Preparation and Characteristics of Activated Carbon from Oil Palm Shell for Removal of Iron and Copper from Patchouli Oil

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Abstract

Activated carbon was prepared from oil palm shell for removal of iron and copper from the patchouli oil. It was designed by pyrolysis at 900°C under nitrogen and continued under carbon dioxide. The result was refluxed into 10 M nitrite acid. The N_2 isotherm exhibits Type I corresponding to the micropores structure. The BET surface area, Langmuir surface area, micropore volume, total pore volume and average pore size distribution were 325.40 m^2/g, 491.60 m^2/g, 0.17 cc/g, 0.19 cc/g and 11.45 Å, respectively. The functional group was determined by FTIR spectroscopy and Boehm titration, and it shows an increasing of oxygen functional groups from 0,04meq/g to 0,19meq/g. The activated carbon showed a higher adsorptive capacity for removal iron compared to copper in patchouli oil

Keywords: Patchouli oil, Activated carbon, Iron, Copper

1. INTRODUCTION

Patchouli (pogostemoncablin) oil contains the patchouli alcohol widely used for medical treatment, food flavouring and perfume. For medical treatment, this oil was used for skin care, aromatherapy and antidepressant. The oil was also used as an additional ingredient in food such as candy, baked food, meat and meat products, alcohol and nonalcoholic beverage. The pleasant aroma was intensively used in perfume and soap[1]. Currently, Indonesia is one of the biggest exporting of essential oil (60 %) in the world and then is producing more than 4000 tons per annum[2]. The oil was obtained by steam extraction process of the dried leaves. Mostly, the oil farmer used conventional tool for extraction using old drum in which it could lower the quality of patchouli oil. It is very important to evaluate the effect of treatment such

as clearness, iron and copper contents including other aromatic volatile compounds in the oil[3].

Activated carbon has been well-known as a porous material with an excellent performance including chemical and physical properties. These properties make them to be prominently used in variety of industrial and environmental applications such as purification and separation[4, 5]. The surface area, pore volume and pore size distribution including surface chemistry are among of which they are strongly associated to the adsorption capacity. Surface area and pore volume are used for liquid and gas separation, medicine and catalyst while total surface area may supports the accessibility of active site relating to the catalytic activity [6]. Pore size of the activated carbon can be separated into the micropores ($d<$ 2nm), mesopores ($d,2-50$ nm) and macropores ($d>$50 nm) which are needed to improve the transport process of particles or molecules inside porous networks and facilitate the adsorption of larger molecules [7].

Due to its excellent characteristic, the world consumption of activated carbon has steadily increased and also not been replaced by zeolite, polymer and other new-adsorbents. This can be seen from the constant increased in number of publications over the years. Recently, considerable efforts have also been increasingly directed to the comprehensive understanding of porous structures with numerous practical applications [8]. Determination of functional group on the surface activated carbon was carried out by the FTIR and then supported by the Boehm titration originally developed in 1994 by Hans Peter Boehm for quantifying organic oxygen-containing surface functional groups of activated carbon [9].

The objective of the present research is to remove the iron and copper contents from patchouli oil using activated carbon prepared from waste of oil palm shell. Analysis of activated carbon was determined by the pore sizeanalyzer Quantachrome NOVA 2200e analyzer, Fourier transform infrared spectroscopy (FTIR), Boehm Titration, SEM and the amount of adsorption of iron and copper were carried out by Atomic Absorption Spectrophotometry (AAS).

2. MATERIAL AND METHODS
2.1 Chemicals
The Patchouli oil was purchased from the oil farmer which was produced by the conventional process. All chemicals were purchased from sigma Aldrich and used without purification.

2.2 Preparation of activated carbon
Activated carbon was prepared from waste of oil palm shell. The sample was washed with hot water and dried at 120°C. The dried sample was grounded with a knife mill into particle size in range of 0.1 – 0.5 mm. A 500 g of sample was pyrolysis in the graphite furnace at 900°C for 3 h. During pyrolysis process, the nitrogen gas was purged into the graphite furnace with a constantly flow rate of 200 cm^3 min^{-1}. Thereafter, the pyrolysis was directly continued with a carbon dioxide for 1.5 h instead of nitrogen gas. After cooling down, the adsorbent was washed with distilled

water for few times to set pH at around 6-7 and then it was dried at 120ºC. A bout 50 g of the activated carbon was refluxed into 10 M of nitrite acid for 6 h. Thereafter, the mixture was filtered and then the activated carbon was washed with hot water few times and neutralize with sodium hydroxide. The activated carbon then carbonized at 300ºC for 3 h. After cooling down, the dried activated carbon was kept for analysis and used as an adsorbent.

2.3 Characterization Technique
The textural characteristics of the activated carbons were investigated by applying nitrogen adsorption desorption isotherm at − 196ºC using the Quantachrome NOVA 2200eA. Prior to analysis, the sample was degassed under vacuum at 200ºC. The nitrogen isotherm data was used to determine the BET surface area (P/Po 0.05 − 0.30), Langmuir surface area (p/po< 0.05), micropore volume (DR method), total pore volume and pore size distribution.
Morphology structure of activated carbon was determined by Scanning electron microscopy (SEM). Prior to measurement, activated carbon were dried overnight at 110ºC.
The surface functional group of the activated carbon was qualitatively identified by Fourier transform infrared spectroscopy (FTIR). The FTIR spectra was obtained between 4000 and 400 nm using an AVATAR 360 spectrophotometer (Thermo Nicolet Co, USA). The transmission spectra of the activated carbon were carried out with KBr pellet.
The surface chemistry of the activated carbon was also analyzed by the Boehm titration method for quantifying organic oxygen-containing surface functional groups [9]. The method based on the procedure for equilibrating 50 ml of 0.05 M solutions of the Boehm reactants ($NaHCO_3$, Na_2CO_3, and NaOH) with 0.5 g activated carbon. The activated carbon is then separated from the solution and the aliquots were titrated with a standardized NaOH solution. The main principle is that the number of acidic sites is determined under the assumptions that NaOH neutralizes carboxylic, lactonic and phenolic groups on the activated carbon surface; that Na_2CO_3 neutralizes carboxylic and lactonic groups; and that $NaHCO_3$ neutralizes only carboxylic groups. The number of basic sites on the activated carbon is calculated from the amount of 0.05 M of HCl required in the titration.

2.4 Batch Adsorption Process
The adsorptive capacity of activated carbon was studied in removal of the Fe and Cu from patchouli oil with batch adsorption model. About 50 mL of the oil was added to each Erlenmeyer flask 250 mL containing 1.0 − 4.0 g activated carbon. The mixtures were shakenat 150 rmpat 30ºC for 24 h. Prior to the analyses, The mixtures were filtered to prevent interference from activated carbon.
The amount of metal removals were expressed as equilibrium (*qe*, mg/L) and the removal efficiency (*E*) of the adsorbent which was defined as

$$qe \ (mg/L) = \frac{(Co - Ce)\text{V}}{m}$$

$$E \ (\%) = \frac{(Co - Ce)}{Co} x100$$

C_o and C_e are the initial and equilibrium concentration (mg/L), respectively, V the volume of solution(L) and m is mass of the activated carbon (g)[10]. Dry ashing method was carried out for preparation of metal determination in the patchouli oil.The total metal contents adsorbed from the patchouli oil were analyzed by an Atomic absorption spectrophotometry (AAS).

3. RESULT AND DISCUSSION

3.1 Nitrogen adsorption isotherm

Fig. 1 shows the nitrogen adsorption isotherm at $-196\ ^oC$ of the activated carbon. The curve sharply increases at low relative pressure and was nearly plateau at higher relative pressure. This curve clearly showed Type I isotherm which is characteristic microporous activated carbon. However, desorption isotherm does not fit into the present classification. The hysteresis loop continues over the entire process exhibiting the inconsequence of failure to reach equilibrium step. As the nitrogen was adsorbed, it stayed inside the pore with a strong bonding and then the desorption process gave a higher curve to pronounce hysteresis[11]. For this reason, it might be that the pores were shrinkage during the desorption process and close the surface of pores of activated carbon. As a result, the surface area of activated carbon could decrease.
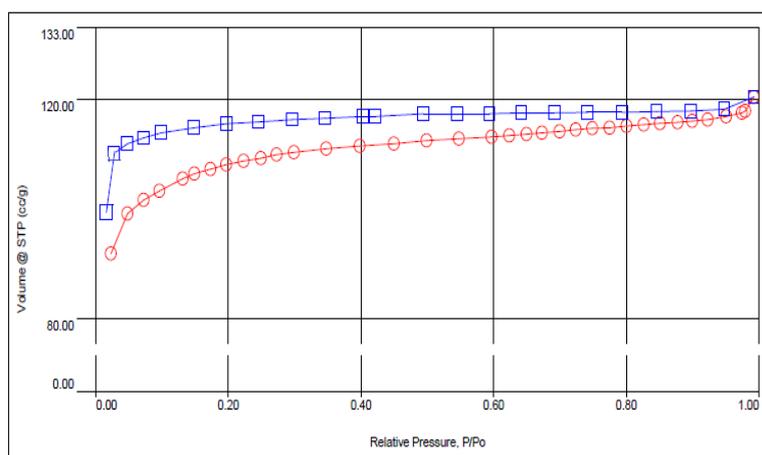

Figure 1: The nitrogen adsorption desorption isotherm of activated carbon at -196^oC

3.2 Pore Structure

To describe the surface area, pore volume and pore size distributions of the activated carbon was subjected to the nitrogen adsorption desorption isotherm data. Table 1 show the textural characteristics of the activated carbon. Based on the nitrogen isotherm curve, the pore clearly shows a predominantly microporous structure with monolayer structure and a small amount of mesoporous structure. This type pores

supported to determine the surface area by 2 methods: the Langmuir at low relative pressure (P/Po, 0.001 – 0.05) and BET at higher relative pressure (0.05 – 0.3) at correlation coefficient, $r^2 = 0.999$.

Table 1: Textural characteristics of activated carbon

Surface area, BET	325.40 m^2/g
Surface area, Langmuir	491.60 m^2/g
Micropore volume, DR	0.17 cm^3/g
Total pore volume	0.19cm^3/g
Average pore size distribution	11.45 Å
Pore diameter, DA	8.00 Å

3.3 pore size distribution

Pore size distribution of the activated carbon was estimated by the Barrett-Joyner-Halenda (BJH) Analysis. Fig. 2 shows the plot of pore size distribution of the activated carbon in the range of 10 – 1000 Å. According to the IUPAC classification, pore diameters can be classified as micropores (d <20 Å), mesopores (d = 20 to 500Å), and macropores (d > 500Å).In general, the formation of pores show a bulky micropore with diameter less than 20 Å or with the average pore size distribution 11,45 Å and a small amount of narrow mesopore with pore diameter between 20-40 Å.This result was confirmed with the Type I isotherm data which indicative microporous materials. The Dubinin-Astakhov (DA) method was used to describe the pore size diameter of micropoes of activated carbon. The value of pore diameter is 8.00 Å indicated a homogeneous narrow micropores[12].
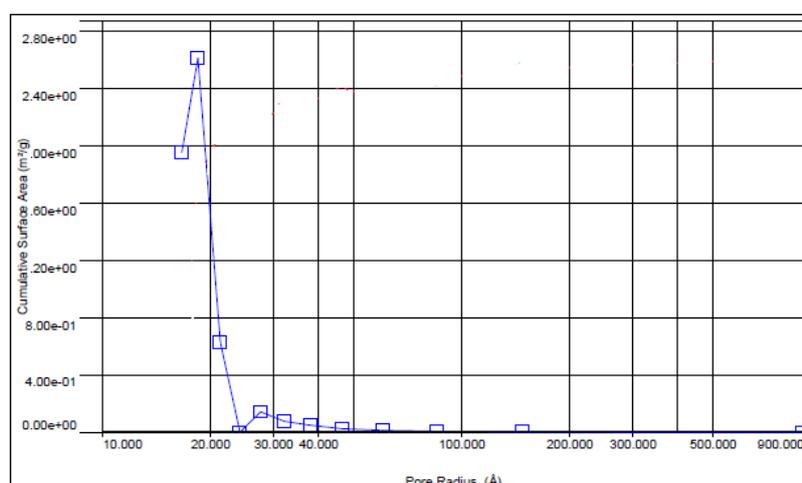

Figure 2: Pore size distribution of activated carbon using the BJH method

3.4 The surface functional group

The Fourier transform infrared (FTIR) transmission spectra were carried out to evaluate the surface functional groups on the activated carbon. Figure 3shows the

FTIR spectra of activated carbon with wave number ranging from 4000–400 cm^{-1}. A wide broad band can be found at 3448 cm^{-1}, especially intense for the O-H stretching vibrations. Treatment of activated carbon using nitric acid produced the formation of carbonyl on the surface by increasing the O-H group. The bands at 2924-2854 cm^{-1} are assigned to the C-H stretching while the bands 1419-1373 cm^{-1} are assigned to asymmetric C-H stretching and symmetric C-H bending, respectively. The bands at 1597 cm^{-1} can be attributed to the stretching vibration of C=C in the aromatic rings. The bands at 1419 cm^{-1} are assigned to C-H bending in alkane or alkyl groups. The peaks at 1267-1187 cm^{-1} were assigned to C-OH stretching vibrations in the carboxylic, phenolic or lactonic groups indicating the presence of oxygen functional group. The bands at 655 – 802 cm^{-1} were assigned to the C – C stretching
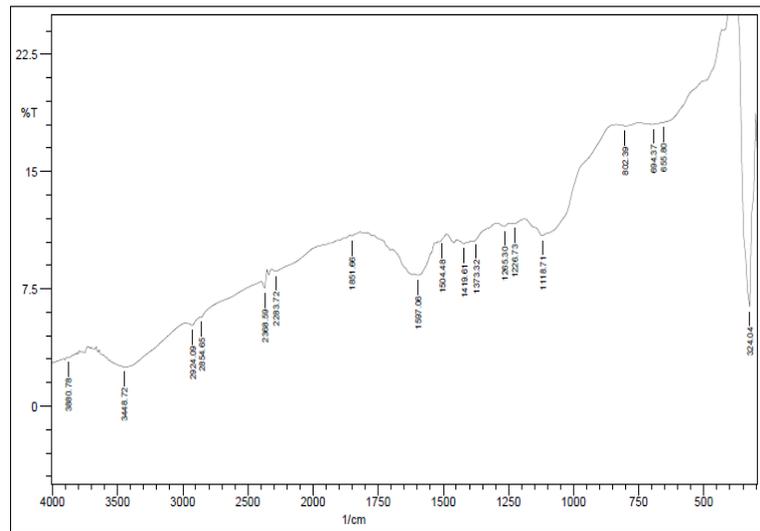

Figure 3: The FTIR spectra of activated carbon

The Boehm titration analysis can support the information of oxygen functional group on the surface activated carbon. Table 2 shows the data of acid functional groups on the surface carbon obtained by Boehm titration analysis. It was clearly mentioned on previous research that the activated carbon treated with nitric acid increased the number of oxygen functional group such as –OH, C=O and C-OH [13]. The result shows that the phenolic functional group has the highest values (0.19 meq/g). It seems that the activated carbon shows the rich oxygen functional group. This result was supported with the FTIR analyses.

Table 2: Total acid and based functional groups on the surface activated carbon

Sample	Acid group (meq/g)			Total acid group (meq/g)	Total based group (meq/g)
	Carboxylic	Lactonic	Phenolic		
Activated carbon	0.02	0.04	0.19	0.24	0.09

3.5 Characteristic Morphology Structure

The scanning electron microscopy (SEM) and the energy disperse X-ray analysis (EDX) was carried to observe the surface morphology and elemental micro-analysis of the activated carbon, respectively. Fig. 4 show the SEM micrograph and elemental composition which were obtained on the surface activated carbon. It was clearly that the external surface of the activated carbon was built up with micropore and mesopore. These pores result from the pyrolysis proses by evaporating all the impurities and rearrangement of carbon to form pores. As a result that the High micropore was observes on the surface. However, the presence of wide mesopore could be happened due to the broken pores during the pyrolysis. The results of typical EDX elemental micro-analysis proved that activated carbon compose from dominant carbon and oxygen. It seems that the activated carbon clearly have oxygen functional groups as an acid group.
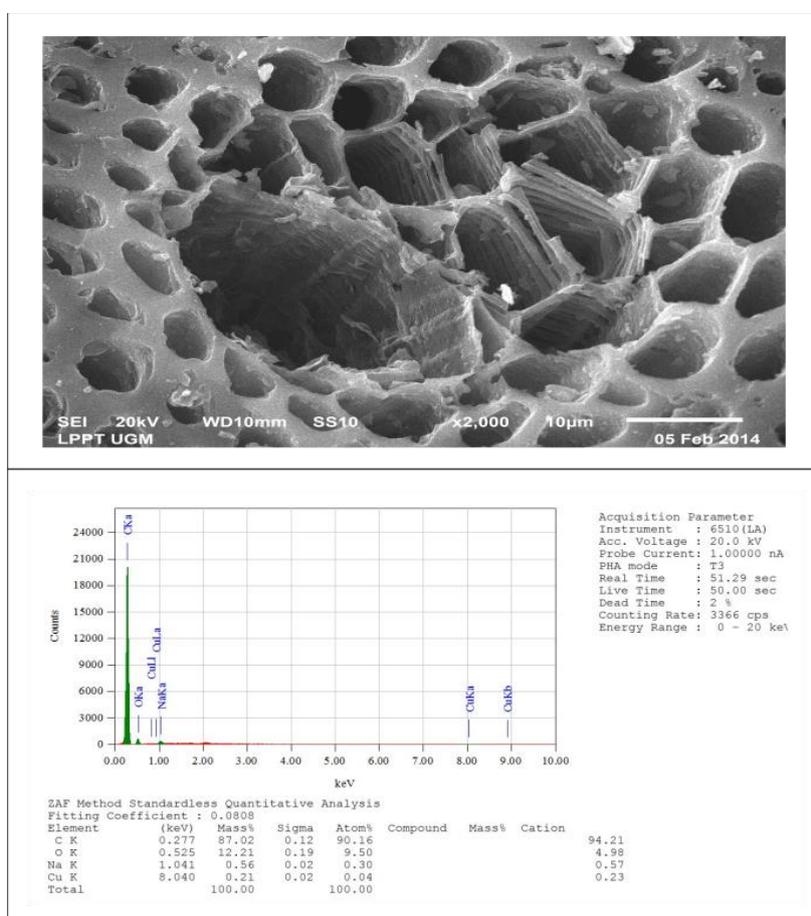

Figure 4: Morphology structure of activated carbon

3.6 Adsorption of Iron and Copper

The effects of activated carbon weight on the removal of Fe and Cu from patchouli oil are shown in Table 3. The percentage removal of the metals sharply increases from

22.07 to 82.59% and 2.11 to 76.18 % for Fe and Cu, respectively. This phenomenon can be occurred due to the increasing the availability of active site (such as pores and oxygen functional groups) or high surface area which it makes easier to adsorb the metals from the patchouli oil. The result found in this study indicates that the activated carbon is more effective in removing Fe as compared to the Cu from patchouli oil.

Table 3. The result for effect of activated carbon mass on removal of Fe and Cu

| Activated Carbon Mass(g)	Initial Fe (mg/L)	Equilibrium Fe (mg/L)	Amount of Fe Absorbed(mg/L)	% Removal of Fe
1.00	47.44	36.97	10.47	22.07
2.00	47.44	23.13	12.16	51.24
3.00	47.44	13.96	11.16	70.57
4.00	47.44	8.26	9.80	82.59
Activated Carbon Mass (g)	Initial Cu (mg/L)	Equilibrium Cu (mg/L)	Amount of Cu Absorbed(mg/L)	% Removal of Cu
1.00	10.90	10.67	0.23	2.11
2.00	10.90	6.12	2.39	43.87
3.00	10.90	2.36	2.85	78.35
4.00	10.90	2.60	2.08	76.18
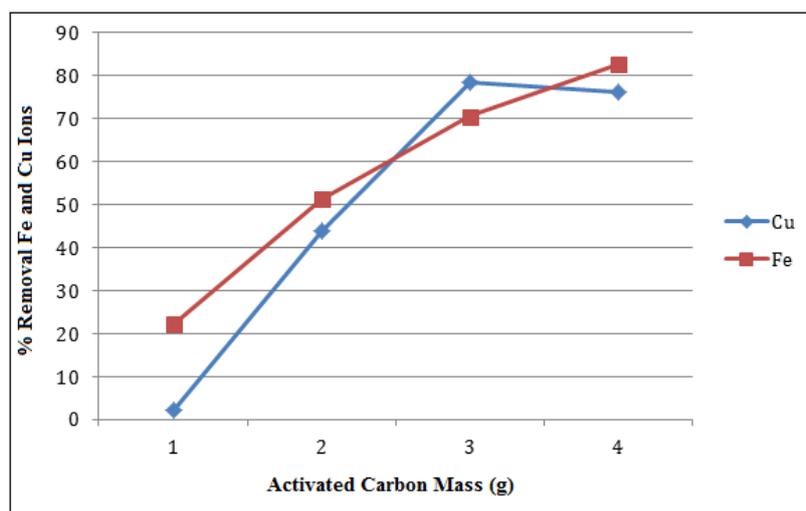
Figure 5: Adsorptive capacity of metal ions using activated carbon

CONCLUSION

The activated carbon was successfully characterized and showed Type I with microporous structure. The BET and Langmuir surface areas of activated carbon were 325.40 m^2/g, and 491.60 m^2/g, respectively. FTIR and Boehm titration results show that the activated carbon prepared contains –OH, C-OH, COOH and Lactones as oxygen containing surface functional group. It was observed that activated carbon

shows very good adsorbent for removing of iron as compared to copper from patchouli oil.

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