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PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBON FROM OIL PALM EMPTY FRUIT BUNCH WASTES USING ZINC CHLORIDE

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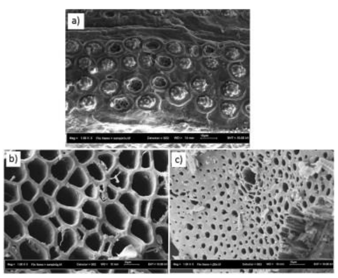
Graphical abstract



Abstract

An oil palm empty fruit bunch-derived activated carbon has been successfully produced by chemical activation with zinc chloride and without chemical activation. The preparation was conducted in the tube furnace at 500°C for 1 h. The surface structure and active sites of activated carbons were characterized by means of Fourier transform infrared spectrometry and field emission scanning electron microscopy. The proximate analysis including moisture content, ash content, bulk density, pH, and pH at zero charge was conducted to identify the psychochemical properties of the adsorbent. The results showed that the zinc chloride-activated carbon has better characteristics compared to the carbon without chemical activation.

Keywords: Activated carbon, chemical activation, oil palm empty fruit bunch, zinc chloride

Abstrak

Karbon teraktif yang diperolehi dari tandan buah kosong kelapa sawit telah berjaya dihasilkan melalui kaedah pengaktifan kimia zink klorida dan juga tanpa pengaktifan kimia. Penyediaan ini dijalankan dalam relau tiub pada suhu 500'C selama 1 jam. Spektroskopi Inframerah Transformasi Fourier dan Mikroskopi Imbasan Elektron Pancaran Medan digunakan untuk menganalisis stuktur permukaan dan juga tapak aktif pada karbon teraktif. Analisis yang lain termasuk kandungan lembapan, kandungan abu, ketumpatan pukal, pH, konduktiviti dan pH pada cas kosong telah dijalankan untuk mengenal pasti ciri-ciri kimia fizik bahan penjerap. Hasil kajian menunjukkan bahawa karbon teraktif-zink klorida mempunyai ciri-ciri yang lebih baik berbanding dengan karbon tanpa pengaktifan kimia.

Kata kunci: Karbon teraktif, aktivasi kimia, tandan buah kosong kelapa sawit, zink klorida

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1.0 INTRODUCTION

Adsorption is the selective removal of impurity in a fluid by contacting the fluid with a solid adsorbent. Among wastewater treatment technologies that have been adopted to remove pollutants, adsorption onto activated carbon is considered as an efficient method for controlling organic pollutants either in drinking water and waste water due to its high efficiency and the ease of operation. It can be applied for the elimination of organic and inorganic pollutants in water with removal up to 99.9% [1-3]. However, the overlying cost of commercial activated carbon has made more researchers looking for the alternative low cost precursors for preparation of activated carbon. A large number of researchers have studied the preparation of activated carbon from agricultural by-products such as maize cob [4], coir pith [5], cassava peel [6], oil palm shell [7], bagasse [8] and rice husk [9].

Palm oil is a major agricultural industry in Malaysia. Malaysian palm oil mills generate an abundance of biomass waste. From one ton of fresh fruit bunch (FFB), palm oil mill produces 14% fibers, 7% shell and 23% empty fruit bunch (EFB). EFB alone accounts for 19.5 million tons in 2008 [10]. These EFB wastes are traditionally used as fuels to generate energy and are burned in incinerators to be used as a fertilizer [11]. However, a large amount of EFB waste is still leftover from plantation and causes environmental problems [12]. As the major agricultural by-product of palm oil extraction, oil palm EFB waste is proposed as a potential precursor for the production of activated carbon. Some researchers have proved that oil palm EFB can be used as adsorbents in the removal of heavy metal and organic compounds. Wahi *et al.* (2009) has conducted study on utilizing oil palm EFB, as an absorbent for removing Hg (II), Pb (II) and Cu (II). Alam *et al.* (2007) has produced activated carbon derived from oil palm EFB to remove organic compound such as 2,4-dichlorophenol. Activated carbon can generally be prepared by physical activation and chemical activation. Physical activation involves carbonization followed by activation using carbon dioxide or steam. Chemical activation involves treatment with dehydrating reagents such as KOH, NaOH, K_2CO_3, $ZnCl_2$, and H_3PO_4 [4, 5, 14, 15]. Chemical activation is an efficient method to produce activated carbons with high surface area and high distribution of porosity.

Several studies have reported the preparation of activated carbon from various raw materials using $ZnCl_2$. However, so far, there is no report comparing the characteristics of activated carbons prepared from oil palm EFB waste by employing chemical activation using $ZnCl_2$ and without chemical activation.

2.0 EXPERIMENTAL

2.1 Materials

The raw oil palm empty fruit bunches (EFBs) used in the experiment was obtained from *Telok Sengat Palm Oil Mill,* Johor, Malaysia. The obtained-oil palm EFB was washed several times using tap water and dried under ambient atmosphere for 24 h then in the oven at 105°C overnight. The dried-EFB was stored in plastic bag at 4°C for further uses. Zinc chloride, hydrochloric acid and sodium hydroxide was supplied by Qrec™.

2.2 Experimental Methods

Activated carbons were prepared using chemical reagent which is zinc chloride and without chemical reagent. For preparation of activated carbon with zinc chloride (ACZ), the dried-EFB samples were impregnated with 10% $ZnCl_2$ for 24 hours. The solution was then decanted off and the impregnated-EFB was dried in the oven at 110°C overnight. The impregnated-EFB was put in a sample holder and then put inside a horizontal furnace under nitrogen flow at 500°C for 1 hour. The activated carbon was washed with 10% HCl to remove residual impurities then with distilled water until water pH become neutral. The activated carbon was dried at 110°C for 3 hours, grinded until fine, and stored in a container. For preparation of activated carbon without chemical activation (AC0), the raw oil palm EFB was heated in a horizontal furnace under nitrogen flow at 500°C for 1 hour.

Moisture content of activated carbon was determined by ASTM E871. 1 g of activated carbon was weighted in a crucible and heated in an oven (Ecocell, USA) at 105 ±5°C for 1 hour. Samples was cooled in a desiccator and then weighed. The process of heating, cooling and weighing was repeated at 30 minutes until the difference between the consecutive weighing less than 5 mg. The moisture content is indicated by the weight loss.

$$Moisture\ content\ (\%) = \frac{(M - X)}{M} \times 100\%$$

Where, M= Mass of the raw material (g)
X= Mass of the material after drying (g)

Ash content was determined according to ASTM D2866. The empty crucible was ignited in the muffle furnace at 650 ± 25°C for 1 hour, cooled to room temperature in the desiccator and weighted the empty crucible. The dried activated carbon was weighed in the ignited crucible and placed in the furnace at 650 ± 25°C for 3 hours. The activated carbon was transferred to the desiccator and then weighed. The processes of heating, cooling and weighing of sample were repeated until constant weight was achieved. The ash content was calculated as follow:

$$Ash\ content\ (\%) = \frac{M}{M_o} \times 100\%$$

Where, M= Mass of the ashed sample (g)
M_o= Mass of the sample (g)

Bulk density was determined by ASTM D 2854-70. An empty cylinder of known volume was weighed accurately. It was then filled with activated carbon. While being filled, the cylinder was constantly tapped and weighed. The bulk density was calculated by dividing the weight of the activated carbon by the volume. The determination of pH value of the activated carbon was in accordance with Dhayabaran *et al*. [16]. 1 g of activated carbon in 50 ml of distilled water was agitated for 1 hour at 200 rpm.

The samples were measured using pH meter (Mettler Toledo, Switzerland)

Surface area of the raw oil palm EFB and EFB-activated carbon were determined using the Brunauer–Emmett–Teller (BET) method based on N_2 adsorption at 77 K using a Micromeritics instrument. The surface morphologies were investigated using Field Emission Scanning Electron Microscope coupled with Energy Dispersive X-Ray (SUPRA™ 40 Carl *Zeiss GEMINI*®). The functional groups on the surface of the activated carbon of EFB was analyzed by Fourier Transform Infrared Spectroscopy (Perkin-Elmer spectrum ONE) at room temperature in the spectral range varied from 4000 to 450 cm^{-1}. Sample was mixed with KBr powder approximately at 100:1 weight ratio.

3.0 RESULTS AND DISCUSSION

Elemental analysis was carried out to determine the elemental content such as carbon, oxygen, silicon, etc. in a sample and the proximate analysis was performed to determine moisture content, ash content, bulk density and pH. This EFB contains 48.73 % of carbon, 44.71 % of oxygen and 6.57 % of silicon [17]. Carbon is important in the production of activated carbon. Table 1 shows physical-chemical properties of EFB-activated carbons.

Table 1 Physical-chemical properties of EFB-activated carbons

Component	AC0	ACZ
Elemental analysis		
Carbon	71.23	87.15 %
Oxygen	%	11.46 %
Mg	22.71	-
K	%	-
Ca	0.33 %	-
Si	0.89 %	-
Al	0.38 %	-
Cl	4.17 %	1.08 %
Zn	0.30 %	0.31 %
	-	
	-	
Proximate Analysis		
Yield	32.07	37.9 %
Moisture	%	13.65 %
Ash	6.24 %	9.21 %
Bulk density	10.56	0.5
pH	%	g/cm³
pH pzc	0.43	6.15
	g/cm³	6.3
	8.21	
	6.9	
Surface area	9.09 m²/g	86.62 m²/g

After carbonization and activation, the oil palm EFB weights were reduced into 32.07% for AC0 and 37.9% for ACZ. Carbon content was also increased, indicating that activated carbon was produced. Activated carbon treated with $ZnCl_2$ gives higher carbon content which is 87.15 % and activated carbon without chemical treatment gives 71.23 % of carbon. AC0 has lower moisture content which is 6.24% and ACZ has higher moisture content which is 13.65%. Ash content of AC0 is 10.56% and ash content of ACZ is 9.21%. pH AC0 is 8.21 and pH ACZ is 6.15. AC0 has lower bulk density ie. 0.43 g/cm^3 and ACZ has 0.5 g/cm^3 of bulk density. pH pzc of AC0 is 6.9 indicating that AC0 has net negative charge and pH pzc of ACZ is 6.3 indicating that ACZ has net positive charge. Surface area of raw oil palm EFB and EFB-activated carbon were analysed based on the nitrogen adsorption at 77 K. The initial surface area of the raw EFB sample was 4.29 $m^2\ g^{-1}$ [17]. Surface area increased slightly to 9.09 $m^2\ g^{-1}$ for AC0 and to 86.62 $m^2\ g^{-1}$ for ACZ. Activated carbon treated with chemical reagent has higher surface area. The other activated carbons treated with zinc chloride was presented in Table 2.

Table 2 Zinc chloride-treated activated carbon prepared from other precursors

Parameter	Maize cob [4]	Rise husk [9]	*Sterculia alata* nutshell [18]
C	80%	67.64%	-
O	7%	-	-
Si	2%	-	-
Zn	2%	-	-
Other elements	-	31.37%	-
Yield	26.42%	-	46%
pH	5.6	6.30	-
Ash content	-	-	7.6%
Moisture content	-	-	9.62%
Density	-	1.984 g/cm³	0.84 g/cm³
Surface area	0.4312 m²/g	480 m²/g	712 m²/g

FESEM images depict the surface structure of samples. Figure 1(a) shows surface morphology of the raw oil palm EFB observed at a magnification of ×1000. The surface of raw oil palm EFB was rough with a very few and closed pores. Figure 1(b) shows the surface morphology of the oil palm EFB without chemical activation (AC0). After carbonization at 500˚C for 1 hour, some cavities were developed on the surface of activated carbon. The FESEM image of AC0 surface clearly showed that the AC0 had amorphous structure with larger pores with sizes ranged from 5-15 µm. Figure 1(c) shows the surface morphology of the $ZnCl_2$-treated activated carbon (ACZ). After activation, the oval-shaped pores were developed on the surface of the ACZ. The FESEM image of ACZ surface clearly showed that the ACZ contained smaller pores with size ranged from 0.5-5 µm. Figure 1(b) and (c) showed that the activated carbon treated with $ZnCl_2$ characterized by smaller pores size and thicker pores wall than the activated carbon without chemical addition. Porosity of activated carbon are varied depend on the ratio of activating agent used [4].

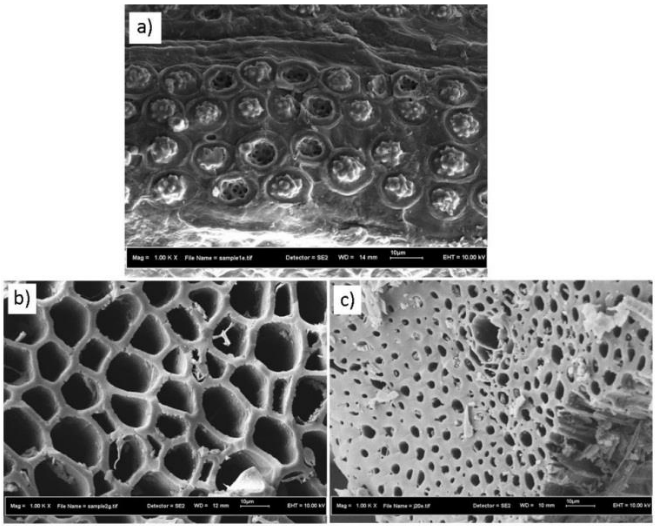

Figure 1 Suface morfology of raw oil palm EFB (a), activated carbon without chemical activation (b), activated carbon treated with $ZnCl_2$ (c)

The smaller cavities developed because the evaporation of $ZnCl_2$ impregnated in the precursor during the carbonization process, forming the spaces that previously occupied by $ZnCl_2$. $ZnCl_2$ acted as dehydrating agent which induces the charring and restricts the formation of tar . In the study of lignin pore structural changes, Hayashi *et al.* (2000) reported that $ZnCl_2$ works effectively as an activating reagent in the temperature range of 500-600 ˚C. The micropore and mesopore of activated carbons prepared by $ZnCl_2$ increased in temperature below 600 ˚C and decreased in temperature above 600 ˚C [4, 19].

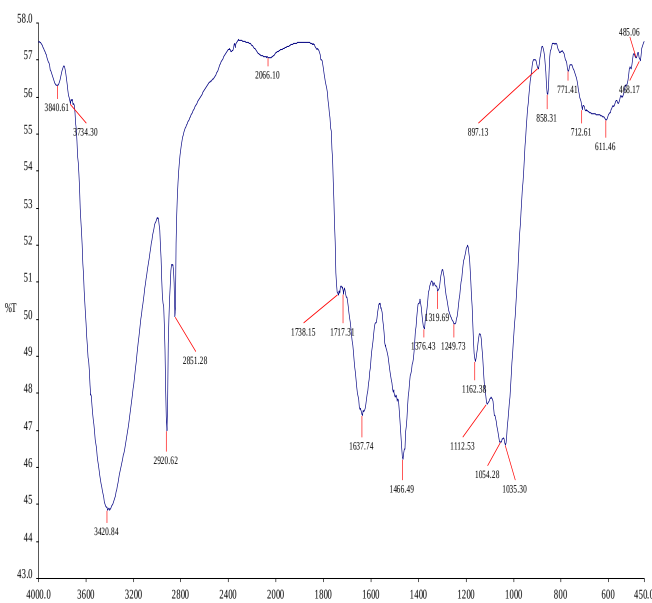

Figure 2 FTIR spectrum of raw oil palm EFB

Figure 2 and 3 show the FTIR spectrum of oil palm EFB, ACZ and ACZ after the adsorption of BPA. The FTIR spectrum presented in Figure 2 shows various absorption peaks on oil palm EFB surface. The broad and strong band at 3420.84 cm^{-1} was assigned to the stretching vibration of the (-OH) hydroxyl group. The absorption peaks at 2930-2850 cm^{-1} was attributed to C-H stretching vibration of the $–CH_3$ group. The small peak at 1740-1700 cm^{-1} were attributed to C=O and C-O stretching of carbonyl, esters and carboxylic acid. The peaks between 1260–1000 cm^{-1} were ascribed to either C-O stretching and Si-O as a yield of silica containing minerals [15]. The peaks at 1637.74 cm^{-1} and 1466.49 cm^{-1} were assigned to amide groups. Peak at 858.31 cm^{-1} was ascribed to the out of plane C–H bending [20].

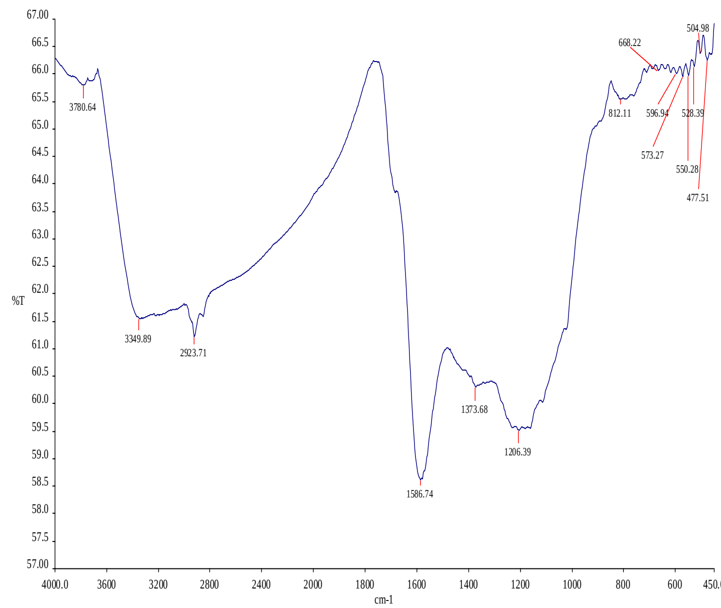

Figure 3 FTIR spectrum of $ZnCl_2$-treated activated carbon (ACZ)

The FTIR spectrum of EFB-activated carbon treated with $ZnCl_2$ is presented in Figure 3. After raw EFB converted to activated carbon, the strong band was observed at 1586.74 cm^{-1}, which may be due to the intensed stretching of conjugated C=C in aromatic ring or oxygen-aromatic bonding in aromatic ether. The band located at 3349.89 cm^{-1}, which is attributed to the –OH stretching vibration was weaker than –OH vibration in Figure 2, probably due to the loss of hydroxyl groups and elimination of volatile molecules from raw EFB. The peak at 1373.68 cm^{-1} was ascribed to C-H bending vibrations.The intensity of the band located at 1740-1700 cm^{-1} ascribed to C=O stretching was also weakened and reduction of complex band at 1260–1000 cm^{-1} was observed which include the reduction of carboxylic acids, alcohol and ester. The surface functional groups of EFB-activated carbon may be the potential active sites for interaction with an adsorbate [21].

4.0 CONCLUSION

Oil palm empty fruit bunch is one of an abundant waste producing from palm oil mills. The advantage of using oil palm empty fruit bunch as a precursor to prepare activated carbon is the use of cheap precursors which is easily obtained in Malaysia. The effects of pre-treatment of oil palm EFB were studied by characterizing the activated carbon. The characterization study showed that the activated carbon treated with $ZnCl_2$ has higher yield (37.9 %), higher carbon content (87.15 %) and higher surface area (86.62 m^2/g) than activated carbon without chemical activation. The results showed that the activated carbon based oil palm empty fruit bunch has a potential as a low-cost adsorbent for water treatment industries.

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