**Microwave-assisted preparation and characterization of mesoporous activated
carbon from mushroom roots by phytic acid (C₆H₁₈O₂₄P₆) activation**

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Abstract

The present study explored the viability of preparing activated carbon from phytic acid (PA, $C_6H_{18}O_{24}P_6$) activation of mushroom roots (MR) via microwave irradiation. Effects of impregnation ratio (IR, g PA: g MR of 1:1, 1.5:1, 2:1) and radiation power (600, 700 and 800 W) on porous activated carbon evolution were investigated. The surface area and porous property, surface morphology, and surface chemistry of activated carbons were investigated by nitrogen adsorption/desorption isotherms, scanning electron microscopy (SEM) and Boehm's titration. The yields obtained at all conditions were relatively high, from ~47% to ~59%. Well-developed mesoporous structure was prepared with the maximum surface area up to 1024 m²/g (IR=1.5:1, 800 W). With increasing IR, the mesoporous structure of the activated carbons was more developed, with S_{ext}/S_{mic} up to 95% at IR of 2. The produced activated carbons also showed favorable to surface chemistry with surface acidity higher than 1.85 mmol/g. The amounts of total surface functional groups were more approachable with IR increasing. These findings provide a strong evidence to support the potential of developing activated carbon alternatives from PA activation of MR via microwave irradiation.

Keywords: Microwave; Phytic acid; Mushroom roots; Activated carbon

1. Introduction

Activated carbon (AC) is a common used adsorbent featured by its high specific surface area, favorable pore structure, and low acid/base reactivity [1]. It has been

widely applied in membrane processes and adsorption of various organic chemicals and heavy metals in water treatment. However, commercial activated carbons are still expensive. Thus, it is of extreme relevance to find suitable low-cost raw materials and methods for sustainable development requirements [2]. Currently, lots of research focused on the production of activated carbons from agricultural products, by-products and/or wastes [3, 4]. Mushroom is very popular in the world, which is widely produced in China. According to Food and Agriculture Organization, China's share of global mushroom production has increased from 57.0% in 2000 to 71.2% in 2013 [5]. The higher production of mushroom means the greater output of byproducts. Unfortunately, mushroom roots are disposed by either burning or discarding in China. Our previous research has revealed that activated carbon with large yield (up to 45%), high surface area (up to 1000 m²/g) and favorable surface chemistry (total acidic groups of 4 mmol/g) can be produced from phytic acid (PA) activation of mushroom roots (MR) via conventional heating method (muffle furnace) [6]. So preparing activated carbons from MR could save the cost of raw materials.

In addition to the raw materials, the heating method also significantly affects the physicochemical properties of activated carbon. In the conventional method, the heat source is located outside the sample, and the heat is transferred to the particles by convection, conduction and radiation mechanisms. So the temperature of the surface is higher than the interior of each particle [7]. Furthermore, there is a considerable risk of overheating or even thermal runaway of local sample, leading to the complete combustion of the carbon and great loss of the yield [1]. Microwave radiation method

is a good way to solve the problems of the thermal gradient for activated carbon preparation. Microwave heating has the advantages of rapid preparation period, uniform temperature distribution, raising the yield and saving of energy over conventional thermal method [8]. In all, preparing activated carbons by microwave could save the energy as well as reduce the cost. There has been a wealth of publications that represent the use of microwaves for producing activated carbons by phosphoric acid activation, KOH and K_2CO_3 activation [9, 10]. However, the preparation and characterization of activated carbon by microwave-induced PA activation have not been reported.

Thus, this paper investigated to prepare activated carbons from MR with PA activation via microwave irradiation. The objectives are to evaluate the effects of IR (1:1 - 2:1) and radiation power (600-800 W) on the carbon evolution. The porous structures were observed by SEM. The pore size distribution parameters of the prepared carbons were characterized by nitrogen adsorption/desorption isotherms, and surface functional groups of the carbons were determined by Boehm's titration.

2. Materials and methods

2.1. Materials

Mushroom roots (MR), received from Shandong Province (China), were cleaned with distilled water, dried, and then ground into powder (particle sizes of 0.15-0.25 mm). Phytic acid (PA, $C_6H_{18}O_{24}P_6$) purchased from Aladin (Shanghai, China) was used as activating agent. The molecular structure of PA is given in Fig. 1. PA is an organic

ester of phosphorus oxyacids, which is also named inositol hexaphosphate. All the chemicals used in this study were of analytical grade and solutions were prepared with deionized water.

2.2. Synthesis of activated carbons

The mushroom root powder was immersed by a certain amount of PA (50 wt.%) at different impregnation ratios (IR, g PA: g MR) of 1:1, 1:1.5 and 2:1 for 10 h. Then, the samples were transferred to a microwave oven at different radiation powers (600 - 800 W) for 15 min. After cooling to room temperature, the samples were washed with deionized water until the pH of the filtrate was steady. Then the activated carbons were filtered and dried at 105°C until reaching a constant weight. Finally, the carbons were ground using a mortar to a particle size between 96 and 125 μm (120-160 mesh) with standard sieves and stored in a desiccator for further experiments. The activated carbons were referred to as MAC-IR-radiation power. For example, MAC-2-700 means activated carbon prepared at IR of 2:1 and 700W.

2.3. Characterization of MACs

The surface morphology of the carbons was identified using scanning electron microscope (SEM) (JEOL, JSM 7600F, Japan). The Brunauer-Emmett-Teller surface area (S_{BET}) and pore structure parameters of the carbons were evaluated by N_2 adsorption/desorption isotherm using a surface area analyzer (Quanta chrome Corporation, USA) at 77 K. Boehm's titration method was used to differentiate and quantify the surface acidic functional groups of the carbons [11]. Triplicates were

performed for each sample and the relative standard error was equal or less than 3%. The yield of carbons was calculated as the quotient of the dry weight of precursor divided by the dry weight of final activated carbon obtained in percentage form.

3. Results and discussion

3.1. Activated carbon yield

Yields of activated carbons were illustrated in Table 1. The yields of all carbons were over 46%. Compared with the conventional heating method (yield from 32.1 to 44.7%), microwave heating method brought about significantly higher carbon yield, mainly because of the shortening of activation time for the microwave heating method [6]. The yield was also much higher than those made from other agricultural wastes with phosphoric acid activation, such as peanut hull of 32.49 - 45.55%, bamboo of 45.5% at 400W and lotus stalk of 40.1% at 700W [9, 12, 13]. Thus, PA activation via microwave irradiation was a promising method to prepare activated carbons with great yield.

It was clearly that IR had a great effect on the yields of activated carbons. Under different powers, the yield increased gradually from ~47 % to ~59% with the increase of IR from 1:1 to 2:1. This was due to the good flame-retardant effect of PA, which promoted formation of carbon materials at lower activation temperature [14]. Besides, as IR increased, PA decomposed into diester or monoester and eventually into phosphorus oxyacids [6]. These abundant free radicals could form organic substances, which could also increase the yield. Similar trends were also found by Foo and Hameed

when they prepared the activated carbon from coconut husk using microwave radiation by increasing the ratio KOH/char [15].

3.2. Morphology of activated carbons

The surface morphology of the samples is depicted in Fig. 2. The surface of raw materials is quite smooth (SEM micrograph not shown here). Some cracks and pores could be observed on the surface of the carbons. These broken bubbles reflected the formation of highly cross-linked structure, decomposition of phosphates, and release of radical species, as reported in our previous papers [16]. PA is a kind of strong acid, exhibited strong chelating ability with protein to form a partial de-polymerization. In addition, PA can easily invade the spaces between the raw materials, and can produce a dehydrating effect on the hemicellulose and cellulose. The decomposition of PA could simultaneously release some radicals, which could promote the oxidative decomposition and accelerate the carbonization at lower activation temperature. This build up the cross-linked structure between inositol and the precursors during the activation process [6]. Consequently, some cracks and pores can be created after activation and washing with DI water.

There is no obvious difference in surface micrographs for the samples prepared under different activation conditions (microwave power and time). However, the increase of IR decreased pores on the surface of the carbons. The reason may be due to that under higher IR, more PA decomposed and produced more organic matters. They would deposit on the carbon surface and block the pores.

3.3. Nitrogen adsorption /desorption isotherms and porosity development

Pore size distributions and N₂ adsorption/desorption isotherms of the carbons were exhibited in Fig. 3. Hysteresis loops of the N₂ adsorption/desorption isotherms suggested the micro-mesoporous structures of the carbons. Pore size distribution demonstrated that the majority of the pores of the carbons fell into the range of micropores (<2 nm) and mesopores (2-50 nm) according to the definition of pore size by International Union of Pure and Applied Chemistry (IUPAC) [17]. The pore diameter (D_p) were all over 2 nm, indicated highly mesoporous carbons.

For each IR, the pore size distributions of the carbons were similar. In general, the surface area of samples produced under 800 W was higher than those produced under 600 and 700 W because the higher microwave power can increase the temperature and cause more pore creation. It should be noted that the highest surface area was achieved at IR of 1.5 at each microwave power. The porous structure was resulted from the release of certain volatile compounds generated by impregnation with PA for the precursors. With IR below 1.5, PA was exhausted before the sample reached higher temperature and the carbonization/activation was incomplete/inadequate. However, the excessive PA addition aggravated such activation effect and destroyed some pores [18]. These were consistent with the results of yield and SEM of the carbons.

The results could also be confirmed by pore structural parameters summarized in Table 1. The S_{BET} and total pore volume (V_{tot}) of the carbons increased as IR increased from 1 to 1.5, then decreased as IR increased to 2, because suitable dose of phosphoric acid had a positive effect on the porous structure, while the excessive dose resulted in

blocking pore structure on the carbon surface. The dramatic decrease of the ratio of micropore surface area and external surface area (S_{mic}/S_{ext}) was observed as the increase of IR, indicating a much higher mesoporosity. This high mesoporosity was attributed to the carbon burnt and destroyed the structure of pores [19]. So the optimum preparation condition of the microwave method was combined condition of IR = 1.5 : 1 (g PA : g MR) and irradiation power at 800 W in terms of surface area and pore structure.

3.4. Surface chemical properties

The surface functional groups of the carbons are listed in Table 2. The samples showed larger amounts of oxygen-containing surface groups (total acidic functional groups > 1.8 mmol/g, basic function groups > 0.9 mmol/g). The amounts of acidic functional groups were more than that of basic function groups. It is known that the acidity of activated carbon mainly comes from the carboxylic acids, lactones and phenolic hydroxyls, and basic groups derive from the complex aromatic system (delocalized π electrons) of graphene surface [20]. For all carbons, the amounts of phenolic groups were higher than carboxylic groups and lactone groups.

The amounts of total groups decreased as the power increased. As well demonstrated above that PA decomposed and volatilized easily at lower activation temperatures, less phosphoric compounds were left in the samples, thus the formed oxygen groups were sensitive to the high temperature and decomposed into carbon gases. At each power, the amounts of total acidic groups increased as IR increased. The

reason was that larger IR promoted the formation of phosphates with high degree of polymerization that tended to be stable at high temperature, whereas the large amount of phosphoric acid could hinder the thermal degradation of the oxygen groups. The results were in coincident with the previous researches [20].

The properties of activated carbon samples prepared in this study were also compared with the results published in the literatures (Table 3). Compared with the reports using H_3PO_4 as an activating agent, activated carbons prepared in this work obtained greater yields with comparative S_{BET} and amounts of surface functional groups. The amounts of surface functional groups in present work were much higher than that reported in previous studies employing $\text{H}_4\text{P}_2\text{O}_7$ or KOH activation. It can be concluded that the yields and amounts of functional groups of the activated carbon prepared in this work were greater than that in previous studies, with comparable S_{BET} . This suggested that MR could form considerable porous structure through microwave-induced PA activation.

4. Conclusion

In this research, effects of impregnation ratio (IR) and radiation power on preparing porous activated carbons were investigated. It was found that the yield, surface area and surface groups of prepared activated carbons were more obviously affected by IR than power. Relatively high yields obtained for the good flame-retardation effects of phytic acid (PA). Well-developed mesoporous structure of the carbons was achieved with the relatively high surface area. A higher mesoporosity

was obtained with increasing IR. The produced activated carbons also showed favorable to surface chemistry, especially surface acidic groups. Greater IR could promote the formation of much more surface functional groups. This work provides a strong evidence to support the potential use of microwave heating as an alternative activation technique for producing activated carbons from mushroom roots employing PA as an activating agent.

Acknowledgements

This work was supported by the National Science Foundation of China (51578321, and 21307078), National Water Special Project (2012ZX07203-004), Shandong Provincial Natural Science Foundation, China (ZR2015BM004) and the Independent Innovation Foundation of Shandong University (2014JC023).

References

- [1] Antonio-Cisneros C, Elizalde-González M. Characterization of Manihot residues and preparation of activated carbon. *Biomass Bioenergy* 2010; 34: 389-95.
- [2] Açıkyıldız M, Gürses A, Karaca S. Preparation and characterization of activated carbon from plant wastes with chemical activation. *Micropor Mesopor Mat* 2014; 198: 45-9.
- [3] Abdolali A, Guo W, Ngo H, Chen S, Nguyen N, Tung K. Typical lignocellulosic wastes and by-products for biosorption process in water and wastewater treatment: A critical review. *Bioresource Technol* 2014; 160: 57-66.

- [4] Karthikeyan S, Magthalin CJ, Mandal A, Sekaran G. Controlled synthesis and characterization of electron rich iron (III) oxide doped nanoporous activated carbon for the catalytic oxidation of aqueous ortho phenylene diamine. RSC Adv 2014; 4: 19183-95.
- [5] Wang XM, Zhang J, Wu LH, Zhao YL, Li T, Li JQ, Wang YZ, Liu HG. A mini-review of chemical composition and nutritional value of edible wild-grown mushroom from China. Food Chem 2014; 151: 279-85.
- [6] Cheng C, Zhang J, Mu Y, Gao J, Feng Y, Liu H, Guo Z, Zhang C. Preparation and evaluation of activated carbon with different polycondensed phosphorus oxyacids (H_3PO_4 , $\text{H}_4\text{P}_2\text{O}_7$, $\text{H}_6\text{P}_4\text{O}_{13}$ and $\text{C}_6\text{H}_{18}\text{O}_{24}\text{P}_6$) activation employing mushroom roots as precursor. J Anal Appl Pyrol 2014; 108: 41-6.
- [7] Hesas RH, Daud WMAW, Sahu J, Arami-Niya A. The effects of a microwave heating method on the production of activated carbon from agricultural waste: a review. J Anal Appl Pyrol 2013; 100: 1-11.
- [8] Guo J, Lua AC. Preparation of activated carbons from oil-palm-stone chars by microwave-induced carbon dioxide activation. Carbon 2000; 38: 1985-93.
- [9] Liu QS, Zheng T, Wang P, Guo L. Preparation and characterization of activated carbon from bamboo by microwave-induced phosphoric acid activation. Ind Crop Prod 2010; 31: 233-8.
- [10] Deng H, Li G, Yang H, Tang J, Tang J. Preparation of activated carbons from cotton stalk by microwave assisted KOH and K_2CO_3 activation. Chem Eng J 2010; 163: 373-81.

- [11] Boehm H. Surface oxides on carbon and their analysis: a critical assessment. *Carbon* 2002; 40: 145-9.
- [12] Huang L, Sun Y, Wang W, Yue Q, Yang T. Comparative study on characterization of activated carbons prepared by microwave and conventional heating methods and application in removal of oxytetracycline (OTC). *Chem Eng J* 2011; 171: 1446-53.
- [13] Zhong ZY, Yang Q, Li XM, Luo K, Liu Y, Zeng GM. Preparation of peanut hull-based activated carbon by microwave-induced phosphoric acid activation and its application in Remazol Brilliant Blue R adsorption. *Ind Crop Prod* 2012; 37: 178-85.
- [14] Zhou Y, Ding C, Qian X, An X. Further improvement of flame retardancy of polyaniline-deposited paper composite through using phytic acid as dopant or co-dopant. *Carbohydr Polym* 2015; 115: 670-6.
- [15] Foo K, Hameed B. Coconut husk derived activated carbon via microwave induced activation: effects of activation agents, preparation parameters and adsorption performance. *Chem Eng J* 2012; 184: 57-65.
- [16] Liu H, Zhang J, Ngo HH, Guo W, Wu H, Cheng C, Guo Z, Zhang C. Carbohydrate-based activated carbon with high surface acidity and basicity for nickel removal from synthetic wastewater. *RSC Adv* 2015; 5: 52048-56.
- [17] Ahmad A, Hameed B. Effect of preparation conditions of activated carbon from bamboo waste for real textile wastewater. *J Hazard Mater*; 2010: 173487-93.
- [18] Liu H, Zhang J, Jiang L, Kang Y, Cheng C, Guo Z, Zhang C. Development of carbon adsorbents with high surface acidic and basic group contents from phosphoric acid activation of xylitol. *RSC Adv* 2015; 5: 81220-8.

- [19] Deng H, Yang L, Tao G, Dai J. Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation—application in methylene blue adsorption from aqueous solution. *J Hazard Mater*, 2009; 166: 1514-21.
- [20] Sun Y, Yue Q, Gao B, Wang B, Li Q, Huang L, Xu X. Comparison of activated carbons from *Arundo donax* Linn with $H_4P_2O_7$ activation by conventional and microwave heating methods. *Chem Eng J* 2012; 192: 308-14.
- [21] Sun Y, Yue Q, Mao Y, Gao B, Gao Y, Huang L. Enhanced adsorption of chromium onto activated carbon by microwave-assisted H_3PO_4 mixed with Fe/Al/Mn activation. *J Hazard Mater* 2014; 265: 191-200.
- [22] Gao Q, Liu H, Cheng C, Li K, Zhang J, Zhang C, Li Y. Preparation and characterization of activated carbon from wool waste and the comparison of muffle furnace and microwave heating methods. *Powder Technol* 2013; 249:234-40.
- [23] Ge X, Tian F, Wu Z, Yan Y, Cravotto G, Wu Z. Adsorption of naphthalene from aqueous solution on coal-based activated carbon modified by microwave induction: Microwave power effects. *Chem Eng Process: Process Intensification* 2015; 91: 67-77.

Figure captions:

Fig.1 The molecular structure of $C_6H_{18}O_{24}P_6$

Fig. 2 SEM micrographs of the samples prepared under different conditions

Fig. 3 N_2 adsorption/desorption isotherms (a) and pore size distributions (b, c & d) of the carbons

Table captions:

Table 1 Yields and the pore structural parameters of the carbons. (Micropore volume (V_{mic}), micropore surface area (S_{mic}) and external surface area (S_{ext}) were calculated using the t-plot method. Total pore volume (V_{tot}) was calculated using DFT method. Average pore diameter (D_p) was calculated as $D_p = 4V_{tot}/S_{BET}$ ($S_{BET} = \text{mean} \pm \text{standard deviation}$)

Table 2 The surface functional groups of the carbons (mean $\pm$ standard deviation)

Table 3 Literature reports of activated carbon samples produced from similar precursors and/or activating agent

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<i>Sample</i>	<i>Yield</i> (%)	S_{BET} (m ² /g)	S_{mic} (m ² /g)	S_{ext} (m ² /g)	V_{tot} (cm ³ /g)	V_{mic} (cm ³ /g)	S_{mic}/S_{ext} (%)	D_p (nm)
MAC-1-600	47.4	810 ± 23	272	592	0.624	0.096	45.9	3.08
MAC-1-700	46.9	737 ± 10	233	504	0.526	0.058	46.2	2.85
MAC-1-800	47.8	818 ± 23	242	576	0.583	0.106	42.0	2.85
MAC-1.5-600	48.9	947 ± 25	147	800	0.774	0.065	18.4	3.27
MAC-1.5-700	51.4	920 ± 17	119	801	0.789	0.052	14.9	3.43
MAC-1.5-800	52.6	1024 ± 22	111	913	0.891	0.049	12.2	3.48
MAC-2-600	59.3	544 ± 16	67	477	0.467	0.030	14.0	3.43
MAC-2-700	59.3	487 ± 12	57	430	0.425	0.024	13.3	3.49
MAC-2-800	56.7	673 ± 15	24	549	0.625	0.010	4.4	3.71

Table 2 The surface functional groups of the carbons (mean $\pm$ standard deviation)

<i>Samples</i>	<i>Carboxyl</i> (mmol/g)	<i>Lactone</i> (mmol/g)	<i>Phenolic</i> (mmol/g)	<i>Total acidic</i> (mmol/g)	<i>Basic</i> (mmol/g)	<i>Total</i> (mmol/g)
MAC-1-600	0.58 $\pm$ 0.013	0.52 $\pm$ 0.012	0.94 $\pm$ 0.015	2.04	1.07 $\pm$ 0.025	3.11
MAC-1-700	0.66 $\pm$ 0.005	0.36 $\pm$ 0.015	0.85 $\pm$ 0.010	1.87	0.95 $\pm$ 0.005	2.82
MAC-1-800	0.75 $\pm$ 0.009	0.30 $\pm$ 0.013	0.80 $\pm$ 0.012	1.85	0.93 $\pm$ 0.018	2.78
MAC-1.5-600	0.53 $\pm$ 0.005	0.56 $\pm$ 0.015	1.04 $\pm$ 0.020	2.13	1.09 $\pm$ 0.025	3.22
MAC-1.5-700	0.65 $\pm$ 0.005	0.35 $\pm$ 0.005	0.99 $\pm$ 0.015	1.99	1.04 $\pm$ 0.019	3.03
MAC-1.5-800	0.76 $\pm$ 0.010	0.32 $\pm$ 0.005	0.89 $\pm$ 0.012	1.97	0.94 $\pm$ 0.026	2.91
MAC-2-600	0.86 $\pm$ 0.005	0.52 $\pm$ 0.006	1.32 $\pm$ 0.031	2.70	1.22 $\pm$ 0.038	3.92
MAC-2-700	0.99 $\pm$ 0.010	0.38 $\pm$ 0.008	1.24 $\pm$ 0.025	2.61	1.46 $\pm$ 0.010	4.07
MAC-2-800	0.73 $\pm$ 0.015	0.40 $\pm$ 0.006	1.10 $\pm$ 0.021	2.23	1.34 $\pm$ 0.015	3.57

Table 3 Literature reports of activated carbon samples produced from similar precursors and/or
activating agent

Precursor	Experimental conditions			Yield (%)	S _{BET} (m ² /g)	Surface functional groups (mmol/g)	Refs.
	Agent	IR	Radiation power (time)				
Arundo donax Linn	H ₄ P ₂ O ₇	1:0.75	700 W (15min)	56.1	1568	1.37	[20]
Arundo donax Linn	H ₃ PO ₄	-	700 W (15min)	44.80	1181	4.35	[21]
Wool	H ₃ PO ₄	1:1.5	700 W (15min)	40.2	519	2.12	[22]
Anthracite	KOH	1:1	300 W (10min)	-	728	~1.3	[23]
			500 W (10min)	-	1062	~1.1	
			700 W (10min)	-	886	~1.1	
Bamboo	H ₃ PO ₄	1:1	200-400 W (5-30 min)	45.5-61.2	970–1432	~1.7	[9]
Mushroom roots	PA	1:1-2:1	600-800 W (15 min)	46.9-59.3	487-1024	2.78 - 4.07	this study