

Removal of Fe and Cu Ions from Patchouli Essential Oil Using ZnCl₂-Activated Carbon Adsorbent Modified With Ammonia

Allwar*, Lily Nurmala Sari, Krisna Merdekawati, Dwiwarso Rubiyanto

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Islamic University of Indonesia, 55584, Indonesia.

Abstract: Activated carbons derived from oil palm shell were used as adsorbents for removal of Fe and Cu from patchouli essential oil. The activated carbon was prepared with chemical activation using 50% zinc chloride under nitrogen and followed by carbon dioxide at 600°C. The activated carbons were converted into modified and non-modified adsorbent using chemical techniques with ammonia solution and without chemical techniques, respectively. Textural characteristics were performed by nitrogen adsorption-desorption isotherm at 77K. The Langmuir surface area and BET surface area were 743.25 and 530.02 m²g⁻¹, respectively. The isotherm curve shows the Type I with a very small hysteresis loop, indicating predominantly micropores and small amount of mesopores. The FTIR and Boehm titration methods were applied for determination of surface functional group showing an increasing basic group after ammonia treatment. The adsorption capacity of adsorbents was observed for removal of ferrate and copper into patchouli essential oil. The results show that modified adsorbent was able to remove 94.96% and 76.39% of Fe and Cu ions, respectively.

Keywords: Activated carbon, adsorbent, patchouli essential oil, Fe and Cu ions

I. Introduction

Patchouli essential oil has unique characterization such as aromatic oily liquids, volatile and strong odor. The oils have a complex composition, containing from a dozen to several hundred components. The majority of components identified in essential oils includes terpenes with monoterpenes and sesquiterpenes prevailing. Nevertheless, allyl- and propenylphenols (phenylpropanoids) are also important components of some essential oils. Essential oil has unique healing and valuable antiseptic properties. Some oils were used in various industries for production of aromatic therapy, food and drink, pharmaceutical industries, cosmetic and soap industry etc [1]. The oil is obtained from the leaves and young shoots of an herbaceous shrub (*Pogostemon cablin*) using distillation process. To obtain high quality of the oil product needs a great effort and well understanding of the oil characteristics. These may be supported by the method and equipment in producing the oil. In the developing countries, many essential oil farmers used a conventional equipment to produce the oil such as metal drum for boiler and then metal containers for storage. Both actions are the major source of impurities in the patchouli essential oil such as metal contents, dirty and dark colour [2].

The presence of metal impurities such as Fe and Cu ions including its compounds are toxic and harmful substances. Those metals can be easily found in the patchouli essential oil due to the conventional equipment during the distillation process. Metal ions may associate with the oil to form chelating metal ions followed by toxic organo-compound formations. In the presence of chelation metal ion, the colour of oil rises to dark brown. In addition, metals also promote the autoxidation process with a substantial negative effect in the yields.

Some industries used the essential oil with redistillation process in order to remove all metals contained and to obtain a fine desirable colour. Some purification methods have been applied to remove metal contents in the patchouli essential oil including adsorption processes using zeolite and complexometry processes [3, 4]. However, adsorption process using activated carbon could be more popular for removal of heavy metals. Some advantages are inexpensive raw materials, less sensitive to moisture, available in large quantity and high adsorption capacity compared to other adsorbents.

Well-known porous materials such as activated carbons are widely used as an adsorbent. Their excellent physical and chemical properties make them to be prominently used for the separation and purification process in a variety of industrial and environmental applications [5, 6]. The important properties such as surface area, pore volume and pore size distribution are among which they are strongly associated to the adsorption capacity. Large surface area and high pore volume are widely used in liquid and gas separation, medicine and catalyst which can support the accessibility of active sites relating to the catalytic activity [7-9]. Pore size distribution with the combinations of the micropores (pore diameter < 2 nm) and mesopores (pore diameter 2 – 50 nm) are requested to improve the transport process of particles or molecules inside porous networks and facilitate the adsorption of larger molecules. In addition, chemical properties are usually developed to the external surface mainly the extension of oxygen, nitrogen, halogen, etc which were chemically bonded to the edges of carbon layers and governed to the surface functional groups [10]. Many researchers are investigating as

how to modify as well as to characterize the surface functional groups in order to improve or extend their practical applications. Previous studies reported that modification using ammonia may increase the basic properties of adsorbent by presenting of nitrogen containing functional group on the surface. The nitrogen might increase the free electron valences on the edges on the external surface as they are very reactive to form coordination bond in attracting heavy metals in aqueous solutions[11, 12].

Activated carbon can be prepared from various types of precursors containing rich carbonaceous materials. Previous publications reported that preparations of activated carbon from palm oil shell using zinc chloride as impregnation agent have been studied. The condition of pyrolysis was set up at high activation temperature and under nitrogen and carbon dioxide atmosphere. The results showed that the adsorbent exhibited highly porous activated carbon with a well developed micro and mesoporous structure[13]. However, the efforts to increase the adsorptive capacity of the adsorbent are still continued, and it will be a good challenge to develop the methods such as to extend the surface functional group on the surface using modification chemical techniques.

This paper is aimed to understand the characteristics and effect of ammonia treatment on the adsorbents. Characterizations of adsorbent were investigated for their porosity and surface area using nitrogen adsorption desorption isotherm data. Surface functional groups were determined by FTIR and Boehm titration. The adsorptive capacity of adsorbents were evaluated on the removal of Fe and Cu from the patchouli essential oil.

II. Experimental Procedure

1.1 Preparation of activated carbon as an adsorbent

Oil palm shell was obtained around palm oil industry. It was washed, dried and grounded into particle size in range of 0.5 – 1.5 mm. The preparation of activated carbon was carried out based on the previous procedure[14]. Approximately, 500 g of palm oil shell was impregnated with 500 ml of 50% ZnCl₂ solution. The mixture was refluxed at 85°C for 24 h. After cooling down, the mixture was filtered, washed few times with hot water to pH around 7 and dried into oven at 120°C. Impregnated sample was carbonized at 600°C for 3 h. under nitrogen with a constant flow rate of 200 cm⁻³ min⁻¹. Thereafter, the carbonization process was continued with carbon dioxide gas of nitrogen gas for 1.5 h. After cooling down, the adsorbent was washed with hot distilled water for few times to pH 6-7 and dried into oven at 120°C. This activated carbon was called as a non-modified adsorbent. For modified adsorbent, this activated carbon then was treated with chemical technique using 10% ammonia. Approximately, 100 g of activated carbon was immersed into 100 ml of 10 % ammonia solution. The mixture was refluxed at 85°C for 3 h. After cooling down, the mixture was filtered, washed for few times with hot distilled water to neutral condition. Sample was dried into oven at 120°C for 24 h and continued into furnace at 250°C for 3 h. The yield was called modified adsorbent. Textural characteristics of both adsorbents were investigated by applying nitrogen adsorption desorption isotherm at 77 K using the Quantachrome NOVA 2200e analyzer. Analysis of surface chemistry was determined by FTIR and Boehm titration. Determination of morphology structure was carried out by SEM.

1.2 Removal of Fe and Cu ions

Patchouli essential oil was obtained from the oil farmer produced from conventional equipment for distillation process. The oil was used without any purification. Both modified and non-modified adsorbent were applied for the removal of Fe and Cu ions associated with patchouli essential oil. The weight of adsorbents was varied starting from 2.0, 4.0, 6.0 and 8.0 g. Each gram of them was placed into column glass in size of 1 x 50 cm prior to put glass wools at a bottom of column. Approximately, 50 ml of patchouli essential oil passed through the column at flow rate 1.0 ml/min. The filtrate was collected and stored to measure the amount of removal of Fe and Cu ions using Atomic Absorption Spectrophotometer.

III. Result And Discussion

1.3 Nitrogen Adsorption Desorption Isotherm

Figure 1 (A) shows the nitrogen adsorption desorption isotherm at 77K. The curve shows a well “knee” form at low relative pressure and tends to nearly plateau at higher relative pressure. Based on the classification of BDDT (Brunauer, Deming, Deming and Teller), the shape is Type I isotherm corresponding to the microporous structure. However, there was a small hysteresis at relative pressure > 0.4 which correspond to multilayer condensation as a mesoporous formation. Figure 1 (B) is the Langmuir plot at low relative pressure < 0.1 having a straight line plot with a correlation coefficient $r^2 = 0.99$. The linear Langmuir plot might support the presence of micropores with a monolayer adsorption. Both curves clearly indicated the modified adsorbent consisting of large pores with a well-developed microporous structure and small amount of mesopores. Previous theories assumed that the Type I isotherm with nearly plateau at higher relative pressure ($P/P_0 > 0.4$) might show a micropore filling indicating physisorption process or “pseudo-Langmuir” isotherm.

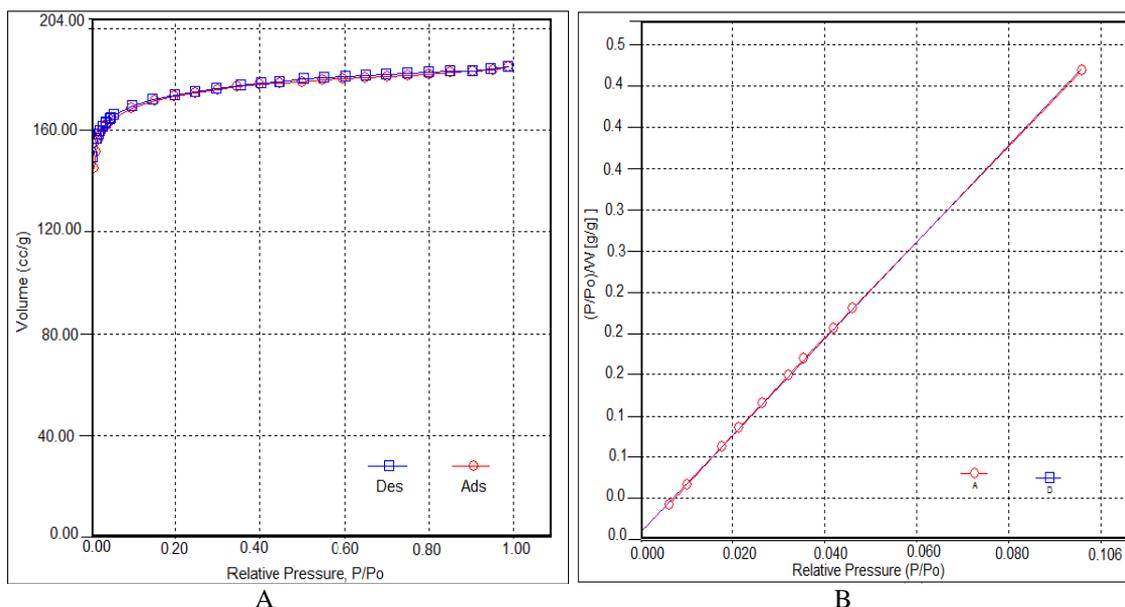


Figure 1:(A)The nitrogen adsorption desorption isotherm, (B)The Langmuir Plot of modified adsorbent

1.4 Specific Surface Area

Determination of surface area was observed by Langmuir and BET methods. The Langmuir surface area was carried out at low relative pressure < 0.1 which was limited to the formation of monolayer adsorption or the Type I isotherm. However, the BET surface area is an extension of the Langmuir method, which was observed at relative pressure in the range of 0.05-0.35. Both methods show convenient straight line plots with correlation coefficient $r^2 = 0.99$. Determination of surface areas of the modified adsorbent using the Langmuir and BET methods were 743.25 and 530.06 m^2g^{-1} , respectively. Table 1 shows the textural characterization of modified adsorbent.

Table 1: Textural characteristics of modified activated carbon

Langmuir Surface Area (m^2g^{-1})	BET Surface Area (m^2g^{-1})	t-plot			DR Micropore Volume (cm^3g^{-1})	Total Pore Volume $P/P_o=0.99$ (cm^3g^{-1})	Average Pore Size Diameter (nm)	D-A Pore Size Diameter (nm)
		Micropore Surface Area (m^2g^{-1})	External Surface Area (m^2g^{-1})	Micropore Volume (cm^3g^{-1})				
743.25	530.06	480.02	21.77	0.26	0.27	0.29	2.28	1.48 (n = 1.9)

1.5 Pore Size Distribution

The t-plot method was applied to the determination of micropore surface areas, external surface areas and micropore volume. The calculation was set at relative pressures in the range of 0.4 – 0.6 and the straight line of correlation coefficient (r^2) was obtained 0.99[15]. The Dubinin Radushkevich (DR) and the Dubinin Astakov (DA) methods were carried out to describe the volume filling of microporous structure of the modified adsorbent and the energetic heterogeneity of pore distributions. The micropore volume filling was calculated by the DR method at low relative pressure < 0.04 . The total pore volume was also interested to determine at the maximum relative pressure ($P/P_o=0.99$)[16]. The Dubinin Astakov method is widely used to describe the pore size diameter of the solid material including modified adsorbent. Fig. 2 shows the DA plot exhibiting the highest peak of pore size diameter around 1.45 nm which related to narrow micropores (micropore diameter < 2.0 nm) and small amount of narrow mesopores (mesopore diameter 2.0-50.0 nm). The DA model needs parameter of an adsorption characteristic energy (E_o), micropore volume (V) and parameter of exponent (n) related to the heterogeneity of micropore system. The value of n exponent was evaluated between 1 and 4. The result shows the modified adsorbent has n exponent value of 1.9 providing the heterogeneous adsorbent with wide range of micropores (Table 1)[17, 18].

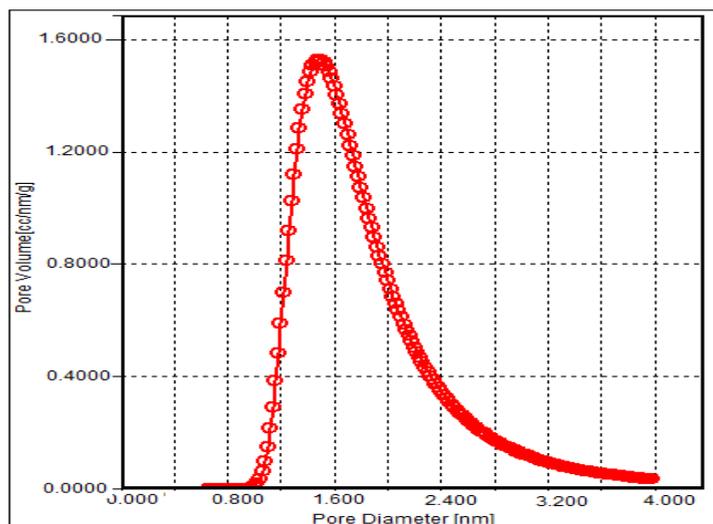


Figure 2. Dubinin Astakhov Plot for the modified adsorbent.

3.2 Functional groups of the adsorbent

3.2.1 FTIR Method

The comparisons of surface functional groups on the modified and non-modified adsorbents were evaluated with the FTIR spectra. The weak bands at 3410 and 3456 cm⁻¹ on non-modified adsorbent changed to strong band at 3417 cm⁻¹ on modified adsorbent which was assigned to N-H stretching vibration in amine group, and it was also associated to the O-H stretching vibration in hydroxyl group. A band at 1751 cm⁻¹ assigned to acid group with C=O stretching vibration in ketones, aldehydes or carboxylic groups (containing O functional group) was disappeared on modified adsorbent after treating with ammonia. This assumed an increasing of basic group on the modified adsorbent. A stronger band at 1635 cm⁻¹ could be assigned to C=O stretching vibration and strongly associated to C=N stretching vibration in pyridine and amide structures. A band at 1581 cm⁻¹ was assigned to C=C stretching vibration or C=N stretching vibration in aromatic rings which were responsible to the ammonia modification. A band at 1381 cm⁻¹ on the modified adsorbent could not be attributed in plane N-H bending vibration. A band at 1098 cm⁻¹ is attributed to N-O stretching vibration and a band at 609 cm⁻¹ is assigned to N-H stretching vibration in cyclic amide groups [19, 20].

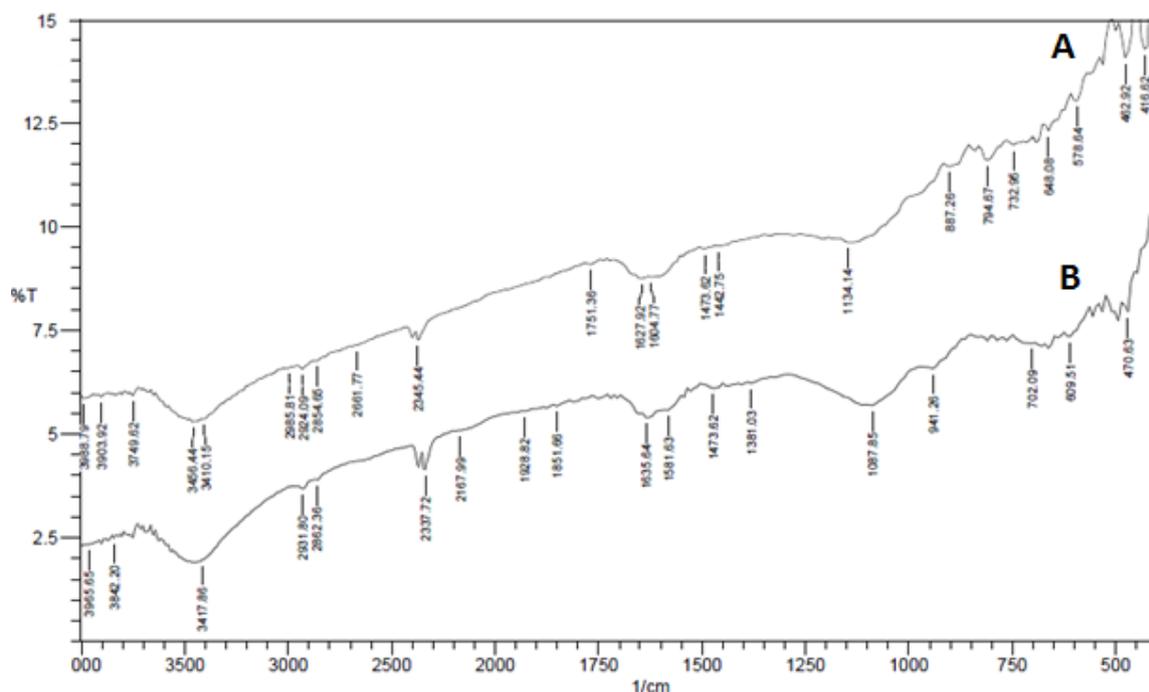


Figure 4. The FTIR Spectra of non modified (A) and Modified (B) adsorbent.

3.2.2 Boehm titration Method

To describe the number of acid and basic functional groups on surface of the adsorbents were determined by the Boehm titration method. The method used a reaction as assumption that NaOH neutralized carboxylic, lactonic and phenolic group; Na₂CO₃ neutralized carboxylic and lactonic group; NaHCO₃ neutralized only carboxylic group; and HCl neutralized the amount number of basic sites. Table 2 shows the concentration of carboxylic, lactonic and phenolic groups of modified and non-modified adsorbent. Introduction of ammonia to the activated carbon (non-modified adsorbent) could initiate the formation of new nitrogen-surface functional groups in the structure such as C-N and C=N groups, cyclic amides, nitrile groups and N-H groups and some of oxygen functional group such as carboxylic groups. This functional group might support an increasing of interaction between functional group and metal ion with chemisorption process. Results show that carboxylic group increased from 0.11 to 0.23 mekg⁻¹ as after ammonia treatment. However, lactonic and phenolic group decreased on modified adsorbent. It was assumed that modified adsorbents have less acid group compared to basic groups.

Table 2: Total acid and basic group on the surface adsorbents

Type of adsorbent	Carboxylic (mekg ⁻¹)	Lactonic (mekg ⁻¹)	Phenolic (mekg ⁻¹)	Basic (mekg ⁻¹)
Non-modified adsorbent	0.11	0.54	0.81	0.13
Modified adsorbent	0.23	0.47	0.59	1.04

1.6 Morphology structure of adsorbents

Morphology structures of adsorbents were determined by the SEM method. Fig. 4(A) shows the surface of non-modified adsorbent that was covered by the residual of zinc chlorides as incomplete pyrolysis process, and then they blocked on the mouth of pores. This occurrence might decrease the amount of surface area, total pore volume and reduced the adsorptive capacity of adsorbent. However, fig 4(B) exhibits the surface of adsorbent after ammonia treatment. It was reported that ammonium treatment might cause an increasing of the amount of surface area, pore volume and basic properties. Therefore, some changes were happened on the surface of adsorbents that all the residuals of zincs have been removed. Consequently, it was assumed that the surface area and pore volume significantly increase and followed by improving capacity adsorption.

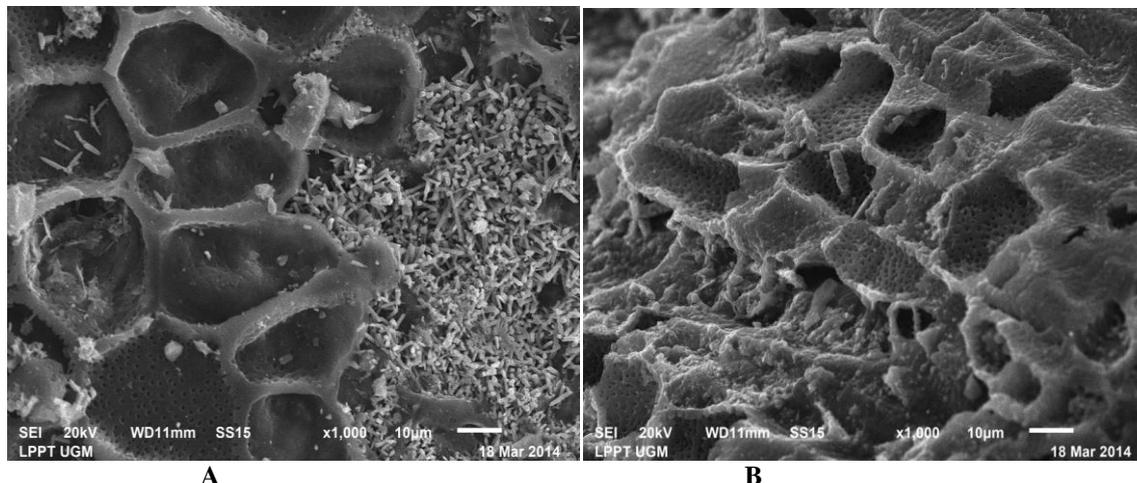


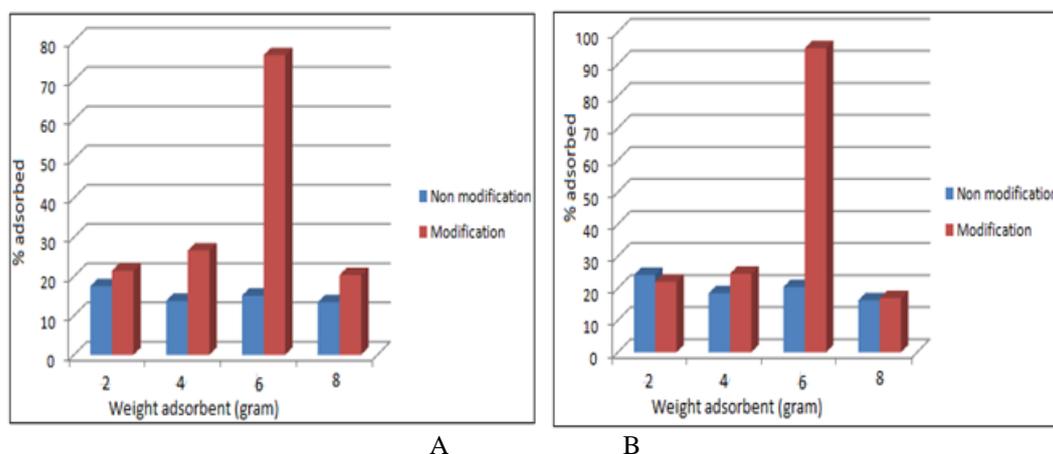
Figure 5: Morphology surface structure of (A) non-modified and (B) modified adsorbent.

3.5 Fe and Cu ions adsorption from patchouli essential oil

The removal of Fe and Cu ions from the patchouli essential oil were performed in a real sample. The results of Fe and Cu removal from the oil were summarized in Table 3. It was clearly seen that modified adsorbent has higher adsorption in removal of metal ions compared to the non-modified adsorbent. It was assumed that this occurrence could be caused by interaction between surface and metal ions. The presence of nitrogen including oxygen as surface functional group on the surface have some lone pair electron and acts as electron donor. The interaction between lone pair electron and metal might occur with coordination bonding with chemisorption process. The results were observed that Fe and Cu removal using the adsorbents reached their maximum values. The amount of percentage removal of Fe and Cu ions from patchouli essential oil was obtained 94.96 % and 76.39%, respectively. Fig. 6 shows the comparison of Fe and Cu removal using both types of adsorbents.

Table 3. The amount of Fe and Cu ions adsorbed by the adsorbents

Type of Metal	Initial metal in the oil (gram)	Weight of adsorbent (gram)	Amount of adsorption			
			Non modified adsorbent		Modified adsorbent	
			The amount of metal ion adsorbed (ppm)	Adsorbed (%)	Amount of metal ion adsorbed (ppm)	Adsorbed (%)
Fe	12.61	2	3.04	24.14	2.78	22.04
		4	2.33	18.45	3.09	24.55
		6	2.57	20.40	11.97	94.96
		8	2.05	16.23	2.13	16.88
Cu	7.24	2	1.27	17.48	1.55	21.43
		4	1.00	13.77	1.93	26.58
		6	1.10	15.09	5.53	76.39
		8	0.97	13.41	1.48	20.36

**Figure 6:** The amount of Fe and Cu ions adsorbed.

IV. Conclusion

Activated carbon derived from oil palm shell was effectively used as adsorbent for removal of Fe and Cu into the patchouli essential oil. Surface areas were evaluated by the Langmuir method and found 743.25 and 530.02 m²g⁻¹ for the modified and non-modified adsorbent, respectively. Functional group properties on surface arise after ammonia treatment proved with the presence of nitrogen and oxygen groups. The effective of adsorbents to remove Fe and Cu from the patchouli essential oil and the effect of ammonia treatment were significant. The adsorption rates of Fe and Cu from patchouli essential oil using modified adsorbent were rapid, and the modified adsorbent was able to remove 94.96 % and 76.39 % of Fe and Co, respectively from the patchouli essential oil. The adsorption process can be assumed due to the presence of functional group through chemisorption method.

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