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CO_2 Adsorption-breakthrough Study on Activated Carbon derived from Renewable Oil Palm Empty Fruit Bunch

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ABSTRACT

The emissions of CO_2 gas lead to the severe environmental pollution especially global warming's effects. In order to minimize the negative impacts from the emission of CO_2 gas, it is necessary to filter and separate the gas. The paper was aimed to synthesize activated carbon from agricultural waste material (EFB) by using basic agent (KOH) and CO_2 activation and to determine the adsorption rate and breakthrough of the CO_2 gas on the different type treatment of activated carbon. EFB-char was produced via carbonization process and then activated through chemical treatment and CO_2 activation. The physical characterization of the samples were investigated by using nitrogen adsorption and scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR) which was used to study the surface chemical properties. Then, adsorption column breakthrough experiment is conducted on the activated carbon prepared while commercial activated carbon (AC) was used as reference. Breakthrough time for KOH-impregnated AC, commercial AC and KOH-impregnated AC with CO_2 activation were 3s, 3s and 2s. Based on the results, KOH impregnated-AC showed longer breakthrough time compared to KOH-impregnated AC with CO_2 activation, which means that KOH-impregnated AC have better performance for CO_2 adsorption and equivalent to the commercial AC. In conclusion, results showed that the EFB base-porous carbon sorbent prepared by carbonization and chemical activation process is a good adsorbent for CO_2 adsorption.

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INTRODUCTION

Biomass is one type of renewable sources which can be utilized further to convert it into value-added products. Furthermore, biomass waste from the disposal of mill residues is abundantly available in Malaysia. Palm oil mills can produce many byproducts such as palm kernels, fibre, and empty fruit bunches. These products are produced in huge quantities. Usage of oil palm unwanted materials as a source of energy will lead to other environmental advantage like decreasing in carbon dioxide that discharged (Lim, 2000). Agro-base solid waste materials have been proven to be suitable precursor for the production of AC due to their availability at a low price. Besides that, they can be utilized for the production of AC with a high adsorption capacity, considerable mechanical strength, and low ash content (Savova *et al*., 2001).

Emission of carbon dioxide gas is increasing yearly which contribute to the negative impact toward environment. Almost 70% of the totally emitted greenhouse gases are CO_2. It is the most important cause of global warming. CO_2 is come from a variety of sources especially from oil and gas industries like refinery process, drilling rigs, general plant operations and others. The rising level of CO_2 can gravely affect our future. The alternative method need to use to reduce the impacts to human and nature. CO_2 can be filtered and separated by using activated carbon as adsorbent moreover nowadays, the usage of activated carbon become increasing and interesting.

Activated carbon is produced from a variety of carbonaceous rich materials such as wood, coal, lignin and coconut shell. The good precursor for production of activated carbon need to have high carbon content, low ash and low cost (Gaur and

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Shankar, 2008).The derivation of biomass-waste for production of activated carbon is an important way in environmental pollution control strategy. Furthermore, using activated carbon which obtained from biomass-waste instead of coal (fossil fuel sources) will minimize environmental effects especially global warming's effect (Norhusna *et al*., 2013). The performance of activated carbon can be highly improved under appropriate condition. The precursors need to undergo first step which involved the production of char with carbonization /pyrolysis process. From the process, the volatile compounds and moisture were removed from the biomass-waste (Ioannidou and Zabaniotou, 2007). Second step involved production of activated carbon which can be produced by using three different processes: physical activation, chemical activation and physiochemical activation. Chemical activation commonly involves the presence of chemical agents like alkaline, acid and metal oxide. Meanwhile, physical activation involves gas activating agents such as steam and CO_2 (Sudaryanto *et al*., 2006). The activation process enhances porosity, surface area, and pore volume of activated carbon.

The objectives of this study were to synthesize activated carbon from agricultural waste material (EFB) by using basic agent and CO_2 activation and to determine the adsorption breakthrough of the CO_2 gas on the EFB-activated carbon and commercial activated carbon. Firstly, EFB was subjected to the carbonization followed by chemical and physical activation. Then, the activated carbon was tested by carbon dioxide uptake through column breakthrough adsorption. Experimental and theoretical studies for adsorption of CO_2 on activated carbon were carried out.

2.0 Methodolgy:

2.1 Material preparation:

Palm empty fruit bunch obtained from Koperasi Kampung Jawi Johor Bahru Berhad, Malaysia. The empty fruit bunch precursor was washed thoroughly and dried for 5-6 hours under sunlight. The washed empty fruit bunch precursor then was dried in the oven at 100-105°C for 24 hours. Dehydration process was applied to remove the moisture. Each sample was prepared and stored for characterization using SEM, FTIR and BET surface area and testing by adsorption breakthrough experiment. Procedure of this experiment was started by sieving of empty fruit bunch grinded particles. Then, the materials undergo the carbonization process to produce char. The carbonization experiment was conducted at temperature of 700^0C under nitrogen flow at 100cm^3/min for 5 hours including pre-heating, heating and cooling phase. Then, biochar was impregnated with potassium hydroxide as chemical agent with ratio 1:1. The mixture was stirred vigorously and being heated for 2 hours at temperature 85 ^{0}C and speed 6 r.p.m. Half amounts of impregnated samples were activated with the CO_2. The chars were activated at temperature of 800℃. The flow was carried out at a flow rate of 100 cm^3/min and heating rate of 10℃/min. After the activation process, the material was stored and labelled with EFB-AC2. Another amount of impregnated samples were labelled as EFB-AC1 and commercial activated carbon labelled with CAC. The three prepared samples then were characterized with SEM, FT-IR analysis and BET surface area and tested with adsorption breakthrough experiment.

2.2 Material Characterization:

There are two distinguish characterization for materials, namely physical and chemical characterization. The characteristics of activated carbon depend on the chemical and physical properties (Guo *et al*., 2007).In this study, the characterization involved BET surface area, SEM technique and FT-IR analysis. Commonly, the specific surface area of porous carbon is determined through gas adsorption measurement using Brunauer, Emmett and Teller theory. This method is used to characterize the structural aspects of the porosity which is based on the interpretation adsorption isotherm. SEM technique was applied to observe the surface physical morphology of oil palm EFB and EFB activated carbon. SEM images are very important to obtain detailed information about pore structure of materials. FTIR is used to study the surface chemical properties. It is an effective analytical instrument for detecting functional groups and characterizing covalent bonding information.

2.3 Single adsorption and breakthrough study:

Adsorption equilibrium data was obtained in a fixed-bed adsorption unit glass. About 2.5 g of adsorbent was used for each run. The adsorption unit was used to monitor the breakthrough curves of CO_2 single gas. In a breakthrough experiment, CO_2 gas was flow first at 200ml/min before it contact with adsorbent while valve of adsorption cell remain closed. The initial reading of concentration CO_2 was taken. Then proceed to the adsorption step in which CO_2 gas was fed through the column. The single CO_2 gas adsorption was measured at room temperature approximately at 30˚C.The feed gas inlet concentration was set at 200 mL/min. The valve located between the adsorption cell and loading cell was opened to enable the gas contact to the adsorbent (N.S.Nasri *et al*., 2014). For detection the compositions of reacted samples, online gas analyzer was set up to the inlet and outlet stream of reactor. The concentration of CO_2 was recorded from first point of CO_2 detected in the effluent. The composition of $C0_2$ was continuously monitored until saturation was reached (S. Sumathi *et al*., 2011).The result was recorded for three different types of samples during the experiment.

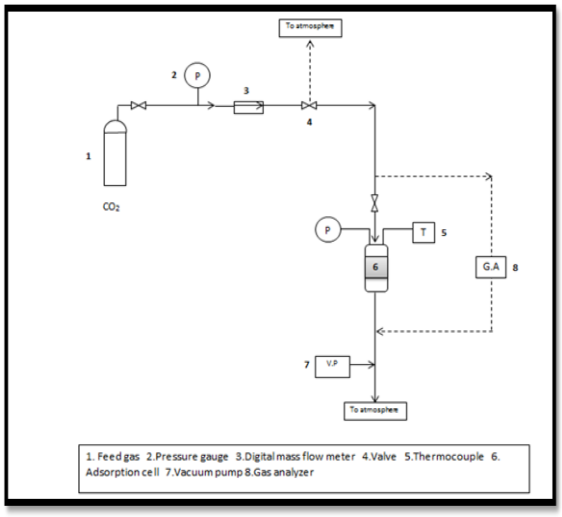


Fig.1: Schematic diagram of the column breakthrough experiment.

2.3 Adsorption capacity:

The adsorption capacity of the porous carbons for CO_2 gas was determined by a dynamic mass balance, through numerical integration of the breakthrough data. The time equivalent (t_t) to the total or stoichiometric capacity of the column for a particular adsorbate is obtained by numerical integration of the following equation:

$$t_t = \int_0^{\infty} \left(1 - \frac{C}{C_0}\right) dt \qquad (1)$$

Where,

t_t is the time equivalent to the total or stoichiometric capacity, t is the time, C is the concentration of adsorbate at time t, and C_o is the feed concentration of adsorbate.

The amount of adsorbate adsorbed by adsorbent (the adsorption capacity) is calculated at non-STP condition from the following equation (S. Sumathi *et al*., 2011).

$$q = \frac{Q_f t_t y_f}{m_c} \qquad (2)$$

Where,

q is the adsorbent adsorption capacity, y_f is the mole fraction of adsorbate in the feed, Q_f is the volumetric feed flow rate at STP, and m_c is the mass of adsorbent used inside the bed.

RESULTS AND DISCUSSIONS

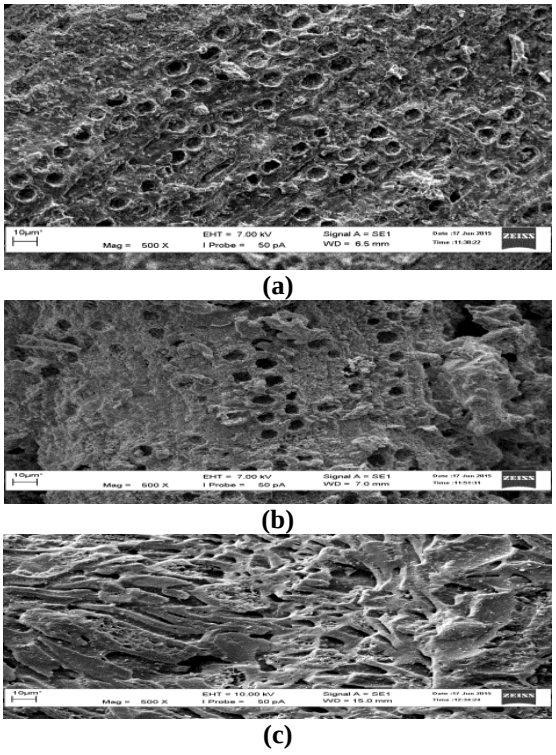
3.1 Material Characterization:

3.1.1 SEM:

SEM micrograph explores the structural changes in activated carbon surface during the carbonization and activation. There was not much different for the results obtained on morphology surfaces of the EFB-AC1 and EFB-AC2. Fig 2(a) and (b) showed that there were many pores created on the surface. The activated carbon which produced from EFB showed the pore arrangement which were quite uniform. The large amount of pores produced and the pore more widen due to the chemical and physical treatment on the sample. Fig 2(c) also demonstrated homogeneous pore size distribution but pore was not arranged uniformly. The formation of well-develop pores on the EFB-AC as a result of the space that has been created by volatilization of moisture and other impurities (Auta and Hameed, 2011).

3.1.2 FT-IR:

Fig. 3 showed the combination of KOH-impregnated AC (EFB-AC1), KOH-impregnated AC with CO_2 activation (EFB-AC) and commercial AC (CAC). It was noticed that some peaks were disappeared for functional group in EFB-AC2 and CAC compared to FT-IR result for EFB-AC1.Several peaks were observed for sample in Fig. 3(a).The peaks located at range 2291.43-2100.48 cm^{-1} were assigned to the C≡C stretch of alkynes. The peaks at wave numbers 2987.74 cm^{-1} , 1571.99 cm^{-1}, 1754 cm^{-1} , 1355.96 cm^{-1}, 1060.85 cm^{-1} and 879.54 cm^{-1} correspond to the funtional group of C-H stretching, C=C stretch in aromatic rings, C=O stretch in ketones, C-H bending, C-O stretching and C-H out of plane bending in benzene derivatives (Foo and Hameed, 2012; Wade, 2010). Alkaline groups of pyrones (cyclic ketone) and other keto-derivatives of pyran were considered as the main surface of functional group on the potassium hydroxide impregnated adsorbent. The spectrum of the activated carbon prepared through KOH impregnation and CO_2 activation (EFB-AC2) displayed the following bands: 2333.87 cm^{-1}, C≡C stretching (alkynes); 1670 cm^{-1}, C=C stretching (alkenes); 1440 cm^{-1}, C-H stretch(alkanes) ; 702.20 cm^{-1} , C-H(aromatic compound). The FT-IR result for commercial activated carbon (Fig. 3c) showed much similarity with the results obtained for EFB-AC2.



(a)

(b)

(c)

Fig. 2: SEM micrograph with magnification of 500X for (a) EFB-AC impregnated with KOH (b) EFB-AC impregnated with KOH and CO_2 activation and (c) Commercial activated carbon.

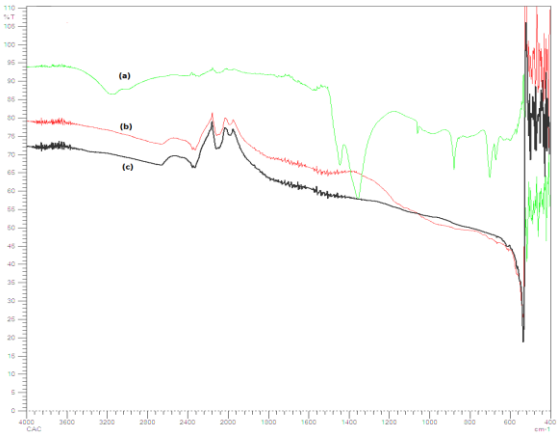


Fig. 3: FTIR spectra of activated carbon a) EFB- AC1, b)EFB-AC2, and c) CAC.

Table 1: Summary table for peak wave number of activated carbon.

Wave number range (cm^{-1})	Peak wave number for EFB-AC1 (cm^{-1})	Peak wave number for EFB-AC2 (cm^{-1})	Peak wave number for commercial AC (cm^{-1})	Group	Compound
3000- 2800	2987.74	-	-	C-H	Alkanes
2000-2500	2291.43,2100.48	2115.91, 2333.87	2335.80,2113.98	C≡C	Alkynes
1675-1575	1571.99,1754	1670.11	1577.23	C=C C=O	Alkenes
1460 - 1350	1355.96,1444.68	1440	1442.65	C-H	Alkanes
1300 - 950	985.62, 1060.85	-	-	C-O	1, 2,3 alcohol, phenol, ester
900 – 650	673.16,702.09,879.54	702.20	-	C-H	Aromatic compound

Table 2: BET surface area, total pore volume, and average pore diameter of activated carbon.

Sample	BET surface area (m^2/g)	Total Pore volume (cm^3/g)	Average pore diameter (A^0)
EFB-AC1	807.54	0.45	20.93
EFB-AC2	720.00	0.34	18.89
CAC	831.10	0.49	23.47

Table 3: CO_2 Adsorption-breakthrough results for CO_2 adsorption on EFB-AC and Commercial AC.

Sample					CO_2			
	Breakthrough time (s)		Breakthrough time (s) – 80g sample	Saturation time (s)		Adsorption capacity (mmol/g)		
EFB-AC1	3		96	82		0.57		
EFB-AC2	2		64	131		0.38		
CAC	3		96	78		0.57		

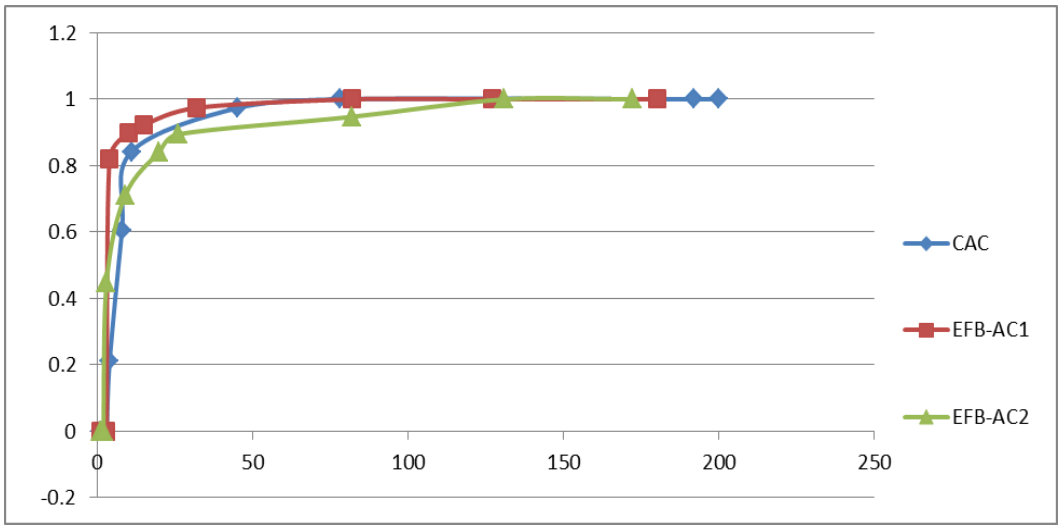


Fig. 4: Breakthrough curves of CO_2 adsorption on different types of activated carbon

3.1.3 BET surface area:

The BET surface area results were obtained by nitrogen adsorption on the samples. The BET surface area for EFB-AC1, EFB-AC2 and CAC were 807.54 mm/g,83.65mm/g, and 831mm/g. The results showed that the surface area for the EFB-AC samples almost equal to the commercial AC sample. The total pore volume of the EFB-AC samples also not much different compared to the total pore volume of commercial AC. Based on classification of pore diameter on activated carbon, generally the pore size that below than 20 A^0 indicated as micropores and the pore size in range of 20-500 A^0 referred to mesopores (Guo and Lua, 2000). The activated carbons produced from this study were microporous so that they suitable for gas-phase application. The results indicated that EFB-AC potentially can be a suitable and good adsorbent for the gas adsorption.

3.2 Material Testing:

3.2.1 CO_2 Breakthrough Adsorption:

Breakthrough adsorption experiments for different type of activated carbon were carried out at room temperature and at pressure 1 bar. The feed gas which contained constant CO_2 concentration was passed through the adsorbent. The results for effluent concentration from the bed were recorded until it reach saturation point or until the effluent concentration equals to the inlet concentration in order to assess the maximum dynamic adsorption capacity of the adsorbent. Fig. 4 showed the breakthrough curves for the EFB-activated carbon and commercial activated carbon. From the results of CO_2 adsorption on different modified AC, it was noticed that the effect of treatment on the activated carbon on the dynamic adsorption process was significant on the sample. The result for AC with KOH treatment (EFB-AC1) showed better performance compared to AC with KOH treatment and CO_2 activation (EFB-AC2) and equivalent to the commercial activated carbon in term of breakthrough time and adsorption capacity. The breakthrough time for CO_2 adsorption on the EFB-AC1 was longer and the amount adsorbed was higher. A longer breakthrough time imply better adsorption capacity. This means it would take a longer time for the adsorbent material to completely saturate with the adsorbate. Besides that, the type of modification on the adsorbent also influenced the adsorption performance. Report by Rafatullah *et al*. (2013) found that the materials treated without additional physical activation showed more extensive pore size distribution and average pore width compared with further CO_2 activation materials. The samples produced lower surface area, pore and micropore volume after been treated by heat treatment under CO_2. It means that that further thermal activation lead to pore shrinkage and produced small micropores which contributed to the lower adsorption capacity produced.

4.0 Conclusion:

In this study, porous carbons were prepared from palm empty fruit bunch by impregnation with KOH and CO_2 activation. The CO_2 gas adsorption and dynamic column breakthrough of three types of

activated carbon was tested. The breakthrough curves were experimentally obtained under constant flow rate (200mL/min).The performance of the KOH-impregnated adsorbent (EFB-AC1) materials found to be superior, in terms of breakthrough times and adsorption capacity. The EFB-AC1 sorbent produced CO_2 capacity of 0.57 mmol/g CO_2/g adsorbent and recorded longer breakthrough times compared to the EFB-AC2 sorbent.

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