Characterization of Activated Carbon Prepared from Oil Palm Empty Fruit Bunch by Chemical Activation using Sulphuric Acid (H_2SO_4)

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Abstract

Activated carbon has been known as an excellent adsorbent and has widely used due to its unique characteristics and large adsorption capacity. In this study, activated carbon produced from oil palm empty fruit bunch by chemical activation with various concentration of sulphuric acid was used. The activated carbon were analyzed using nitrogen adsorption isotherm as BET for specific surface area and Fourier Transform Infra Red (FT–IR) Spectroscopy. The experimental results indicated that improvement on carbon physicochemical characteristics was obtained by a activation process using sulphuric acid material (H_2SO_4). Analysis data showed that the specific surface area of activated carbon using sulphuric acid concentration at 2 M, 2.5 M, dan 3.5 M were 4.341 m^2/g, 2.190 m^2/g, 1.914 m^2/g respectively.

Keywords : *activated carbon, oil palm empty fruit bunch*

Introduction

Activated carbon is one type of adsorbent which most effective for the adsorption of heavy metals in water and gas pollution due to its unique characteristics and large adsorption capacity such as large surface area, high porosity and functional groups such as hydroxyl (OH), carboxyl (–COOH) and carbonyl (–CO) on its surface (Sumathi et al, 2009; Alkatib et al, 2011; Devi et al., 2012).

Recently, the development of activated carbon from agricultural wastes was widely used and more advanced in future. Agricultural wastes containing lignincellulose materials which rich carbon have been used as precursors of activated carbon is oil palm empty fruit bunches (EFB). EFB was containing lignocellulose by 55–65% dry weight. Through the production of palm oil per hectare of 20–24 tons of fresh fruit bunches per year that means its would produced 2.5 to 3.3 ton of lignocellulose materials. According to Mohamed et al. (2010) and Silvestre–Albero et al. (2012), materials containing lignocellulose can be used as the precursor material of activated carbon. Some advantages of activated carbon as precursor material of EFB is cheaper and easier to obtained.

The quality of activated carbon prepared from oil palm empty friut bunch (EFB) has been affected by the used method of carbonization and activation process. In general, activated carbon can be activated by two ways, namely chemical activation with alkali metal hydroxide, salts of carbonates, chlorides, sulfates, phosphates of alkaline metals and especially $ZnCl_2$, $CaCl_2$, inorganic acids such as H_2SO_4 and H_3PO_4 (Auta et al., 2012; Kurniawan et al, 2014) and physical activation which is the process of breaking the carbon chains of organic compounds with heating materials at a temperature of 800 °C to 900 °C and steam (Alam et al., 2008; Hidayu et al ., 2013). The types of activation methods have been used affected the physicochemical characteristics of activated carbon prepared oil palm empty fruit bunch.

According to Hsu and Teng (2000) the production of activated carbon by chemical activation using organic acid activator such H_2SO_4 is better applied to materials containing high ligninsellulose. It is because ligninsellulose materials containing high functional group of oxygen could be react with proton (H^+) from activator.In this work, characterization of activated carbon prepared from oil palm empty bunch (EFB) by chemical activation was studied. As reported previous research, some activation methods affect the physicochemical characteristics of activated carbon. In this study, the effect of sulphuric acid concentration on the physicochemical characteristics of activated carbon is focused. Characterizations using BET and FTIR were respectively used to determine specific surface area and surface functional groups. Proximate analysis was performed according to ASTM D7582–10 and the results showed the moisture, volatile content, fixed carbon, and ash content of activated carbon.

Experimental/Methods

Material

The oil palm empty fruit bunch (EFB) was supplied by the Oil Palm Mill PKS Aramiah, Bireum Bayeun, East Aceh residence, Langsa. The materials were cleaned with distilled water several times to remove dust and impurities. Then, EFB samples were dried in oven at 110°C for 24h to remove any surface moisture. The dried EFB samples were crushed with grinder and sieved to a small particle sizes.

Activated carbon preparation

The activated carbon from oil palm EFB was prepared by chemical activation with various concentration of sulfuric acid; 2 M, 2.5 M, and 3.5 M. Then, the mixture was separated from slurry by filtration and neutralization. The process was proceeded by countinous rinsing of the suspension with water until the filtrate absenced from H^+ (tested by universal indicator). Finally, the activated carbon obtained from this step was dried and calcined at 600°C.

Characterizations of activated carbon

In this experiment, the physicochemical characteristics of the activated carbon from EFB prepared under the optimum conditions were determined. Proximate analysis was performed according to ASTM D7582–10 and the results showed the moisture, volatile content, fixed carbon, and ash content of activated carbon.

Nitrogen gas sorption analysis for BET isotherm was performed by Quantachrom Autosorb–1. The spesific surface areas of samples was calculated by the BET (Brunauer, Emmett, and Teller) method while volume of micropore was estimated using Dubinin Radushkevich (DR) equation.

The surface functional groups of raw EFB and activated carbon EFB were analyzed using Fourier Transform Infrared (FT–IR) spectroscopy. Firstly, the samples were mixed with potassium bromide (KBr) and the mixture was pressed as pellet prior to analysis. The IR spectrum was obtained at a resolution of 4 cm^{-1} over range of 500–4000 cm^{-1}.

Results and Discussions

Proximate analysis of raw sample and activated carbon

The results of the proximate analysis of raw EFB and activated carbon EFB are represented in Table 1. As described in Table 1, the proximate analysis of the raw EFB showed fixed carbon and ash content that lower than activated carbon EFB. This is due to phsyical activation at the high temperature that caused volatile matter content was released. Table 1 showed that volatile content was decreased due to the activation process from 71.95 %w/t become 15.23 %w/t. According to De et al (2013) fixed carbon and volatile contents of EFB make this material become a good precursor for production of activated carbon.

Table 1. Proximate analysis of raw EFB and activated carbon EFB

Sample	Proximate analysis (wt%)			
	Moisture	Volatile	Fixed carbon	Ash
Raw EFB	7.32	71.95	16.93	3.80
Activated carbon EFB	2.44	15.23	67.66	9.58

N_2 adsorption isotherm in activated carbon

The types of N_2 adsorption desorption isotherms activated carbon is given in Fig. 1. Based on Fig. 1, activated carbon shows isotherms type I. This type indicates that the activated carbon is microporous materials (diameter of < 20 Å in size), according to International Union of Pure and Applied Chemistry (IUPAC) classification. This means that microporous materials most adsorb nitrogen molecules. Usually, isotherms type I display a convex curve and the platform of this type come out horizontal or virtually horizontal. The adsorption isotherms directly intersects with the line P/Po = 1 (Tang et al., 2012).

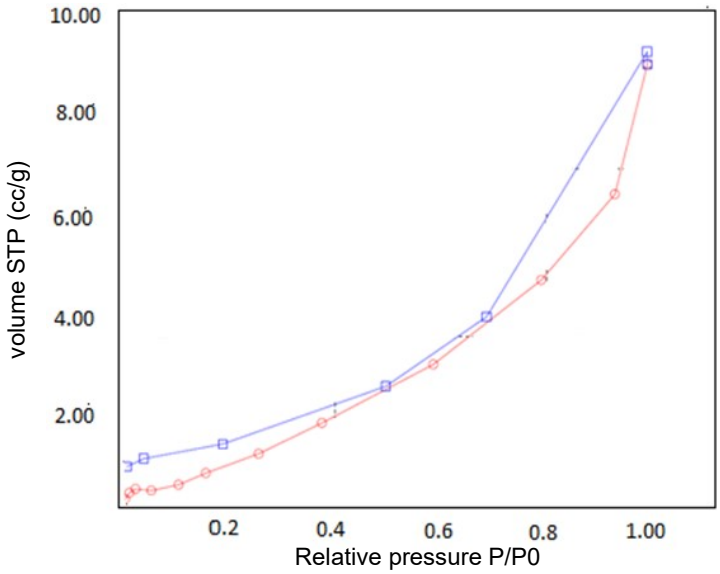


Figure. 1 The types of isotherm adsorption activated carbon from EFB

The BET specific surface areas of raw EFB and activated carbon EFB are presented in Table 2. It showed that the specific surface areas were increase after activation under optimum conditions. It occured because of activation process will enlarge the pore structure of EFB samples with breaking of hidrocarbon or oxidizing of surface molecules, so the carbon will change physically dan chemically, such the increasing of surface areas and absorption abilities.

Table 2. BET surface area of raw EFB and activated carbon EFB

Samples	S_{BET} (m^2/g)
Raw EFB	0,00
Activated carbon EFB	4,341

Fourier Transform Infrared (FT–IR) Spectrocopy

The FT–IR spectra of the raw material EFB and activated carbon EFB were given in Fig. 2a and 2b respectively. The EFB sample shows a broad adsorption peak at 3302 cm^{-1} which attributed to O–H stretching functional group. This indicates the presence of bonded hydroxide in the raw EFB. The adsorption band at 1743,65 cm^{-1} was corresponding to C=O functional group and peak at 1265,3 cm^{-1} and 1045 cm^{-1} refer to C–O stretching functional group. The result of identification functional groups based on Figure 2(a) showed that raw material of EFB has any functional groups, such as hydroxl (−OH), metoxy ($-CH_3O$), and carbonil (C=O) on its surface.

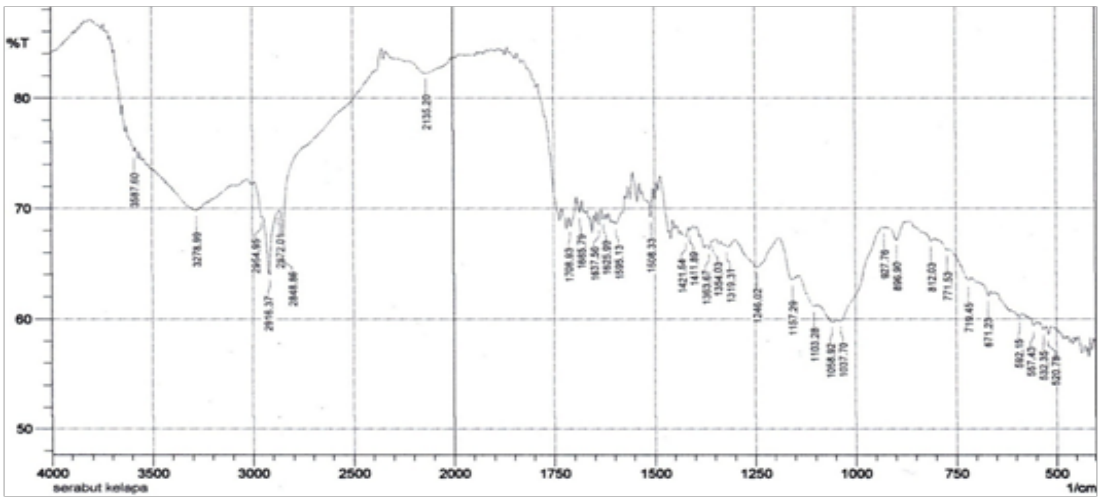


Figure 2. The FT–IR spectra of the raw material EFB (a).

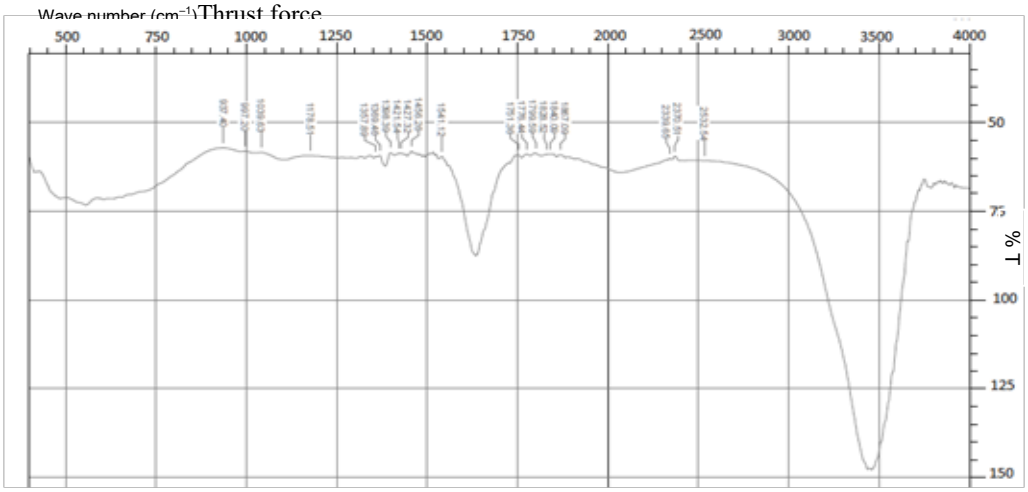
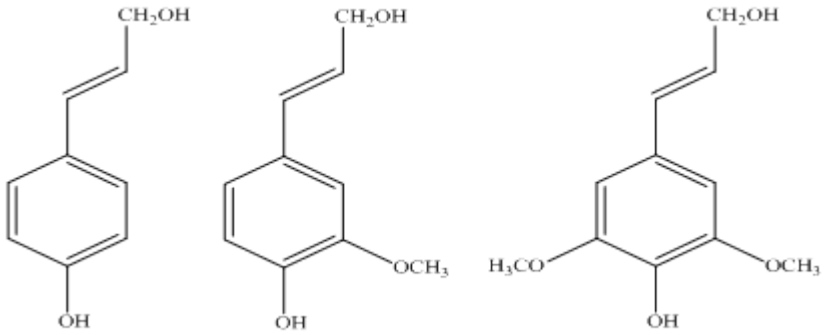


Figure 2. The FT–IR spectra of the activated carbon EFB (b)

The FT–IR spectra of activated carbon EFB was represented in Figure 2(b). The adsorption peak in Fig. 2 indicate that carbonization and activation process caused some of the adsorption peak of functional groups in activated carbon were dissapeared. This is occured because the heating at high temperature cause some of functional groups in raw material EFB were vaporized as volatile materials. This proved that the activation process was successfully converted raw material EFB into carbon. FTIR spectra show similiarties of some peaks; adsorption peak at 1751,36 cm^{-1} which attributed to C=O functional group and adsorption peak at 1043,49 cm^{-1} which attributed to C–O stretching functional group but adsorption peak at 1265,3 cm^{-1} was vaporized while activation process. It can be noticed that the adsorption peak of activated carbon EFB shift to the smaller wavenumber compare with raw material EFB.

Therefore, FTIR spectra of activated carbon EFB showed that the activated carbon has some functional groups such as hydroxyl (OH), carboxyl (–COOH), carbonyl (–CO) and aromatic structure which come from lignin and seluluce on its surface. The lignin of activated carbon EFB consists monomers of koniferil alcohol, p–kumaril alcohol, and sinapil alcohol as shown in Figure 3, respectively.



(a) (b) (c)

Figure 3. The structure of lignin activated carbon EFB samples (a) koniferil alcohol (b) kumaril alcohol (c) sinapil alcohol.

Effect of the sulphuric acid concentration to specific surface area of activated carbon

The effect of sulphuric acid concentration on the spesific surface areas of activated carbon shows in Figure 4. Based on Figure 4, the specific surface areas of activated carbon EFB was decreased with increasing the concentration of sulfuric acid used in the activation process. It showed that the increasing concentration of sulfuric acid in the activation process of activated carbon from the EFB would damaged the pore structure, so it cause the decreasing of specific surface area.

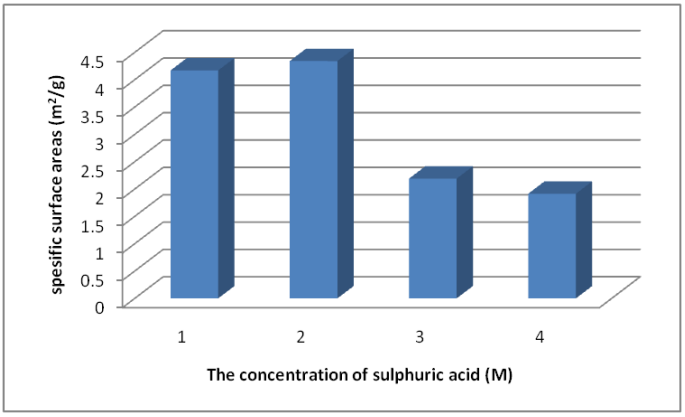


Figure 4. The effect of sulphuric acid concentration to spesific surface areas

Conclusions

The result of this research showed that the improvement on physicochemical characteristics of the raw EFB samples was obtained by a activation process. The activated carbon has specific surface area more higher than raw EFB samples yaitu 4,341 m^2/g. The result of FTIR analysis showed that the activated carbon has some functional groups such as hydroxyl (OH), carboxyl (–COOH), carbonyl (–CO) and aromatic structure which come from lignin and seluluce on its surface. The concentration of the sulphuric acid has effect on the pyhsicochemical characteristics of activated carbon. Analysis data showed that the specific surface area of activated carbon using sulphuric acid concentration at 2 M, 2.5 M, dan 3.5 M were 4.341 m^2/g, 2.190 m^2/g, 1.914 m^2/g respectively. It is concluded that the specific surface areas of activated carbon EFB was decreased with increasing the concentration of sulfuric acid used in the activation process.

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References

Alam Z.M., Muyibi S.A., Kamaldin N. 2008. Production of Activated Carbon From Oil Oil Palm Empty Fruit Bunches For Removal of Zinc. *Twelfth International Water Technology Conference*. 373–383. Alexandria. Egypt.

Alam M Z., Muyibi S A., and Mansor M. F. 2007. Activated carbons derived from oil palm empty–fruit bunches: Application to environmental problems. *J. Environ Sci*, 17: 103–108.

Alkhatib, M.A., Muyibi, S., and Amode, J. 2011. Optimization of activated carbon production from empty fruit bunch fibers in one–step steam pyrolysis for cadmium removal from aqueous solution, *The Environmentalist*, 31: 349.

Auta, Manase., Jibril, Muhammad., Philip, Tamuno, B.L., and Audu, A.A. 2012. Preparation of Activated Carbon from Oil Palm Fruit Bunch for Adsorption of Acid Red 1 Using Optimize Response Surface Methodology. *J. Engineering Research and Application*. Vol. (2): 1805–1815.

De, M., Azargohar, R., Dalai, A.K., Shewchuk, S.R.. 2013. Mercury removal by biochar based modified activated carbons. *Fuel 103*. p 570.

Devi, B. V., Jahargidar, A. A. and Ahmed M. N. Z.. 2012. Adsorption of Chromium on Activated Carbon Prepared from Coconut Shell, *Int. J. Eng. Research Applications*, Vol. 2 (5) : 364–370.

Hidayu, A.R., Mohammad, N.F., Matali, S., Sharifah, A.S.A.K. 2013. Characterization of Activated Carbon Prepared From Oil Palm Empty Fruit Bunch Using BET and FT–IR Techniques. *Procedia Engineering*. 379–384.

Hsisheng, Teng, Yu–Chuan Lin , Li–Yeh Hsu. 2000. Production of Activated Carbons from Pyrolysis of Waste Tires Impregnated with Potassium Hydroxide. *Journal of the Air & Waste Management Association*. Vol. 50 (10) : 1940–1946.

Kouotou, D., Manga, H. N., Bacaoui, A., Yaacoubi, A. and Mbadcam, J. K. 2013. Optimation of Activated carbon Prepared by H_3PO_4 and Steam Activation of Oil Palm shells, *J. Chem*., Vol. 2013: 1–10.

Kurniawan, Riski., Mustofa, Lutfhi, dan Wahyunanto Agung, N.. 2014. Karakterisasi Luas Permukaan BET (Braunanear, Emmelt and Teller) Karbon Aktif dari Tempurung Kelapa dengan Aktivasi Asam Posphat (H_3PO_4). *Jurnal Keteknikan Pertanian Tropis dan Biosistim*. Vol. 2 (1) :15–20.

Mohamed, A. R., Mohammadi, M. and Darzi, G. N. 2010. Preparation of Carbon Molecular Sieve from Lignocellulosic Biomass: A review, *Renewable and Sustainable Energy Reviews,* Vol. 14 (6): 1591–1599.

Rahmalia,W., Fitria, Y., Janiar, N., Mahwar, Q., dan Muhammad, I. 2009. Pemanfaatan Potensi Tandan Kosong Kelapa Sawit (*Elais guinensis* Jacq) sebagai Bahan Dasar C–Aktif Untuk Adsorpsi Logam Perak dalam Larutan.

Sumathi,S., S. Bhatia, S., Lee,K. T., Mohamed, A. R. 2009. Optimization of microporous palm shell activated carbon production for flue gas desulphurization: Experimental and statistical studies, *Bioresource Technology* 100, 1614.

Tang, Y–b., Liu, Q., Chen, F–y., 2012. Preparation and characterization of activated carbon from waste ramulus mori. *Chemical Engineering Journal*. 203: 19.

Wahi, R., Ngaini, Z. and Jok, V. U. 2009. Removal of Mercury, Lead and Copper from Aqueous Solution by Activated Carbon of Palm Oil Empty Fruit Bunch, *World Applied Sciences J*., Vol. 5 : 84–91.