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PREPARATION AND CHARACTERIZATION OF ADSORBENTS FROM OIL PALM FRUIT SOLID WASTES

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*Preparation and characterization of activated carbons from **oil** palm **fruit** solid wastes were studied. The effects of activation conditions (CO_2 flow rate, activation temperature and retention time) on the characteristics of the activated carbons, namely density, porosity, BET surface area, pore size distribution and surface chemistry were investigated. The optimum conditions for activation were an activation temperature of 800°C and a retention time of 30 min for fibre or 50 min for shell, which gave the maximum BET surface area. Adsorption tests showed that the activated carbons from oil palm fibre and shell could be used as adsorbents for both liquid-phase and gas-phase adsorption.*

INTRODUCTION

Extracted mesocarp fibre (or exocarp) and fruit shell (or endocarp) are two major solid wastes from palm oil mills (Singh, 1994). In Malaysia, the largest palm oil producer in the world, about two million tonnes (dry weight) of shell and one million tonnes of extracted fibre are generated annually (Tay, 1991). Normally, they are used as boiler fuels or building materials. To make better use of these cheap and abundant wastes, it is proposed to make them into effective adsorbents or activated carbons. Preliminary characterization has shown it feasible to prepare chars with sufficient densities and high porosity from oil palm fruit wastes (Lua and Guo, 1998; Guo and Lua, 1998). In fact, some oil palm solid wastes have already been successfully made into activated carbons. Normah *et al.* (1995) prepared activated carbon from oil palm shell by steam gasification. The optimum duration of activation was 45 min which gave a specific surface area of 710 m^2 g^{-1} and a yield of 21%. Hussein *et al.* (1996) found

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that activated carbon from palm shell by $ZnCl_2$ activation was essentially microporous with a fairly high surface area of 1500 m^2 g^{-1}. However, this method involves using some chemicals, which may generate secondary environmental pollution.

The aim of this work was to prepare and characterize activated carbons from oil palm fruit fibre and shell for adsorption in gaseous- and/or aqueous-phases. The effects of CO_2 activation conditions, such as CO, flow rate, activation temperature and retention time, on the textural and chemical properties of the activated carbons were investigated to optimize the process.

EXPERIMENTAL

Sample Preparation

As - received oil palm fruit fibre and shell were first dried at 110°C for 24 hr to reduce the moisture content, The dried fibre and shell were then cut, ground and sieved. Size fractions of 0.5-1.0 mm for fibre and 2.0-2.8 mm for shell were used. Both pyrolysis and activation were carried out in a stainless steel reactor (550 mm length and 38 mm internal diameter) placed in a vertical tube furnace (818P, Lenton). About 15 g of the materials were placed on a metal mesh in the reactor. During pyrolysis, purified nitrogen at a flow rate of 150 cm^3 min^{-1} was used as purge gas. The furnace temperature was increased from room temperature to 600°C and held at this temperature for two hours. The resulting chars were then activated at 500°C 900°C for 10-60 min under a CO, flush of various flow rates. In both processes, a heating rate of 10°C min^{-1} was used. The characteristics of the starting materials and chars are listed in *Table 1.* Oil palm fibre and shell appeared to he suitable raw materials for making high quality activated carbons because of their inherent high densities and carbon contents, especially after pyrolysis.

Textural Characterisation

A thermogravimetic analyser (TA-50, Shimadzu) was used for proximate analysis of volatile matter (VM), fixed carbon (FC) and ash (AS). An ultra-pycnometer (UPY-1000, Quantachrome) and a mercury intrusion porosimeter (Poresizer-9320, Micromeritics) were used to measure the solid and apparent densities, respectively. For a known solid density, ρ_s, and apparent density, ρ_a, the porosity, ε, can be calculated by $\varepsilon = [(\rho_s-\rho_a) / \rho_s] \times 100\%$. Adsorption characteristics were determined by nitrogen adsorption at -196°C with an accelerated surface area and porosimeter (ASAP-2000, Micromeritics). The BET surface area (S_{BET}) was calculated from the adsorption isotherms and the pore size distribution calculated using the BJH model (Gregg and Sing, 1982). A scanning electron microscope (S360, Cambridge Instruments) and a transmission electron microscope (JEM2010, Leco) were used to verify the presence of porosities on the sample surface and to study the atomic structure of the sample, respectively.

Chemical Characterization

An X-ray diffractometer (PW-1830, Philips) was used to investigate the surface inorganic components of the activated carbons. The X-ray patterns were recorded in the scan range 26 = 10°-70°, at a scan rate of 0.1 min^{-1} The surface organic functional groups were studied by Fourier

TABLE 1. CHARACTERISTICS OF OIL PALM FRUIT SOLID WASTES AND DERIVED CHARS

Sample	Density and porosity			Proximate analysis (wt.%)			Surface area (m^2 g^{-1})
	ρ_s ($g\ cm^{-3}$)	ρ_a ($g\ cm^{-3}$)	ε (%)	VM	FC	AS	S_{BET}
Oil palm fibre	1.66	1.62	2.4	80.8	18.3	0.9	1.2
Fibre char	1.73	1.29	25.4	30.9	62.4	6.7	266
Oil palm shell	1.53	1.47	3.9	77.6	19.8	2.6	1.5
Shell char	1.62	1.31	19.1	34.5	59.4	6.1	147

transformed infrared spectroscopy (FTIR-2000, Perkin Elmer). The spectra were recorded from 4000 to 400 cm-‘.

Adsorption Test

Adsorption of NO, and SO,, two representative gaseous pollutants, was also carried out in the TGA. NO, or SO, (2000 ppm, balanced by N_2) was introduced into the analyser chamber, where a platinum sample holder with about 20 mg sample was suspended. At room temperature (30°C), the subsequent sample weight gain due to the amount of NO, or SO, adsorbed was recorded. In addition, adsorption of iodine from solution was determined. Samples of 100 mg were equilibrated with 25 cm^3 of I_2/KI solution for one hour. The value taken for monolayer coverage was the amount adsorbed at a free concentration of 0.5 mmol dm^{-3}.

RESULTS AND DISCUSSION

Density and Porosity

The density of an activated carbon depends on not only the nature of its raw material but also its preparation (Pandolfo *et al.,* 1994). *Table* 2 shows the weight losses, densities and porosities of the activated carbons prepared from oil palm fibre and shell under different activation conditions. For the same retention time (30 min for fibre and 50 min for shell), increasing the activation temperature up to 800°C increased the solid densities (nevertheless all were less dense than pure graphite at of 2.25 cm^3 g^{-1}) and decreased the apparent densities, resulting in the development of porosity. However, with an activation temperature of 900°C, the apparent density increased and porosity decreased. This was probably due to excessive burn off of carbon, accompanied by a marked weight loss, resulting in a reduction of porosity.

Surface Area

The most important property of activated carbon is its adsorptive capacity, which is related to its specific surface area. Generally, the higher the surface area, the larger is its adsorptive capacity (No11 et al., 1992). The effects of CO, flow rate on the BET surface areas of the fibre and shell derived activated carbons prepared at 800°C for 30 and 50 min, respectively, are shown in ***Figure 1.*** With a low CO, flow rate, the BET surface area was small due to an insufficient amount of CO, reacting with the carbon to produce pores. But, with a flow rate which was too high, the carbon-CO, reaction was so severe that excessive carbon was burnt off, reducing the quality of the activated carbon. From the results, a flow rate of 100 cm^3 min^{-1}, which yielded the highest BET surface area, was used for subsequent experiments.

Figures 2 and 3 show the BET surface areas of the activated carbons prepared from shell and fibre under various activation temperatures, respectively. For shell at the low temperature of 500°C, increasing retention time resulted in a proportionate increase in BET surface area. At 800°C, for up to 50 min retention time, the

TABLE 2. DENSITIES AND POROSITIES OF ACTIVATED CARBONS PREPARED

Sample	Activation temperature °C	Retention time (min)	Weight loss (%)	ρ_s ($g\ cm^{-3}$)	ρ_a ($g\ cm^{-3}$)	ε (%)
	500	30	**42.1**	1.87	1.13	39.6
	600	30	51.3	**1.95**	**0.97**	50.3
Palm fibre	700	30	58.4	2.02	0.92	54.5
	800	30	60.7	2.09	0.88	57.9
	900	30	78.3	2.14	1.24	42.1
	500	50	52.4	1.80	**1.10**	**38.9**
	600	50	**58.9**	**1.83**	**0.90**	50.8
Palm shell	700	50	64.2	1.90	0.83	56.3
	800	50	66.8	**1.95**	**0.71**	63.6
	900	50	75.7	2.03	1.02	49.8

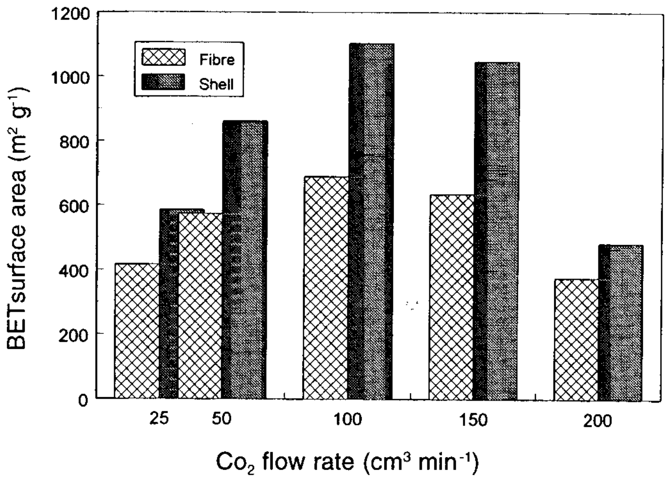

Figure 1. Effect of CO_2 flow rate on BET surface area.

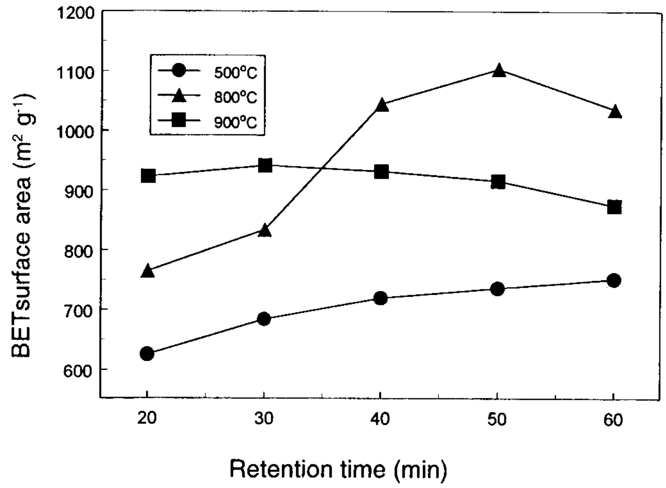

Figure 2. BET surface areas of activated carbon prepared from oil palm shell at various activation temperatures.

surface area increased progressively due to development of new pores, then decreased because of carbon burnt off from excessive exposure. At a higher temperature of 900°C, the surface area deteriorated from an initial high value with retention time. Oil palm fibre showed a similar trend. The optimum conditions for CO_2 activation to obtain maximum BET surface area were found to be an activation temperature of 800°C and a retention time of 50 min for oil palm shell and 30 min for fibre.

Pore Size Distribution

In the classification by the International Union of Pure and Applied Chemistry (IUPAC), pores are classified as micropores (<2 nm diameter), mesopores (2-50 nm diameter) and macropores (>50 nm diameter) (IUPAC, 1982). This classification is important because most molecules of gaseous pollutants vary from 0.4 to 0.9 nm in diameter. Gas-phase activated carbons usually consist predominantly of micropores whilst liquid-phase activated carbons have significant mesopores because of the larger sizes of liquid molecules.

Figure 4 shows the pore size distributions of activated carbons from oil palm fibre and shell prepared under different activation conditions. The shell activated carbon was a predominantly microporous. This predominance was more significant for the carbon prepared at 800°C for 50 min, and less so for the carbon prepared at

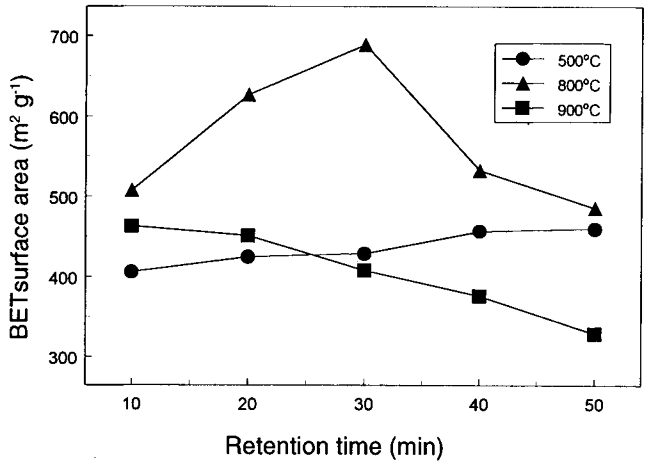

Figure 3. BET surface areas of activated carbons prepared from oil palm fibre at various activation temperatures.

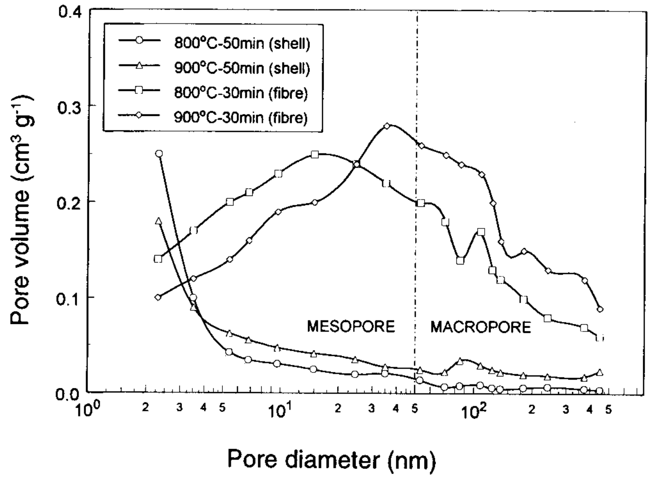

Figure 4. Pore size distributions of activated carbons from oil palm fibre and shell.

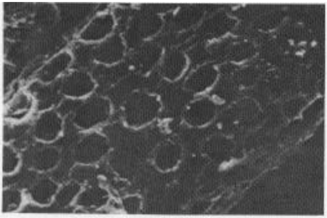

Figure 5a.

Figure 5b.

Figure 5. SEM micrographs of activated carbon surfaces: a) fibre; b) shell.

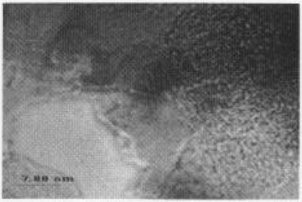

Figure 6a.

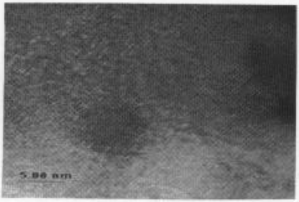

Figure 6b.

Figure 6. TEM micrographs of activated carbons a) fibre; b) shell.

900°C for 50 min which had more mesopores and macropores because of the severe reaction of carbon-CO, The high microporosity in shell activated carbon suggests potential applications in gas-phase adsorption for air pollution control However, fibre activated carbons had predominantly mesopores and macropores, which make them more suitable for liquid-phase adsorption in wastewater treatment Low magnification SEM micrographs (×1000) of the surfaces of the fibre and shell activated carbons (*Figures 5a* and *5b*) clearly showed the differences The fibre carbon had a more porous structure with abundant macropores, whereas the shell carbon had few cavities It could be seen from the TEM micrographs at high magnification (×10^6) that the shell carbon (*Figure 6b*) was a typical amorphous carbon. The gaps between different carbon atom layers (parallel lines) can be considered slit-shaped micropores, of mostly less than 2 nm. However, in the fibre carbon (*Figure 6a*), there was no regular carbon lattice, resulting in lower microporosity.

Surface Chemistry

The adsorptive capacity of the activated carbon is also influenced by its surface chemical structure (Bansal et al, 1988) X-ray diffraction (XRD) patterns of the chars and activated carbons from oil palm fibre and shell are shown in *Figure 7* For both chars, $CaCO_3$ as calcite

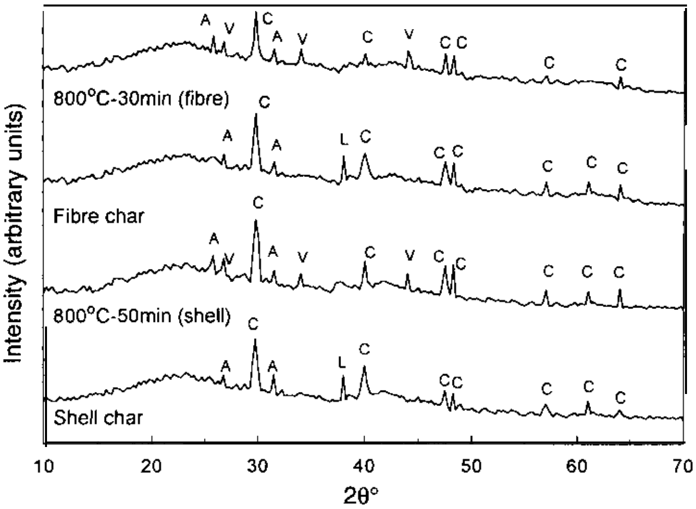

Figure 7. XRD patterns of the chars and activated carbons from oil palm fibre and shell.

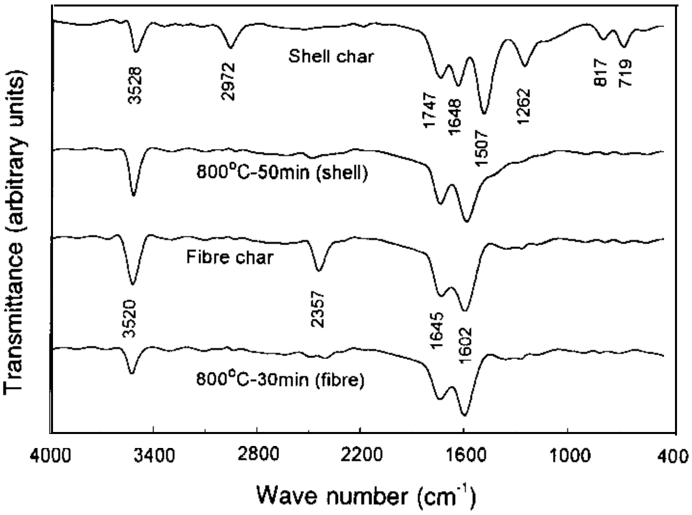

Figure 8. FTIR spectra of the chars and activated carbons from oil palm fibre and shell.

(C), $CaSO_4$ as anhydrite (A) and CaO as lime (L) were present. After activation, $CaCO_3$ as calcite and vaterite (V), and $CaSO_4$ as anhydrite were the dominant components without any lime peaks. The difference between the fibre and shell carbons was insignificant, but activation changed the inorganic surface component by transforming CaO into $CaCO_3$ by combining with atmospheric CO,.

The FTIR spectra of the chars and activated carbons are shown in Figure 8. The spectrum of the char from shell displayed the following bands: 3528 cm^{-1}: O-H stretching in alcohols; 2972 cm^{-1}: C-H stretching in alkanes, 1747 cm^{-1}: C=O stretching in ketones; 1648 cm^{-1}: C=O stretching in quinones; 1507 cm-i: C=C stretching in aromatic rings; 1262 cm-i: C-O stretching in ethers; 817 and 719 cm^{-1}: C-H out-of-plane bending in benzene derivatives. The spectrum of the fibre char displayed the following bands: 3520 cm^{-1}: O-H stretching in alcohols; 2357 cm^{-1}: C=O stretching in ketones; 1645 cm-i: C=O stretching in quinones; 1602 cm^{-1}: C=C stretching in aromatic rings. The main oxygen groups were suggested to be carbonyl groups (such as ketones and quinones), ethers and phenols in the shell char, and ketones, quinones and phenols in the fibre char. These results agree with the surface chemistries of other agricultural by-products, such as peach stones (Arriagada et al., 1997) and rockroses (Gomez-Serrano et *al.*, 1996). After CO, activation, the ether and ketonic groups were not found due to their instabilities in the slightly oxidative atmosphere, and only the quinones and phenols remained. These groups are typical organic functional groups on the activated carbon surface (Mattson and Mark, 1975). Hence, the difference in the surface chemistry between the shell activated and fibre activated carbons was insignificant.

Adsorptive Capacity

Both gaseous- and aqueous-phase adsorption onto the activated carbons prepared and some commercial activated carbons were carried out (*Table 3*). The commercial activated carbons tested include Microcarb® (Grade: FY5, surface area: 1150 m^2 g^{-1}) and Carbochem® (Grade: LQ-830, surface area: 950 $m^2 g^{-1}$). *Table* 3 shows that

TABLE 3. ADSORPTIVE CAPACITIES OF THE ACTIVATED CARBONS

Phase	Adsorbate	Adsorbent	Amount adsorbed ($mg\ g^{-1}$)
Gaseous	SO_2	Fibre activated carbon	38
		Shell activated carbon	76
		Microcarb®	71
	NO_2	Fibre activated carbon	136
		Shell activated carbon	219
		Microcarb®	194
Aqueous	Iodine	Fibre activated carbon	692
		Shell activated carbon	721
		Carbochem®	850

the shell activated carbon adsorbed much more gaseous pollutants and slightly more iodine from solution than the fibre carbon. Generally, the adsorptive capacities or the quality of the activated carbons from oil palm fruit solid wastes were comparable to those of commercial carbons.

CONCLUSION

Experimental results have shown that it is possible to prepare activated carbons with a high density and well developed porosity from oil palm fruit solid wastes. The CO, flow rate, activation temperature and retention time had important influences on the BET surface area. The optimum conditions for CO, activation to obtain maximum BET surface area were an activation temperature of 800°C and a retention time of 50 min for oil palm shell and 30 min for fibre. For inorganic components, $CaCO_3$ as calcite and vaterite, and $CaSO_4$ as anhydrite, were the dominant components. Quinones and phenols were detected as the main organic functional groups on the surfaces of both the activated carbons. The predominance of microporosity in shell activated carbon suggests its possible application as granular adsorbent in gas-phase adsorption for air pollution control; the fibre activated carbon consisted predominantly of mesopores and macropores, suggesting its application as powder adsorbent in liquid-phase adsorption for wastewater treatment. Gas-phase adsorption of SO, and NO, and liquid-phase adsorption of iodine onto the activated carbons, as well as comparison with some commercial activated carbons, confirmed these potential applications.

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