

Porous structure and adsorptive properties of hide waste activated carbons prepared via potassium silicate activation

Jiaojiao Kong^a, Qinyan Yue^{a,*}, Baoyu Gao^a, Qian Li^a, Yan Wang^a, Huu Hao Ngo^b,

Wenshan Guo^b

a Shandong Provincial Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Jinan 250100, China

b Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology, Broadway, Sydney, NSW 2007, Australia

* Corresponding author, E-mail address: qyyue58@aliyun.com (Q. Yue); Tel.: +86 531 88365258;

Fax: +86 531 88364513.

Abstract

A novel activating agent, potassium silicate, was employed in the preparation of hide waste activated carbon. Effects of different activation temperatures and impregnation ratios on porous activated carbon evolution were evaluated by nitrogen adsorption/desorption. The BET specific surface area and pore volume of prepared activated carbon could attain 2046.12 m²/g and 1.068 cm³/g, when the process of preparation carried out at the best conditions (activation temperature of 700°C and the impregnation ratio of 2:1). Methylene blue (MB) was selected as the adsorbate to evaluate its adsorption property. Adsorption results can be fitted well by the Langmuir isotherm, indicating the maximum monolayer adsorption capacity of MB reached to 769.23mg/g.

Keywords: Activated carbon; Potassium silicate; Hide waste; Methylene blue

1. Introduction

Activated carbon, the most common and effective adsorbent, has large specific surface area, complex aperture structure and variety of functional groups, which can be prepared by any carbonaceous materials. Today, waste materials such as macadamia nut endocarp [1], lotus stalk [2], waste tires [3] etc. are transformed into activated carbons, which has become one of the research focuses. When raw hide and skin convert into leather, solid and liquid wastes would produce. The solid waste such as hide waste (HW) had keratin ingredient which was often discarded due to the low economic benefits, thus the reasonable application of this solid waste should be studied further. Nevertheless, according to the literature, there is little information about the preparation of activated carbon from HW.

There are two main activation methods in the preparation of activated carbon, namely physical and chemical methods. As to chemical method, KOH, NaOH, H₃PO₄ and ZnCl₂ were often used as the activating agents [4]. The carbon produced by KOH or NaOH generally has microporous structure, whereas KOH or NaOH can corrode apparatus whose life would be shortened and thus limit the development and application of this activating agent. Actually, silicone material is widely used as flame retardants in the field of extinguishing as a result of hindering the combustion of materials from originating [5]. However, to our knowledge, there are no papers using potassium silicate (K₂SiO₃) as the activating agent for preparing activated carbon. The purpose of this study was to prepare hide waste activated carbon (HWAC), using K₂SiO₃ as the activating agents to evaluate the pore structure and adsorption properties.

2. Materials and methods

2.1. Preparation of activated carbons

HW was provided by a tanning industry from Shandong province in China. The raw material was first soaked with ethanol for 48 h to remove some fat, then washed and dried at 60 °C. The dried materials were cut into particles of 0.5 cm × 0.5 cm, then dipped with a certain concentration of K₂SiO₃ solution to a varying impregnation ratio of 1:1–3:1 (R, g K₂SiO₃/g HW). After impregnation for 12 h, the mixtures were heated at 105 °C for 30 min to evaporate some of water. Samples were heated to the desired temperatures (400, 500, 600, 700, and 800 °C) in a tube furnace, and maintained for 1 h under a stable nitrogen flow (100 mL/min). The products were washed with hot water and distil water to ensure the pH of washing liquid attained neutral, and then dried at 105 °C for 12 h. Finally, the desired carbons were sieved to a particle size of 0.076–0.15 mm, and stored in a desiccator for the next study.

2.2. Characterization of HW-K₂SiO₃ and HWAC

The thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves of HW after K₂SiO₃ impregnated were acquired by an SDT-simultaneous TGA–DTA model, which were performed in pure N₂ atmosphere (100 mL/min). The mixture was heated at the heating rate of 10 °C from room temperature to 700 °C, and held this temperature for 1 h. The BET specific surface area (S_{BET}) and pore size distribution of HWACs were characterized using a surface area analyzer (JW-BK122W, China) by N₂ adsorption–desorption isotherm at 77 K. The surface morphology of activated carbon was determined by scanning electron microscopy (SEM) (HitachiS-520, Japan).

2.3. Equilibrium adsorption experiment

Activated carbon under the conditions of the activated temperature of 700 °C and the impregnation ratio of 2:1 with the highest S_{BET} (AC) was selected to perform the adsorption experiments. Batch experiments were conducted in a series of 150-mL conical flasks containing 50 mL MB and 0.05 g adsorbents with different initial concentrations ranging from 75 to 900 mg/L. The flakes were placed in a thermostatic shaker (SHA-B, Shanghai, China) and shaken at 25 °C with a speed of 160 rpm for 24 h to ensure the equilibrium. Finally, the concentrations of MB solution after filtrating were determined by a UV-vis spectrophotometer (UV-754, Shanghai) at $\lambda_{\text{max}} = 665$ nm. Blank experiments without adsorbents were also performed as described above. The adsorption isotherm experiments were carried out in duplicate and the mean value was reported. The adsorption capacity, q_e (mg/g), could be calculated by the equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of MB solutions. V (L) is the solution volume of MB solutions. W (g) is the mass of activated carbon.

2.4. Equilibrium modeling

The equilibrium data of MB adsorption were modeled using Langmuir [6] and Freundlich [7] equations as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (2)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

where q_m and q_e (mg/g) are the maximum and the equilibrium adsorption capacities, respectively. K_L (L/mg) is the Langmuir constant related to the free energy of

adsorption. K_F (mg/g) $(L/mg)^{1/n}$ and n are the Freundlich constants associated with adsorption intensity.

3. Results and discussion

3.1. Characterization of HW- K_2SiO_3 and HWAC

3.1.1. Thermogravimetric analysis of HW- K_2SiO_3

The TGA and DTG curves of HW- K_2SiO_3 are shown in Fig. 1. TGA profile shows that the process of weight loss contained three sections. The weight loss in the first 20 min could be due to the water evaporation and the degeneration of keratin, reflected in the DTG curve two small peaks. The second stage occurred between 20 min and 45 min, which attributed to the volatile of organic matter and moisture. The peaks at the temperatures of 287 °C and 450 °C in the DTG curve were corresponded with the thermal decomposition of denatured proteins under the catalysis of silicate. After 40 min, the weight loss decreased slightly, illustrating that the catalytic action of K_2SiO_3 completed.

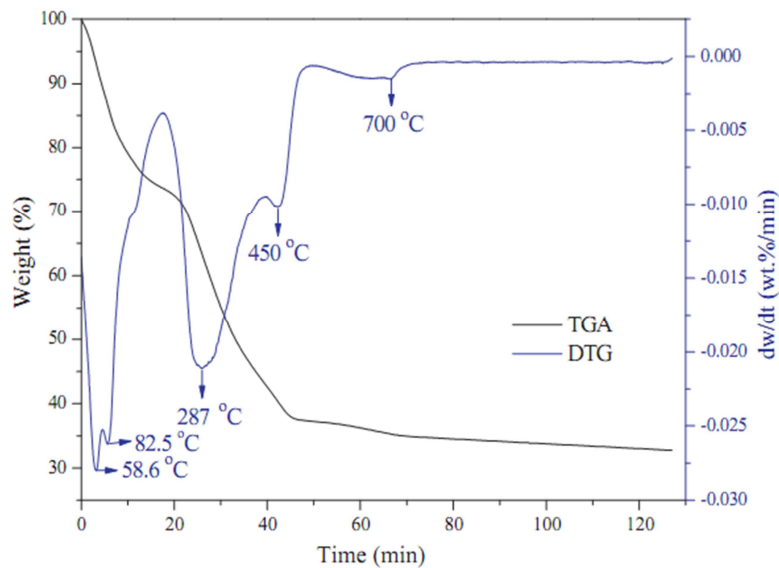


Fig. 1. TGA and DTG curves for the pyrolysis of HW- K_2SiO_3 .

3.1.2. Nitrogen adsorption behavior and porosity development

The N₂ adsorption/desorption isotherms and pore size distributions of the prepared activated carbons under different conditions are shown in Fig. 2. The N₂ adsorption/desorption isotherms reflected different adsorption capacities of nitrogen and hysteresis loops, indicating the appearance of mesopores and presence of majority micropores (AC). The N₂ adsorption/desorption curves were mixture of type I and type IV isotherms [8], illustrating the pores of the carbons were micropores and mesopores. Table 1 shows the BET surface areas, pore volumes, and average pore sizes of the prepared activated carbons. It can be concluded that HW and K₂SiO₃ were excellent precursor and activating agent respectively in the preparation of activated carbon. S_{BET} first increased then decreased with the activated temperature, and it showed the same trend with the impregnation ratio. This may be attributed to high activation energy between carbon atom and K₂SiO₃. Consequently, under the conditions of the activated temperature of 700 °C and the impregnation ratio of 2:1, HWAC had the highest specific surface area (2046 m²/g) and total pore volume (1.068 cm³/g). Table 1 also reflects that the high proportion of micropores was beneficial to the high specific surface area, and the majority of pore size was micropores and mesopores. The pore sizes distribution (Fig. 2) reveals that most of the pores ranged around 2 nm, which indicates the activated carbons had micro–mesopores structure, corresponding to the N₂ adsorption/desorption results.

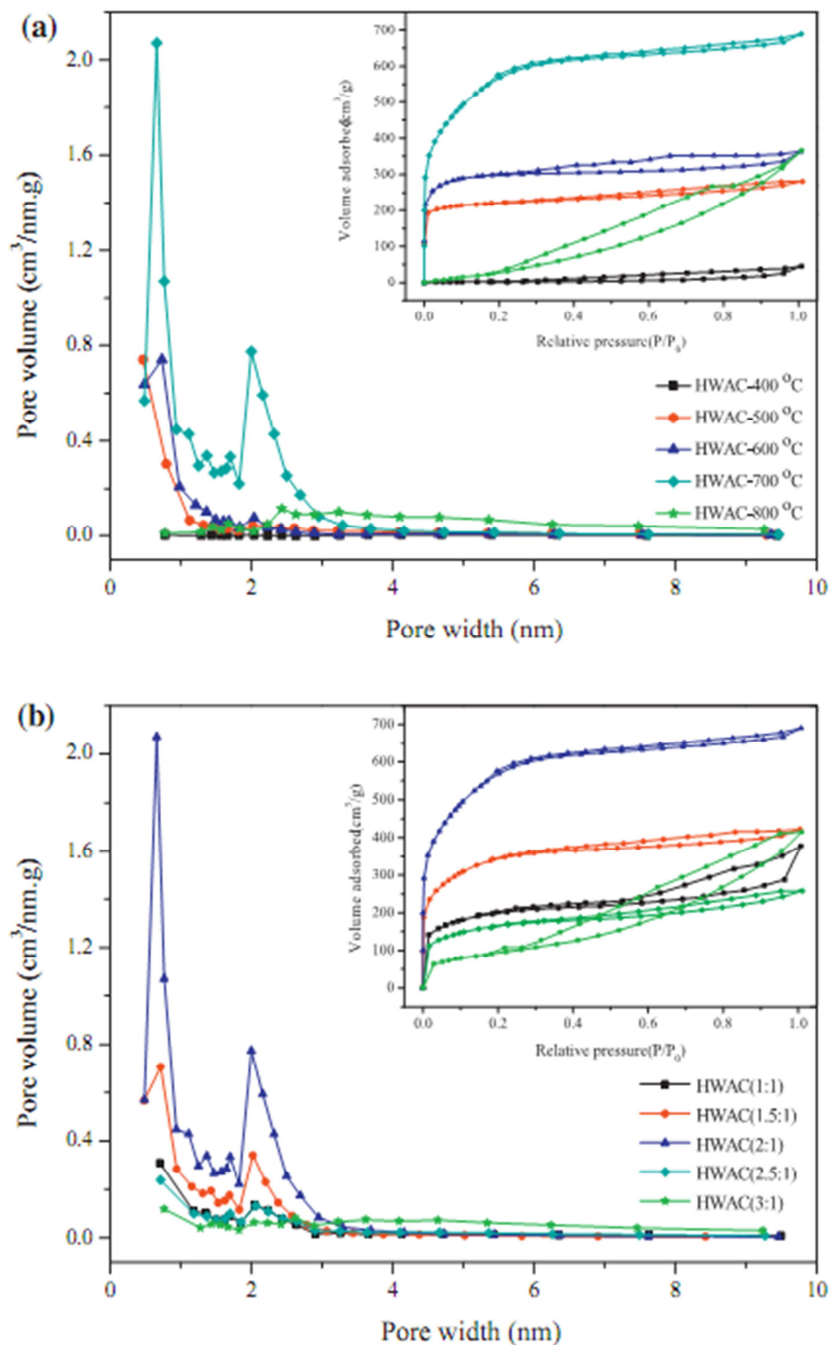


Fig. 2. Effects of (a) activating temperature (preparation condition: $R = 2:1$; activating time = 1 h), (b) impregnation ratio (activating temperature = 700 °C; activating time = 1 h) on pore size distributions and nitrogen adsorption/desorption isotherms (inset) for HWAC.

Table 1

The effect of activation temperature and impregnation ratio on BET surface areas, pore volumes, average pore sizes of activated carbons activated by K_2SiO_3 .

Activated temperature (°C)	R	S_{BET}^a	S_{mic}^b (m ² /g)	S_{mic}/S_{BET}	V_{tot}^c (cm ³ /g)	V_{mic}^d (cm ³ /g)	V_{mic}/V_{tot} (%)	D_p^e (nm)
400		7.93	0.318	4.01	0.071	0.0025	3.52	35.89
500		791.64	697.21	88.07	0.436	0.3371	77.32	2.20
600	2:1	1071.84	1031.29	96.23	0.563	0.4574	81.24	2.10
700		2046.12	1803.20	88.13	1.068	0.8103	75.87	2.09
800		175.05	11.22	6.41	0.567	0.0307	5.41	12.95
700	1:1	716.69	616.38	86.00	0.585	0.2961	50.62	3.27
	1.5:1	1245.70	1115.70	89.56	0.653	0.5054	77.40	2.10
	2.5:1	594.51	495.09	83.28	0.399	0.2435	61.03	2.69
	3:1	333.34	91.87	27.56	0.644	0.1301	20.20	7.72

a S_{BET} : BET specific surface area.

b S_{mic} : micropore specific surface area.

c V_{tot} : total pore volume.

d V_{mic} : micropore volume.

e D_p : the mean pore.

Table 2 shows the element contents of C, N, O, S, and Si of HW and AC. It can be seen that both of HW and AC had high content of C, N, O, and S but low Si content. HW contains the protein substance, which explained the higher contents of N, S, O for HW than AC, but the content of C increased after activation.

Table 2

Elemental change between HW and AC.

	C (%)	N (%)	O (%)	S (%)	Si (%)
HW	65.69	18.55	13.51	2.25	0
AC	87.15	6.05	6.76	0.01	0.03

SEM micrographs of AC (Fig. 3) shows that the prepared activated carbon had a smooth surface and highly developed pores. It is indicated that K_2SiO_3 favored for the generation of porous structure. K^+ could transform into elemental potassium, thus massive pores produced [9].

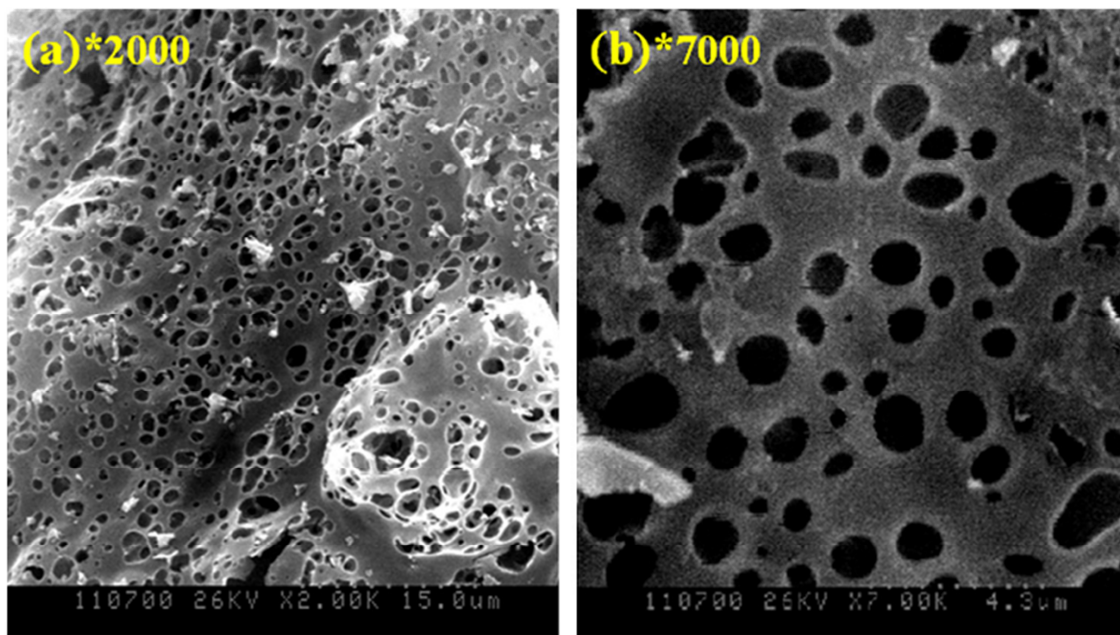


Fig. 3. SEM micrographs of AC at different magnifications (2000 \times and 7000 \times).

3.2. MB adsorption analysis

The adsorption properties of AC were evaluated by MB adsorption to test its adsorption performance. Table 3 shows that Langmuir isotherm was more suitable to describe the adsorption with high correlation coefficient ($R^2 = 0.9999$), indicating monolayer coverage of MB molecules and uniform energy. The comparisons of specific surface area and maximum monolayer adsorption capacity of various adsorbents are displayed in Table 4. Compared with the previous study, AC in this work showed high MB adsorption capacity (769.23 mg/g) which was much higher than that of the other adsorbents prepared from other materials and different activating agents. According to the results, AC as an excellent adsorbent could be

applied in the removal of dye in wastewater. Hence, HW and K_2SiO_3 were preferable raw material and activating agent in the process of activated carbon preparation.

Table 3

Langmuir and Freundlich isotherm constants for the adsorption of MB onto AC.

Langmuir isotherm model			Freundlich isotherm model		
q_m (mg/g)	K_L ^a (L/mg)	R^2	K_F ^b (mg/g) (L/mg) ^{1/n}	n ^c	R^2
769.23	14.44	0.9999	538.02	7.83	0.8336

^a K_L : Langmuir constant.

^b K_F : Freundlich constants which relate to the adsorption capacity.

^c n : Freundlich constants which relate to the adsorption capacity intensity.

Table 4

Comparisons of BET specific surface area and MB adsorption capacity of various adsorbents.

Precursor	Activating agent	S_{BET} (m ² /g)	Adsorption capacity (mg/g)	Reference
Rice husks	KOH	752	362.6	[10]
<i>Jatropha curcas</i> fruit shell	NaOH	1873	499.17	[11]
Rice husks	K_2CO_3	1165	441.52	[10]
Peach stones	H_3PO_4	1298	412	[12]
Black liquor lignin	Steam	310.15	92.51	[13]
Cocoa shell	CO_2	85.09	212.77	[14]
Walnut shells	$ZnCl_2$	1800	315	[15]
Leather waste	$H_4P_2O_7$	638.57	303.03	[16]
Hide waste	K_2SiO_3	2046	769.23	In this study

4. Conclusion

This study highlighted the potential of potassium silicate and hide waste as the efficient activating agent and raw precursor for preparation of activated carbon, respectively. The prepared carbon possessed BET specific surface area as 2046.12 m²/g and total pore volume as 1.068 cm³/g at the best condition ($T = 700$ °C, $R = 2:1$). K_2SiO_3 activation enhanced the development of aperture and benefited the production of micro–mesopores carbon. The

adsorption isotherm results fitted the Langmuir equation with the monolayer adsorption capacity for MB of 769.23 mg/g.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (21007034), Technology Foresight Program of Shandong province (2012GGE27011), and Foundation for Young Excellent Scientists of Shandong Province (BS2009NY005).

References

- [1] O. Pezoti Junior, A.L. Cazetta, R.C. Gomes, É.O. Barizão, I.P.A.F. Souza, A.C. Martins, T. Asefa, V.C. Almeida, Synthesis of ZnCl₂-activated carbon from macadamia nut endocarp (*Macadamia integrifolia*) by microwave-assisted pyrolysis: optimization using RSM and methylene blue adsorption, *J. Anal. Appl. Pyrol.* 105 (2014) 166–176.
- [2] H. Liu, Q. Gao, P. Dai, J. Zhang, C. Zhang, N. Bao, Preparation and characterization of activated carbon from lotus stalk with guanidine phosphate activation: sorption of Cd(II), *J. Anal. Appl. Pyrol.* 102 (2013) 7–15.
- [3] A. Undri, B. Sacchi, E. Cantisani, N. Toccafondi, L. Rosi, M. Frediani, P. Frediani, Carbon from microwave assisted pyrolysis of waste tires, *J. Anal. Appl. Pyrol.* 104 (2013) 396–404.
- [4] S. Karagöz, T. Tay, S. Ucar, M. Erdem, Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption, *Bioresour. Technol.* 99 (2008) 6214–6222.
- [5] R. Song, L. Chang, B. Li, Flame retardancy and thermal properties of carboxyl-containing polysiloxane derivatives in polycarbonate, *J. Appl. Polym. Sci.* 131 (2014).

- [6] I. Langmuir, The constitution and fundamental properties of solids and liquids. Part I. Solids, *J. Am. Chem. Soc.* 38 (1916) 2221–2295.
- [7] M. Šćiban, B. Radetić, Ž. Kevrešan, M. Klačnja, Adsorption of heavy metals from electroplating wastewater by wood sawdust, *Bioresour. Technol.* 98 (2007) 402–409
- [8] R. Pierotti, J. Rouquerol, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity, *Pure Appl. Chem.* 57 (1985) 603–619.
- [9] H. Deng, G. Li, H. Yang, J. Tang, J. Tang, Preparation of activated carbons from cotton stalk by microwave assisted KOH and K₂CO₃ activation, *Chem. Eng. J.* 163 (2010) 373–381.
- [10] K.Y. Foo, B.H. Hameed, Utilization of rice husks as a feedstock for preparation of activated carbon by microwave induced KOH and K₂CO₃ activation, *Bioresour. Technol.* 102 (2011) 9814–9817.
- [11] W. Tongpoothorn, M. Sriuttha, P. Homchan, S. Chanthai, C. Ruangviriyachai, Preparation of activated carbon derived from *Jatropha curcas* fruit shell by simple thermo-chemical activation and characterization of their physico-chemical properties, *Chem. Eng. Res. Des.* 89 (2011) 335–340.
- [12] A.A. Attia, B.S. Girgis, N.A. Fathy, Removal of methylene blue by carbons derived from peach stones by H₃PO₄ activation: batch and column studies, *Dyes Pigments* 76 (2008) 282–289.
- [13] K. Fu, Q. Yue, B. Gao, Y. Sun, L. Zhu, Preparation, characterization and application of lignin-based activated carbon from black liquor lignin by steam activation, *Chem. Eng. J.* 228 (2013) 1074–1082.

- [14] F. Ahmad, W.M.A.W. Daud, M.A. Ahmad, R. Radzi, Cocoa (*Theobroma cacao*) shell-based activated carbon by CO₂ activation in removing of cationic dye from aqueous solution: kinetics and equilibrium studies, *Chem. Eng. Res. Des.* 90 (2012) 1480–1490.
- [15] J. Yang, K. Qiu, Preparation of activated carbons from walnut shells via vacuum chemical activation and their application for methylene blue removal, *Chem. Eng. J.* 165 (2010) 209–217.
- [16] J. Kong, Q. Yue, B. Wang, L. Huang, B. Gao, Y. Wang, Q. Li, Preparation and characterization of activated carbon from leather waste microwave-induced pyrophosphoric acid activation, *J. Anal. Appl. Pyrol.* 104 (2013) 710–713.