

## PREPARATION OF ACTIVATED CARBON FROM LIGNIN OBTAINED BY STRAW PULPING BY KOH AND K<sub>2</sub>CO<sub>3</sub> CHEMICAL ACTIVATION

XIAO-JUAN JIN,<sup>\*,\*\*</sup> ZHI-MING YU<sup>\*</sup> and YU WU<sup>\*</sup>

<sup>\*</sup>*School of Material Science and Technology, Beijing Forestry University, 100083, Beijing, China*

<sup>\*\*</sup>*Key Laboratory of Pulp and Paper Engineering of Ministry of Education, Shandong Polytechnic university, Jinan, China*

*Received October 29, 2010*

Activated carbon was prepared through chemical activation of lignin from a straw pulping precursor, using K<sub>2</sub>CO<sub>3</sub> and KOH as chemical agents. To optimize the preparation method, the effect of the main process parameters (such as impregnation ratio, activation temperature and activation time) on the performance of the obtained activated carbon (expressed in terms of iodine number and yield of activated carbon) was investigated, and the actions of the activating agents were compared. The activated carbon prepared by K<sub>2</sub>CO<sub>3</sub>, under optimum conditions, permitted to obtain a BET surface area of 1104 m<sup>2</sup>/g, including an external or non-microporous surface of 417 m<sup>2</sup>/g, an average adsorption pore width of 2.0 nm, the amount of methylene blue, iodine number and the yield of activated carbon being of 10.6 mL/0.1 g, 1310 mg/g and 19.8%, respectively. As to the carbon activated by KOH under optimum conditions, its BET surface area was of 917 m<sup>2</sup>/g, including the external or non-microporous surface of 231 m<sup>2</sup>/g, the average adsorption pore width of 2.5 nm, while the amounts of methylene blue, iodine number and yield of activated carbon were of 9.6 mL/0.1 g, 1180 mg/g and 18.7%, respectively.

**Keywords:** lignin, K<sub>2</sub>CO<sub>3</sub>, KOH, activated carbon

### INTRODUCTION

Lignin is the second most abundant natural polymer, making up 15-30% of the woody cell walls of gymnosperms (softwood) and angiosperms (hardwood). Lignocellulose represents approximately 50% of the wastes from agriculture, municipal sources, forest and agricultural-based industries. As a result, several systems have been proposed for the utilization of lignin as a renewable polymeric material. However, lignin utilization is still limited – less than 2% of the produced lignin is used in commercial applications.<sup>1-3</sup> An enormous amount of lignin is separated from wood during pulp and papermaking operations, the black liquors being commonly processed through evaporation and calcinations, to recover the energy and the remaining chemical reactant. Nevertheless, within the last several decades, lignin has gained an increasing interest as a potential raw material for the chemical industry.

According to a widely accepted definition, lig-

nin is an amorphous, polyphenolic material arising from an enzyme-mediated dehydrogenative polymerization of three phenylpropanoid monomers, coniferyl, sinaphyl and p-coumaryl alcohols, which are the main sources for the formation of graphite microcrystallites of activated carbon.

As to the preparation of carbon, lignin is particularly advantageous due to its high phenolic content, leading to higher carbon yields than those obtained from the two other main macromolecular compounds of biomass: cellulose and hemicellulose.<sup>4,7</sup> Activated carbon is a high-porosity material, very useful in the adsorption of both gases and solutes. Therefore, it has been widely used for the separation of gases, recovery of solvents and removal of organic pollutants from drinking water, as well as a catalyst carbon. As environmental pollution is becoming an issue of increasing concern, the need for activated carbon is growing. The development

of methods for re-using waste materials is highly desired, and the production of activated carbon from wastes is an interesting possibility.<sup>8</sup> In China, straw is still one of the materials for paper production, because of the scarcity of the existing forest resources; the utilization of lignin from these effluents can reduce significantly the environmental impact and afford attractive products.<sup>9</sup>

In this paper, the action of two alkaline potassium compounds commonly used for the chemical activation of various precursors has been thoroughly investigated, on commercially available straw lignin obtained from alkaline straw pulping. All parameters of active carbon synthesis, which could be varied, were investigated, and namely, activation temperature, mass ratio of the alkaline potassium compound to lignin and activation time. Also, the suitable preparation conditions of the material having been given, desired porous characteristics could be identified, and an insight into the activation mechanisms was obtained. The characterization of the activated carbon prepared under optimal conditions with the 2 activating agents was discussed comparatively.

## EXPERIMENTAL

### Materials

Chinese straw lignin was purchased as fine dark brown powder from Haiming Scientific & Technical Co. Ltd., Henan province, China. Analytical grade KOH and K<sub>2</sub>CO<sub>3</sub> were purchased from Beijing Lanyi Chemicals. The ash and Klason lignin content were evaluated according to the Chinese standard methods GB/T 2677.3-93 and GB/T 2677.8-94, which agree with the standard test ASTM D 1102-84 and ASTM D 1106-96 methods, respectively.<sup>10</sup> Two replicates were used for all samples. The acid-soluble lignin was determined by the GB/T 10337-89 method,<sup>11</sup> which is a Chinese standard for the determination of acid-soluble lignin in raw material and pulp.

### Methods

#### *Preparation of lignin-based activated carbon*

The preparation of activated carbon from lignin was carried out in four steps, as follows: (i) prior to the experiments, the samples were oven-dried for 4 h at 105 °C; (ii) the oven-dried lignin (3 g) was mixed with KOH and K<sub>2</sub>CO<sub>3</sub> (40% aqueous solution), in various mass ratios, in a crucible, for 16 h; (iii) the mixture was put in an electric furnace, the impregnated sample was pyrolyzed at temperatures from 500 to 900 °C, at a heating rate of 20 °C min<sup>-1</sup>, on maintaining it for some time at a certain temperature, to complete activation (the KOH- and K<sub>2</sub>CO<sub>3</sub>-to-lignin ratios, the activated

time and activated temperature were decided by the design of the experiment), and to cool down; (iv) the carbonized samples were washed several times with hot distilled water, to remove the chemical active agent, then with cold distilled water, until the pH of the filtrate became neutral, and finally oven-dried for 6 h at 105 °C, to prepare lignin-based activated carbon. The yield of the activated carbon was calculated with the equation:

$$Y = \frac{M_1}{M_2} \times 100\% \quad (1)$$

where M<sub>1</sub> is the weight of the activated carbon and M<sub>2</sub> is the weight of oven-dried lignin.

The entire activation process was divided into three parts. During activation, the influences of parameters, such as the ratio of KOH- or K<sub>2</sub>CO<sub>3</sub>-to-lignin, the activation time and activation temperature, on the yield and iodine number were examined. In the first case, the ratio of KOH- or K<sub>2</sub>CO<sub>3</sub>-to-lignin was varied from 0.8 to 2.4, while the activation temperature (800 °C) and activation time (50 min) were kept constant. In the second case, the activation temperature (800 °C) and ratio of KOH- or K<sub>2</sub>CO<sub>3</sub>-to-lignin (2/1) were set and the activation time was varied from 20 to 60 min. In the last case, the activation temperature was varied from 500 to 900 °C, along with the preset values of activation time (50 min) and ratio (2/1). All activation processes were performed at a heating rate of 20 °C/min.

#### *Characterization of lignin-based activated carbon*

Some properties of activated carbon were measured, including the iodine number, the Brunauer-Emmet-Teller (BET) specific surface area, the amount of methylene blue adsorption and the yield. (i) The methylene blue adsorption of lignin-based activated carbon was evaluated according to the procedure of GB/T 12496.10-1999, and the iodine number was determined at 303K, based<sup>12-13</sup> on the Standard Test Method ASTM Designation: D4607-86. Also, the yield was calculated as the ratio of the weight of the final activated carbon to that of the initial raw materials. (ii) The N<sub>2</sub> adsorption-desorption isotherms of activated carbon prepared under optimum conditions were measured with an accelerated surface area and porosimetry system (ASAP 2010, Micromeritics), for determining the surface areas. Prior to the measurements, the samples were outgassed at 573K, under nitrogen flow, for at least 2 h. The nitrogen adsorption-desorption data were recorded at a liquid nitrogen temperature of 77 K. The nitrogen adsorption isotherm was measured over a relative pressure (p/p<sub>0</sub>) range, from approximately 10<sup>-6</sup> to 1. The BET surface area was calculated using the BET equation from the selected N<sub>2</sub> adsorption data, within a range of relative pressure, p/p<sub>0</sub>, from 0.1 to 0.3. Pore size distribution in the micropore range was obtained by the Barrett-Joyner-Halenda (BJH) method.<sup>14-17</sup>

## RESULTS AND DISCUSSION

### Characterization of purchased straw lignin

Table 1 shows that the Klason lignin content accounted for 44.93% in the raw material, with a larger amount of ash (20.29%), compared to that of Kraft lignin (11.2%), reported by V. Fierro,<sup>7</sup> while the carbohydrate content ratio was of 29.73%. This was mainly due to the evaporation used to concentrate the black liquor, the straw lignin powder being obtained by the method of sponging drying. Therefore, all carbohydrate and inorganic materials were present in the dried lignin powder, which explains the relatively lower Klason lignin content and higher ash content.

### Influence of activating agent/lignin ratio on yield and iodine number

The ratio of KOH or  $K_2CO_3$  to lignin was varied from 0.8 to 2.4, while the activation temperature (800 °C) and activation time (50 min) were kept constant.

The effects of the activating agent/lignin ratio were studied at five different  $K_2CO_3$  and KOH/lignin ratios, ranging between 0.8 and 2.4. Figure 1 shows that a ratio of  $K_2CO_3$  and KOH/lignin below 2:1 led to insufficiently activated carbons (*i.e.*, the iodine adsorption value was relatively low). However, higher values led to materials with too wide pores (*i.e.*, the iodine adsorption value was also low). Consequently, with increasing the ratio of  $K_2CO_3$  and KOH/lignin, more pores would be formed while, when the ratio arrived at a certain value, the pores would be widened and burnt off. So, the adsorption capacity of the activated carbon would increase to a certain value and then decrease with the  $K_2CO_3$ - and KOH-to-lignin ratio. Figure 2 shows that the best adsorption capacity of activated carbon was obtained at a  $K_2CO_3$ - and KOH-to-lignin ratio of 2:1. Within a ratio range of

0.8-1.6, with increasing the  $K_2CO_3$ - and KOH-to-lignin ratio, the activation reaction was more intense, enhancing the adsorption capacity of iodine; when the ratio of  $K_2CO_3$ - and KOH-to-lignin reached 2.0, the carbons on the active sites reacted completely and the adsorption capacity of iodine reached its maximum value. Similar trends were also found by V. Fierro *et al.* when preparing activated carbon from Kraft lignin using  $H_3PO_4$ . As for the iodine number,  $K_2CO_3$  was more effective than KOH, which agrees with previously reported results.<sup>18</sup>

### Influence of activation time on yield and iodine adsorption

The activation temperature (800 °C) and KOH- and  $K_2CO_3$ -to-lignin ratio (2/1) were set and the activation time was varied from 20 to 60 min, to examine the effects of activation time on yield and iodine number.

The effects of activation time on the yield and iodine adsorption capacity of activated carbon were evaluated under the following experimental conditions: activation temperature = 800 °C, and ratio of KOH- and  $K_2CO_3$ -to-lignin = 2.0, as shown in Figures 3 and 4, respectively.

It was evidenced that the yield of activated carbon decreased with increasing the activation time. In the case of  $K_2CO_3$ , the iodine number increased gradually from 1008 to 1312 mg/g, with increasing the activation time from 20 to 50 min, after which the amount of iodine decreased from 1312 to 1260 mg/g, with increasing the activation time from 50 to 60 min.

As for KOH, the iodine number increased gradually from 953 to 1165 mg/g with increasing the activation time from 20 to 50 min, and then it decreased from 1165 to 960 mg/g with increasing the activation time from 50 to 60 min.

Table 1  
Characterization of purchased straw lignin

Composition	Content (%)
Klason lignin	44.93
Acid soluble lignin	4.25
C	51.78
H	3.83
O	18.31
N	0.01
Ash	20.29
Carbohydrate	29.73
pH	11

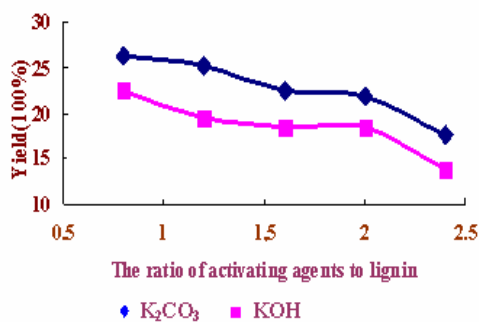


Figure 1: Effects of K<sub>2</sub>CO<sub>3</sub>- and KOH-to-lignin ratios on yield of activated carbon

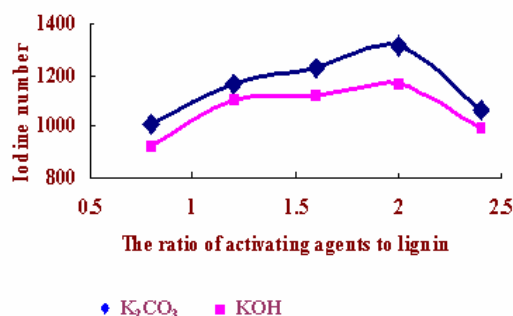


Figure 2: Effects of K<sub>2</sub>CO<sub>3</sub>- and KOH-to-lignin ratios on iodine number of activated carbon

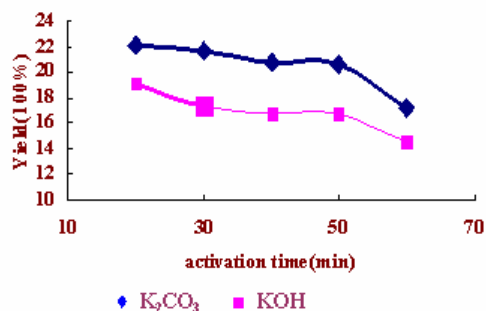


Figure 3: Effects of activation time on yield of activated carbon

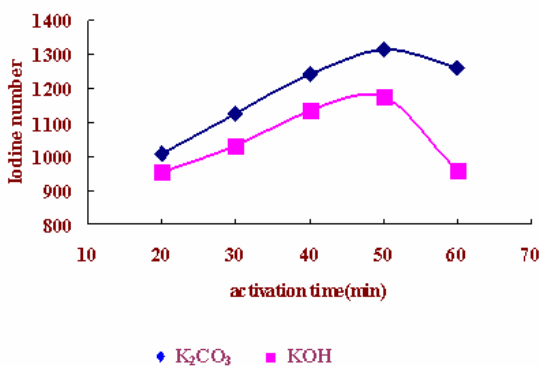


Figure 4: Effects of activation time on iodine number of activated carbon

The main explanation is that, after the activation time reached a certain value, any further increase in the activation time would cause the carbon pores to burn off, thus reducing the adsorption capacity and yield of activated carbon.

### Influence of activation temperature on yield and iodine adsorption

The activation time (50 min) and KOH- and K<sub>2</sub>CO<sub>3</sub>-to-lignin ratio (2/1) were kept constant, while the activation temperature was varied from 500 to 900 °C, to explore the effects of activation time on yield and iodine adsorption.

The yield and iodine number of activated carbon prepared at different temperatures using different activating agents are illustrated in Figures 5 and 6, respectively. The experimental

data provided in Figure 5 show that the yield of activated carbon decreased progressively with increasing the activation temperature, as due to the more numerous pores formed; when the activation temperature increased, the pores would widen and then burn off. Consequently, the adsorption capacity of activated carbon increased to a certain value and then decreased with increasing temperature (Fig. 6), the iodine adsorption of the activated carbon prepared by K<sub>2</sub>CO<sub>3</sub> activation increasing with an increase in temperature within 500-800 °C, and then decreasing with the increase in temperature from 800 to 900 °C. The result is similar to that reported by Y. Sun *et al.*, who found out<sup>19</sup> that the optimal temperature for preparing activated carbon using lignin from reed black liquors with K<sub>2</sub>CO<sub>3</sub> was 800 °C.

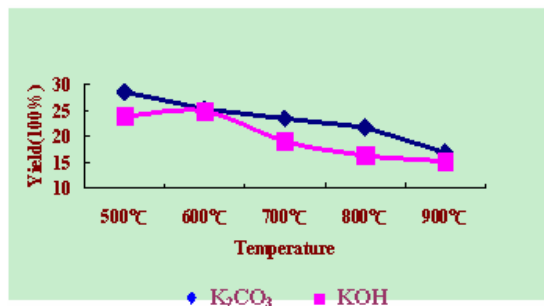


Figure 5: Effects of activation temperature on activated carbon yield

When using KOH as an activating agent, the iodine adsorption of the activated carbon prepared by KOH activation increased with increasing the temperature within the 500-700 °C range, and decreased with increasing the temperature from 700 to 900 °C. As to the iodine number, KOH indeed activates lignin more rapidly and at lower temperatures than K<sub>2</sub>CO<sub>3</sub> does: 800 °C and 700 °C for K<sub>2</sub>CO<sub>3</sub> and KOH, respectively, yet the yield of activated carbon when using K<sub>2</sub>CO<sub>3</sub> was higher than that for KOH activation. Similar trends were found by Turgay Taya *et al.*,<sup>20</sup> when preparing activated carbon from waste biomass using K<sub>2</sub>CO<sub>3</sub> and KOH activation. Jun'ichi Hayashi *et al.* reported that, when using K<sub>2</sub>CO<sub>3</sub>, the yield of activated carbon from Kraft lignin was of about 23%, when temperature increased to 900 °C (a slightly higher value than that obtained in the present experiment), which may be possibly due to the higher ash content of the raw material.<sup>21</sup>

### Activation mechanism

#### Activation using KOH

Several researchers<sup>22-24</sup> have investigated the mechanism of KOH activation of carbonaceous materials. After carbonization, the KOH added to coal remains as K<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>O. The dehydration of KOH at temperatures higher than 500 °C also generates K<sub>2</sub>O. The catalytic reaction mechanism of K-containing compounds in carbon materials during combustion and steam gasification processes has been thoroughly studied.<sup>25-28</sup> At relatively lower temperatures, the catalytic effect of K-containing compounds leads to a fast char gasification, by the steam adjacent to the active points (location of K-containing compounds), which leads to the formation of macropores. The macropores contribute slightly to the adsorption capacity of activated carbon, as proved by iodine adsorption. With increasing the activation

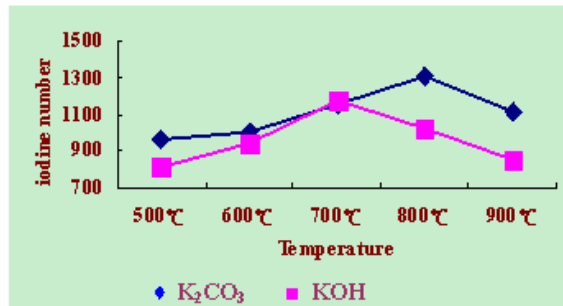


Figure 6: Effects of activation temperature on activated carbon iodine number

temperature, K-containing compounds are gradually evaporated. As a result, the influence of K-containing compounds fades. At the same time, the effect of KOH on carbonization plays an important role at the end of activation, the amorphous gradients formed by means of control coal carbonization by KOH permitting the formation and development of micropores, as proved by iodine adsorption.

The increase in the porosity of KOH activated carbons is associated with the gasification reaction. It is assumed that, during carbonization, KOH is reduced to metallic potassium. The reaction of KOH and carbon occurs as follows:<sup>29-30</sup>



#### Activation using K<sub>2</sub>CO<sub>3</sub>

Adinata *et al.*,<sup>34</sup> who studied the activated carbon from palm shells by chemical activation with K<sub>2</sub>CO<sub>3</sub>, found out that graphite gasification by alkali metals occurs as:



K<sub>2</sub>CO<sub>3</sub> was reduced by carbon above 600 °C, consequently the carbon was removed as CO, while the surface area and pore volume increased. However, with excess activation, the pores were combined, the mesopore volume increased and iodine adsorption decreased.

#### Characterization of optimally activated carbon

The optimally activated carbon was fully characterized, as to its adsorption properties, as well as its yield.

The observations above show that the ratio of K<sub>2</sub>CO<sub>3</sub>- and KOH-to-lignin, the activation time and activation temperature have significant effects on the yield and iodine number of the activated carbon obtained from lignin by K<sub>2</sub>CO<sub>3</sub> and KOH activation. The optimum conditions applied when

using  $K_2CO_3$  as an activation agent were the following:  $K_2CO_3$ -to-lignin ratio = 2.0, activation time = 50 min, activation temperature = 800 °C. These conditions allowed to obtain a BET surface area of 1104  $m^2/g$ , including the external or non-microporous surface of 417  $m^2/g$ , an average

adsorption pore width of 2.0 nm, an ash content of 12.5%, while the amount of methylene blue, the iodine number and the yield of activated carbon were of 10.6 mL/0.1 g, 1310 mg/g and 19.8%, respectively.

Table 2  
Comparison of preparation conditions and main parameters of activated carbon from black liquor

Preparation conditions	Raw material	$S_{BET}$ ( $m^2/g$ )	Reference
$K_2CO_3$ activation at 800 °C for 1 h	Reed lignin	1217	[31-32]
$K_2CO_3$ activation at 800 °C for 1 h	Spruce wood kraft lignin	2000	[31,8]
$K_2CO_3$ activation at 800 °C for 1 h	Cornstalk lignin	1410	31
KOH activation at 800 °C for 1 h	Spruce wood kraft lignin	1500	[31,8]
KOH activation at 700 °C for 1 h	Indulin lignin	514	[33,8]
Chemical activation using $ZnCl_2$ , $H_3PO_4$ , $K_2CO_3$ , $Na_2CO_3$ , KOH, NaOH	Kraft lignin	800-2000	[33-34]
$K_2CO_3$ activation at 800 °C for 50 min	Straw lignin	1104	This work
KOH activation at 700 °C for 50 min	Straw lignin	917	This work

As for KOH activation, the optimum conditions were as follows: KOH-to-lignin ratio = 2.0, activation time = 50 min, activation temperature = 700 °C. These conditions allowed to obtain a BET surface area of 917  $m^2/g$ , including an external or non-microporous surface of 231  $m^2/g$ , an average adsorption pore width of 2.5 nm, an ash content of 11.2% and an amount of methylene blue, iodine number and yield of activated carbon of 9.6 mL/0.1 g, 1180 mg/g and 18.7%, respectively. The results showed that  $K_2CO_3$  activation, under optimal conditions, led to more microporous materials, with a BET surface area 1.2 times higher than that obtained with KOH.

Table 2 shows that the BET area of straw lignin-based activated carbon using  $K_2CO_3$  activation was similar to that of reed lignin while, for KOH activation, the BET area was higher than that of Indulin lignin and lower than others, possibly due to the higher ash content of the raw material.

## CONCLUSIONS

1) Iodine absorption and the amount of methylene blue for activated carbon from lignin obtained from straw pulping by  $K_2CO_3$  activation can reach 1310 mg/g and 10.6 mL/0.1 g, after the optimization of the following three parameters:  $K_2CO_3$ -to-lignin ratio – 2:1, activation temperature – 800 °C, activation time – 50 min; under such conditions, the yield of activated carbon is of 19.75%.

2) Iodine absorption and the amount of methylene blue for activated carbon from lignin

obtained from straw pulping by KOH activation can reach 1180 mg/g and 9.6 mL/0.1 g, after the optimization of the following three parameters: KOH-to-lignin ratio – 2:1, activation temperature – 700 °C, activation time – 50 min; in this case, the yield of activated carbon is of 18.7%.

3) Applied under identical conditions,  $K_2CO_3$  was found to be a more effective chemical reagent for the preparation of activated carbon of lignin from straw pulping than KOH, in terms of both iodine number and yield of activated carbon.

In other studies now in progress, we are investigating the application of lignin-based activated carbon.

**ACKNOWLEDGEMENTS:** The authors gratefully acknowledge the financial support of the State Forestry Administration under Project 201204807: the study on the technology and mechanism of the activated carbon electrode preparation from waste hard board, and the Project (No. 0807) of Key Laboratory of Pulp and Paper Science and Technology of Ministry of Education (Shandong Polytechnic University).

## REFERENCES

- <sup>1</sup> V. Singhal and V. S. Rathore, *J. Microbiol. Biotechnol.*, **17**, 235 (2001).
- <sup>2</sup> J. H. Lora and W. G. Glasser, *J. Polym. Environ.*, **10**, 39 (2002).
- <sup>3</sup> S. Kubo and J. F. Kadla, *J. Polym. Environ.*, **13**, 97 (2005).
- <sup>4</sup> Q. Lu, X. R. Qian, G. Yu and H. C. Li, *Paper and Papermaking*, **2**, 61 (2005).

- <sup>5</sup> S. E. Gonzalez, T. Cordero and M. J. Rodriguez, *J. Water Res.*, **38**, 3043 (2004).
- <sup>6</sup> P. Ariyadejwanich, W. Tanthapanichakoon and K. Nakagawa, *Carbon*, **41**, 157 (2003).
- <sup>7</sup> V. Fierro, V. Torné-Fernández and A. Celzard, *Micropor. Mesopor. Mater.*, **101**, 419 (2007).
- <sup>8</sup> J. Hayashi, A. Kazehaya, K. Muroyama and A. P. Watkinson, *Carbon*, **38**, 1873 (2000).
- <sup>9</sup> L. Y. Zhao, J. M. Lü, Q. Li, G. F. Fan and Y. C. Wen, *J. Sci. Technol. Eng.*, **11**, 2914 (2008).
- <sup>10</sup> The State Bureau of Quality and Technical Supervision, China GB/T 2677.3-93 (1993); GB/T 2677.8-94 (1994).
- <sup>11</sup> The State Bureau of Quality and Technical Supervision, China GB/T 10337-89 (1989).
- <sup>12</sup> The State Bureau of Quality and Technical Supervision, China GB/T 12496.10 (1999).
- <sup>13</sup> American Society for Testing Materials (ASTM), ASTM D 4607-94, Philadelphia, PA.
- <sup>14</sup> S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).
- <sup>15</sup> S. Gregg and K. S. W. Sing, in “Adsorption, Surface Area and Porosity”, Academic Press, London, 1982, pp. 42-112.
- <sup>16</sup> W. Li, L. B. Zhang, J. H. Peng, N. Li and X. Y. Zhu, *Ind. Crop. Prod.*, **27**, 341 (2008).
- <sup>17</sup> E. P. Barret, L. G. Joyner and P. P. Halenda, *J. Am. Chem. Soc.*, **73**, 373 (1951).
- <sup>18</sup> V. Fierro, V. Torné-Fernández and A. Celzard, *Micropor. Mesopor. Mater.*, **92**, 243 (2006).
- <sup>19</sup> Y. Sun, J. P. Zhang, G. Yang and Z. H. Li, *J. Chem. Biochem. Eng.*, **20**, 429 (2006).
- <sup>20</sup> T. Taya, S. Ucarb and S. Karag, *J. Hazard. Mater.*, **165**, 481 (2009).
- <sup>21</sup> V. Fierro, V. Torné-Fernández and A. Celzard, *Micropor. Mesopor. Mater.*, **101**, 419 (2007).
- <sup>22</sup> J. Hayashi, A. Kazehaya, K. Muroyama and A. P. Watkinson, *Carbon*, **38**, 1873 (2000).
- <sup>23</sup> M. A. Lillo-Ródenas, D. Cazorla-Amorós and A. Linares-Solano, *Carbon*, **41**, 267 (2003).
- <sup>24</sup> H. Jankowska, A. Swiatkowski and J. Chorea, “Active Carbon”, New York, Ellis Horwood, 1991.
- <sup>25</sup> T. Wignmns, *Carbon*, **27**, 13 (1989).
- <sup>26</sup> Q. Xie and B. X. Bian, “Principles of Control over Coal Carbonization and its Application in Preparation of Coal-based Activated Carbon”, Xuzhou, China University of Mining and Tech. Press in China, 2002.
- <sup>27</sup> Q. Xie, Q. R. Chen, G. Z. Gong, X. L. Zhang and D. P. Xu, *J. Coal. Eng.*, **9**, 84 (2003).
- <sup>28</sup> M. A. Lillo-Ródenas, J. Juan-Juan, D. Cazorla-Amorós and A. Linares-Solano, *Carbon*, **42**, 1371 (2004).
- <sup>29</sup> Y. B. Ji, T. H. Li, Z. Li, X. X. Wang and Q. L. Lin, *Appl. Surf. Sci.*, **254**, 506 (2007).
- <sup>30</sup> D. Adinata, W. M. A. W. Daud and M. K. Aroua, *Bioresource Technol.*, **98**, 145 (2007).
- <sup>31</sup> Y. Sun, J. Wei, Y. S. Wang, G. Yang and J. P. Zhang, *J. Environ. Technol.*, **31**, 53 (2010).
- <sup>32</sup> Y. Sun, J. P. Zhang, G. Yang, and Z. H. Li, *J. Chem. Biochem. Eng.*, **20**, 429 (2006).
- <sup>33</sup> P. J. Suhas, M. Carrott and M. M. L. Ribeiro, *Bioresource Technol.*, **98**, 2301 (2007).
- <sup>34</sup> L. Khezami, A. Chetouani, B. Taouk and R. Capart, *Powder Technol.*, **157**, 48 (2005).