

Surface Image of Charcoal and Activated Charcoal from Banana Peel

S. Mopoung

Department of Chemistry, Faculty of Science, Naresuan University, Phitsanulok, Thailand
e-mail: sumritm@nu.ac.th

Abstract

In this research, the results of the SEM morphology and XRD pattern studies of charcoals and activated charcoals prepared from banana peel are used to describe the effects of pyrolysis temperature and the mass ratios of KOH. In the carbonization process, banana peel charcoal carbonized at 300°C to 400°C has incomplete carbonization and the cell structure is maintained. Complete pore evolution occurred at temperatures of 500°C. The surface image of activated carbon from banana peel charcoal obtained at a pyrolysis temperature between 500°C and 700°C and with mass ratios between 1:2 and 1:5 showed increased porosity with increasing temperature. Increase KOH ratios slightly raised the pore size and porosity of activated charcoals. The change of pyrolysis temperature from 500°C to 700°C for ratios ranging between 1:2 and 1:4 has a big effect on the pore size. However, the 1:5 ratio of activated charcoal suppressed the pore size. This result showed that the over KOH ratio resulted in an insulating layer, covering the particles of banana peel charcoal. The XRD pattern showed that the constituents of banana peel activated charcoal were probably graphite, amorphous C, amorphous SiO₂, K₂O, K and K₂CO₃.

Background

Organic matter may be converted by controlled thermal decomposition into carbon. The mechanisms involved in the conversion of organic matter to carbon are: (1) desorption of adsorbed water up to 150°C, (2) splitting of matter structure water between 150°C and 260°C, (3) chain scissions, or depolymerization, and breaking of C-O and C-C bonds within ring units evolving water, CO and CO₂ between 260°C and 400°C, (4) aromatization forming graphitic layers above 400°C, and (5) above 800°C, the thermal induced decomposition and the rearrangement reaction are almost terminated leaving a carbon template structure. The major components of organic matter break down in a stepwise manner at 200-800°C (hemicellulose), 260-350°C (cellulose) and 280-500°C (lignin). Between 260°C and 400°C almost 80% of the total weight loss occurs which may vary between 40% (lignin) to about 80% (cellulose) due to evolution of H₂O, CO₂, and volatile hydrocarbon species from fragmentation reactions of the polyaromatic constituents [1]. Chemical activation of carbons is a very common method for obtaining activated carbons with very high surface areas. KOH is one of the most effective agents employed for organic materials. KOH might be more selective in the activation process, causing a more localized reaction with the carbon precursor and is more effective for the highly ordered materials [2]. Thus, it can be stated that direct KOH activation of a lignocellulosic material is not necessarily an advantage [2]. The temperatures of pyrolysis and activation are considered to be the most important parameters controlling the activated carbon

production. There are many precursors from which activated carbons can be obtained. The use of organic materials for activated carbon is common. These materials are obtained as by-products of the agricultural and food industries and, hence, they are cheap and their use contributes to the conservation of the environment [3]. Banana peels are a solid waste from finished food products, such as chips, slices, and dried banana. They are high organic carbon (41.37%). This waste has been subjected to biomethanation [4] and biogas production [5].

The banana peel charcoals have been prepared by carbonization at 300-700°C. It was found that the percentage of charcoal from banana peel was decreased with the increase of carbonization temperature. However, the percentage of fixed carbons was reversed. The maximum of iodine numbers of charcoal from banana peels were found to be at the carbonized temperature of 500°C. The charcoals of banana peels with carbonization at 500°C were activated with KOH in ratios of 1:2 to 1:5 by weight. Then, these activated charcoals were recarbonized at 600° to 900°C. The iodine number of activated charcoals increased with increasing ratios of KOH, but the ethylene blue absorptions were increased a little [6]. These results suggest that activated carbons prepared from banana peel using KOH activation may be developed for adsorbents.

In this study, the results of the SEM morphology and XRD pattern studies of charcoals and activated charcoals prepared from banana peel are used to describe the effects of pyrolysis temperature and the mass ratios of KOH.

Materials and Methods

Preparation of Charcoals and Activated Charcoals

Banana peel as the precursor material was obtained from the Banggrathum district, Phitsanulok, Thailand. It was well washed with H₂O several times and used after oven drying at 110°C for 3 h. The dried sample was used for charcoal and activated charcoal preparation. The charcoal was prepared by a carbonized temperature of 300°C to 600°C for 1 h under a closed system in a porcelain crucible and then cooled to room temperature. The charcoal was then subjected to KOH activation. The charcoal was agitated in KOH (CARLO ERBA Reagent) at a ratio of 1:2, 1:3, 1:4 and 1:5 charcoal : KOH weight by weight basis. After the agitation was finished, the pre-carbonized charcoal slurry was left overnight at room temperature and, then, dried at 110°C for 24 h. The samples were then activated in a closed system. Consequently, the samples were heated to optimize temperatures of 500, 600 and 700°C and maintained at a constant temperature for 1 h before cooling. After cooling down, the activated charcoal was washed successively several times with 0.2 N HCl (AR Merck), then with hot water until the pH became neutral, and finally with cold water to remove the excess KOH compounds. The washed samples were dried at 110°C to get the final product. The charcoal and activated charcoal were characterized by SEM and XRD.

Surface Morphology

Scanning electron microscopy was used to visualise the surface morphology of the charcoal and activated charcoal samples. A LEO 1455 VP scanning electron microscope was used. The samples were coated with gold by a gold sputtering device for a clear visibility of the surface morphology.

XRD Analysis

X-ray diffraction (XRD) was measured on a PW 3040/60, X' Pert Pro MPD X-ray diffractometer to determine the crystalline phases formed in banana peel activated charcoal.

Results and Discussion

Influence of Carbonized Temperature on the Development of Porosity of Charcoal

In the carbonization process, the development of porosity of banana peel charcoal starts at 300°C and increases with increasing carbonized temperature (figures 1 (a) - (d)). Figures 1 (a) and (b) show a pore and a cellular structure of banana peel charcoals which was carbonized at 300°C to

400°C. A temperature of 300°C to 400°C led to incomplete carbonization of banana peel and the cell structure is maintained. There are some rudimentary pores due to the release of volatiles. Evident pore evolution occurred in carbonization temperatures of 500°C. Raising the temperatures from 500°C to 600°C has a good influence on the banana peel with the generation moderately developed for charcoal production and shows characteristics open cellular structure in the original banana peel (figures 1 (c) and (d)). It can also be seen that the distribution of the open pores is uniform and forms a honeycomb structure. The scanning electron micrograph of charcoal (figures 1 (c) and (d)) clearly showed its complete porous structure and the opening of cell pores on the surface. The study of Mendez et al. [7] showed that the main important weight change of sewage sludges had been produced due to the light compounds volatilization and pyrolysis transformations at 450°C. This stage is primary pyrolysis (in the 300°C to 500°C range) with evolution of most gases and tars with formation of the basic structure of the char [8]. A temperature of 500°C was found sufficient for banana charcoal production. Therefore, considering economical and manufacturing factors, it was recommended the use of 500°C carbonization temperature for banana charcoal production. Thus, we selected banana charcoal carbonized at 500°C for subsequent KOH activation and characterization.

Influence of Activation Pyrolysed Temperature and Ratios of KOH on the Development of Porosity of Activated Charcoal

Figures 2-5 shows the surface images of activated carbon from banana peel charcoal obtained at pyrolysis temperature between 500°C and 700°C and mass ratios between 1:2 and 1:5. In this study it was established that the activated charcoal activated by KOH lost its original cellular structure and looked broken, therefore it was more fragmented during activation pyrolysis than carbonized charcoal. Generally, with the increase of activation temperature and the ratio of KOH, pore widening should occur. An increase in KOH ratio slightly raises the pore size and porosity of activated charcoals which is due to the aggressive action on the cellular structure, indicating that carbon gasification was enhanced by the increased KOH ratios.

By increasing the temperature from 500°C to 700°C and ratios of KOH from 1:2 to 1:5, the amount and size of porosity of activated charcoal increased. Increasing of the temperature raised the C-KOH reaction rate, resulting in an increased carbon burn-off. Concurrently, the volatiles from the charcoal continue to evolve with increasing activation temperature, whereas the C-KOH

reaction enhances the existing pores and creates new porosities [9]. The pore size depends on the banana charcoal : KOH ratios. Because the KOH reagent is a strong base, it is able to interact with carbon atoms and thus catalyze the dehydrogenation and oxidation reaction, leading to the increment of tar evolution and development of porosity [10]. The change of pyrolysis temperature from 500-700°C for ratios ranges between 1:2 and 1:4 has a big effect on pore size. However, the 1:5 ratio of activated charcoal suppressed pore size. It is seen that the white sphere and some fluffy materials appear in the pores of activated charcoal (figures 2-5). The white spheres and fluffy materials may be due to the presence of K_2O , K_2CO_3 or K residues and increase with increasing ratios of KOH. It could be supposed that during the KOH activation process, various reactions can be considered with such products as H_2 , K, K_2CO_3 , and K_2O [11]. At higher temperature, the formation of K_2O is thermodynamically the most stable. The increase of KOH ratios on samples containing a large amount of potassium suggests that the high ratio KOH may give more K_2CO_3 and K_2O during pyrolysis. They were analyzed to be possibly either K_2CO_3 or K_2O from the corresponding EDS spectra (figure 6). Elemental analysis on the white point of activated charcoal shows that large amounts of K and O. The K_2CO_3 formation may not only occur on the outermost carbon surface, whereby K_2CO_3 forms a shell around the carbon and has no effect on the carbon structure, but also in the pores and cavities of the carbon where molten KOH could be located [3]. K_2CO_3 formed here would cause carbon lamellae separation, deformation and structure crumbling.

In the impregnated samples, increasing pyrolysis temperature at a constant impregnation ratio gives rise to an enhancement of the pore size. The same behavior was observed in activated carbon which ratios of KOH 1:2 to 1:4 (figures 2-4). It appears that a larger amount of K_2CO_3 formed causes a larger pores size and the structural deformation. However, the surface image of banana peel activated charcoal with KOH activation of ratio 1:5 (figure 5) showed smaller pore size than activated charcoal with ratios of KOH 1:2 to 1:4. It might be explained that the larger ratio of KOH probably forms an insulating layer, covering the particles, thus reducing the activation process and the contact with the surrounding atmosphere [8].

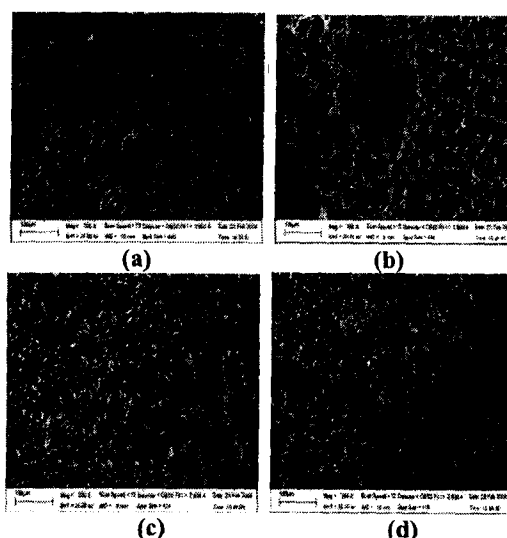


Fig. 1 Surface images of banana peel charcoal with carbonized temperature at (a) 300°C (b) 400°C (c) 500°C and (d) 600°C.

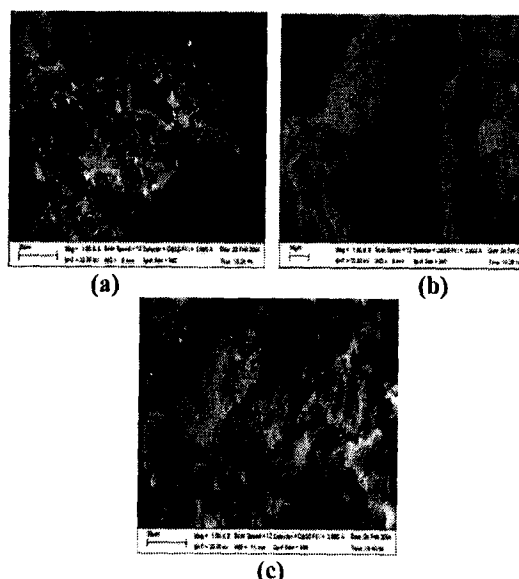


Fig. 2 Surface images of banana peel activated charcoal with KOH activation of ratio 1:2 and pyrolysed temperature at (a) 500°C (b) 600°C and (c) 700°C.

XRD Pattern of Banana Peel Activated Charcoal

Figure 7 illustrates the XRD pattern of the activated carbon prepared from banana peel with an activated temperature of 700°C. The activated carbon exhibited two peaks at around $2\theta = 26^\circ$ and 44° which correspond to the peak of graphite [9]. At the same time, it exhibits noise of the powder XRD signals. This reveals a predominantly amorphous structure of carbon. In this result, it can be explained that the pyrolytic reaction of organic compounds consists of the breaking of chemical bonds with temperature and repolymerization of radicals condensing further into active compounds. These compounds form typical graphitic layers and

stacks of planes during carbonization [12]. The XRD pattern showed that the compounds formed were probably K_2O and K_2CO_3 in the peaks of $2\theta = 28^\circ$, 31.4° and 42° . Formation of K_2CO_3 occurs by the reaction of KOH with CO_2 . The K_2O is left in the carbon as the end product [10]. The appearance of a broad peak at $2\theta = 24^\circ$ indicated that the silica in activated charcoal was amorphous SiO_2 .

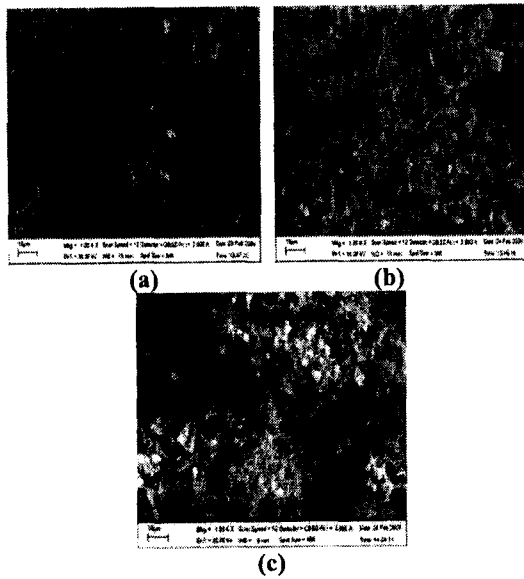


Fig. 3 Surface images of banana peel activated charcoal with KOH activation of ratio 1:3 and pyrolysed temperature at (a) 500°C (b) 600°C and (c) 700°C.

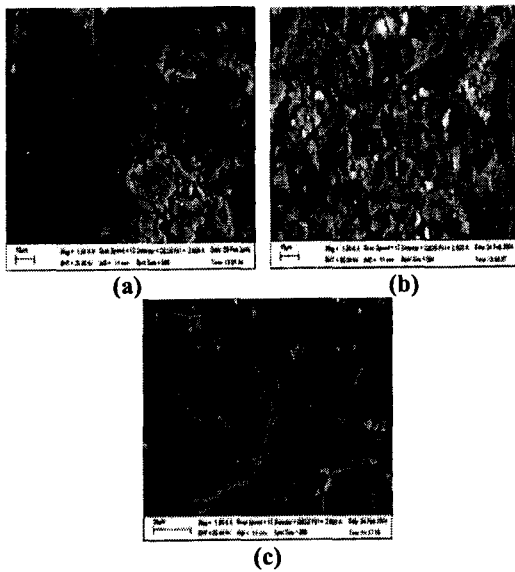


Fig. 4 Surface images of banana peel activated charcoal with KOH activation of ratio 1:4 and pyrolysed temperature at (a) 500°C (b) 600°C and (c) 700°C.

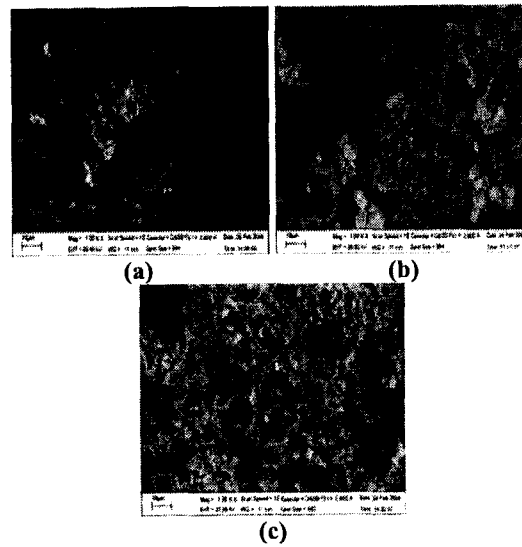


Fig. 5 Surface images of banana peel activated charcoal with KOH activation of ratio 1:5 and pyrolysed temperature at (a) 500°C (b) 600°C and (c) 700°C.

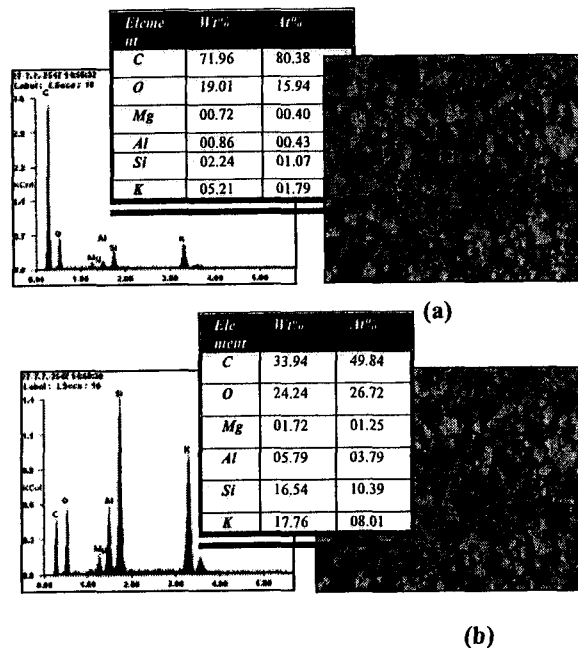


Fig. 6 SEM-EDS analysis of activated charcoal with activated KOH ratio of 1:5 and temperature at 700°C, (a) point on activated carbon granular (b) point on K_2O granular.

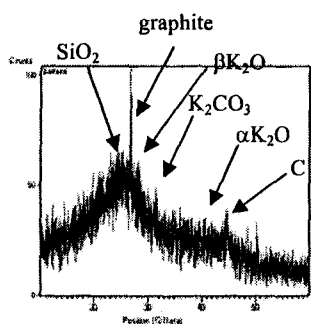


Fig. 7 XRD pattern of banana peel activated charcoal with pyrolysis at 700°C.

Conclusion

As the carbonization temperature increases, the resulting banana peel charcoal is better in clearly structure and ordering. Raising the temperatures from 500°C to 600°C has a good influence on the banana peel with generation of moderately developed charcoal production and shows characteristic due to open cellular structure in the original banana peel.

Increased KOH ratios slightly raises the pore size and porosity of activated charcoals which is due to aggressive action on the cellular structure, indicating that carbon gasification was enhanced by the KOH ratios increase to widen the pores.

The change of pyrolysis temperature from 500°C to 700°C for ratio ranges between 1:2 and 1:4 has a large effect on the pore size. However, the 1:5 ratio of activated charcoal suppressed the pore size. It is seen that the white sphere and some fluffy materials appear in the pores of activated charcoal. The white spheres and fluffy materials may be due to the presence of K_2O , K_2CO_3 or K residues and increase with increasing ratios of KOH. K_2CO_3 formed would cause carbon lamellae separation, deformation and structure crumbling. However, the surface image of banana peel activated charcoal with KOH activation of ratio 1:5 showed smaller pore size than activated charcoal which ratios of KOH 1:2 to 1:4.

The XRD pattern showed that the constituents of banana peel activated charcoal were probably graphite, amorphous C, amorphous SiO_2 , K_2O , K and K_2CO_3 .

Acknowledgment

This research was supported by the Faculty of Science, Naresuan University and the National Research Council of Thailand. Instrumentation used in this research was purchased with partial funding from the Department of Chemistry, Faculty of Science, Naresuan University.

References

1. Qian, J.-M., Wang, J.-P., Qiao, G.-J., and Jin, Z.-H. Preparation of porous SiC ceramic with a woodlike microstructure by sol-gel and carbothermal reduction processing. *J. Eur. Ceram. Soc.* 2004, 24, 3251-3259.
2. Lillo-Rodenas, M.A., Marco-Lozar, J.P., Cazorla-Amoros, D., and Linares-Solano, A. activated carbon prepared by pyrolysis of mixtures of carbon precursor/alkaline hydroxide. *J. Anal. Appl. Pyrol.* 2007, 80, 166-174.
3. Diaz-Teran, J., Nevskaja, D.M., Fierro, J.L.G., Lopez-Peinado, A.J., Jerez, A. Study of chemical activation process of a lignocellulosic material with KOH by XPS and XRD. *Micropor. Mesopor. Mater.* 2003, 60, 173-181.
4. Bardiya, N., Somayaji, D., and Khanna, S. Biomethanation of banana peel and pineapple waste. *Bioresour. Technol.* 1996, 58, 73-76.
5. Mopoung, S., Udeye, V., Mopoung, R., Boonphong, S., O' Donnohuy, J., Production of biogas from banana peeling. *Nation. Res. Council. Thail.* 2000, 432, 23-28.
6. Mopoung, S. Chemical composition and physical properties of charcoal and activated charcoal from peel and bunch of banana. *NU Sci. J.* 2005, 2(1), 107-119.
7. Mendez, A., Gasco, G., Freitas, M.M.A., Siebielec, G., Stuczynski, T., and Figueiredo, J. Preparation of carbon-based adsorbents from pyrolysis and air activation of sewage sludges. *Chem. Eng. J.* 2005, 108, 169-177.
8. Girgis, B.S., and El-Hendawy, A.-N. A. Porosity development in activated carbons obtained from date pits under chemical activation with phosphoric acid. *Micropor. Mesopor. Mater.* 2002, 52, 105-117.
9. Lua, A.C., and Yang, T. Effect of activated temperature on the textural and chemical properties of potassium hydroxide activated carbon prepared from pistachio-nut shell. *J. Colloid. Interface. Sci.* 2004, 274, 594-601.
10. Hsu, L.Y., and Teng, H. Influence of different chemical reagents on the preparation of activated carbons from bituminous coal. *Fuel Process. Technol.* 2000, 64, 155-166.
11. Babel, K., and Jurewicz, K. KOH activated carbon fabrics as supercapacitor material. *J. Phys. Chem. Solid.* 2004, 65, 275-280.
12. Kurosaki, F., Ishimaru, K., Hata, T., Bronsveld, P., Kobayashi, E., and Imamura, Y. Microstructure of wood charcoal prepared by flash heating. *Carbon*, 2003, 41, 3057-3062.