

PREPARATION AND PHENOLS ADSORPTION PROPERTY OF POROUS CARBON FROM OIL PALM EMPTY FRUIT BUNCHES

Yap Yee Ling, Mohamad Deraman, Mohamad Hafizuddin Jumali, Ramli Omar, Astimar Abdul Aziz, Abubaker Elshiekh Abdelrahman, Tang Hon Peng, Julia Tan Meihua, Masliana Muslimin and Mazliza Mohtar

*School of Applied Physics, Faculty of Science and Technology,
Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor Darul Ehsan*

ABSTRACT

Porous carbons were prepared from the potassium hydroxide (KOH) treated self-adhesive carbon grains (SACG) produced by ball milling and sieving of the pre-carbonized oil palm empty fruit bunch (EFB). The SACG were treated with KOH at different percentages (0-70 % by weight). The treated SACG was carbonized at 700 °C in nitrogen environment using a multi-steps heating profile. After carbonization, the carbon powders were cooled to room temperature, washed with distilled water and hydrochloric acid solution. Characterization by nitrogen adsorption isotherm at 77 K showed that the surface area and pore volume of the carbon powders increased as the percentages of KOH increased, they are dominated by micropores. The maximum surface area of 432 m²/g was obtained for the sample treated with KOH 70 wt %. Batch adsorption was carried out at room temperature to determine the adsorption of phenols by the carbon powders. Percentages removal of phenols by the carbon powders using adsorption isotherms found to be increased as the surface area and pore volume increased. The percentages removal of phenol for sample treated with KOH 70 wt % is 72 %, which is only 22 % inferior to the commercial carbon. In order to describe the isotherm mathematically, the experimental data of the removal equilibrium were correlated by the Freundlich and Langmuir equations and the result showed that the phenol adsorption isotherm of all samples seen to fit the Freundlich and Langmuir adsorption isotherm model satisfactorily and indicated that the adsorption condition is favourable. The scanning electron microscopy (SEM) study of the carbon powders showed the enhancement of porous structures as the percentages of KOH increased.

INTRODUCTION

There are many forms of carbon products in the market, for example, cokes, graphites, carbon and graphites fibers, carbon fibers-carbon matrix composites, adsorbent carbons and monoliths, glassy carbon, engineering carbons, carbon blacks, carbon films, diamond like films, carbynes, fullerenes, carbon nanoparticles, carbon nanotubes, carbon nanocones and multiwall carbon spheres. Typical categories of precursor for

carbon product are hydrocarbons, petroleum, coal, polymer and biomass from palm oil industry such as oil palm stones [1] and oil palm empty fruit bunches (EFB) [2]. Annual production of EFB is estimated about 8.5 million metric tonnes [3].

Porous carbons such as activated carbons are particularly useful and commonly used owing to their large adsorption capacity, fast adsorption kinetics and relative ease of regeneration. They adsorb organic and other non-polar compounds from liquid and gaseous phases. In practice, activated carbon is found in two general forms: granular activated carbon (GAC) and powdered activated carbon (PAC). GAC by definition is composed of particles with sizes greater than 0.8 mm, whereas PAC is composed of particles smaller than that value. GAC is generally said to have a larger internal surface area and smaller internal pores, while PAC is thought to have larger pores and a smaller internal surface area [4].

There are two principal methods for making activated carbon, namely a high temperature oxidation with steam of a previously charred carbonaceous substance (coal, char and charcoal) and a lower temperature chemical dehydration or chemical reaction of a carbonaceous raw material [4]. Inexpensive sources and cost-effective preparation methods are in demand because of the importance of adsorption in pollution control.

Result from previous studies showed that KOH treatment is able to increase the surface area and pore volume of the porous carbon pellet prepared from SACG [5,6]. The porosity of these carbon pellet changed with the concentration of KOH. The mechanism of reaction between KOH and carbon samples can be found elsewhere [7-9].

In this study, the porous carbon from SACG was prepared in powder form. The objective of this study is to investigate the effect of KOH concentration on the morphology and porosity of carbons powder prepared from SACG and also their ability to adsorb phenols. Studies on adsorption of phenols from aqueous solutions by activated carbon from others precursors have been widely reported [10-13].

MATERIAL AND METHOD

The raw material used in this study is oil palm empty fruit bunch (EFB). EFB fibres were pre-carbonized at low temperature based on method previously reported [14]. Then, the pre-carbonized EFB was ball milled for 20 h and sieved in order to obtain SACG with particle sizes $\leq 53 \mu\text{m}$. Next, the SACG was treated with potassium hydroxide (KOH) with 5 different percentages of concentrations (0 %, 10 %, 30 %, 50 % and 70 % by weight, designated as samples A, B, C, D, E respectively) at room temperature. For each concentration, 100 g of SACG was mixed with 325 ml of water and stirred by a magnetic stirrer for 1 h at room temperature. The treated SACG was left for 24 h for reaction before it was dried in an oven at 110 °C for 48 h. The dried mixture was ball milled again for 5 h to form fine powder that can pass through 53 μm sieve. Carbonization of the treated SACG powder was carried out in a furnace (Vulcan Box Furnace 3-1750) using a multi step heating profile. The samples were heated in a nitrogen stream of 1.0-1.5 l per minute at the rate of 1 °C per minute from room temperature to 375 °C at which they were kept for 1 h, followed by 3 °C per minute from 375 °C to 700 °C. After carbonization, the samples were cooled down under

nitrogen flow and then washed with distilled water to remove residual chemical. Subsequently, the samples were transferred to a beaker containing 300 ml of 0.5 M hydrochloric acid solution, soaked for 24 h, and then washed with distilled water again until the pH of the washed solution was about 6 to 7. The carbon powder was then dried in an oven at 110 °C for a 24 h. The dried carbon powder was then ball milled again for 1 h into fine powder that can pass through 250 µm sieve before subjecting them to characterization and phenol adsorption test.

The N₂ adsorption-desorption isotherms data for the samples S0 to S7 were recorded at liquid nitrogen temperature (77 K) using volumetric adsorption apparatus (Micromeritics ASAP 2010) in order to determine their surface areas and pore volumes. The specific surface area and micropore volume of the samples were determined from nitrogen adsorption isotherms by the standard BET and s t-plot methods respectively. The microstructure of the samples was recorded, with the magnifications of 2000X and 10000X, using a scanning electron microscope (LEO 1450 VPSEM).

Wastewater containing traces of organic compounds is a serious environmental problem. The presence of phenol and phenolic compound in water is of great public concern, because they can cause toxicity on human health even when present in small concentration. The threshold value of phenol in water is 4000 µg/l [10]. Considering this limit, it is necessary to remove the phenol from industrial effluents before discharging into the water stream. Studies on the adsorption of phenol by activated carbon are numerous [10-13]. In the present study, adsorption isotherms were determined using the batch equilibration technique at room temperature [4]. A series of 250 ml conical flasks containing 0.05 g of carbon sample and 100 ml of phenols solution were sealed and shaken at room temperature until equilibrium was obtained. Subsequently, the adsorbents were removed by filtration using 0.45 µm nylon membrane filter. The residual concentration of phenol in the solution was measured by UV-visible spectrophotometer (Double beam, Shimadzu UV-160A) using wavelength of 269 nm. The percentage adsorption of phenol was computed in the usual way.

RESULTS AND DISCUSSION

The plot in Figure 1 shows that all the samples have the characteristic of microporous solids, since they exhibited type I isotherm according to the IUPAC classification [15]. The isotherms of the all treated samples, B to E, have more rounded knee, indicating a wider pore size distribution compared with that of the untreated sample, A. The treated samples also show higher adsorption capacity for higher KOH percentages, suggesting that pore volume increases significantly due to KOH treatment.

The values of the BET surface area, micropore surface area, mesopore surface area and micropore volume obtained from the adsorption data are listed in Table 1. The data suggest that all the samples are made up of highly microporous structures with very low mesoporosity, and in such a case it is obvious that the dominant portion of surface area comes from the micropore [4]. The values of these parameters, except for the mesopore surface area, seem to increase sharply for the treatment up to 10 % KOH, and beyond this, the data show a very gradual increase. For higher increases of phenol adsorption,

the treatment requires 30 percent or higher KOH component, but in this region the adsorption level appear to vary with small increment. This demonstrates that at higher concentration, the BET and phenol adsorption data are more consistent.

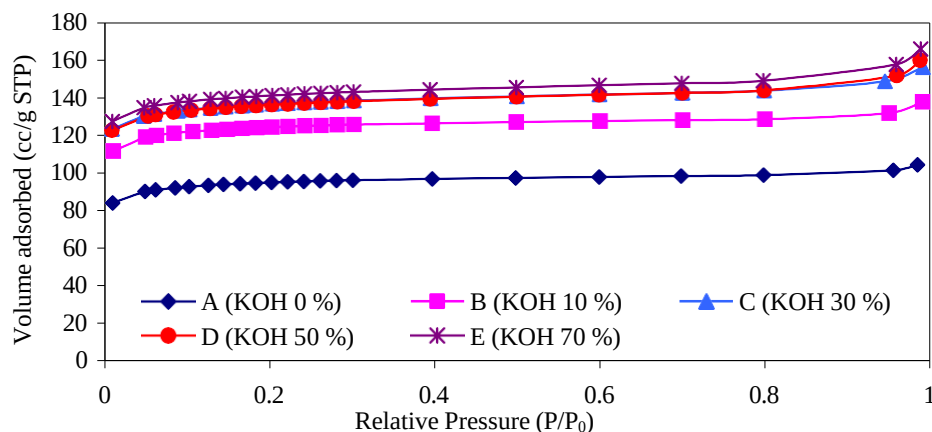


Figure 1: N₂ adsorption isotherms (77 K) corresponding to the porous carbons prepared with KOH treatment using different KOH weight percentage.

Table 1: Surface areas, pore volumes and phenol adsorption capability of SACG-derived carbons and commercial carbon

Sample ID		A	B	C	D	E	Filtrisorb 100 *
BET Surface Area (m ² /g)		290.35	378.55	417.70	415.84	431.52	937.00
Micropore Surface Area (m ² /g)		245.66	328.66	357.03	354.08	369.30	-
Mesopore Surface Area (m ² /g)		44.69	49.88	60.67	61.75	62.22	-
Micropore Volume (cm ³ /g)		0.1271	0.1703	0.1847	0.1836	0.1910	-
Phenol Adsorbed (mg/g)		13.09	21.32	61.10	64.46	68.01	89.27
Concentration Of Phenol Solution (mmol/l)	Initial	0.5	0.5	0.5	0.5	0.5	0.5
	Final	0.4305	0.3867	0.1754	0.1575	0.1387	0.0257
Loading (mmol/l)		0.0695	0.1133	0.3246	0.3425	0.3613	0.4743
Efficiency (%)		13.91	22.65	64.92	68.50	72.27	94.86

*The Data source for Fitratorb 100, a commercial carbon is from reference [12]

It is well known that the adsorption of low-polarity or non-polar organic compounds onto activated carbons is normally depend on the surface area and pore volume [11]. As can be seen in Table 1, the commercial carbon, which can removed 94.86 % of phenols, has a very high BET surface area. For example, the adsorption capacity of the sample E

is 22 % inferior compared to the commercial carbon. However, improvement can still be made in order to produce high quality carbon from SACG.

The adsorption isotherms of phenol for the samples C to E were tested with the logarithmic form of Freundlich model

$$\log \frac{x}{m} = \log q_e = \log K_f + \frac{1}{n} \log C_e \quad (1)$$

where q_e is the mass of the adsorbate adsorbed per unit mass of adsorbent (mg adsorbate/g adsorbent), K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively, while C_e is the equilibrium concentration of the adsorbate (mg/l) [17].

The plot of $\log (x/m)$ against $\log C_e$ for the samples C, D and E are given in Figure 2, which clearly shows that the data is well fitted to the Freundlich model. The values of the Freundlich constants K_f and n are estimated from the best-fit line and they are presented in Table 2.

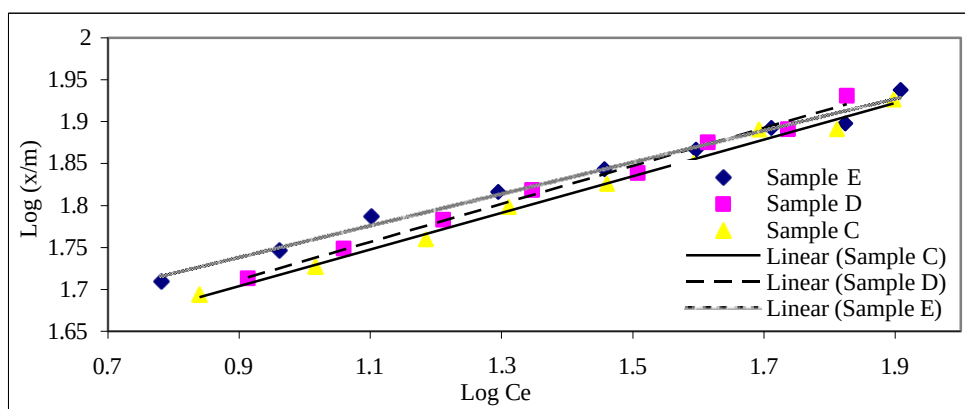


Figure 2: Freundlich adsorption isotherm for phenols on samples C, D and E.

Table 2: Parameter of phenol adsorption isotherms according to the Freundlich model.

Sample ID	Freundlich model				Recommended isotherm
	K_f	n	$\frac{1}{n}$	R^2	
C (KOH 30 %)	32.16	4.577	0.2185	0.9914	$\frac{x}{m} = 32.16C_e^{0.2185}$
D (KOH 50 %)	32.18	4.417	0.2264	0.9911	$\frac{x}{m} = 32.18C_e^{0.2264}$
E (KOH 70 %)	36.96	5.294	0.1889	0.9894	$\frac{x}{m} = 36.96C_e^{0.1889}$

The magnitude of the Freundlich exponent $1/n$ is an indication of the favourability and capacity of the adsorbent-adsorbate systems [16]. The values of $0 < 1/n < 1.0$, shown in

Table 2, indicate that activated carbon from the treated SACG exhibit a favourable condition for phenol adsorption.

The Langmuir model is represented by a linear equation in the following form

$$\frac{C_e}{(x/m)} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (2) \quad \text{or} \quad \frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (3)$$

where C_e is the equilibrium concentration of the adsorbate (mg/l), q_e is the mass of the adsorbate adsorbed per unit mass of adsorbent (mg adsorbate/g adsorbent), and Q_o and b are the Langmuir constants related to adsorption capacity and energy of adsorption respectively [17]. When $C_e/(x/m)$ were plotted against C_e , a straight line with slope $1/Q_o$ is obtained (Figure 3), which shows that the adsorption of phenol follows the Langmuir isotherm. The Langmuir constants, b and Q_o are determined and the values are given in Table 3.

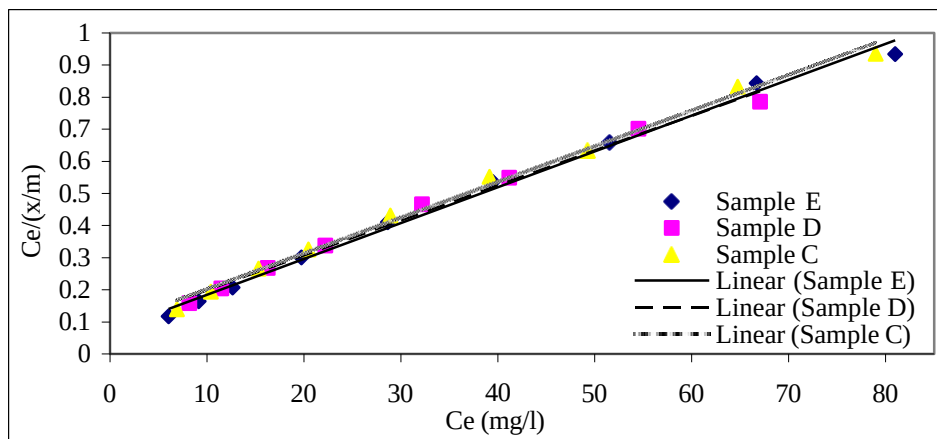


Figure 3: Langmuir adsorption isotherm for phenols on samples C, D and E.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , and is defined as follows

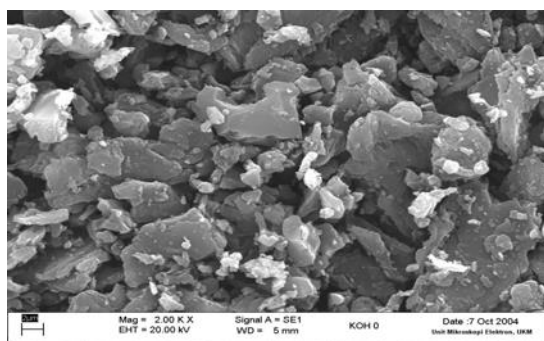
$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

where C_0 is the initial concentration of phenol (mg/l) and b is the Langmuir constant (l/mg) [18]. The parameter R_L indicates the shape of the isotherm accordingly, and if $0 < R_L < 1$, the isotherm is favourable. The values of R_L shown in Table 3 indicate a favourable adsorption.

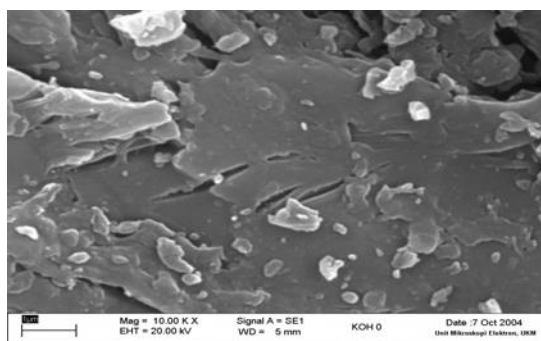
Table 3: Parameter of phenol adsorption isotherms according to the Langmuir model.

Sample ID	Langmuir model				Recommended isotherm
	Q_0 (mg/g)	b (l/mg)	R_L	R^2	
C (KOH 30 %)	90.09	0.1217	0.0790	0.9942	$\frac{x}{m} = \frac{10.96C_e}{1 + 0.1217C_e}$
D (KOH 50 %)	91.74	0.1208	0.0756	0.9925	$\frac{x}{m} = \frac{11.09C_e}{1 + 0.1208C_e}$
E (KOH 70 %)	89.29	0.1530	0.0623	0.9941	$\frac{x}{m} = \frac{13.66C_e}{1 + 0.1530C_e}$

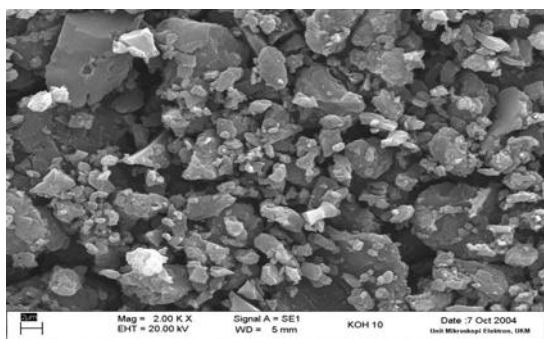
The SEM micrographs of the carbon powders are shown in Figure 4. These micrographs show the changes of their porous structures, that is, increase of more pores and spot of pores, as the percentages of KOH increased. Rounded pores are the spaces from the removal of impregnated KOH and KOH-derived compounds. These are not present in the untreated SACG carbon, where it has more compact structure and smoother surface, indicating that less pore development occurs inside the particles.



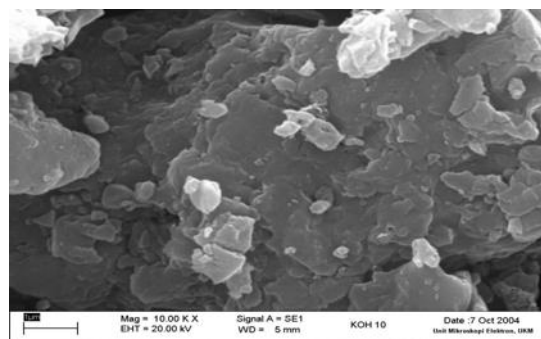
(a) Sample A (KOH 0 %) (magnification 2000X)



(b) Sample A (magnification 10000X)

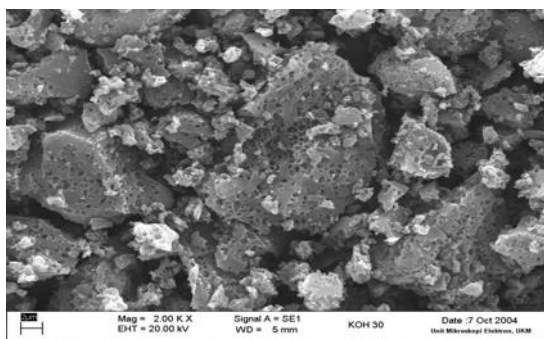


(c) Sample B (KOH 10 %) (magnification 2000X)

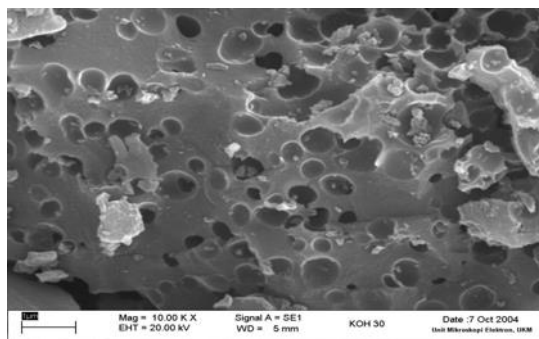


(d) Sample B (magnification 10000X)

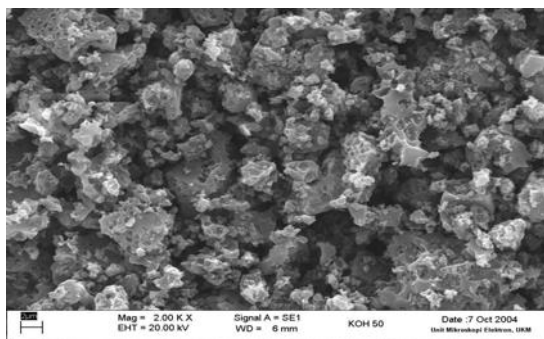
This study shows that treatment of the SAGC with KOH increase the porosity of porous carbon from SAGC and affect the final porous texture of the porous carbon. The surface area and pore volume of the resulting porous carbons increased with increasing amount of KOH added to the SAGC. The BET surface area and micropore volume increase significantly from 10 percent KOH, but further increase in the BET surface area and micropore volume are very small for treatment with higher percentage of KOH. All the samples are highly microporous with very low mesoporosity. As expected, the adsorption capacity of the porous carbon was found to increase with the percentage of KOH treatment and surface area. These shows that the adsorption of low-polarity or non-polar organic compounds onto activated carbons is dependent on the surface area and pore volume. Data from the adsorption isotherm of phenols seem to fit the Langmuir and Freunlich adsorption isotherm model satisfactorily. This indicates that the porous carbons produced from SAGC are good adsorbent.



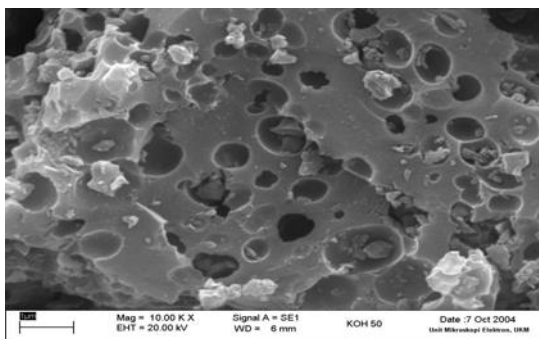
(e) Sample C (KOH 30 %) (magnification 2000X)



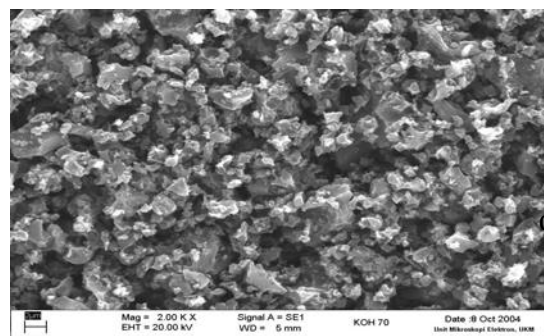
(f) Sample C (magnification 10000X)



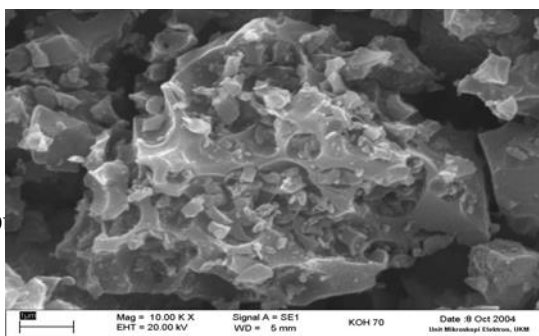
(g) Sample D (KOH 50 %) (magnification 2000X)



(h) Sample D (magnification 10000X)



(i) Sample E (KOH 70 %) (magnification 2000X)



(j) Sample E (magnification 10000X)

CONCLUSIONS

ACKNOWLEDGEMENT

IRPA grant (Code 09-02-02-0022-EA077) for the project entitles “Advanced Carbon Product from Oil Palm Bunches” and scholarship of NSF (Ref: KSTAS.S190.080, th. 2003) from MOSTE for Yap Yee Ling, and the assistance of Mr. Saini Sain are gratefully acknowledged.

REFERENCES

- [1] Lua, A. C. and Guo, J. (2000); *Carbon*. **38**, 1089-1097.
- [2] Deraman, M., Omar, R., Zakaria, S., Talib, M., Mustapa, I. R., Azmi, A. and Abdul Aziz, A. (2004); *Advances in Polymer Technology*. **23 (1)**, 51-58.
- [3] Palm Oil Registration and Licencing Authority [PORLA]. (1997); *Review of the Malaysian Palm Oil Industry 1996*. (1997); Malaysia: Ministry of Primary Industry. pp. 9.
- [4] Jerry, R. P. (1981); *Activated Carbon Adsorbtion For Waste Water Treatment*. CRC Press Inc., United States.
- [5] Abdul Rahman, R. M. and Deraman, M. (2004); *Proceeding of the Postgraduate Colloquium, FST, UKM*. 106-108.
- [6] Abdelrahman, A. E., Deraman, M. and Omar, R. (2003); *Suranaree J. Sci. Technol.* **10(3)**, 191-197.
- [7] Teran, J. D., Nevskaia, D.M., Fierro, J. L. G., Peinado, A. J. L. and Jerez, A. (2003); *Microporous and Mesoporous Material*. **60**, 173-181.
- [8] Guo, J. and Lua, A. C. (2002); *Journal of Colloid and Interface Science*. 254, 227-233.
- [9] Rodenas, M. A. L., Amoros, D. C. and Solano, A. L. (2002); *Carbon*. **41**, 267-275.
- [10] Qadeer, R. and Rehan, A.H. (2002); *Turk. J. Chem.* **26**, 357-361.
- [11] Hu, Z. and Srinivasan, M.P. (1999); *Microporous and Mesoporous Materials*. **27**, 11-18.
- [12] Castilla, C.M., Utrilla, J. R., Ramon, M.V.L. and Marin, F.C. (1995); *Carbon*. **33**, 845-851.
- [13] Lu, Q. and Sorial, G.A. (2004); *Carbon*. **42(15)**, 3133-3142.
- [14] Deraman, M. Omar, R. and Harun, A. G. (1998); *J. Mater. Sci. Letters*. **17**, 2059-2060.
- [15] Gregg, S.J. and Sing K.S.W. (1982); *Adsorption, Surface Area and Porosity*. Academic Press Inc., United States.
- [16] Krishnan, K.A. and Anirudhan, T.S. (2003); *Water South Africa*. **29(2)**, 147-156.
- [17] Metcalf and Eddy. (2003); *Waste Water Engineering: Treatment and Reuse*. McGraw-Hill Higher Education, New York.

- [18] Weber, T.W. and Chackravorti, R.K. (1974); *Amer. Inst.Chem. Eng. J.* **20**, 228-238.