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Production of Palm Shell-Based Activated Carbon with More Homogeneous Pore Size Distribution

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Abstract: Oil palm shell as a raw material was used for the preparation of activated carbon adsorbents. The precursor was first activated chemically with small proportion of zinc chloride and phosphoric acid and then the prepared samples were treated with CO₂ flow at 850°C at different activation time. The samples activated chemically with phosphoric acid showed higher surface area and pore volume compared to the samples activated using zinc chloride as chemical agent, at the same duration. In addition, it was shown that extra physical activation will granteees more developed pore structure. In terms of pore size distribution the combined preparation method resulted in a better and more homogenous pore size distribution than the commercial palm shell based activated carbon.

Key words: Palm shell, activated carbon, chemical activation, physical activation, pore size distribution

INTRODUCTION

Activated carbons with highly developed internal surface area and porosity are described as solid sponges (Zanzi *et al.*, 2001). The large surface area of these carbonaceous materials results in a high adsorption capacity for gases or liquids. Activated carbons are versatile materials that are employed in a multitude of gas purification, gold purification, sewage treatment, water purification, metal extraction, medicine, air filters in gas masks and filter masks, filters in compressed air and many other applications. The storage and transport activity of fluids in these porous sorbents largely depend on the pore size distribution in the material. Hence, in order to develop the adsorptive and catalytic properties of these adsorbents, it is important to have the suitable Pore Size Distribution (PSD) as the sorbent. In fact, the potential of activated carbons to obtain both high surface area and homogeneous pore size distribution made these microporous materials more applicable for adsorption of various materials (Sing *et al.*, 1985). Table 1 shows the IUPAC convention in dividing the range of pore sizes into different groups.

The production of activated carbon can be assorted into two methods: chemical and physical treatments. Chemical activation has become widely employed because of the lower activation temperature (400-500°C compared to >850°C for physical activation) and higher carbon product yield. Among the commonly used chemical agents, H₃PO₄ and ZnCl₂ are used on a relatively large

Table 1: IUPAC Classification of pore sizes

Type	Pore size (Å)
Ultramicropore	≤7
Supermicropore	7 to 20
Mesopore	20 to 500
Macropore	≥500

scale (Baker, 1992). On the other hand, it was shown by Prauchner and Rodriguez-Reinoso (2008) that chemical activation generates carbons with more developed mesoporosity. Extra physical activation creates more homogeneous pore size distribution. Using low concentration of the chemical agents allows narrow micropores to develop without a significant decrease in bulk density. The primary pore structure generated by low proportion of chemicals would be develop more homogeneously by subsequent thermal activation (Prauchner and Rodriguez-Reinoso 2008).

Due to increasing usage of AC, exploring the economical supplies for the production of AC is necessary. Generally, agricultural by-products as waste are ignored in most countries, their disposal is costly and causes serious environmental problems. Due to high carbon and low ash contents of these products, many of them are appropriate to be used as precursors for AC production. Examples of such bio-materials are; oil palm shell (Daud and Ali, 2004), coconut shell (Gratuito *et al.*, 2008), pistachio shells (Yang and Lua, 2006), olive stones (Nakagawa *et al.*, 2007), date stones (Bouchelta *et al.*, 2008), rice bran (Suzuki *et al.*, 2007), coffee residua (Boonamnuyvitaya *et al.*, 2005), apricot

stones (Sentorun-Shalaby *et al.*, 2006), jackfruit peel (Prahas *et al.*, 2008), arundo donax (Vernersson *et al.*, 2002).

It is accepted that the differences in material composition, i.e., lignin, cellulose and halo-cellulose, largely influences the pore structure and pore size distribution of AC (Daud and Ali, 2004; Gergova *et al.*, 1994). Palm shell as by-product of the palm oil industries is abundantly available mainly in South East Asia (Malaysia, Indonesia and Thailand). Many previous studies have been done on the utilization of palm shell as raw material of AC production and it was reported that due to its high density, high carbon contents and low ash, this material can be used for the production of good quality AC (Daud *et al.*, 2000; Guo and Lua, 2002; Rodriguez-Reinoso, 2002).

In the present study, chemically activated carbons from oil palm shell as a precursor were prepared using low concentration of zinc chloride or phosphoric acid as chemical agent (Prauchner and Rodriguez-Reinoso, 2008). The prepared samples were heated under CO₂ (Daud and Ali, 2004) for physical activation at different durations to prepare microporous activated carbons with high surface area and narrow Micropore Size Distribution (MPSD).

MATERIALS AND METHODS

Preparation: Palm shell as raw material collected from Malaysian Oil Palm Shell (MOPS) was crushed and then sieved to a particle size in the range of 1-2 mm. After that, it was washed and dried at 110°C for 24 h. First, a standard solution of phosphoric acid or zinc chloride (2 mL g⁻¹ of the precursor) was used to impregnate the precursor. The chemicals per gram palm shell mass ratios are showed as X_p and X_{zn} for the phosphorous and zinc, respectively. A mixture of precursor and chemical solution of X_p = 0.09 or X_{zn} = 0.25 was stirred at 85°C for 2 h (Prauchner and Rodriguez-Reinoso, 2008). Next, the impregnated samples with H₃PO₄ and ZnCl₂ were heated up to 450 and 500°C, respectively for 2 h under N₂ flow rate of 100 mL min⁻¹ (Noor and Nawati, 2008; Prauchner and Rodriguez-Reinoso, 2008). To remove the excess activating agent and increase the pH over 6, the chemically produced ACs were washed several times with abundant amount of distilled water. For the ZnCl₂ samples, ACs were first washed with 0.1 N solution of HCl (Moreno-Castillaa *et al.*, 2001). The products were first carbonized at 900°C for 1 h and heating rate of 10°C min⁻¹ (Ahmad *et al.*, 2008; Daud and Ali, 2004). After carbonization, the resulting material was used for thermal activation under carbon dioxide stream. For the physical activation, samples were heated up to 850°C, then carbon dioxide stream with flow rate of

100 mL min⁻¹ was used for 1-7 h (heating rate of 10°C min⁻¹) to obtain ACs with different burn-off degrees.

The commercial granular palm shell based activated carbon was obtained from Bravo Green Sdn Bhd, a local manufacturer based in Sarawak, Malaysia. This activated carbon was first sieved to the desired particle size (1-2 mm) and then washed and dried at 110°C overnight.

Characterization: The characterization of AC samples was carried out using N₂ adsorption and desorption at -196°C using Micromeritics ASAP 2020 surface area analyzer to assess the pore morphology of the produced activated carbons. The BET surface area, micropore and total pore volume and pore size distribution were obtained by analyzing the N₂ adsorption-desorption. The specific surface areas were determined according to the BET method at the relative pressure in the range of 0.05-0.30 (Kenneth, 2001; Sing, 1998; Terzyk *et al.*, 2001):

$$\frac{P/P_0}{V[1-P/P_0]} = \frac{1}{V_m C} + \left[\frac{C-1}{V_m C} (P/P_0) \right] \quad (1)$$

where, V is the volume of adsorbed at a relative pressure of P/P₀, P₀ is the saturation pressure (vapor pressure of liquid gas at adsorption temperature), V_m is the volume of gas (stp) required to form one monolayer of adsorbate and C is the constant related to energy of adsorption.

Pore volume was directly calculated from the volume of nitrogen held at the highest relative pressure (p/p₀ = 0.99). The volume of micropore was estimated using the Dubinin-Radushkevich (DR) equation (Rouquerol *et al.*, 1999). This equation has been widely used for activated carbon and other microporous adsorbents:

$$V = V_0 \exp \left[- \left(\frac{RT}{\beta E} \ln \frac{P_0}{P} \right)^2 \right] \quad (2)$$

where, V is the volume of adsorbed at a relative pressure of P/P₀ and temperature T, V₀ is micropore volume, E is the energy of the adsorption, β is the affinity coefficient of the adsorbate and R is the universal gas constant.

Pore size diameters were determined by the Dollimore-Heal adsorption pore distribution method.

Classification of produced activated carbon: In order to make the description of the prepared systems easy, the following nomenclature is used. CP and CZ indicate palm shell-based activated by phosphoric acid and zinc chloride followed by carbon dioxide activation, respectively. Activation time (expressed in hours) is

coming as a suffix for the two letters (example: CZ3 represent zinc chloride activated sample with extra activation under carbon dioxide for 3 h).

RESULT AND DISCUSSION

N₂ adsorption isotherms: Figure 1 shows the nitrogen adsorption isotherms of CZ activated carbons. Similar to typical AC, all CZ samples show almost flat plateau at higher relative pressures, showing type I isotherm.

According to the IUPAC categorization this indicates extremely microporous materials with a narrow pore size distribution (Yang *et al.*, 2007). The evolution of the isotherms shapes for these series indicates that the adsorption capacity increases with increasing activation time. This signifies the widening of microporosity. The similar isotherms for all of CZ series, shows that all of these samples include micropores and the size of these micropores widens with the increase of the activation length. There is small variation between the uptake of CZ1 and CZ3 at low and high relative pressures which indicates common microporosity either in narrow or large micropores. As the activation time increases, nitrogen adsorption and micropore volume enlarge as well. As it can be seen, the commercial activated carbon adsorbed lower amount of nitrogen than the CZ7 sample. Moreover, the slope of this plateau and the increase in adsorption at higher relative pressures are the major differences with other samples though, its isotherm shows type I. Hence, it can be concluded that this sample includes wide range of micropores in comparison with the CZ series. Like the CZ series, CP carbons in Fig. 2 demonstrate the same form of adsorption isotherm at low burn-off degree. CP1 and CP3 with similar type I adsorption isotherm show the difference in the uptake at low relative pressure. CP3 achieved higher adsorption capacity as compare to CP1, at low relative pressure. This shows that the increase in burn-off causes some degree of micropores widening. This raise in nitrogen adsorption is continued up to CP5. The isotherms of CP3 and CP5 have similar tendency at very low relative pressure and parallel at relative pressure above $P/P_0 = 0.4$. This indicates that the differences are in the large size micropores (Nakagawa *et al.*, 2007). In addition, throughout the entire pressure range, CP7 reveals a gradual increase in nitrogen uptake; therefore, the resulting isotherm is more likely of type 2.

The nitrogen uptake in this case is less than the other three preparation methods in this series of ACs at low relative pressure ($P/P_0 < 0.3$). This is followed by an increase in adsorption at higher pressures and then it

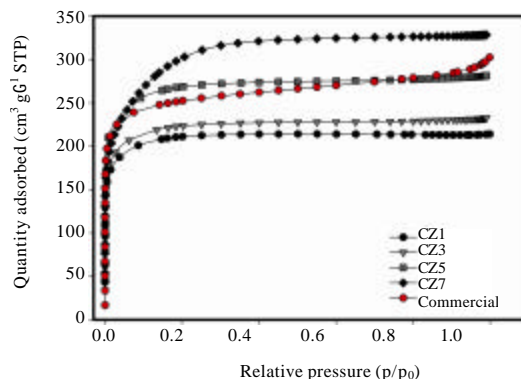


Fig. 1: N₂ adsorption isotherms of ZnCl₂ activated carbons followed by CO₂

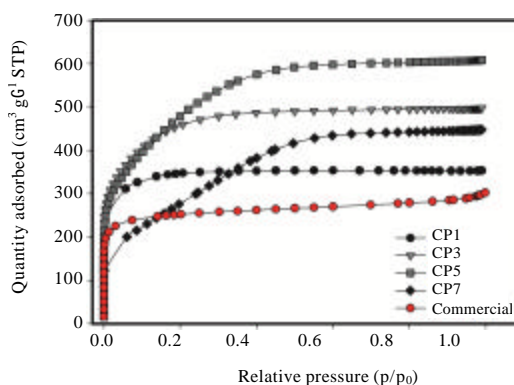


Fig. 2: N₂ adsorption isotherms of H₃PO₄ activated carbons followed by CO₂

Table 2: Preparing condition, production burn-off, surface area, pore volume

Samples	Burn-off (%)	S _{BET} (m ² g ⁻¹)	V _{Micro} (cm ³ g ⁻¹)	V _{total} (cm ³ g ⁻¹)
CZ1	0	727.91	0.35	0.360
CZ3	7.2	736.84	0.36	0.380
CZ5	11.6	863.08	0.43	0.440
CZ7	12.61	1118.00	0.42	0.510
CP1	21.75	1065.59	0.56	0.570
CP3	38.25	1542.45	0.78	0.800
CP5	61.75	1652.89	0.89	0.940
CP7	73	1034.77	0.54	0.690
Commercial	-	837.80	0.52	0.470

turns into similar form with the other plateaus. This suggests that CP7 is not a highly microporous substance, indeed a mesoporous material.

Textural characterization: Table 2 lists the burn-off percentage, surface area, micropore and pore volume of AC samples. Although, the CZ samples have expected surface area values within the normal range, all of the preparation techniques show high relative micropores. On the other hand, CZ5 demonstrates higher rate of

micropore volume and surface area compared to other conditions in this series. As the time of activation increases from CZ1 to CZ3, there is a small variation between CZ1 and CZ3 micropore volume values. However, there is a observable increase in BET surface area and micropore volume values from CZ3 to CZ5. It can also be observed that all products except CP7, show low mesopore volume. This could be because of the use of carbon dioxide as activating agent. Larger mesopore volume could be created if steam is used as the activating agent (Czechowski *et al.*, 1979). Although, all of samples in this series demonstrate lower pore volume value in comparison to the commercial AC ($0.52 \text{ cm}^3 \text{ g}^{-1}$), CZ5 results higher micropore volume. It confirms that the produced ACs are highly microporous.

In the CP series, the entire pore volume of all samples are higher compared with $0.47 \text{ cm}^3 \text{ g}^{-1}$ for commercial activated carbon. In particular, CP3 and CP5 samples have values as high as $0.80 \text{ cm}^3 \text{ g}^{-1}$. Increases in both surface area and micropore volume from CP1 to CP3 is very noticeable. Although, there is a raise in micropore volume in CP5 compared to CP3, this increase is lower than that of the two previous samples. CP5 has a higher mesopore and total pore volume than that of CP3, proposing that increasing burn-off higher than 38% produces some new pores being mesoporous and extends some micropores to form mesopores. The rate of mesopore formation is higher for CP5 to CP7 and the BET surface area is lower with a microporosity of 78% ($V_{\text{Micro}}/V_{\text{Total}}$). It is obvious that CP3 is a highly microporous substance with a microporosity value of 97% while CP7 has a lower microporosity of 78% and therefore more mesopore volume as shown in Table 2. However, CP5 had the highest surface area, pore volume and micropore volume between all CP series. It also achieved better microporous ACs compared to previously publish biomass raw material based AC.

Pore size distribution: The pore size distribution is described as structural heterogeneity of the porous material and closely related to both equilibrium characteristics and kinetics of these materials used in industrial purposes (Adinata *et al.*, 2007). Figure 3 shows the pore size distribution of CZ series and the commercial AC. All of the pore size distribution curves of prepared activated carbons have their maximum at the pore diameter around 2 nm signifying the presence of micropores.

From this figure, it is apparent that the activation method had significant effect on the pore formation of the produced activated carbons. The commercial activated carbon shows wide range of pore size distribution including mesopores. In comparison with this AC, the produced samples presenting more micropore percentage and homogenous pore size distribution.

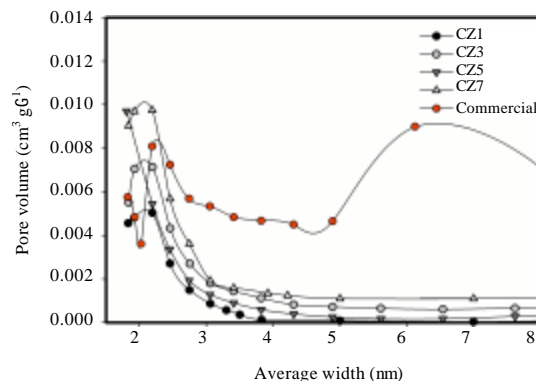


Fig. 3: Pore size distribution of ZnCl_2 activated carbons followed by CO_2

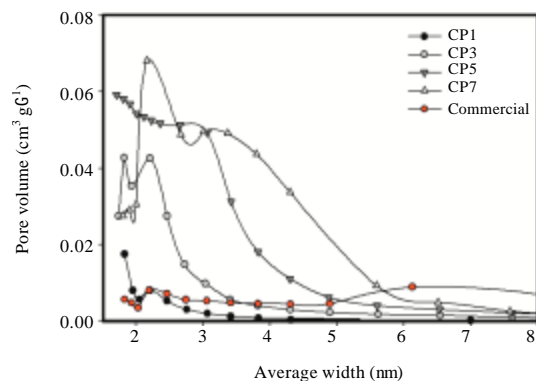


Fig. 4: Pore size distribution of H_3PO_4 activated carbons followed by CO_2

Figure 4 demonstrates the pore size distribution of CP series. In these samples, it is obvious that increasing the time of thermal activation has considerable effect on pore size distribution. When the period increases, the pore size distribution develops into wider and the curves moving to the mesoporous area (more than 2 nm). In CP7 sample, the highest point of adsorption is in the pores with diameters between 2-3 nm.

By increasing the activation duration from 1 to 7 h, the mesopore volume increases. It demonstrates that although the formation of micropores increases up to 5 h of activation, widening of these micropores to mesopores carries out continuously in all the samples.

CONCLUSION

Combined physical and chemical activation of palm shell revealed that H_3PO_4 impregnated samples attained higher surface area and micropore volume than those prepared using ZnCl_2 or the physically activated samples. Using small amount of ZnCl_2 and H_3PO_4 creates some

small pores that can be developed homogenously by extra physical activation. Combination of physical and chemical activation creates more homogenous pore size distribution. Consequently, this method of activation is a powerful technique for controlling and developing similar micropores which enhances the overall adsorption capacity of the ACs.

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