

TREATMENT OF LANDFILL LEACHATE IN KAYU MADANG, SABAH: TEXTURAL AND PHYSICAL CHARACTERIZATION (PART 1)

Collin G. Joseph, Hasnul Fazli Md. Zain, & Siti Fatimah Dek

*Industrial Chemistry Program, School of Science & Technology,
Universiti Malaysia Sabah, 88999 Kota Kinabalu, Sabah.*

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Abstract. Activated carbons from two agro-industrial wastes; oil palm shells (OPS) and coconut husk (CH); were prepared by chemical activation using potassium hydroxide as the dehydrating agent. A two-stage process was used; with semi-carbonization stage at 200°C for 15 minutes as the first stage followed by an activation stage at 500°C for 45 minutes as the second stage. The precursor material with the impregnation agent was exposed straightaway to semi-carbonization and activation temperature unlike the specific temperature progression as reported in the literature. All experiments were conducted in a laboratory scale muffle furnace under static conditions in a self generated atmosphere. We found that by using this method, the OPS prepared with the KOH impregnation ratio of 25% had the highest Iodine Number which was 466.1mg/g but CH with the similar impregnation ratio had the highest Methylene Blue adsorption capacity and percentage of yield, which were 10.9mg/g and 74.68% respectively.

Abstrak. Karbon teraktif daripada tempurung kelapa sawit dan sabut kelapa disediakan melalui pengaktifan fizikal dan kimia dengan menggunakan KOH. Satu proses dua peringkat telah digunakan; dengan peringkat separa pengkarbonan pada suhu 200°C untuk 15 minit sebagai peringkat pertama diikuti oleh peringkat pengaktifan pada suhu 500°C untuk 45 minit sebagai peringkat kedua. Sampel precursor yang telah diimpregnasikan didedahkan kepada dua peringkat proses itu secara terus dan bukan secara progresif. Semua eksperimen dijalankan dengan menggunakan 'Muffle Furnace' pada keadaan pegun. Kami dapati dengan kaedah penyediaan ini, karbon teraktif yang daripada OPS 25% KOH, mempunyai Nombor Iodine terbesar iaitu 466.1mg/g tetapi CH dengan nisbah impregnasi yang sama mempunyai kapasiti penyerapan Metilene Biru dan peratus hasil yang terbesar iaitu 10.9mg/g dan 74.68% masing-masing.

Introduction

Activated carbons are carbons of highly microporous form with both high internal surface area and porosity, which find extensive use in the industrial sector for adsorption of pollutants from air and water streams. This material can be designed for adsorption of specific adsorbate, by using appropriate precursor [1-4], dehydrating agent and by optimizing the activation process conditions. Several activating agents have been reported for chemical activation process; however the most important and commonly used activating agents are zinc chloride, potassium hydroxide and alkaline metals. This agent, which has dehydrating properties, will influence the pyrolytic decomposition and retard the formation of tars during the carbonization process, increasing the carbon yield [5]. A number of activation methods have been reported in the literature using KOH as an activating agent. Chemical activation by KOH was first reported in the late 1970s by AMOCO Corporation [6], and these carbons were commercialized by the Anderson Development Company in the 1980s [7]. Since then, there have been many studies reporting on the activation of carbons using KOH [8-14]. The chemical nature of activated carbon significantly influences its adsorptive, electrochemical, catalytic, and other properties. However, few papers report on the effects of chemical preparation conditions and preparation methods on the carbon. Generally, activation methods can be classified as single-stage or two-stage activation process carried out either in inert medium or a self-generated atmosphere as shown in Table 1. This paper explains the effect of KOH impregnation to the precursors prepared by using a two-stage process in a self-generated atmosphere. Trial and error methods are also used to achieve a high surface area carbon with desired pore size by optimizing the process parameters such as the activation time, activation temperature and impregnation ratio. Table 1 summarizes

efforts by researchers to prepare activated carbons using various methods with reference to the precursors, experiment conditions and results.

Table 1. Summary of earlier work by researchers to prepare activated carbons using various methods.

Researcher	Precursor	Experimental Condition	Results
Kirubakaran et al. [15]	Coconut Shell	Two stage in N ₂ atm; A.T=400 to 600°C; A.time=2hrs.	S.A > 1000m ² /g at I.R=1.5
Toles et al. [16]	Macadamia shell, pecan, walnut and almond	Single and two stage; N ₂ and self-generated atm.; S.C.T.=170°C; S.C. time=30min.; A.T.=450°C; A. time=1h	S.A=1100 to 1600 m ² /g. Activation in self-generated atm gave the highest S.A.
Dastgheib and Rockstraw [17]	Pecan Shells	Three stage activation: 1) liquid-stage activation at 160°C 2) primary activation at 160-210°C 3) secondary activation at 300-500°C for 30 min, I.R.=3	S.A=1071 m ² /g. S.A. increases until secondary A.T of 450°C and reduces when temperature increases above 450°C.
Lafi [18]	Acorns and olive seeds	A single stage with self-generated atmosphere. A.T=400-800°C. A.time=1h	A.T=800°C produced the highest Methylene Blue no. of 130mg/g

S.A =surface area; S.C.T=semi-carbonization temperature; S.C. time=semi-carbonization time; A.T=activation temperature; A. time=activation time; I.R. impregnation ratio.

Agricultural by-products such as oil palm shells (OPS) and coconut husk (CH) are renewable source of raw materials for activated carbon production. In some countries these by-products are considered as wastes and have caused significant disposal problems. Their utilization in the activated carbon industries is a viable solution to this environmental issue. In Malaysia, oil palm shell is one of the main agricultural wastes from palm oil industries. It is estimated that for every one million tonnes of palm oil produced, 0.8 million tonnes of palm shells are created [20]. Based on a total oil production of 7.4 million tonnes in 1993, the amount of palm shells generated in that year alone was about 6 million tonnes. Realizing the scale of these wastes, several studies were initiated to utilize palm shells including the possibility of using it as fuel to boilers [21, 22]. Its use as a raw material for activated carbon production was first highlighted by Chan et al. [23] and concluded that a good quality product can be obtained. OPS used in this study was taken from Lumadan Mills in Beaufort, Sabah. Coconuts grow abundantly in coastal areas of tropical countries. The coconut husk is available in large quantities as residue from coconut copra or coconut milk production in many areas, which gives the coarse coir fibre. The husk comprises of 30 wt.% coir fibres and 70 wt.% pith. Both fibre and pith are high in lignin and phenolic content. Most of coconut trees in Sabah are of the local tall coconut type. This tree has a big trunk and broad fronds. The size of the coconuts is big and the yield is between 35- 45 coconuts for each tree a year. Each of coconut can produce 320 g of copra [24]. CH used in this study was taken from Tuaran, Sabah. This paper describes a study on the use of KOH as a dehydrating agent and the effects of two stage processes in self-generated atmosphere on the textural and physical properties and comparison between the activated carbons (OPS and CH) prepared. Adsorption studies regarding the treatment of landfill leachate with these activated carbons, surface area and porosity studies were presented in our next paper [27].

Experimental

Prior to the impregnation process, precursors were washed with distilled water and dried in an oven at 110°C for 24 hours. This was done to remove sand, branch fibers and dirt from contaminating the samples as explained in our previous papers [1-4]. Impregnation process was done using KOH as the dehydrating agent. 5g, 10g, 15g, 20g and 25g of granular KOH were placed separately into 2 sets of 5 Erlenmeyer flask (250ml). 100ml of distilled water and 20g of precursor (OPS or CH) were added into each of the flask. The flask was then placed in orbital shaker model 721 Protech for a week. The samples were dried overnight in an oven at 110°C. A muffle furnace model Carbolite RHF 1500 was used to semi-carbonized the samples at 200°C for 15 minutes as the first stage followed by an activation stage at 500°C for 45 minutes as the second stage. The precursor material with the impregnation agent was exposed straightaway to semi-carbonization and activation temperature unlike the specific temperature progression methods as described in earlier works [1-4, 15-18]. After that, the activated carbons were refluxed in an acid solution (0.1M HNO₃) to remove metals ions, tar and ash followed by distilled water (10 times) to remove the acid. The activated carbons were dried in an oven at 110°C for a week, after which, yield percentage, moisture and

ash content, pH [19], scanning electronic microscopy and surface area analysis of the selected activated carbon were determined. The scanning electronic microscopy was done using JEOL JSM 5610 whereas surface area analysis was done by PETRONAS RESEARCH & SCIENTIFIC SERVICES SDN. BHD.

Result and Discussions

Temperature, heating period, materials, dehydrating agent and the method of carbonization and activation play an important role in determining the properties of the resulting activated carbon. Previous work in our laboratories [1-4] suggested that the temperature played an important role to produce optimum surface area for the carbons.

Percentage of yield, pH, moisture and ash contents

The overall yield of the activated carbon was calculated based on the initial weight of the predried precursor. Relatively high yields of the final products are expected in manufacturing commercial adsorbents. Figures 1 and 2 shows the effect of KOH impregnations (wt%) on the percentage of yield, pH, moisture and ash content of OPS and CH respectively. The percentage for yield for OPS was between 33-58% with OPS25% giving the highest percentage of 58%, whereas the percentage of yield for CH was between 25-75% with CH25% giving the highest percentage of yield of 75%. Increasing the KOH-to-precursor ratio increased the overall yield for both the OPS and CH activated carbons. This was because the potassium ions attached onto the carbon surface, acting as catalyst to accelerate direct reaction between the carbon and KOH. OPS and CH are typical carbonaceous biomass, the following reaction occurred during KOH impregnation process:

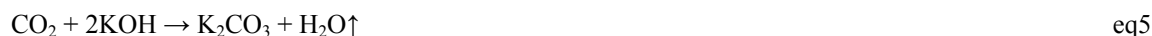
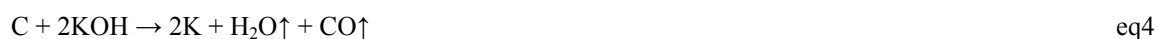


During semi-carbonization (1st stage) will result in the following products:



Char usually contains a majority of carbon, C(~75-80%); some oxygen, O(~15-17%) and some hydrogen, H(< 3%). Tar consists of phenols, CH₃COOH, CH₃OH, (CH₃)₂CO, and other high molecular weight hydrocarbons. Gaseous components include H₂O, CO₂, CO, etc [25].

The following reaction occurred during the activation (2nd stage) process:



At activation temperature, metallic potassium intercalated with the carbon matrix, resulting in the widening and formation of new pores. Secondary reactions possibly took place as well between H₂O (eq3), C and KOH resulted in the formation of 'extra' K₂CO₃ as shown in the following equation:



Potassium carbonate (K₂CO₃) is known to prevent excessive sample burn-off, resulting in high yield and well-developed internal porosity [26].

Our observation recorded that the pH of the activated carbons ranged from mildly acidic to mildly basic. This is due to the basic nature of the dehydrating agent, coupled with the washing process using nitric acid. Near neutral activated carbon is important for the leachate adsorption studies. Moisture and ash content for the OPS activated carbon ranged from 2.78-6.41% and 5.85-3.95% respectively, whereas for CH activated carbon, the percentage ranged from 3.5-5.9% and 9.2-6.2% respectively. Both OPS and CH activated carbons showed a reducing pattern for the ash content and an increasing pattern for the moisture content as the impregnation ratio of KOH was increased. This was because higher concentration of KOH inhibits excessive burn-off, giving high yield and lowering ash formation. KOH also has an affinity for adsorbing water, this account for the increasing pattern of the moisture content as the concentration of KOH increases.

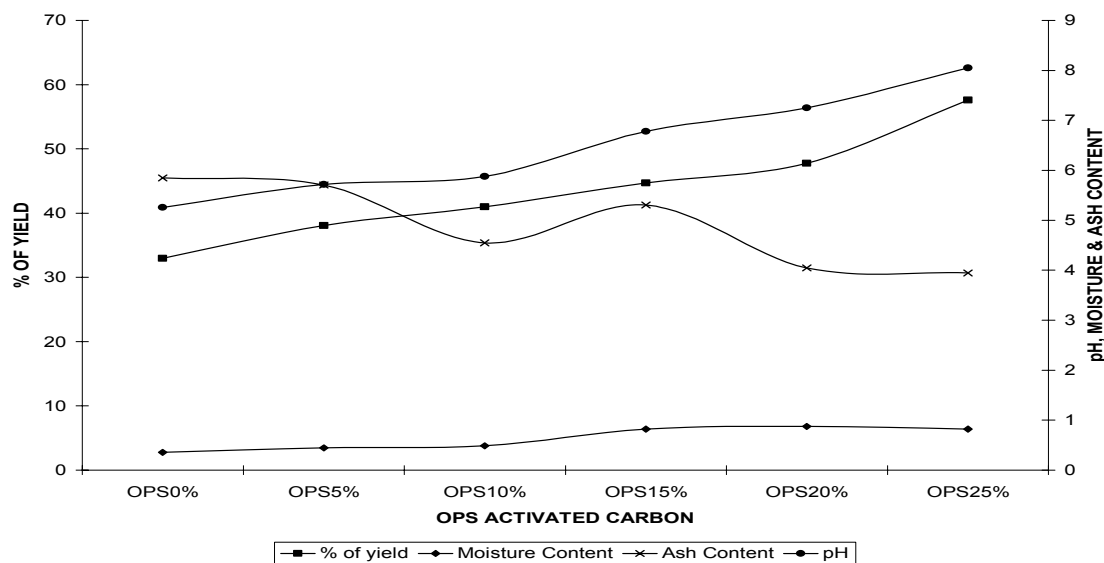


Figure 1. The effect of KOH impregnations (wt%) on the percentage of yield, pH, moisture and ash contents of the OPS activated carbons.

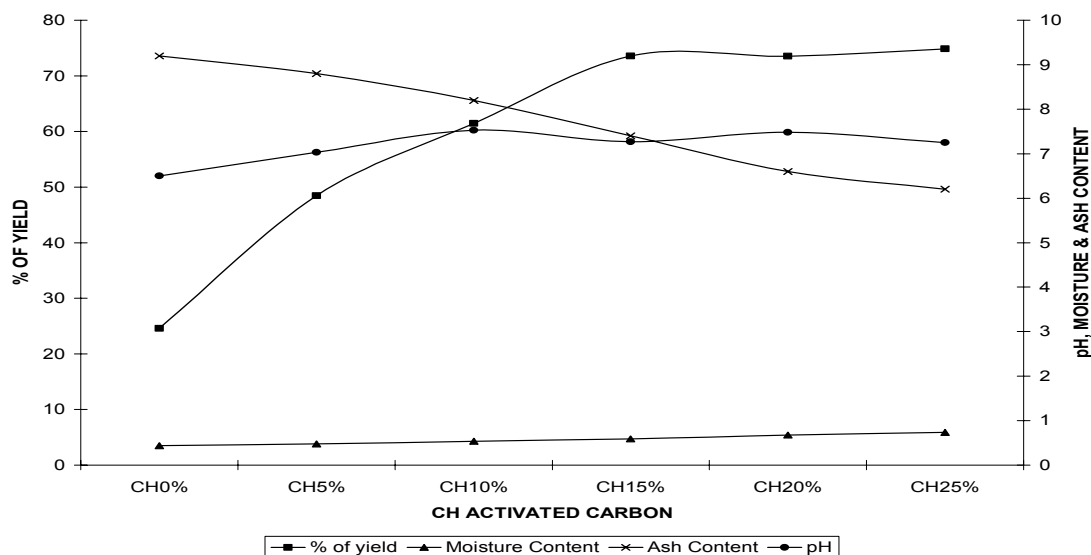


Figure 2. The effect of KOH impregnations (wt%) on the percentage of yield, pH, moisture and ash contents of the CH activated carbons.

Physical Appearance

The OPS and CH activated carbons were photographed after activation, and these photographs showed an interesting physical appearance. Figure 3 shows the photographs of the untreated OPS, OPS0%, OPS25%, untreated CH, CH0% and CH25%.

The untreated OPS, CH and CH0% were light brownish in colour whereas the chemically activated CH25% was dark brown in colour. OPS0% and OPS25% were black in colour. The OPS0% and CH0% maintain the similar shape and structure as untreated OPS and CH but OPS25% underwent remarkable physical change whereas CH25% only had a slight physical change as shown in figure 3. The shape of the palm shells was completely lost and the OPS25% took the shape of the crucible that was used as a reactor. OPS25% had a sponge-like appearance and was very brittle. It is possible that KOH deposition on the surface of the material according to eq1 during impregnation and eq4 during activation contributed to extensive gasification that produced the sponge-like appearance. Why CH25% did not change physically unlike OPS25% is subject to further studies.

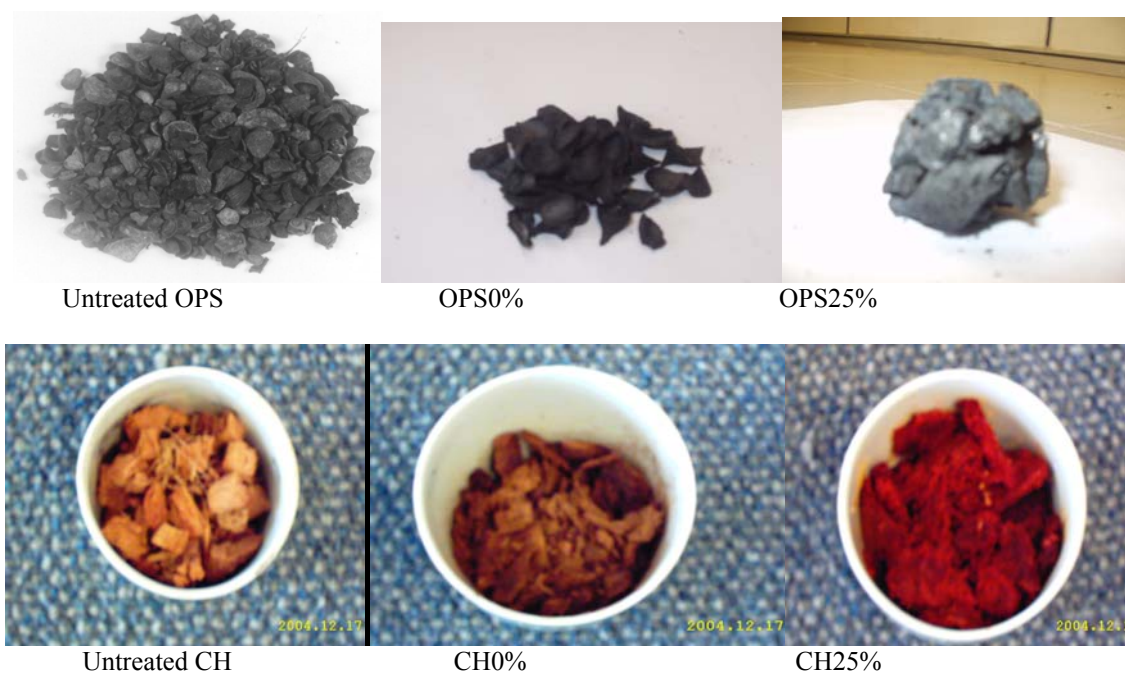


Figure 3: Photographs of the untreated OPS, OPS0%, OPS25%, untreated CH, CH0% and CH25%

Scanning Electron Microscopy

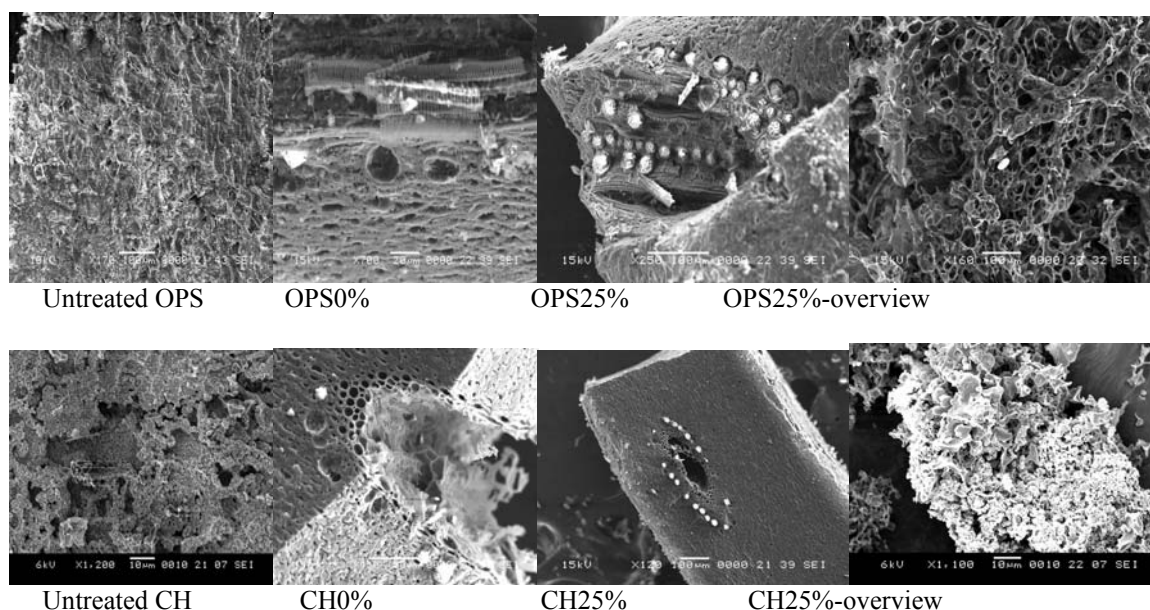


Figure 4: The electron micrographs of untreated OPS, OPS0%, OPS25% OPS25%-overview, untreated CH, CH0%, CH25% and CH25%-overview.

SEM was used to study the morphological structure on the prepared activated carbons. The surface structures of the untreated OPS and CH have dirt-covered and unclear pores. The surface structures of the physically activated carbons (OPS0% and CH0%) have clean and burnout pores with tunnel or honeycomb-like structures. The chemically impregnated activated carbons, OPS25% and CH25% also showed similar traits but some of the pores were clogged with potassium salts even after undergoing washing process. If the morphological structures are viewed as a whole (OPS25%-overview and CH25%-overview), we can see that the structure is completely different as compare to OPS and CH respectively. This was due to the reaction of KOH with the lignocellulosic material (OPS and CH) giving a burn-out sponge-like structure. These findings correspond with the physical appearance results of the activated carbons. Our results suggest that the chemical activators played an important part in clearing, restructuring and producing better pores. These findings are consistent with the findings of other researchers. Potassium compounds are effective catalyst for activation [26].

Conclusion

In conclusion, this study showed that the use of dehydrating agent and the two-step process in a self-generated atmosphere played a major role in shaping and transforming precursors into activated carbons. Granular KOH was used as a dehydrating agent, produced a very different activated carbon, changing not only the pore structure and morphology of the activated carbon but also giving the sponge-like physical appearance of the precursor itself. The precursors (OPS and CH) were changed from their natural forms to take the shape of the reactors. It is our opinion that extensive gasification coupled with activation temperature of 500°C contributed to this change.

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Reference

1. Anuar, K., Collin, G. J., Zulkarnain, Z., Hussein, M. Z., Haron, M.J. dan Abdullah, A. H. (2003) "Surface area and porosity studies of activated carbons prepared from oil palm shells (*Elaeis Guineensis*) using physical and chemical activators such as CO₂, H₃PO₄, K₃PO₄ and KOH" *ASEAN J. of Sci. And Tech. For Dev.*, 20(2), 149-158.
2. Anuar, K., Collin, G. J., Zulkarnain, Z., Hussein, M. Z., Haron, M.J. dan Abdullah, A. H. (2004) "Activated carbons prepared from oil palm shells : application for column separation of heavy metals" *Indian Chem. Soc.*, 81(12), 946-949.
3. Anuar, K., Collin, G. J., Zulkarnain, Z., Hussein, M. Z., Haron, M.J. dan Abdullah, A. H. (2002) "Preparation and characterization of activated carbon from Resak wood (*Vatica Hullettii*): surface area and porosity studies" *Oriental J. of Chem.*, 18(1), 43-46.
4. Anuar, K., Collin, G. J., Zulkarnain, Z., Hussein, M. Z., Haron, M.J. dan Abdullah, A. H. (2001) "Preparation and characterizations of activated carbon from Resak wood (*Vatica Hullettii*)" *Res. J. of Chem. Environ.*, 5(3), 21-24.
5. Gergova, K., Petrov, N., Eser, S. (1994) "Adsorption properties and microstructure of activated carbons produced from agricultural by-products by steam pyrolysis" *Carbon*, 32, 693-702.
6. Marsh, H., Crawford, T.M., O'Grady, T.M., Wennerberg, A.N. (1982) "Carbons of high surface area. A study by adsorption and high resolution electron microscopy" *Carbon*, 20, 419-426.
7. O'Grady, T.M., Wennerberg, A.N. (1986) Petroleum-Derived Carbons, High-Surface-Area Active Carbon, in: ACS Symposium Series, 303, *American Chemical Society*, 302.
8. Ottawa, T., Nojima, Y., Miyazaki, T. (1997), "Development of KOH activated high surface area carbon and its application to drinking water purification" *Carbon*, 35, 1315-1319.
9. Ottawa, T., Tanibata, R., Itoh, M. (1993) "Production and adsorption characteristics of MAXSORB: High-surface-area active carbon" *Gas Sep. Purif.*, 7, 241-245.
10. Ahmadpour, A., Do, D.D., (1996) "The preparation of active carbons from coal by chemical and physical activation" *Carbon*, 34, 471-479.
11. Ahmadpour, A., Do, D.D. (1997) "The preparation of activated carbon from macadamia nutshell by chemical activation" *Carbon*, 35, 1723-1732.
12. Hu, Z.H., Vansant, E.F. (1995) "Chemical activation of elutrilite producing carbon-aluminosilicate composite adsorbent" *Carbon*, 33, 1293-1300.
13. Laine, J., Calafat, A. (1991) "Factors affecting the preparation of activated carbons from coconut shell catalized by potassium" *Carbon*, 29, 949-953.
14. Hu, Z.H., Srinivasan, M.P. (1999) "Preparation of high-surface-area activated carbons from coconut shell" *Micropor. Mesopor. Mater.* 27, 11-18.
15. Kirubakaran, J.C., Krishnaiah, K., Sheshadri, S.K. (1991) *Ind. And Eng. Chem. Res.*, 30, 2411.
16. Toles, C. A., Marshall, W.E., Johns M.M. (1998) *J. Chem. Tech.*, 72, 255.
17. Dastgeib S.A., Rockstraw D.A. (2001) "Pecan shell activated carbon: synthesis, characterization, and application for the removal of copper from aqueous solution" *Carbon*, 39, 1849-1855.
18. Lafi W.K. (2001) "Production of activated carbon from acorns and olive seeds" *Biomass and Bioenergy*, 20, 57-62.
19. SIRIM (1984). Specification of powdered activated carbon MS 873: Standard and Industrial Research Institute Malaysia.
20. Kirkaldy, J.L.R., Sutanto, J.B. (1976) *Planter Kuala Lumpur*, 52, 118.
21. Wigmans, T. (1989) "Industrial aspects of production and use of activated carbons" *Carbon*, 27, 13-22.
22. Lamond, T.G., Marsh, H. (1963) "The surface properties of carbon—III the process of activation of carbons" *Carbon*, 1, 293-302.
23. Chan, K.C., Goh, S.H., Ing, T.W. (1976) *Planter Kuala Lumpur*, 52, 127
24. Fong, A.W., (1999) Panduan Penanaman Kelapa, Jabatan Pertanian Sabah. No. 112/IC/1999.
25. Jankowska, H., Swiatkowski, and Choma, (1991) J., *Active Carbon*, Elis Horwood Ltd.
26. Anuar, K., Collin, G. J., Dzulkefly, K., Zulkarnain, Z., Hussein, M. Z., Haron, M.J. dan Abdullah, A. H. And Jamaluddin D. (2004) "Activated carbons from oil palm shells (*Elaeis Guineensis*)-preparation and characterization" *Mal. J. Of Anal. Sci.*, 8(1), 130-134.
27. Collin G. Joseph, Fauziah Hj. Abdul Aziz, Hasnul Fazli Md. Zain, dan Siti Fatimah Dek, 2005, Treatment of Landfill Leachate In Kayu Madang, Sabah: Porosity and Adsorption Studies (Part 2), *Asian Chem. Letters*, 10(3), (in press). ↵