Manufacture of Low-cost Activated Carbon Using Sago Palm Bark and Date Pits by Physiochemical Activation

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Two raw materials, sago palm bark (SPB) and date pits, were utilized as precursors to prepare high porosity activated carbon (AC). The porosity of these two raw materials was compared with that of commercial AC made from coconut shells. The physicochemical activation method was used for AC preparation, and it consisted of two steps, carbonization and activation. The activation process was performed using zinc chloride ($ZnCl_2$) as an activation agent. N_2 adsorption-desorption analysis was carried out to characterize the porosity of AC. Thermogravimetric analysis (TGA) was conducted for the two raw materials. The adsorbent made from SPB, which showed the maximum surface area of 1634 m^2/g at the 700 °C activation temperature for one hour, while the surface area of prepared AC from date pits was 1367 m^2/g. Both prepared ACs had a larger surface area than commercial AC made with coconut shell (1348 m^2/g).

Keywords: Activated carbon; Date pits; Sago palm bark; Porosity characterization; Activation

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INTRODUCTION

Activated carbon (AC) is prepared to have very large surface area so that it can be widely applied in applications such as the treatment of water and wastewater and sanitary and hazardous landfill leachates. AC is produced from carbonaceous materials such as palm oil wastes (Ahmad *et al*. 2012), coconut shell (Bhatnagar *et al.* 2008), sugarcane bagasse (Orlando *et al.* 2002), rice husks (El-Shafey 2007), bamboo (Ohe *et al.* 2003), and raw wheat residues (Wang *et al.* 2007). Many researchers studied on activated carbon characterization (Rahman *et al.* 2013; Shaheed *et al.* 2015; Tadda *et al.* 2016) and on utilization of it (Ahsan *et al.* 2014; Khaleel *et al.* 2015).

Different methods used to prepare AC involve physical, chemical, and physicochemical activation processes. Physical methods involve carbonization and activation at elevated temperature using an activating agent such as steam, air, CO_2, or their mixtures. Physicochemical activation is a new method to prepare AC that combines physical and chemical methods (Aber *et al.* 2009).

The sago palm belongs to the Palmae family and the genus *Metroxylon*. The sago palm grows well in humid tropical climates such as those of Oceania and Southeast Asia. It can reach a maximum height of 25 m and a diameter of 40 cm. In Malaysia, the area with

the largest sago plantations is located outside the Peninsula and is found in the state of Sarawak (Singhal *et al*. 2008). The sago starch industry discards over 20,000 tons of SPB per year. SPB is Malaysia's main carbohydrate. It is about 60 to 70% cellulose and hemicellulose (Ethaib *et al*. 2016).

This study examined the porosity of AC prepared from two different raw materials; sago palm bark and date pits. These materials were compared with commercial AC made from coconut shells.

EXPERIMENTAL

Preparation of AC

Sago palm bark (SPB) and date pits (DP) were used as precursor materials (Fig. 1). The SPB was purchased from a local plantation in Melaka, Malaysia. The preparation of the precursor included the removing of pith (the inner portion) from sago palm trunks to obtain the bark fraction (the outer layer), and the collected bark was dried at 105 °C for 24 h. After drying, the bark of sago palm was chopped and screened to 20 to 30 mm and stored in sealed plastic bags at 20 °C. The small particles were crushed and grinded (Fig. 2). Ground samples were sieved to the particle size of 0.3 to 0.6 mm. The DP were washed with tap water several times, dried overnight at 105 °C, crushed, and sieved into sizes from 0.3 to 0.6 mm.

(a) SPB (b) DP

Fig. 1. Raw materials

(a) SPB (b) DP

Fig. 2. Raw materials after milling

The preparation of AC included two steps; carbonization and chemical activation. In carbonization, the sample was transferred to a cylindrical stainless steel reactor. The reactor was inserted into an electric horizontal tubular furnace under continuous nitrogen gas flow (100 mL/min). The furnace tube dimensions are 800 mm length and 50 mm in diameter. The heating started by adjusted the furnace temperature to the desired value. The furnace took about 2 to 2.5 h to reach the desired temperature (the average heating rate was 10 ^{o}C/min).

The temperature of carbonization was 300 ^{o}C and the total duration of the reaction was 4 h. The second step of the preparation was the activation using the chemical agent ($ZnCl_2$) with impregnation ratio of 1/1 (weight of $ZnCl_2$ per weight of precursor). The precursor and chemical agent were mixed thoroughly for 24 h, and the sample was then dried overnight at 100 °C. After drying, the impregnated material was inserted into a tubular regulated furnace at an activation temperature of 700 °C for 1 h under continuous nitrogen flow (100 mL/min). After cooling, the sample was washed with boiling and cold distilled water thoroughly until the pH reached a neutral value. Finally, the sample was dried at 100 °C overnight and stored in a desiccator.

Activated Carbon Characterization

Moisture and ash contents

The moisture and ash contents were calculated using the oven-drying test according to ASTM D2867-09 (2009) and ASTM D2866-94 (1999), respectively.

Yield

$$Yield\ (\%) = \frac{weight\ of\ AC\ after\ carbonisation}{weight\ of\ the\ raw\ material} \times 100 \quad (1)$$

Ultimate analysis

The ultimate analysis for measuring the percentage of four elements of raw materials (carbon (C), hydrogen (H), nitrogen (N), and sulfur (S)) was conducted using CHNS analyzer (Elementar Vario El CUBE). While the percentage of oxygen (O) was calculated by the following formula,

$$Oxygen\ (\%) = 100 - (C\% + H\% + N\% + S\%) \quad (2)$$

Thermogravimetric analysis (TGA)

The TGA was performed using a thermogravimetric analyzer (SDTA851e, Mettler Toledo, Switzerland). The sample was heated from 25 to 800 °C at the rate of 10 °C/min.

Porosity characterization

Porosity characterization involves the determination of the surface area of the prepared activated carbon, total pore volume, and pore size distribution through N_2 adsorption-desorption isotherms at -195.6 °C using an automatic adsorption instrument. The surface area (S_T) of the sample was evaluated using the BET (Brunauer, Emmett and Teller) method over a relative pressure range of 0.01 to 0.3 (Brunauer *et al*. 1938).

RESULTS AND DISCUSSION

Table 1 presents the proximate and ultimate analysis of these three raw materials. The proximate analysis of SPB and date pits showed low ash content (2.09 and 1.35%, respectively), which is an important factor in the AC preparation method.

Table 1. Ultimate and Proximate Properties of Precursors

Proximate Analysis (%)	(Mozammel *et al.* 2002)		
Property	Coconut Shells	Sago Palm Bark	Date Pits
Moisture content	10.46	9	10.3
Yield	-	65	58
Ash content	3.58	2.09	1.35
Ultimate Analysis (%)	(Yusup *et at*. 2010)		
Element	Coconut Shells	Sago Palm Bark	Date Pits
C	40.12	45.16	45.63
H	2.56	6.306	7.118
N	0.61	-0.0144	0.724
S	0.23	0.013	0.062
O	56.48	48.54	46.47

The ultimate analysis indicated that the SPB and date pits have high content of carbon (45.16 and 48.54%, respectively), and oxygen (48.54 and 46.47%, respectively) and a low content of sulfur and nitrogen.

Thermogravimetric Analysis

The weight loss of the raw materials with respect to temperature was approximated by TGA. As an example, Fig. 3 presents the TGA profile of date pits. The first step represents 3.96% of weight loss in temperatures ranging from 55 to 160 °C; this loss represented moisture release. The second step represents weight loss of 72.68% in the temperature range from 167 to 667 °C. This weight loss was due to the decomposition of cellulose and other main components. Up to 670 °C, slow weight loss was registered due to the decomposition of hemicellulose and lignin. Hence, the carbonization temperature is considered in the range of 300 to 700 °C.

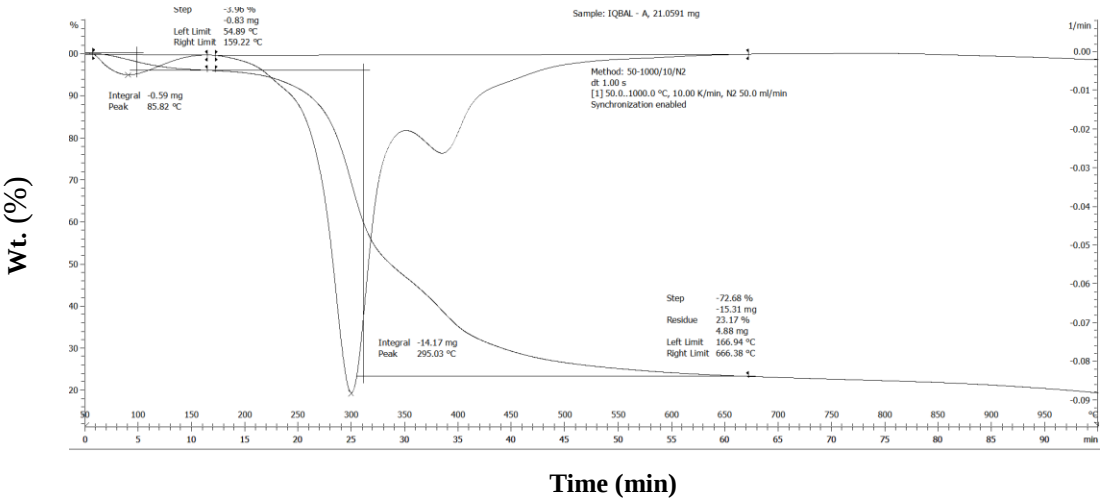

Fig. 3. TGA profile of date pits (as an example)

Isotherms of Nitrogen Gas Adsorption-Desorption

The porous characteristics of AC were investigated through isotherms of nitrogen gas adsorption in prepared AC activated with $ZnCl_2$ at impregnation ratio of 1/1. As an example, the volume of N_2 adsorbed by the date pits is illustrated in Fig. 4.

The volume of N_2 adsorbed by AC-SPB is reached (259.97 cm^3/g). While in the case of AC made from date pits and commercial coconut shells, the volume of N_2 adsorbed were 244.45and 238.82 cm^3/g, respectively. The highest value of adsorbed volume of N_2 indicated the evolution of pores during activation process for SBP.

Internal surface area of AC

The raw precursor materials played a critical role in producing AC with high porosity. Figures 5 and 6 show the porosity characteristics of AC using three different precursors: AC made from sago palm bark (AC-SPB), AC made from date pits (AC-DP), and AC made from coconut shell (AC-CN). The surface area for AC-SPB, AC-DP and AC-CN were 1634, 1367 and 1348 m^2/g, respectively (Fig. 5). The pore volume of AC-SPB, AC-DP and AC-CN were 0.649, 0.480, and 0.486 cm^3/g, respectively (Fig. 6). The maximum porosity characterization of AC-SPB using $ZnCl_2$ with an impregnation ratio of

1.5/1 at 700 °C for a holding time of 1 h may reflect that $ZnCl_2$ acts as a dehydrating agent and inhibits the formation of char, which can clog up sample pores (Guo and Lua 2000).

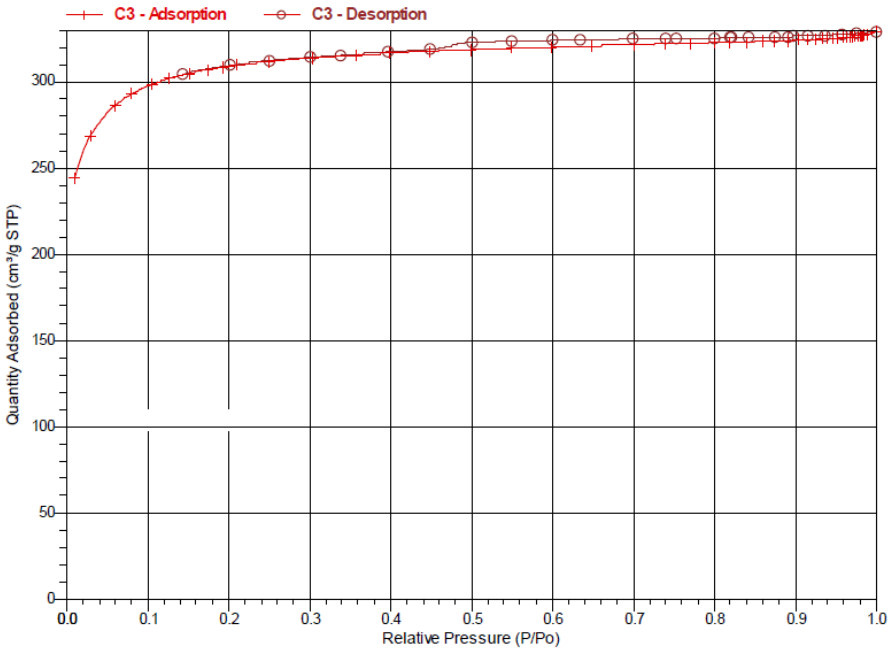

Fig. 4. N_2 gas adsorption-desorption isotherm of AC from date pits (as an example)

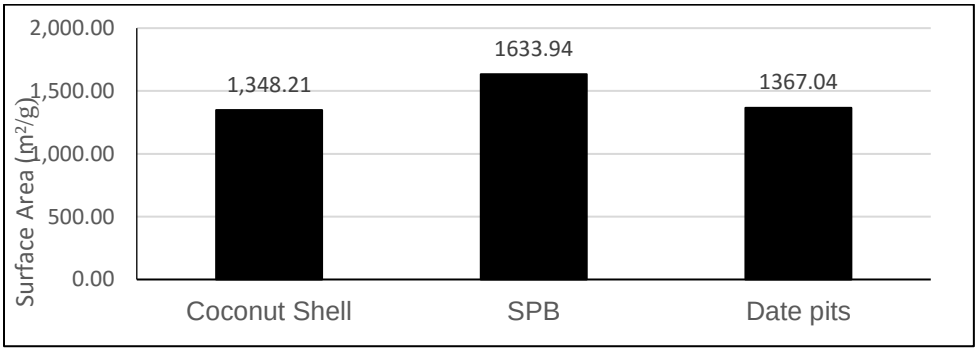

Fig. 5. Surface area for the prepared AC using different precursors

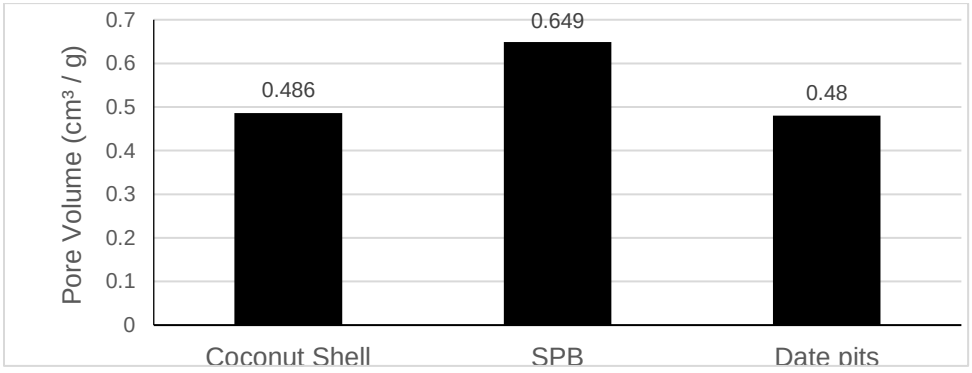

Fig. 6. Pore volume for the prepared AC using different precursors

Microporosity Characterizations of AC

Figures 7 and 8 show the microporosity volume for AC. AC-SPB had the maximum micropore surface area of 1148.58 m^2/g and micropore volume of 0.335 cm^3/g. AC-DP presented a micropore surface area of 600.41 m^2/g, while its micropore volume was 0.319 cm^3/g. AC-CN had a micropore surface area of 600.18 m^2/g and micropore volume of 0.271 cm^3/g.

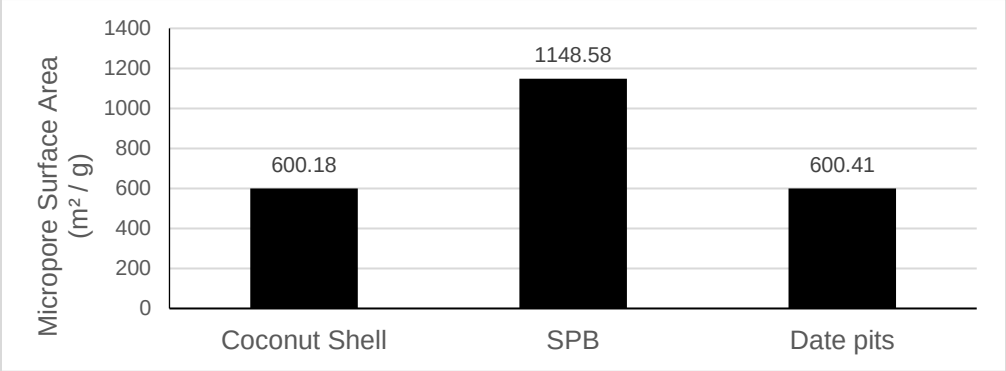

Fig. 7. Micropore surface area for the prepared AC using different precursors

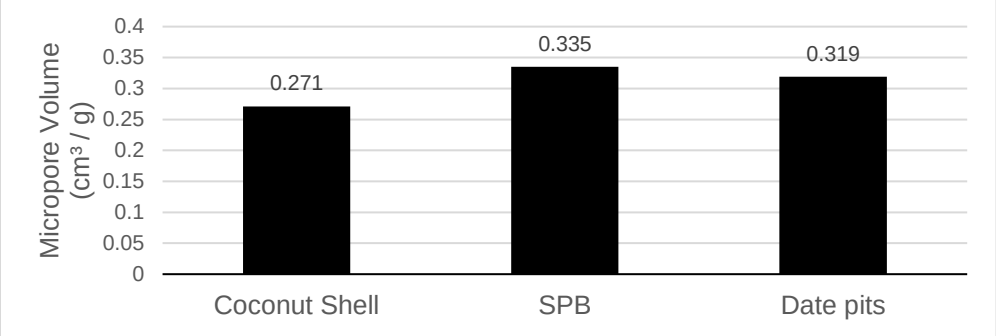

Fig. 8. Micropore volume for the prepared AC using different precursors

CONCLUSIONS

1. Experimental results indicated that adsorbent using date pits with activation by chemical agent of $ZnCl_2$ at 700 °C for 1 h resulted in high surface area, which indicates good adsorption for inorganic contaminates and heavy metals when using AC as adsorbent for wastewater treatment.
2. Development of AC was influenced by different factors such as low ash content of raw material. The two precursors that used in this study have low ash content (2.09 and 1.35%, respectively).
3. Important factor that affect the preparation method of AC to get good adsorbent is the content of carbon and oxygen. Both precursors prepared in study indicated high content of carbon and oxygen.

4. The activation process of AC with $ZnCl_2$ exhibited maximum porosity characterization such as pore volume, micropore surface area and micropore volume of the prepared AC using SPB in comparison with AC prepared using date pits and commercial AC.

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