CHARACTERIZATION OF NITROGEN-ENRICHED ACTIVATED CARBONS PREPARED FROM WASTE MEDIUM DENSITY FIBERBOARD BY H_3PO_4 ACTIVATION

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ABSTRACT

The nitrogen atoms of waste medium density fiberboard originates from urea-formaldehyde resin adhesive used in the manufacturing process, so nitrogen-enriched activated carbons could prepared easily. Nitrogen-enriched activated carbons were prepared from waste medium density fiberboard using H_3PO_4 as an activating agent. The influence of impregnation ratio (gram chemical agent/gram wood fiberboard waste of 1, 2, 3, 4) and activation temperature (600, 700, 800, 850ºC) on the iodine adsorption capacity and yield of the prepared activated carbon were investigated. The pore properties of the activated carbons were determined by N_2 adsorption at 77 K. Elemental analysis and XPS were used to study how nitrogen functional groups changed with different activation conditions. The results showed that the adsorption of iodine number was ranged from 553 to 1073 mg.g^{-1}. BET of activated carbons was differed from 706 to 1473 m^2.g^{-1} and total pore volume was from 0.34 to 0.71 cm^3.g^{-1}.

KEYWORDS: Nitrogen-enriched activated carbon; waste medium density fiberboard; H_3PO_4 activation.

INTRODUCTION

Activated carbon is commonly defined as a carbonaceous material showing a well-developed surface area and porous texture. So, this material has been widely used as adsorbent (Hung et al. 2005) and in catalysis (Lee et al. 2006) or separation processes (Dabrowski 2001). The main disadvantages of this material are its high cost. Therefore, in recent years, there has been a growing research interest in the low-cost procurers such as waste materials or renewable sources for activated carbon preparation (Demirbas 2009, Girods et al. 2009).

In principle, the methods for preparing an activated carbon can be divided into two categories: Physical activation and chemical activation (Demiral and Demiral 2010; Rodriguez-Reinoso and Molina-Sabio 1992). Chemical activation has become widely applied because of its lower activation temperature and high carbon product yield as compared to physical processing

(Guo and Rockstraw 2006). Phosphoric acid is widely used as an activating agent. This is because of its advantages such as its non-polluting character compared to zinc chloride and its ease of elimination by leaching with water, with the recovered phosphoric acid being recycled for further use (Zhang et al. 2008).

In China, most of the waste wood is burnt which could releases toxic gases and pollutes to the environment. In the waste wood fiberboard, nitrogen is introduced to the wood matrix because of the use of nitrogen-containing aminoplastic adhesives such as urea-formaldehyde and melamine-formaldehyde resins (Yu et al. 2011). Therefore, the utilization of waste wood can reduce significantly the environmental impact and afford attractive products. Nitrogen-enriched activated carbon could easily absorb acid gased (Li et al. 2001; Bimer et al. 1998) and phenolic compounds (Przepiórski 2006).

The present study is to use waste medium density fiberboard (MDF) to prepare nitrogen-enriched activated carbon by H_3PO_4 activation. The objective of this work is to study the effect of various operative parameters such as activation temperature and impregnation ratio on the adsorption characteristics. Also, pore structures and BET surface area were investigated. Elemental analysis and XPS were used to study how nitrogen functional groups changed with different activation conditions.

MATERIAL AND METHODS

Material

Waste MDF was collected from wood processing factory in Beijing Forestry University. MDF was consisted of the poplar wood and urea-formaldehyde resin (12 %). H_3PO_4 and HCl were analytical grades and were purchased from Beijing Lanyi Chemical reagent. Distilled water was utilized throughout the experiments.

Preparation of activated carbon

The activated carbon (AC) was prepared using a two-step process. In carbonization step, MDF was heated up to a carbonization temperature of 500ºC at a heating rate of 100ºC.h^{-1}, and were held at this temperature for 1 hour. The samples were then ground and screened out with sieves. The fraction in the particle diameter ranged from 40 to 60 mesh. The particle samples were dried in a 105ºC oven for 4 h.

In activation step, 3 grams of the oven-dried samples were soaked in a 50 % H_3PO_4 solution for 16 h at the investigated impregnation (gram chemical agent/gram wood fiberboard waste) (1:1, 2:1, 3:1, 4:1). The soaked samples were then put in an electric furnace and heated up a desired temperatures (600, 700, 800, 850ºC). Samples were held at this temperature for 2 h before cooling down, and followed by washing sequentially with a 0.5 N HCl solution. The activated carbons were repeatedly washed with hot distilled water until the pH of solution reach to about 6-7. Finally, these activated carbons were dried in a 105ºC oven for 6 h.

Characterization methods

The yield of AC was calculated by equation:

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

where: M_1 - weight of AC,
          M_2 - weight of oven-dried MDF.

Iodine number was determined at 303 K based on the Standard Test Method ASTM Designation: D4607-86.

The elemental analysis was carried out using a CHNS Analyzer (Thermofinnigan Flash, EA, 1112 series).

The pore structure characteristics of ACs were measured by N_2 adsorption isotherm at 77 K using an ASAP 2010 Micromeritics. The surface areas, pore volumes and micropore surface areas of the ACs were determined by the application of the Brunauer–Emmett–Teller (BET) and t-plot method (El-Hendawy et al. 2001). The pore size distributions of the ACs were determined by density functional theory (DFT) method (Sudaryanto et al. 2006).

Chemical surface composition was investigated by X-ray photoelectron spectroscopy (XPS) on an ESCALAB250 (VG Scientific, UK) instrument. The sample charging was corrected using the C1s peak (284.6eV) as an internal standard. A non-linear, Shirley-type baseline and an iterative least-squares fitting algorithm were used to deconvolute the peaks. The surface atomic ratios were calculated from the ratio of the corresponding peak areas after correction with the theoretical sensitivity factors based on the Scofield_s photoionisation cross-sections.

RESULTS AND DISCUSSION

Effect of H_3PO_4/MDF

The ratio of impregnation agent/raw material has been found to be the most important parameter in a chemical activation process (Ahmadpour and Do 1996, 1997). The adsorption capacities towards iodine and yield of AC prepared from MDF impregnated H_3PO_4 with different impregnation ratio, activation temperature 700ºC, activation time 120 min. were shown in Fig. 1.
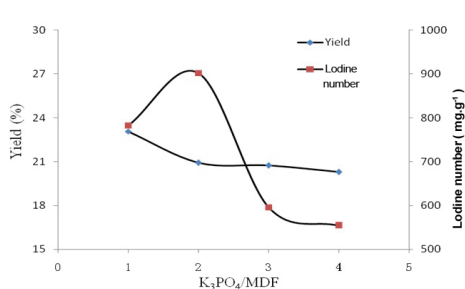

Fig. 1: Effect of impregnation ratio on the yield and the iodine number (Experimental conditions employed: Activation temperature=700ºC, activation time=120 min.).
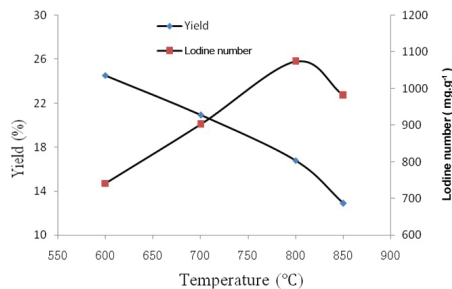
Fig. 2: Effect of temperature on the yield and the iodine number (Experimental conditions employed: Impregnation ratio=2, activation time=120 min).

It was observed from Fig. 1, increasing the impregnation ratio from 1 to 4, the yield of AC decreased from 23.08 to 20.29 %. This may because the loss of volatile materials.

The highest iodine number, 902 mg.g^{-1}, was obtained at the impregnation ratio of 2. At a value more or less than 2, the iodine number decreased. Phosphoric acid promoted the pyrolytic decomposition of the starting material and the formation of cross-linked structures. The decomposition was promoted by the catalytic effect of H_3PO_4 on the bond cleavage reactions

(Budinova et al. 2006; Jagtoyen and Derbyshire 1998). However, excessive phosphoric acid could not further promote the pore enlargement further as an insulating layer might be formed (Guo and Rockstaw 2007). The similar trends could be found in several reports, such as Jun Wang et al. (2010).

Effect of activation temperature

The effect of activation temperature was studied by preparing ACs using MDF impregnated with H_3PO_4 at a constant H_3PO_4/MDF ratio of 2:1 and activating by heating for 120 min. at different temperatures. The yield of AC and the iodine number were measured. The corresponding experimental data were shown in Fig. 2.

Activation temperature played an important role on the yield of AC. It could be seen from Fig. 2 that, as activation temperature increased from 600 to 850°C, the yield of AC decreased from 24.53 to 12.88 %. This was due to the loss of the volatile materials with increasing temperature.

When temperature increased from 600 to 800°C, the iodine number increased from 740 to 1073 mg.g^{-1}. However, when temperature increased from 800 to 850°C, the iodine number decreased from 1073 to 981 mg.g^{-1}. This was probably because that the pores would be widened and burnt off when activation temperature reached a certain value. This was in agreement with the results obtained Huiping et al. (2008) by for chemical activation of sawdust using H_3PO_4.

Elemental analysis

C, H, N contents of the ACs prepared from MDF were shown in Tab. 1, respectively.

As can be seen from Tab. 1, increasing the activation temperature and the impregnation ratio, the content of N, H decreased and the content of C increased. The reason of the decreased of N was probably due to the volatilization of unstable functional groups containing N. From Tab. 1, it could be seen that the content of N was ranged from 3.13 to 4.28 %.

Tab. 1: Elemental analysis of the Acs.

ACs prepared from MDF		Elemental analysis		
H$_3$PO$_4$/MDF	Activation temperature (°C)	C	H	N
		(wt %)		
1:1 (AC1)	700	60.36	2.18	4.28
2:1 (AC2)	700	62.03	2.34	3.83
3:1 (AC3)	700	66.95	2.04	3.76
4:1 (AC4)	700	67.1	1.96	3.55
2:1 (AC5)	600	60.71	2.56	4.03
2:1 (AC6)	700	62.03	2.34	3.83
2:1 (AC7)	800	62.86	2.23	3.74
2:1 (AC8)	850	73.04	1.99	3.13

In the waste MDF, N was provided by the adhesive: urea-formaldehyde resins. So, the content of N in the ACs prepared from MDF was high, while the content of N in commercial AC was normally lower than 0.5 %.

XPS study

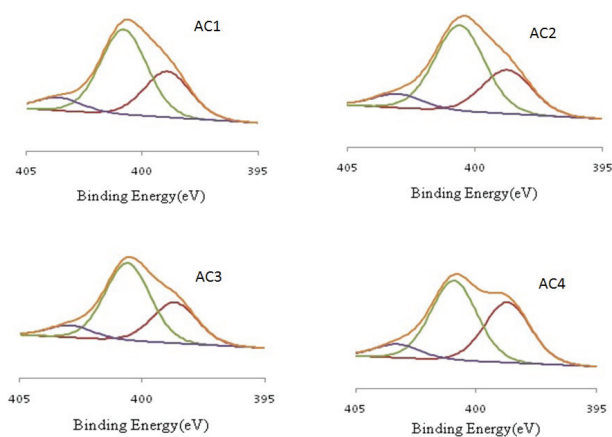Fig. 3 and Fig. 4 showed the complex XPS N1s spectra of nitrogen-containing AC.

Fig. 3: N1s XPS spectra of AC of different impregnation ratio (1, 2, 3, 4).
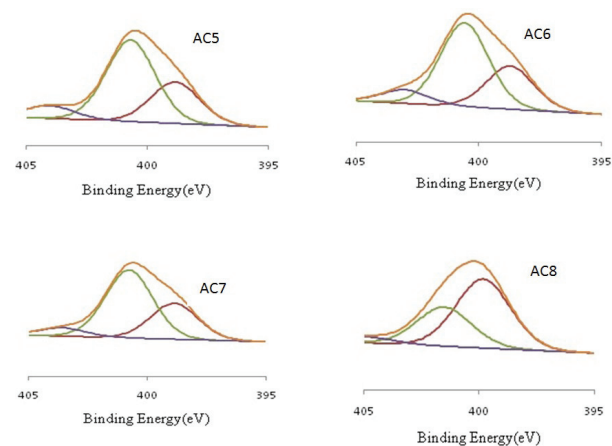

Fig. 4: N1s XPS spectra of AC of different activation temperature (600, 700, 800, 900ºC).

The peaks were assigned to different forms of nitrogen atoms substituted for carbon in graphene layer: N-6, N-5, N-Q and N-X, respectively (Pels et al. 1995). Hence, N-6 (398.7±0.3eV) was pyridinic-N, i.e. nitrogen bonded to two carbon atoms in sixmembered rings at the edge of graphene layer. N-5 (400.3±0.3eV) represented pyrrolic-N in five-membered ring and/or pyridonic-N. N-Q (401.4±0.4eV) corresponded to quaternary-N, i.e. nitrogen bonded to three carbon atoms in central or valley position of graphene layer. Finally, N-X (402-405eV) was pyridine N-oxide (Grzyb et al. 2009).

Types of nitrogen surface functional groups were presented in Tab. 2. It could be seen from Tab. 2, N-5 and N-6 accounted for the majority of nitrogen functionalities. And, N-Q was not found in all AC. According to the experimental data, the chemical state of nitrogen could be sensitively changed by the activation temperature and the impregnation ratio.

Tab. 2: Distribution of N species obtained from the deconvolution of the N1s peaks.

Sample	N-6,Pyridinic nitrogen (398.7±0.3eV)	N-5,Pyrollic nitrogen,pyridone (400.3±0.3eV)	NQ,Quaternary nitrogen (401.4±0.4eV)	N-X,Oxidized nitrogen (402-405eV)
AC1	31.83	59.12	-	9.05
AC2	32.03	60.53	-	7.44
AC3	31.25	59.56	-	9.20
AC4	39.33	51.86	-	8.80
AC5	30.53	60.07	-	9.39
AC6	30.53	59.85	-	9.62
AC7	32.03	60.53	-	7.44
AC8	60.41	34.39	-	5.19

Pore structure analysis

The analyses of the N_2 isotherms were performed by applying the BET equation, t-plot and DFT methods. Physical properties of the AC, such as surface areas, total pore volumes, were shown in Tab. 3, respectively. As can be seen from Tab. 3, when the impregnation ratio increased from 1 to 2, BET surface area and pore volume increased. The maximum BET surface and micropore volume could get 1228 $m^2.g^{-1}$ and 0.598 $cm^3.g^{-1}$, respectively. After that, increasing the ratio, the BET surface area decreased. When temperature increased, surface areas were generated gradually during the activation processes. The maximum BET surface area of 1473 $m^2.g^{-1}$ and the 0.714 $cm^3.g^{-1}$ of micropore volume were obtained at 850ºC.

Tab. 3: Physical properties of the Acs.

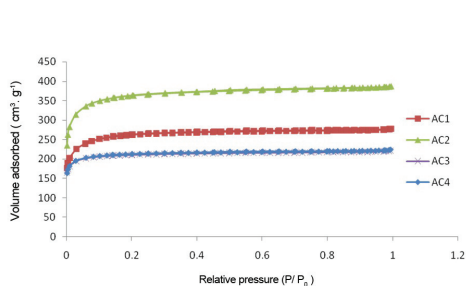| H_3PO_4/ MDF	Activation temperature (ºC)	S_{BET}	S_{mi}	S_{me}	V_{tot}	V_{mi}	V_{me}
		($m^2.g^{-1}$)			($cm^3.g^{-1}$)		
1:1 (AC1)	700	894	693	201	0.428	0.317	0.111
2:1 (AC2)	700	1228	931	297	0.598	0.431	0.167
3:1 (AC3)	700	706	611	95	0.342	0.283	0.059
4:1 (AC4)	700	716	614	102	0.347	0.285	0.062
2:1 (AC5)	600	849	701	148	0.412	0.325	0.087
2:1 (AC6)	700	1228	931	297	0.598	0.431	0.167
2:1 (AC7)	800	1444	1123	321	0.692	0.516	0.176
2:1 (AC8)	850	1473	847	627	0.714	0.384	0.330

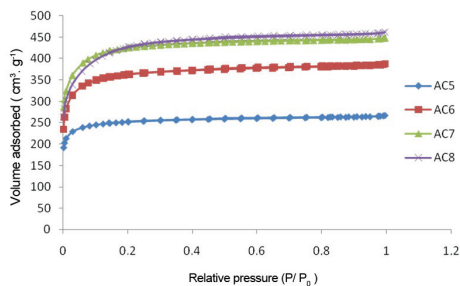*Fig. 5: Nitrogen adsorption–desorption isotherms of activated carbons with variable impregnation ratio.*

Fig. 6: Nitrogen adsorption–desorption isotherms of activated carbons with variable activation temperature.

Fig. 5 and Fig. 6 plotted the nitrogen adsorption-desorption isotherms of ACs. The curve trends among all the ACs for volume adsorbed were very similar. The isotherms displayed an abrupt increase in adsorbed volume at a low relative pressure (P/P_0). As the relative pressure increased, the nitrogen uptake increased across the entire pressure range. The shape of isotherm corresponded to type I, indicating that the AC was essentially microporous (Liou 2004). From Fig. 5, it could be seen that the adsorption capacity attained a maximum value at impregnation ratio of 2. From Fig. 6, with temperature increasing, the adsorption capacity increased.

CONCLUSIONS

Nitrogen-enriched activated carbons were prepared from waste MDF by H_3PO_4 activation. The effect of impregnation ratios and activation temperatures were investigated. The adsorption of iodine number could get 1073 $mg.g^{-1}$ and BET surface area was 1473 $m^2.g^{-1}$ at optimized condition. The content of N changed from 3.13 to 4.28 % which were higher than commercial activated carbon (lower than 0.5 %). Since introducing of N-containing surface groups makes activated carbon more alkaline, increased adsorption of acidic agents is expected.

According to the experimental results, waste MDF is a suitable material for nitrogen-enriched activated carbon. On one hand, the utilization of waste MDF reduce significantly the environmental impact .On the other hand, nitrogen-enriched activated carbon could absorb acid gases and phenolic compounds more easily. In future, we will study phenol adsorption on nitrogen-enriched activated carbon. Also, we will investigate how the content of N and nitrogen species affect the adsorption capacity of nitrogen-enriched activated carbons prepared from waste medium density fiberboard.

ACKNOWLEDGMENT

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