# ACTIVATED CARBON FIBER DERIVED FROM SINGLE STEP CARBONIZATION-ACTIVATION PROCESS

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## Abstract

The properties of activated carbon are influenced by the conditions of carbonization and activation. Activated carbon is normally produced through a conventional two-step process. This two-step process comprises the carbonization of precursor followed by activation of the carbonaceous char at elevated temperatures with the presence of suitable oxidizing gases. However, such process is very time consuming and energy intensive. The present study attempted to synthesize activated carbon fiber (ACF) derived from oil palm empty fruit bunches (EFB) fiber by using single step activation process. The properties of the produced ACF were investigated and analyzed by SEM, EDS, FTIR and XRD. Nitrogen adsorption was carried out to characterize the porosity of the produced ACF. EDS results indicated the carbon content of raw oil palm EFB fiber was 63.33 wt % with oxygen content of 36.67 wt %. After activation, ACF has a higher carbon content of 93.63 wt % and oxygen content of 5.19 wt %. The BET and Langmuir surface area for the produced ACF were 432 $m^2$/g and 670 $m^2$/g, respectively. The results revealed the possibility to prepare ACF from oil palm EFB fiber by using single step activation process.

**Keywords**: Activated carbon fiber, Adsorption, Oil palm empty fruit bunch fiber, Porosity, Single step activation

## Introduction

Activated carbon (AC) is an amorphous carbonaceous material that exhibits a high degree of porosity and large surface area [1]. AC is found in the form of powder, granular, spherical, fiber and cloth forms. Activated carbon fiber (ACF) has many advantages compared to the conventional powdered and granular activated carbon. Such advantages include large surface area and high adsorption capacity [1]. Coal, lignite, peat, wood and coconut shell are common raw materials used for the production of AC [2]. However, the increasing demands of AC used for adsorption have lead to the research and studies on production of AC derived from agricultural wastes and biomass.

In Malaysia, an estimation of more than two million tonnes (dry weight) of empty fruit bunches (EFB) is generated annually [3]. This oil palm waste is normally used as low energy fuel for the boilers in the oil palm mills or disposed in landfills. Improper management of this waste will only increase the generation annually and may affect the quality of the air. Therefore, research and studies have been done on the effective utilization and conversion of oil palm EFB to become efficient adsorbents. Alam and coworkers (2007) have shown the possibility of synthesizing AC using oil palm EFB as starting materials [4]. The result indicated that AC activated at 800ºC showed maximum adsorption capacity in aqueous phenol solution. In another study, AC with BET surface area of 807 $m^2$/g and average pore size of 2.1 nm was prepared from oil palm EFB [5]. The conversion of oil palm waste into activated carbon with good properties would reduce the

problems of wastes disposal and contribute towards the production of low cost but value added adsorbents.

The properties of AC produced are greatly influenced by the precursors used and conditions of activation. Activated carbon was normally produced by conventional two-step process. The two-step process comprises carbonization of precursor and followed by activation of carbonaceous char at elevated temperature with the presence of suitable oxidizing gases such as carbon dioxide, steam or air. However, such process is very time consuming and energy intensive. Research has been done on the production of activated carbon by using single step process, which both carbonization and activation steps are carried simultaneously. Single step activation offers a simple and efficient preparation of AC from carbonaceous materials, eliminate the separate carbonization step used in conventional two-step activation process and consume lower energy for the preparation of AC [6]. Lua and Guo (2007) showed that activated carbon can be produced using single step $CO_2$ activation method [7]. Oil palm stones were used as starting materials for the production of AC and the BET surface area of the produced AC was 1410 $m^2/g$. Guo and Rockstraw (2007) also produced activated carbon from rice husk using single step phosphoric acid activation and the produced AC surface area was 1295 $m^2/g$ [8].

However, not many reports on the production of ACF derived from oil palm EFB fiber using single step activation process in the literature. Thus, characteristics of ACF derived from EFB fiber through single step activation are unknown. The potential applications of this ACF could be identified via the study and understanding of its characteristics. The main objective of this work was to report on the synthesis and the properties of ACF from oil palm EFB fiber using single step activation process

## Materials and Methods

### Preparation of Activated Carbon Fibers

Oil palm empty fruit bunch (EFB) fiber used for the preparation of activated carbon fiber was collected from United Palm Oil Mill, Penang, Malaysia. EFB fiber was cleaned and soaked in diluted 5% nitric acid to remove dirt attached on it and dried overnight inside an oven. The clean and dried EFB fiber was used as precursor for the production of ACF using single step activation process. In this method, the clean EFB fiber was mixed with sulphuric acid at ratio of 1: 0.75 (wt %). Then, the acid treated EFB fiber was activated in a horizontal tube furnace under nitrogen gas flow at constant heating rate of 10ºC/min to 900ºC. Throughout the activation process, nitrogen gas was flown at flow rate of 100 ml/min. Upon achieving 900ºC, nitrogen gas supply was switched to carbon dioxide ($CO_2$) gas at flow rate of 100 ml/min and soaked for 1 hour. After that, the activated sample was cooled to room temperature under nitrogen gas flow to yield sample ACF-S.

### Characterization

Field Emission Scanning Electron Microscope (FESEM) was used to study surface morphology of the oil palm EFB fiber and ACF-S. EDS was used to determine the elemental composition of the samples. All the samples were coated with gold of electrically conductive layer by using a BIO-RAD SEM coating system. FTIR was applied to detect the surface functional groups present in ACF from the scanning range of 4000 to 400 $cm^{-1}$ using KBr technique. X-ray diffractometer (XRD) with Copper anode (Cu-K$\alpha$, $\lambda$ = 1.5406 Å) was used to identify the phases formed in the ACF sample. ACF was characterized by $N_2$ adsorption at 77K using Autosorb IQ (Quantachrome) via BET and DFT method.

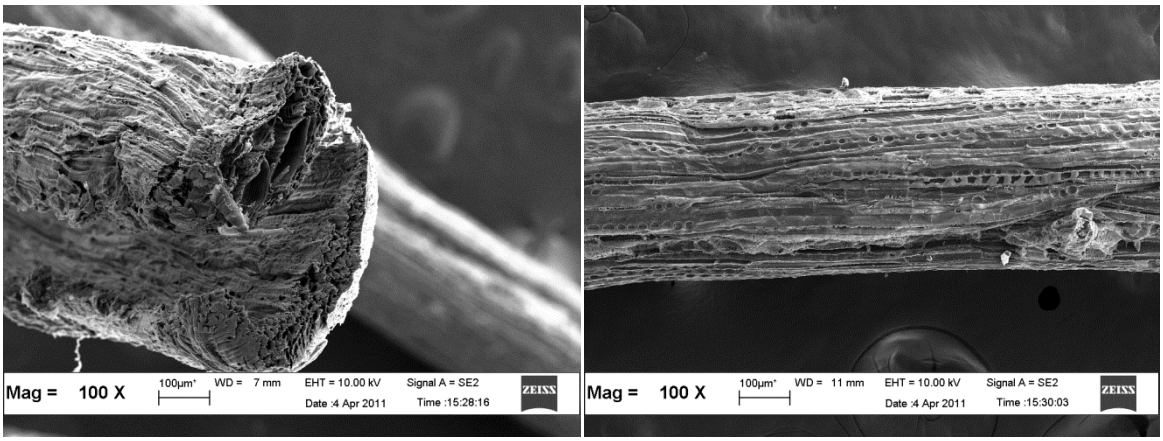
## Result and Discussion

### Textural Characterization of Activated Carbon Fiber

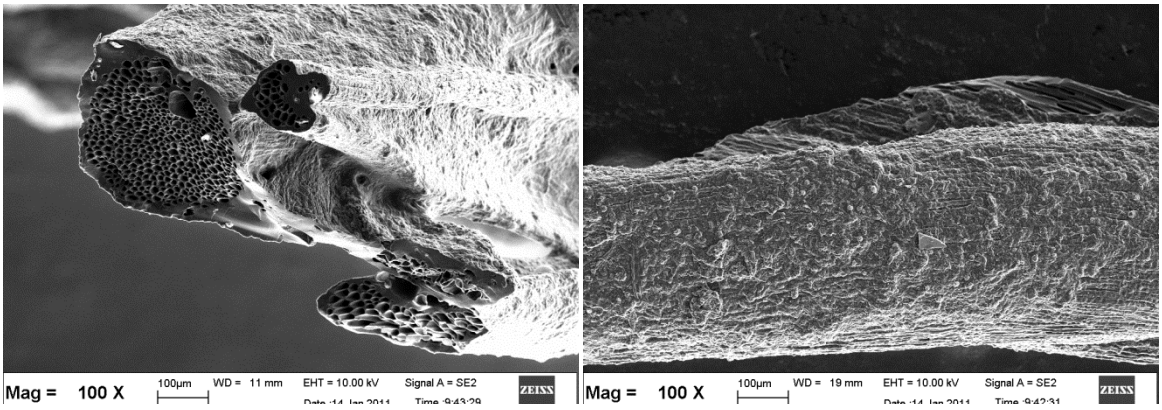
Figure 1 (a) shows the SEM cross sectional image of a raw oil palm EFB fiber at 300x magnification. Figure 1 (a) shows that EFB fibers were made up from numerous microfibrils and many opening pore channels appeared on it. Figure 1 (b) shows that the surface texture along the external surface of the oil palm EFB fiber was rough, uneven and full of pin-holes. Figure 1 (c) shows the cross sectional SEM micrograph of ACF-S has flat and smooth surface. After activation, the microfibrils rounded up to form channels, fusing together and could not be distinguished from each other. Such trend was also exhibited by the activated carbons derived from coconut shells prepared by Achaw and Afrane [9]. These changes were due to the cross-linking of reactive points of channels. During the activation process, disruption occurred on the original polymeric structure of the precursor and formed new structure [9, 10]. Figure 1 (d) shows that ACF-S has irregular and rough surface. Numerous pores were observed on the surface of ACF-S.

### Surface Chemistry

The EDS results for raw EFB fiber and ACF-S are shown in Figure 2 and Figure 3. Table 1 shows the elemental composition for raw EFB fiber and ACF-S summarized from EDS results. The raw oil palm EFB fiber consists of 63.33 wt % of carbon and oxygen content of 36.67 wt %. The single step activated ACF-S has much higher carbon content, 93.63 wt %, oxygen content of 5.19 wt % and sulphur of 1.18 wt %. This result was further confirmed by the ultimate analysis of EFB based AC carried out by Ma'an and co-workers [11]. The result showed that ACF derived EFB fiber via single step activation contained 87.9 wt % of carbon and 4.56 wt % of oxygen. ACF-S has higher amount of carbon content compared to raw oil palm EFB fiber. This was due to removal of volatile matters such as oxygen and sulphur during high temperature carbonization and activation processes and hence leaving a high carbon content. The presence of sulphur element in ACF was due to the sulphur residue remaining after the pretreatment of precursor with sulphuric acid.




(a) (b)




(c) (d)

Figure 1. SEM images of

(a) Raw oil palm EFB at the edge of the fiber
(b) Raw oil palm EFB along the surface of the fiber
(c) ACF-S at the edge of the fiber
(d) ACF-S along the surface of the fiber

**Table 1. Elemental Composition for Raw Oil Palm EFB Fiber and ACF-S Obtained from EDS Results**

| Sample | Element (wt %) | | |
|---|---|---|---|
| | C | O | S |
| Raw EFB fiber | 63.33 | 36.67 | - |
| ACF-S | 93.63 | 5.19 | 1.18 |

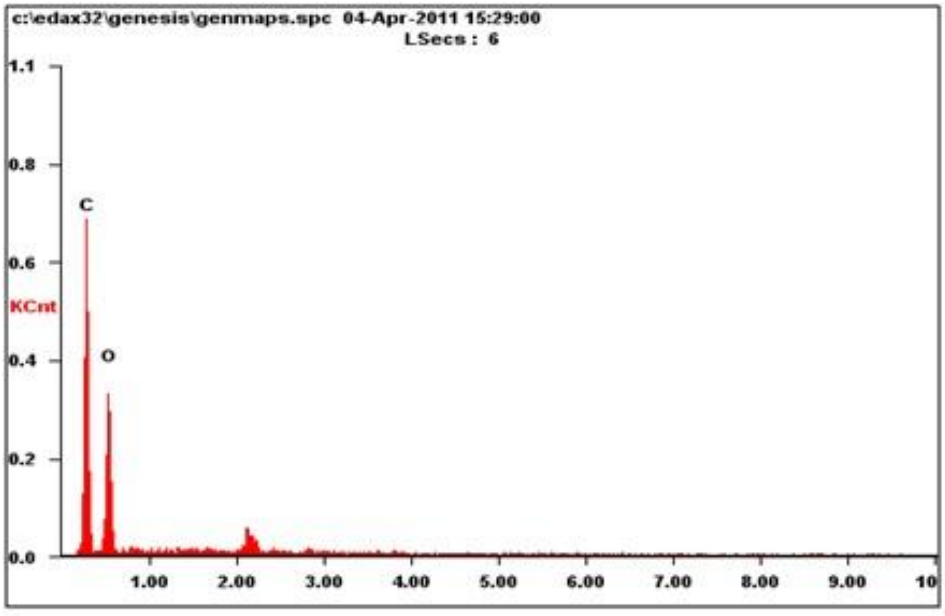



Figure 2. EDS result of raw oil palm EFB fiber

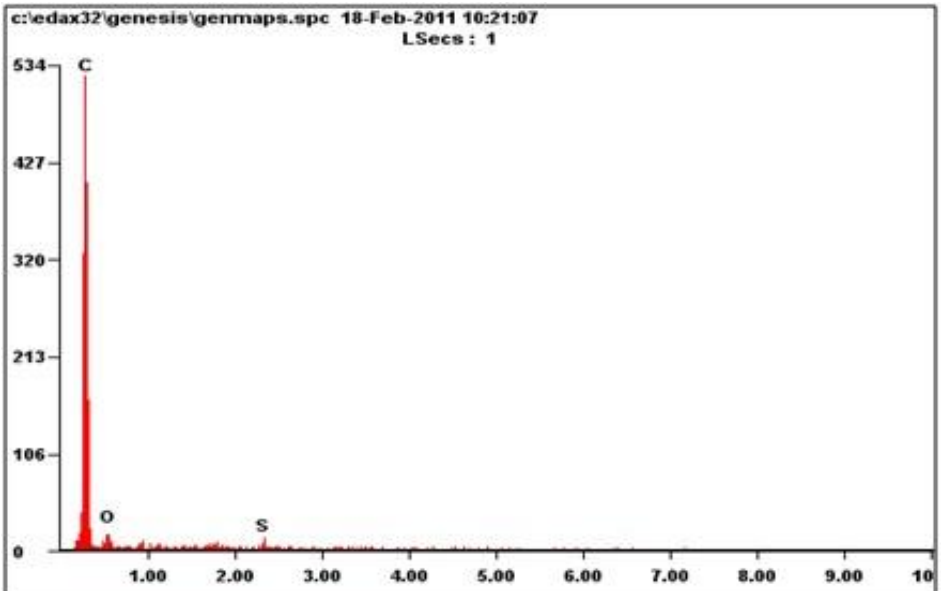



Figure 3. EDS result of ACF-S

Figure 4 shows the FTIR spectra for raw oil palm EFB fiber and ACF-S. Oil palm EFB fiber showed an absorption band at 3400 $cm^{-1}$ and it was assigned to O-H stretching mode of hydroxyl functional group. The O-H group was caused by the adsorbed moisture content in the EFB fiber. An absorption band at 3400 $cm^{-1}$ was also detected in ACF-S sample. Its intensity was greatly reduced due to the vaporization of moisture content during activation process. From the literature, O-H stretching functional group was detected in most of activated carbons [10], including commercial activated carbon [12] and activated carbon derived from cherry stones [13]. These were due to adsorption of water from atmosphere onto the surface of activated carbon. The absorption band at 1638.24 $cm^{-1}$ shows the presence of carbonyl groups as their stretching frequencies fall in this range [14, 15]. The peak at 1052.79 $cm^{-1}$ suggested the presence of C-O-C [15]. ACF-S shows different spectrum from raw oil palm EFB fiber due to decomposition of volatile matter during activation process.

An absorption band at 3240 $cm^{-1}$ was detected for ACF-S and this band was assigned to O-H hydroxyl group overshadowed by moisture content in EFB fiber. The low intensity of this absorption band suggested the adsorbed of moisture content on the surface of AC or existence of –OH functional group. The absence of absorption band at 1638.24 $cm^{-1}$ for ACF-S sample indicated that carbonyl group was greatly reduced after acid pretreatment and activation [16]. Absorption bands at 464, 735 and 1105 $cm^{-1}$ are associated the silicon atom attached initially to oxygen in the precursor material [14]. From previous study, about 0.653 wt % of silicon was found in the EFB fiber [17]. The small absorption bands at the region 926 $cm^{-1}$ may be due to the out of plane OH bending in carboxylic acid dimmers and band at 827 $cm^{-1}$ could be due to silica [14].

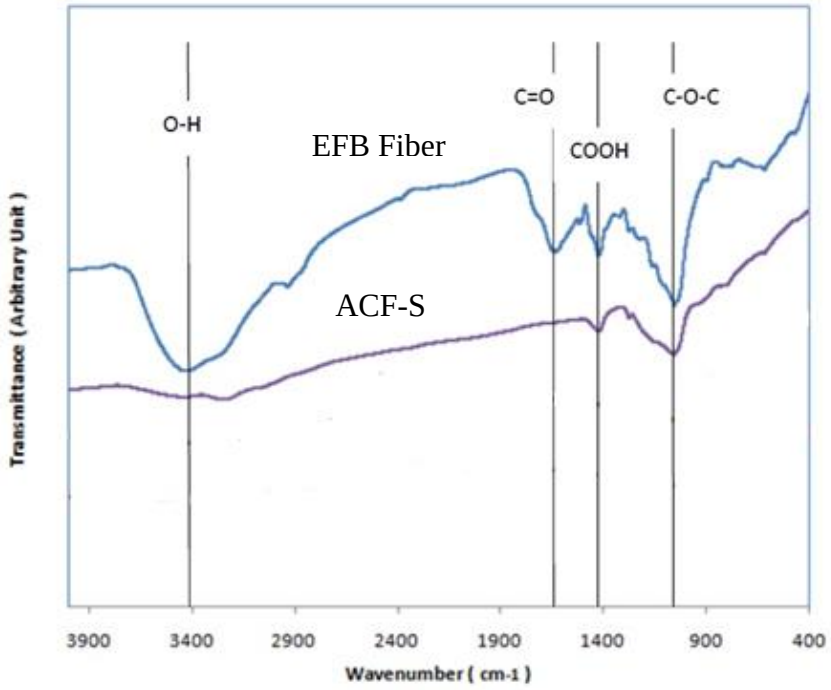



Figure 4. FTIR spectra for raw oil palm EFB fiber and ACF-S

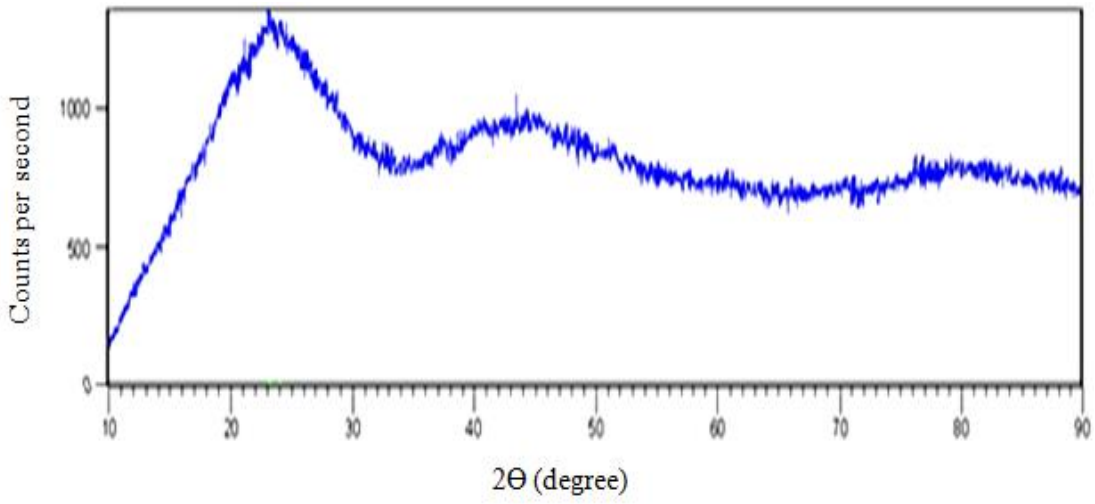



Figure 5. X-ray diffraction pattern of ACF-S

**XRD Characterization**

Figure 5 shows the X-ray diffraction pattern for ACF-S. No sharp characteristic peak was observed in this diffractogram. However, two broad peaks were found at 23.7º and 44º. These two angles are assigned to disordered graphitic (002) plane and (100) plane respectively [18]. Similar XRD patterns were observed for activated carbon derived from rice husk [14] and commercial granular activated carbons [12]. This indicated that the ACF-S produced from single step activation process was rather amorphous but may possess some microcrystallite structure. This XRD pattern indicated that such activated carbon exhibited turbostratic structure of disordered carbon materials [12, 14]. Turbostratic structures are disorder microcrystallite layers that form due to the presence of heteroatoms

like hydrogen, oxygen or vacant lattice site in activated carbon [1]. Elemental analysis indicated the presence of 0.06 wt % of hydrogen found in AC derived from EFB fiber [5].

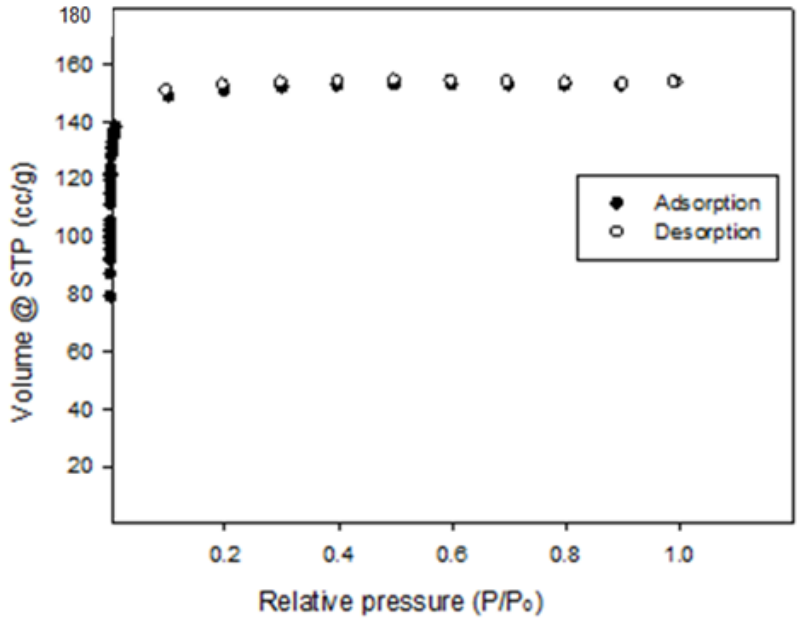



Figure 6. Nitrogen adsorption isotherm of ACF-S

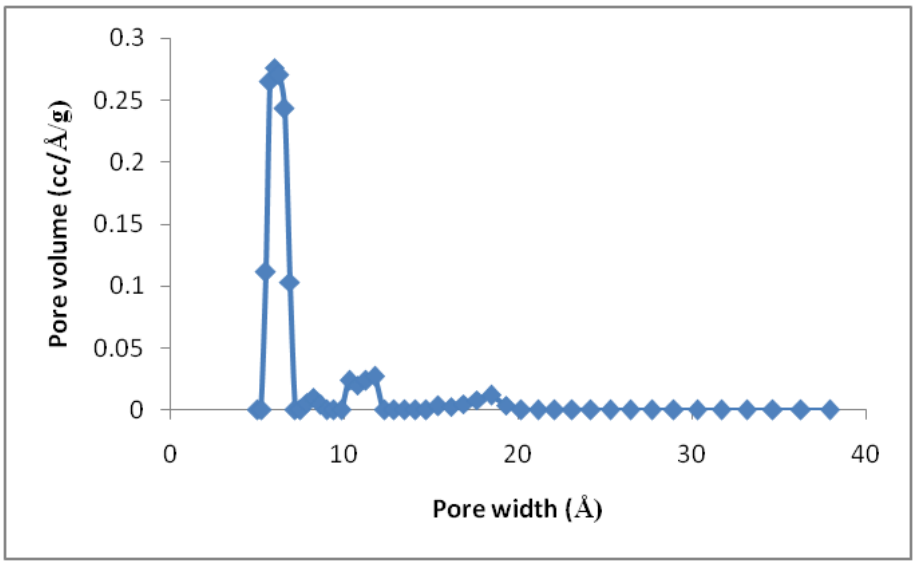



Figure 7. DFT pore size distribution of ACF-S

**Table 2. BET Surface Area of Activated Carbon Derived from Different Precursors**

| Precursor | Activation Temperature (°C) | Activation Time (min) | Activating Agent | BET Surface Area ($m^2/g$) | Reference |
|---|---|---|---|---|---|
| EFB fiber | 900 | 60 | $H_2SO_4$ | 432 | Present study |
| Coconut shell | 750 | 120 | $CO_2$ | 638 | [19] |

| | | | | | |
|---|---|---|---|---|---|
| Pulp pith | 150 | 1440 | $H_2SO_4$ | 380 | [20] |
| Sugarcane Bagasse | 150 | 1440 | $H_2SO_4$ | 312 | [20] |
| Rice hull | 350 | 90 | $H_3PO_4$ | 903 | [8] |

**Nitrogen Adsorption Isotherm**

Adsorption capacity of an absorbent is dependent on the surface area and volume of micropores. Activation process develops porosity in the EFB by creating orderly porous structure [21]. During activation by carbon dioxide ($CO_2$) gas, the diffusion of this oxidizing agent through carbonaceous matrix in solid form enhances gasification of the matrix into CO gas and creating porosity according to Equation 1 [22]. $CO_2$ was effective in creating well-developed pores on the surfaces of precursor and hence leading to the activated carbon with large surface area.

$C + CO_2 = 2\ CO$ (Equation 1)

Nitrogen adsorption isotherm is a popular and widely used method for the estimation of porous nature of activated carbon. Figure 6 shows the nitrogen adsorption isotherm exhibited by ACF-S prepared from one-step activation process. It can be ascertained from Figure 6 that the isotherm of ACF-S pertain to type I of the referred IUPAC classification [1]. This type of isotherm suggested that the activated carbon fiber mainly comprises micropores. The BET and Langmuir surface area measured were 432 $m^2/g$ and 670 $m^2/g$ respectively.

Figure 7 shows the DFT pore size distributions (PSD) of ACF-S. Density Functional Theory (DFT) is use to determine the pore size distribution (PSD) of AC. DFT provides a microscopic treatment of sorption phenomena in micro and mesopores on a molecular level based on statistical mechanics [23]. From Figure 7, a sharp peak was detected at pore width between 0.5 and 1 nm for ACF-S. The ACF shows a narrow pore size distribution with a pore size at 0.6 nm. Pore size in this range with narrow PSD could enhance organic compound adsorption from aqueous solution. Studies by Newcombe and co-workers (1997) showed that adsorption strength increases with the decreasing of pore size [24]. When the pore size decreased, the contact points between the adsorbent and adsorbate surfaces increase and the adsorption potential between opposing pore walls begin to overlap when the micropore width is less than twice the adsorbate diameter [24]. Hence, ACF-S could potentially be used for selective adsorption of target adsorbate with size in range of micropores. For example, Li and co-worker (2002) utilized ACF for the adsorption of drinking water contaminants, methyl tertiary-butyl ether (MTBE) and trichloroethene (TCE) [25]. In the latter study, ACFs with three activation levels were used for the adsorption of the two drinking water contaminants. The kinetic diameters for TCE and MTBE were 0.56 nm and 0.62 nm respectively. TCE adsorbed primarily in micropores in the pore width range of 0.7 - 1 nm while MTBE adsorbed primarily in micropores in the pore width range of 0.8 - 1.1 nm. The results suggest that an effective adsorbent should exhibit large volume of micropores with width that is about 1.3 to 1.8 times larger than the kinetic diameter of target adsorbate. Table 2 above shows a comparison of BET surface area of activated carbons derived from different precursors. The BET surface area of ACF-S was lower than rice hull and coconut shell but higher than others.

## Conclusions

The present study showed ACF can be synthesized from oil palm EFB fiber using single step activation method. The surface of ACF-S was brittle, rough, irregular and densified after activation. The ACF-S has a higher carbon content of 93.63 wt % compared to raw oil palm EFB fiber (63.33 wt %). XRD diffractogram showed that ACF-S was amorphous. The BET and Langmuir surface area for ACF-S were 432 $m^2/g$ and 670 $m^2/g$ respectively. All the results indicated that ACF-S prepared from single step activation process was a suitable adsorbent to be used in adsorption applications. It could potentially be used for selective adsorption of target adsorbate due to its size in the nanometer range. The single step activation process offer shorter treatment time, lower heat treatment temperature and reduce in the consumption of energy. This in turn will result in cheaper production of ACF when the process is scaled up to industrial scale.

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