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CHARACTERIZATION OF PHOSPHORIC ACID IMPREGNATED ACTIVATED CARBON PRODUCED FROM HONEYDEW PEEL

Zalilah Murni Yunus[a*], Norzila Othman[b], R. Hamdan[a], N. N. Ruslan[b]

[a]Dept. Of Sci., Fac. of Sci., Tech. & Human Development, University Tun Hussein Onn Malaysia
[b]Dept. Of Water Eng. Fac of Civil and Env. Eng., University Tun Hussein Onn Malaysia, Malaysia

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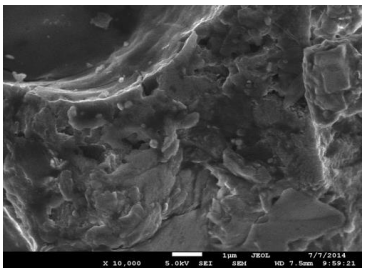
*Corresponding author
zalilah@uthm.edu.my

Graphical abstract



Abstract

The role of waste materials in producing activated carbon (AC) used in adsorption has been identified as an alternative to substitute commercial expensive wooden starting materials. The present study has chosen honeydew peel as an alternative starting material in activated carbon production because of it's low cost, availability and incurs minimal cost for waste management. The production involved chemical impregnation using 20% diluted phosphoric acid (H_3PO_4) prior to activation. To optimize the activation method, the effect of different activation temperatures (470°C - 550°C) on the physicochemical properties of the AC was studied. The results showed that the AC carbonized at 490°C possessed 942 mg/g iodine number, 997 m2/g surface area SBET and 0.56 ml/g total pore volume. FESEM images showed a high pore development as the activation temperature increased. FTIR indicated the presence of –OH, C=O bond in carboxylic acids, ketones, aldehydes, lactones and ester functional groups on the AC. The experimental results presented the potential use of honeydew peel as a precursor material in the preparation of inexpensive adsorbent for wastewater remediation.

Keywords: Agricultural waste, alternative adsorbent, BET, FESEM, wastewater

1.0 INTRODUCTION

Among the various techniques, adsorption is the most widely applied method to wastewater treatment due to its easy operation, simplicity and efficiency [1, 2]. The activated carbons (AC), is a carbonaceous material that has a porous structure and excellent internal surface area. It has the ability to adsorb various substances from liquid phases, thus, it remains the prime adsorbent in water treatment. AC can be obtained by using either the chemical activation or physical activation method. There are two significant factors contributing to the choice of the production method – lower activation temperature and higher product of carbon. Previous studies had proved that the chemical process is now widely preferred over the physical process according to these considerations [3, 4]. It was explained that chemical activation with phosphoric acid works outstandingly at moderate temperatures and produces a range of agricultural waste materials, thus, preventing a high percentage of ash formation. This type of activation results in a high surface area and microporosity [3]. In recent years, researchers have focused on converting agricultural waste into AC, since this technology offers a promising solution to the waste disposal problem by converting potential waste into a valuable product that can be used as an adsorbent for wastewater treatment [4]. However currently very little data are available on the physicochemical properties of acid-activated carbons from honeydew peel (HDP). This study aimed to look at the characteristics of honeydew peel activated carbon (AC-HDP) produced by phosphoric

activation and optimization of activation temperature.

2.0 MATERIALS AND METHOD

The HDP from local stalls was sorted and washed with tap water, pretreated with 5% nitric acid (HNO_3), soaked in distilled water and was oven dried. The impregnation step used 20% phosphoric acid (H_3PO_4) and oven dried at 110. Optimization of activation process was undertaken at 470°C, 490°C, 510°C, and 530°C for 30 min. The AC-HDP was washed until pH neutral then dried at 110°C and kept in a tight container for further use. Surface functional groups of dried raw HDP were determined by fourier transform infrared spectra (FTIR) SHIMADZU IR Prestige21. The thermogravimetric analysis was performed by using a LINSEIS THERMOBALANCE with simultaneous recording of TG and differential thermogravimetric analysis (DTG). Field emission-scanning electron microscope (FE-SEM) images of AC-HDP were recorded usinga JEOL JSM-7600F Field Emission Scanning Electron Microscope (USA). Textural characterization was performed using nitrogen adsorption-desorption isotherm determination with a multiple-point Brunauer, Emmet and Teller (BET) gas adsorption measurement using the SA 3100 Surface Analyser (Beckman Coulter) at 77 K. Before the measurement, the sample was degassed at 100°C for 1 h. Iodine number analysis (mg iodine/g carbon) analysis of a 0.1 g sample was equilibrated for 1 h with a 0.1 N standardized iodine solution.

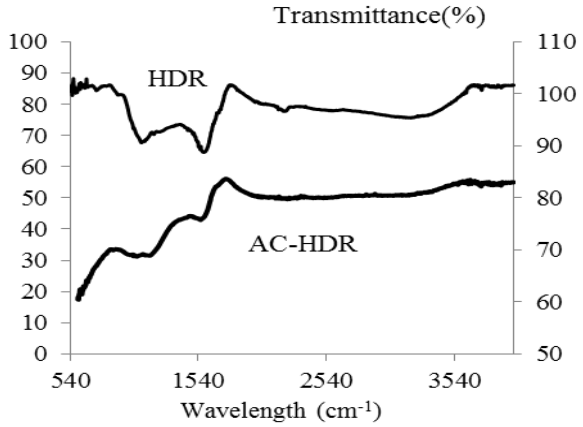
3.0 RESULTS AND DISCUSSION

3.1 Fourier Transform Infrared Analysis

FTIR is a method to identify functional groups of honeydew peel HDP and activated carbon honeydew peel (AC-HDP). [Figure 1(a)] shows the existence of carboxyl, hydroxyl and alcoholic functional groups as a broad peak detected at 3200-3600 cm^{-1} which is believed to be the stretching of the hydroxyl band and the amine N-H functional group shows the presence of bonded hydroxide in the raw sample [5]. The bands located at 2800-2900 cm^{-1} correspond to the C-H vibrations of the methyl and methylene groups while the band at 2335 cm^{-1} is assigned to the vibration of C≡C bond from the alkyne groups. The band at 1700 cm^{-1} denotes the existence of carbonyl/carboxyl groups. The band at 1120 cm^{-1} indicates the C-O stretching vibrations in alcohols, phenols or ester groups. From the observations it can be concluded that AC made from honeydew peel and from other agricultural products has the common functional groups. The AC-HDP spectra shown at the 1600–1500 cm^{-1} band identify the existence of an aromatic C=C ring stretching. Similar results have been found in other research suggesting that the presence of phosphoric acid during activation promotes depolymerisation and dehydration and favours the rearrangement of aliphatic to aromatic compounds [6]. A slight difference was detected between the spectrums by which a broad band corresponding to C=O groups at around 1700cm^{-1} suggests that AC-HDP contains less C=O groups than the HDP. The amount of carbonyl groups diminished may be due to the effect of H_3PO_4 hydrolysis, causing to gasification to occur [7].

3.2 Thermogravimetry

The decomposition of honeydew peel is shown by the TG and DTG curves [Figure 1(b)]. Temperature ranging between 30°C -100°C allowed the moisture in the sample to evaporate resulting in an approximate weight loss of 9 wt.%. A higher range of temperature between 100°C -200°C was suggested for the release of volatiles at 7 wt.% resulting from the decomposition of biopolymer compounds. The weight loss from the temperature in the range of 300°C –480°C was contributed by the decomposition of cellulose and lignin with the highest loss of 46 wt.%. This is due to the decomposition of chemically bonded water, biopolymer to carbon [6.] However, no significant weight loss was observed above 490°C which suggested that 490°C is a suitable temperature for the preparation of the AC.



(a)

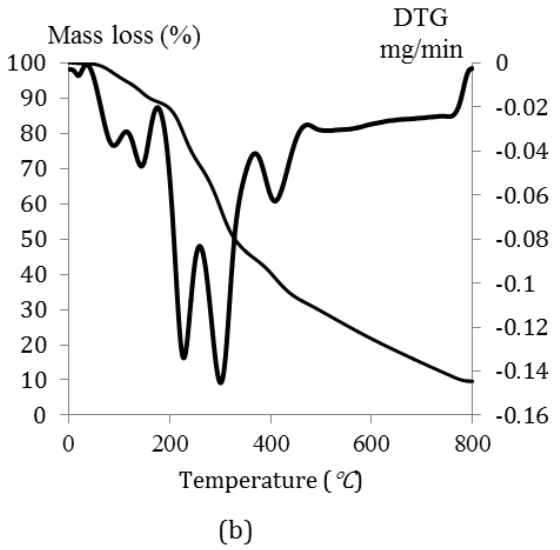


Figure 1 (a) FTIR spectra of HDP and AC-HDP and (b) TG and DTG curve of dried HDP

3.2 BET Analysis

Iodine number and textural analysis of BET are presented in Table 1. Based on the porosity data, increasing the activation temperature leads to the vast development of the BET surface area and micropores but low improvement of mesopores. The SBET (m^2/g) of the ACs is 706, 997, 954, 959 and 920 at each studied temperatures. It was observed that the value increased with increasing activation temperature presumably because of intensive interaction between the impregnation agent and precursor at a higher temperature. This remarked development of pore widening occured as the activation temperature increased [8].

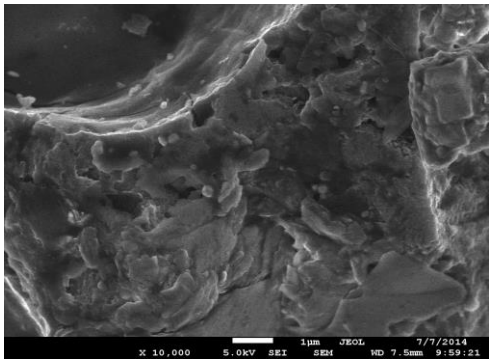
Meanwhile unimpregnated-AC attained S_{BET} 73. The result of the surface characterization analysis from unimpregnated-AC was compared to impregnated-ACs and showed that the reaction between the starting materials and activation agent may lead to the formation of most of the micropores and mesopores [9]. This observation also identified the relationship between the surface area and iodine number whereby both values decreased at a higher temperature. The highest iodine number was obtained at activation temperature of 490°C and decreased at higher temperature. Therefore, 490°C is the suitable activation temperature leading to the best iodine number and $S_{BET,}$ consequently, to the best development of the microporous structure.

3.2 FESEM Analysis

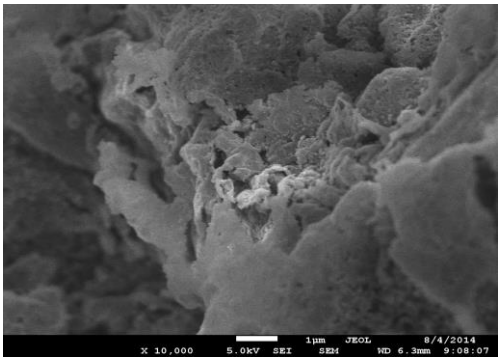
The FESEM [Figure 2] shows images of the smooth surface of unimpregnated-AC with no porosity except some occasional cracks while morphology of AC-HDP attests to substantial changes provoked by H_3PO_4 and the adsorbent surface clearly shows a porous nature with a predominant microporous character, which is responsible for the developed surface area. Figure 2(c) shows a roughly texture with a heterogeneous surface and distributed pore size. By comparison, there was a significant pore development trend as the temperature increased whereby they were progressing positively until they reached higher temperatures and became wider and consequently collapsed at 550°C. This result is probably due to both the chemical composition of the precursor and H_3PO_4 induce depolymerization, dehydration, and redistribution of elemental biopolymers, generating significant revolution in the pyrolytic decomposition of the material [9, 10]. From the micrograph AC-HDP of 490°C produced the desired pore distribution supported by the highest value of S_{BET} and iodine number, and thus, was selected as the optimum activation temperature.

Table 1 Iodine number and textural properties of phosphoric activated honeydew peel AC

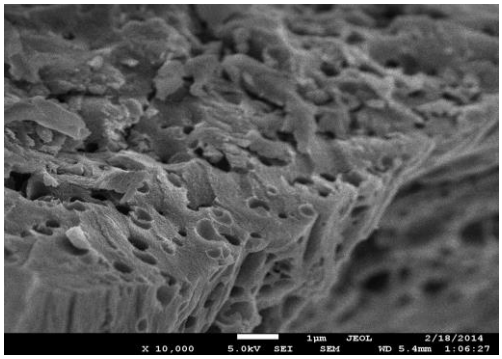
Activation temperature, °C	Iodine number (mg/g)	S_{BET} (m^2/g)	V_{micro} (ml/g)	V_{meso} (ml/g)	V_{total} (ml/g)
470	769	706	0.24	0.14	0.38
490	942	997	0.33	0.22	0.56
510	923	954	0.28	0.12	0.47
530	793	950	0.30	0.13	0.44
550	734	920	0.29	0.11	0.41



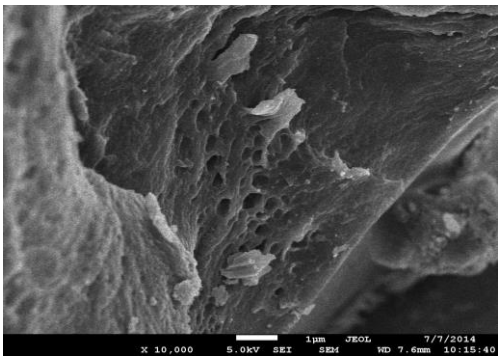
(a) unimpregnated AC



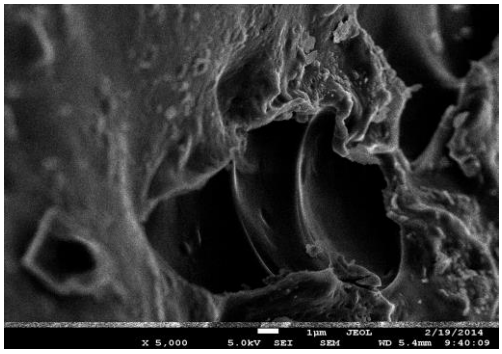
(b) 470°C



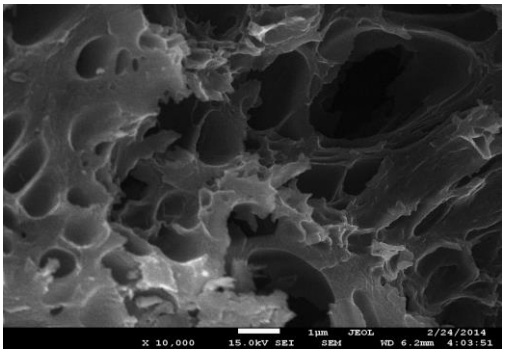
(c) 490°C



(d) 510°C



(e) 530°C



(f) 550°C

Figure 2 FESEM micrograph of (a) unimpregnated AC and AC-HDP at activation temperature (°C).(b) 470 (c) 490 (d) 510 (e) 530 (f) 550. (magnification=10000x)

4.0 CONCLUSION

Based on this work, the optimal production of 20% H_3PO_4 impregnated AC-HDP was determined at 490°C Activation for 30 min resulted in 942mg/g iodine number, 997m^2/g S_{BET} and 0.56ml/g total pore volume. The FESEM images showed a high pore development as the activation temperature increased. This study showed the potential use of honeydew peel as a precursor material in the preparation of a low cost adsorbent for wastewater treatment. Nevertheless, future study is suggested to investigate the effects of other production parameters to expand the knowledge of the AC-HDP process.

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References

[1] Francesca, P. Sara, M. Luigi, T. 2008. New Biosorbent Materials For Heavy Metal Removal: Product Development Guided by Active Site Characterization. *Water Research*. 45: 2953-2962.

[2] Soleimani, M. & Kaghazchi, T. 2007. Agricultural Waste Conversion to Activated Carbon by Chemical Activation with Phosphoric Acid. *Chemical Engineering & Technology*. 30: 649-654.

[3] Kanchi, S. Bisetty, K. Kumar, G. Lin, C. Chin, T. 2014. Development of Green Energy Waste Activated Carbon for Removal of Trivalent Chromium: Equilibrium and Kinetic Modeling. *Separation Science and Technology*. 14: 513-522.

[4] Baccar, R. Bouzid, J. Feki, M. Montiel, A. 2009. Preparation of Activated Carbon From Tunisian Olive-Waste Cakes and Its Application for Adsorption of Heavy Metal Ions. *Journal of Hazardous Materials.* 162: 1522-1529.

[5] Hadoun, H. Sadaoui, Z. Souami, N. Sahel, D. Toumert, I. 2013. Characterization of Mesoporous Carbon Prepared From Date Stems By H_3PO_4 Chemical Activation. *Applied Surface Science.* 280: 1-7.

[6] Yun, C. Shang-Ru, Z. Na, L. Yu, S. Qing-Da, A. Xiao-We, S. 2014. Dye Removal Of Activated Carbons Prepared From Naoh-Pretreated Rice Husks by Low-Temperature Solution-Processed Activation and H_3PO_4 Activation. *Bioresource Technology*. 144: 401-409.

[7] Sych, N. V. Trofymenko, S. I. Poddubnaya, O. I. Tsyba, M. M. Sapsay, V. I. Klymchuk, V. O. Puziy, A. M. 2012. Porous Structure and Surface Chemistry of Phosphoric Acid Activated Carbon From Corncob. *Applied Surface Science*. 261: 75-82.

[8] Lu, X. Pellechia, P. J. Flora, J. R. V., Berge, N. D. 2013. Influence of Reaction Time and Temperature on Product Formation and Characteristics Associated with The Hydrothermal Activation of Cellulose. *Bioresource Technology*. 138: 180-190.

[9] Ekpete, O. A. Horsfall, M. 2011. Preparation and Characterization of Activated Carbon derived from Fluted Pumpkin Stem Waste (*Telfairia occidentalis Hook F*). *Research Journal of Chemical Science*. 1: 10-17.

[10] Girgis, B. S. Abdel-Nasser, E. 2002. Porosity Development In Activated Carbons Obtained From Date Pits Under Chemical Activation With Phosphoric Acid. *Microporous and Mesoporous Materials*. 52: 105-117.