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Preparation of High-butane-working-capacity Granular Activated Carbon from China Fir Sawdust

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Abstract: A simple route has been developed for preparing granular activated carbon (GAC) with high butane working capacity (BWC). Concentrated sulfuric acid was used during phosphoric acid activation for the production of the activated carbon. A granular activated carbon with high BWC of 165 g/L and an apparent density of 241 g/L was obtained from China fir sawdust. Simultaneously specific surface area, total pore volume, micropore volume and average pore diameter of the GAC reached 2 627 m^2/g, 1.574 cm^3/g, 0.941 cm^3/g and 2.397 nm, respectively. The results of orthogonal test showed that the adopted combination of factors is: phosphoric acid concentration 56 %, impregnation ratio 1.9∶1, sulfuric acid amount 6 %, sulfuric acid concentration 80 %, drying temperature 300 ℃, drying time 3 h, activation temperature 450 ℃ and activation time 60 min. It was also seen that the dosage of concentrated sulfuric acid and activation temperature were the most important factors for preparing GAC for butane adsorption. Finally, compared to previous studies, this study can shorten the preparation period from 20–70 h to less than 5 h.

Key words: granular activated carbon; butane-working capacity; orthogonal test; China fir; phosphoric acid; sulfuric acid

杉木屑制备高丁烷工作容量颗粒活性炭

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摘 要：研究提出了一种简单的高丁烷工作容量(BWC)颗粒活性炭(GAC)的制备方法。在磷酸法制备活性炭的工艺中通过添加浓硫酸作为助催化剂，以杉木屑为原料制备了 BWC 高达 165 g/L 的产品，其表观密度为 241 g/L，比表面积、总孔容、微孔孔容和平均孔径分别为 2 627 m^2/g、1.574 cm^3/g、0.941 cm^3/g 和 2.397 nm。正交试验结果表明较佳的工艺条件为：磷酸浓度为 56 %，浸渍比为 1.9∶1，硫酸添加量为 6 %，硫酸浓度为 80 %，干燥固化温度为 300 ℃，干燥固化时间为 3 h，活化温度为 450 ℃，活化时间为 60 min，并且浓硫酸和活化温度是制备丁烷吸附用颗粒活性炭的重要影响因素。通过本研究可将高 BWC 颗粒活性炭制备时间从 20 ~ 70 h 缩短在 5 h 以内。

关键词：颗粒活性炭；丁烷工作容量；正交试验；杉木；磷酸；硫酸

Cunninghamia lanceolata (China fir) is one of the most important timber species in China. According to the Fourth National Forest Inventory Statistics, the planted forest area of China fir is up to 9.11 million hm^2, accounting for 30.4 % of the artificial commercial forest area. The stocking volume of mature forest which occupyies an important position in the national economy[1] is up to 105 m^3/hm^2. With the consumption of the non-renewable fossil oil resources, the emission control of gasoline surely attracts more and more attention all over the world. Just as what is pointed out by Environmental Protection Agency (EPA) USA that activated carbon adsorption is the best method available to recycle the volatile organic compounds (VOCs). Thus large quantities of granulatar activated carbon (GAC) will be demanded. Many US patents [2-6] disclosed the preparation of GAC, with BWC ranging from 160-180 g/L by chemically activating carbonaceous material fragments. However the preparation period reached 20-70 h and/or some binders [6] were needed to improve the BWC by increasing the apparent density. Furthermore the process is difficult to control, such as using periodic addition of water to maintain fluidity[5] and keeping the 1 ℃/min heating rate from 35 to 95 ℃, etc. [3-4]. In this work, a simple method for the preparation of GAC with high BWC performance from China fir sawdust impregnated with phosphoric acid and concentrated sulfuric acid is proposed from the view of economic benefits.

1   Experimental Methods

1.1   Preparation of GAC

China fir sawdust was used as raw material. It was ground and sieved to obtain particles with a size range of 0.25-1.4 mm. Each impregnation was typically performed as follows. About 50 g of starting materials with a water content of 22 % were mixed simultaneously with H_3PO_4 solution of concentration range 50 %-65 % by weight and an impregnation ratio (g : g, the same as follows) range of 1.8 : 1-2.4 : 1 was also adopted and 2 %-6 % sulfuric acid (based on the weight of known H_3PO_4 concentration solution) with a concentration of 80 %-98 % was added in the mixture above. After sufficient blending, the impregnated-material was placed in an electric thermostatic drying oven at 120 ℃ until the impregnated material was transformed into a plastic-like high viscous mass. After enough kneading, the mass was shaped in a mould by vacuum hydraulic machine in the absence of a binder additive, then dried and solidified at 200-300 ℃ for 1-3 h in the drying oven. An activation process was followed in a Muffle furnace i. e. the materials were heated from ambient temperature up to a final activation temperature range of 400-500 ℃ at a rate of 10 ℃/min and resided for a range of 30-90 min without N_2 flow. At the end of activation, the sample was taken out immediately to cool down sharply to room temperature. Then, the sample was extensively washed with hot water until filtrate pH value 6-7. Finally, the sample was dried at 150 ℃ to constant weight.

1.2   Characterization

The pore characteristics of GAC were determined by nitrogen adsorption at −196 ℃ using a Micromeritics ASAP 2020 volumetric adsorption analyzer at a relative pressure of 0.975. Prior to analysis, the samples were degassed at 350 ℃ for 2 h under vacuum. The surface area was evaluated using the Brunauer-Emmet-Teller (BET) equation by the nitrogen adsorption data. Total pore volume (V_{tot}) was calculated by converting the amount of nitrogen adsorbed at a relative pressure of 0.95 to the volume of liquid nitrogen (density: 0.807 g/mL). Micropore volume (V_{mic}) was determined by nitrogen adsorption isotherms using Dubinin-Astakhov equation. Pore size distribution (PSD) of GAC was estimated based on the nitrogen adsorption isotherms, using the Density Function Theory (DFT) Plus Software.

According to the ASTM method D5228-93 the BWC test of GAC was performed. The sample was packed

in a constant volume bed as directed by the ASTM D2854-89 standard procedure. The bed was then held within a constant temperature bath at 25 ℃ and butane flow rate at (250 ± 5) mL/min for 15 min. The sample was then weighed and butane was adsorbed for additional 10 min, stopping at nearest 0.01 g gap between two adjacent weighs. When a constant sample weight had been reached, desorption was affected by passing dry air through the sample bed at (300 ± 5) mL/min for (2 400 ± 20) s. The mass difference between the saturated and desorbed adsorbent is the BWC in grams of butane per 100 mL carbon.

1.3　Orthogonal tests

The author adopted 8 factors, 3 levels in orthogonal test. The following $L_{27}(3^{13})$ orthogonal test in Table 1 was designed using the software Orthogonal Design Assistant Professional Ⅱ V3.1 to optimize these factors and confirm the degree of influence for each factor.

Table 1　Factors and levels of orthogonal test

| levels | factors | | | | | | | |
| | A | B | C | D | E | F | G | H |
	phosphoric acid concentration /%	impregnation ratio (g:g)	sulfuric acid amount/%	sulfuric acid concentration /%	drying temperature /℃	drying time/h	activation temperature/℃	activation time/min
1	50	1.6:1	2	80	200	1	400	30
2	56	1.9:1	4	90	250	2	450	60
3	65	2.2:1	6	98	300	3	500	90

2　Results and Discussion

2.1　Results of orthogonal tests

According to the experimental schemes in Table 1, GAC with different BWC were prepared and orthogonal test results were analyzed by range analysis, as shown in Table 2. The value of range reflects the significance of the corresponding factor on the performance of GAC. The bigger the value of R is, the greater the degree of influenceis is.

The descending order of the degree of influence for factors is given as follows: sulfuric acid amount (C), activation temperature (G), impregnation ratio (B), phosphoric acid concentration (A), drying temperature (E), drying time (F), activation time (H), sulfuric acid concentration (D). Thus, it is concluded that the addition of sulfuric acid is the most important factor for the preparation of the GAC for n-butane adsorption.

With regard to BWC, the best preparation technology is the combination of the maximum level of each factor i. e. $A_2B_2C_3D_2E_3F_3G_2H_2$. Due to the 0.01 % difference between k_1 and k_2 for the sulfuric acid concentration (D), the adopted combination of factors is $A_2B_2C_3D_1E_3F_3G_2H_2$ from the point of industrialization. That is phosphoric acid concentration 56 %, impregnation ratio 1.9:1, sulfuric acid amount 6 %, sulfuric acid concentration 80 %, drying temperature 300 ℃, drying time 3 h, activation temperature 450 ℃, activation time 60 min.

2.2　Optimization experiment

Experiment was carried out according to the optimal combination of factors(No.15 in Table 2) except for drying time 3 h, activation time 60 min.

Comparing with No.15 in Table 2 the repeated experiment's butane activity was 0.78 g/g and BWC was 165.41 g/L. It is seen that the analysis result of the orthogonal test is correct. The repeated experiment only has an apparent density of 241 g/L compared with the 254 g/L of No.15 due to the longer drying and activation time. Furthermore, longer time at high activation temperature may lead to more phosphorus-bearing groups

（C-O-P）leaving the carbonaceous surface [7]. It indicates the enlargement of primary pores to wider diameter pores which are favor of higher BWC.

Table 2　Results and data range analysis of orthogonal test

experimental number	A phosphoric acid concentration /%	B impregnation ratio (g:g)	C sulfuric acid amount /%	D sulfuric acid concentration /%	E drying temperature /℃	F drying time/h	G activation temperature /℃	H activation time/min	BWC/ (g·L⁻¹)
1	1	1	1	1	1	1	1	1	135.56
2	1	1	1	1	2	2	2	2	147.44
3	1	1	1	1	3	3	3	3	141.45
4	1	2	2	2	1	1	1	2	151.81
5	1	2	2	2	2	2	2	3	153.28
6	1	2	2	2	3	3	3	1	155.84
7	1	3	3	3	1	1	1	3	152.80
8	1	3	3	3	2	2	2	1	157.66
9	1	3	3	3	3	3	3	2	152.25
10	2	1	2	3	1	2	3	1	144.07
11	2	1	2	3	2	3	1	2	149.97
12	2	1	2	3	3	1	2	3	151.08
13	2	2	3	1	1	2	3	2	157.52
14	2	2	3	1	2	3	1	3	157.51
15	2	2	3	1	3	1	2	1	161.97
16	2	3	1	2	1	2	3	3	138.58
17	2	3	1	2	2	3	1	1	142.38
18	2	3	1	2	3	1	2	2	157.60
19	3	1	3	2	1	3	2	1	149.58
20	3	1	3	2	2	1	3	2	140.01
21	3	1	3	2	3	2	1	3	153.17
22	3	2	1	3	1	3	2	2	150.44
23	3	2	1	3	2	1	3	3	139.46
24	3	2	1	3	3	2	1	1	141.17
25	3	3	2	1	1	3	2	3	155.28
26	3	3	2	1	2	1	3	1	140.23
27	3	3	2	1	3	2	1	2	145.10
k_1	149.79	145.81	143.79	149.12	148.40	147.84	147.72	147.61	
k_2	151.19	152.11	149.63	149.14	147.55	148.67	153.81	150.24	
k_3	146.05	149.10	153.61	148.77	151.07	150.52	145.49	149.18	
R	5.14	6.30	9.82	0.37	3.52	2.68	8.32	2.63	

Fig. 1 shows adsorption-desorption isotherm of N_2 at 77 K on GAC prepared under optimal experiment condition. It can be seen that the resulting GAC gives a mixed type isotherm in the IUPAC classification. At the initial p/p_0, large amount of N_2 adsorption happens at very low relative pressures. It indicates the characteristic of microporous materials (type Ⅰ). However at intermediate p/p_0, the knee of the isotherm becomes wide. It shows that the pores are widened. At high p/p_0, a certain slop is observed and a plateau is not clearly attained, It means that a wide range of pore sizes (type Ⅳ) appears. The isotherm exhibits type H_4 hysteresis loops which are, typical for slit-shaped pores [8-12].

For micropores and mesopores, the adsorptive capacity of the activated carbon as well as the rate of adsorption depend upon the internal surface area and pore size distribution (PSD) [13]. GAC readily adsorb large amounts of butane in both micropores and mesopores [14]. However, easy and fast desorption indicates mesoporosity [15]. n-Butane has a molecular diameter of 0.5 nm and it will be most strongly adsorbed in pores of slightly larger width. The enhanced adsorption interaction energy will disappear for pores which are slightly larger than 1 nm [14,16]. This indicates that the optimal pore width for cyclic butane adsorption-desorption is

possessed by larger micropores and small mesopores[14-15]. Just as what is shown in the PSDs of GAC prepared under the better experiment condition (Fig. 2), the GAC is abundant in lager micropores and small mesopores especially the pore range from 1.8 to 5.0 nm corresponding to the literatures[5,17].
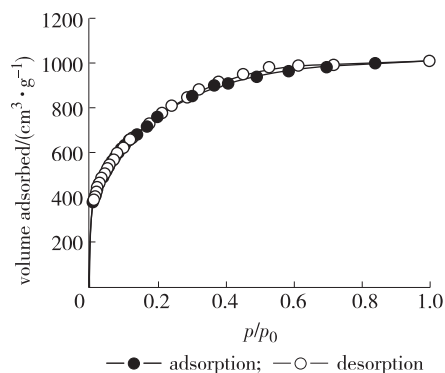

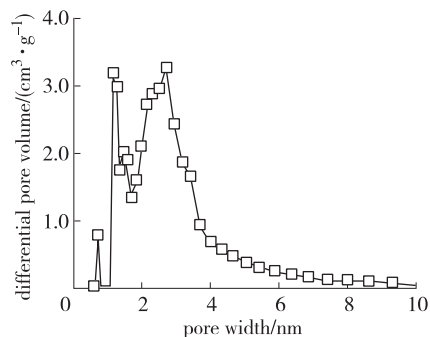Fig. 1 N$_2$ adsorption-desorption isotherm on GAC prepared under optimal experiment condition

Fig. 2 PSDs of GAC prepared under optimal experiment condition

2.3 Comparison of different preparation processes

As shown in Table 3, the preparation period of GAC 1 (C1) which is added sulfuric acid in this study is apparently shorter than those of GAC 2 (C2) and GAC 3 (C3)[3]. Although the BWC value of C1 is smaller than that of C2, it is still large enough to satisfy the market demand and particularly competitive due to the superiority in simplified production process and lower apparent density.

Table 3 Properties of activated carbon

samples	heating history[1]	properties			
		BET surface area /(m^2·g^{-1})	apparent density /(g·mL^{-1})	butane activity /(g·g^{-1})	BWC /(g·L^{-1})
C1	120 ℃ (1.5 h)/300 ℃ (3 h)/450 ℃ (1 h)	2627	0.24	0.78	165
C2	70 ℃ (36h)/85 ℃ (36h)/480 ℃		0.30	0.69	181
C3	50 ℃ (1h)/120 ℃ (45min)/140 ℃ (0.5h)/85 ℃ (16h)/480 ℃	2490	0.26	0.68	158

1) temperature(time) denotes that the impregnated material was hold at the given temperature for a given time.

Molina-Sabio et al[18] suggested that the amount of phosphorus X_p introduced into the interior of the particle during impregnation was the main factor to govern the development of porosity of the final carbon. Thus, it becomes critical for obtaining high performance activated carbon that effective method to increase the amount of phosphorus X_p in the interior of the particle is carried out. At present, two methods can be adopted, i.e., impregnation with activator at low temperature for a longer duration[3,19-20] and adding concentrated sulfuric acid during the phosphoric acid activation process[21-23]. The combination of both methods above (which could intensify the dehydration and degradation process of biopolymer in the material at the catalyzing of the combination of phosphoric acid and sulfuric acid at low temperature) was adopted in this study. Due to this combination, there is a dramatic decrease of preparation period compared to the previous study[2-6].

3 Conclusion

From the viewpoint of economic benefits, the preparing condition was optimized in this study on the basis of the property of products. The final analysis results of orthogonal test demonstrate that the optimal preparation technology is as follows: phosphoric acid concentration 56 %, impregnation ratio 1.9:1, sulfuric acid amount 6 %, sulfuric acid concentration 80%, drying temperature 300 ℃, drying time 3h, activation temperature 450 ℃, activation time 60 min. The sulfuric acid amount(C) is the most important factor as for BWC. The

descending order of other factors for their effects on BWC is: activation temperature (G), impregnation ratio (B), phosphoric acid concentration (A), drying temperature (E), drying time (F) or activation time (H), sulfuric acid concentration (D). Under the optimal preparation conditions, a GAC with maximum BWC of 165 g/L, apparent density of 241 g/L, pore volume of 1.574 cm^3/g, micropore volume of 0.941 cm^3/g, average pore diameter of 2.397 nm and BET of 2 627 m^2/g was prepared. It was seen that the preparation period was shortened from 20－70 h to less than 5 h.

References：

[1]傅星星,郑德勇.浅谈杉木精油的开发前景[J].福建林业科技,2008,35(4):267-269.

[2]EDWARD D T,MITCHELL S D,CHARLES C M. High activity,high density activated carbon:US,5204310[P].1992-02-21.

[3]EDWARD D T. Preparation for high activity high density carbon:US,5206207[P].1992-03-18.

[4]ZHIQUAN Q Y. Preparation of high activity,high density carbon:US,5250491[P].1992-08-11.

[5]MITCHELL S D. Preparation for high activity,high density carbon:US,5304527[P].1992-11-16.

[6]JOHN C M,ZHIQUAN Q Y,EDWARD D T. Method of preparation of gasoline vapor adsorptive activated carbon:US,5324703[P].1993-07-21.

[7]HAIMOUR N M,EMEISH S. Utilization of date stones for production of activated carbon using phosphoric acid[J]. Waste Management,2006,26(6):651-660.

[8]HARRY M,FRANCISCO R. Activated Carbon[M]. London:Elsevier,2006:153-233.

[9]ROOP C B,MEENAKSHI G. Activated Carbon Adsorption[M]. Boca Raton :Taylor & Francis,2005:100-112.

[10]SUÁREZ-GARCÁA F,MARTÓNEZ-ALONSO A,TASCÓN J M D. Porous texture of activated carbons prepared by phosphoric acid activation of apple pulp[J]. Carbon,2001,39(7):1111-1115.

[11]ALEXANDER M P,OLGA I P,AMELIA M,et al. Surface chemistry of phosphorus-containing carbons of lignocellulosic origin[J]. Carbon,2005,43(14):2857-2868.

[12]EDWARD D T. Preparation for high activity high density carbon:US,5206207[P].1992-03-18.

[13]CHARLES C M,EDWARD D T. Preparation for high activity high density carbon:US,5276000[P].1992-10-28.

[14]JAN L A,JENNIFER L G,PETER C E. Applications for activated carbons from used tires:Butane working capacity[J]. Carbon,1999,37(9):1485-1489.

[15]JAGTOYEN M,DERBYSHIRE F. Some considerations of the origins of porosity in carbons from chemically activated wood[J]. Carbon 1993;31(7):1185-1192.

[16]YENISOY-KARAKA S,AYGÜN A,GÜNE M,et al. Physical and chemical characteristics of polymer-based spherical activated carbon and its ability to adsorb organics. Carbon 2004;42(3):477-484.

[17]蒋剑春,王志高,邓先伦,等.丁烷吸附用颗粒活性炭的制备研究[J].林产化学与工业,2005,25(3):5-8.

[18]MOLINA-SABIO M,RODRÍGUEZ-REINOSO F,CATURLA F,et al. Porosity in granular carbons activated with phosphoric acid[J]. Carbon,1995,33(8):1105-1113.

[19]MACÍAS-GARCÍA A,DÍAZ-DÍEZ M A,GÓMEZ-SERRANO V,et al. Preparation and characterization of activated carbons made up from different woods by chemical activation with H_3PO_4[J]. Smart Materials and Structures,2003,12(6):24-28.

[20]JIBRIL B,HOUACHE O,AL-MAAMARI R,et al. Effects of H_3PO_4 and KOH in carbonization of lignocellulosic material[J]. Journal of Analytical and Applied Pyrolysis,2008,83(2):151-156.

[21]蒙冕武,蒋治良.磷酸-微波法活性炭的工艺研究[J].林产化工通讯,1999,33(3):14-17.

[22]谢仁智,汪秀英.大、中孔高性能活性炭的制备方法:中国,CN200810070148.7[P].2008-08-21.

[23]DÍAZ-DÍEZ M A,GÓMEZ-SERRANO V,GONZÁLEZ C F,et al. Porous texture of activated carbons prepared by phosphoric acid activation of woods[J]. Applied Surface Science,2004,238(1/2/3/4):309-313.