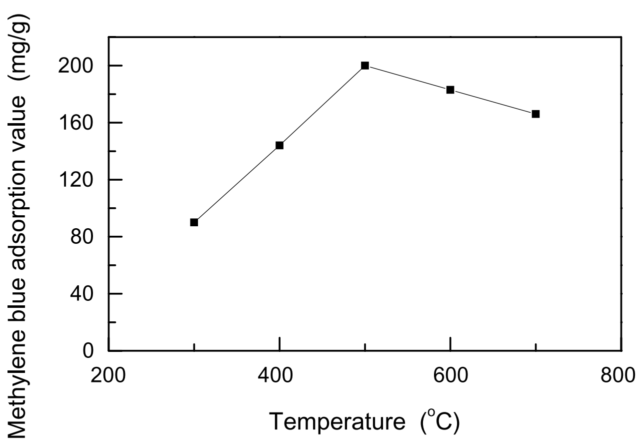

Fig. 10 The effect of activation temperature on methylene blue adsorption value of activated carbon

because the increase of activation temperature has resulted in the burn-off of carbon. Figure 9 shows that the iodine adsorption value of activated carbon sharply increase with increasing the activation temperature from 300 to 500 °C and reach a maximum at 500 °C. Then the iodine adsorption value decreases with increasing the activation temperature from 500 to 700 °C, the decrease is not very pronounced. The similar behavior has been observed too for the methylene blue adsorption of activated carbon demonstrated in Fig. 10. The methylene blue adsorption value increases sharply by increasing the activation temperature from 300 to 500 °C, and reach a maximum at 500 °C. The methylene blue adsorption value decreases with increasing the activation temperature when the activation temperature is over 500 °C, but only slightly as shown in Fig. 10.

The experimental results illustrated from Fig. 2 through Fig. 10 show that in zinc chloride activation process relatively lower activation temperature (500 °C), an impregnation ratio of $ZnCl_2$/sawdust for 100% and the activation time of 60–90 minutes provide a better conditions for making activated carbon with good adsorption characteristics if carbon yield is also taken into account.

4 Conclusions

Wood activated carbons are prepared from the chemical activation of sawdust impregnated with zinc chloride. The effects of various operation parameters such as impregnation ratio, activation temperature and time on the adsorption properties of activated carbons were measured and analyzed in order to optimize these operation conditions. The most important operation parameter in chemical activation with zinc chloride was found to be the impregnation ration of $ZnCl_2$/sawdust. The activation temperature is the second important variable which had significant effect on the yield of carbon and the adsorption capacity of prepared activated carbon for iodine and methylene blue. The yield of activated carbon increases with increasing the impregnation ratio, but the increase of yield is not very pronounced when the impregnation ratio is larger than 100%, that is to say, the weight loss of the activated carbon products in the lower impregnation ratio (<300%) almost keeps constant with increasing the impregnation ratio. The yield of activated carbon decreases by increasing the activation time and temperature. The increase in the yield of activated carbon by increasing activation temperature is much more sharply than by increasing activation time. The similar adsorption behaviors for iodine and methylene blue of activated carbon prepared in different operation variables had been observed. The adsorption of activated carbon for iodine and methylene blue can reach a maximum value in each case of different impregnation ratio, different activation time and/or different activation temperature. The better adsorption properties of activated carbon can be obtained in the zinc chloride activation process under the optimum operation conditions activated with the impregnation ratio of 100% $ZnCl_2$/sawdust at the activation temperature of 500 °C for 60–90 minutes (activation time).

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