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BIO-SORBENT AND ACTIVATED CARBON ADSORPTION COMPARATIVE STUDY OF *JATROPHA CURCAS* LEAVES IN REDUCING FREE FATTY ACID (FFA) AND PEROXIDE VALUE (PV) TO IMPROVING OF USED COOKING OIL QUALITY

HAFNI INDRIATI NASUTION[1], JASMIDI[1], MARINI DAMANIK[1], SITI RAHMAH[1], WASIS WUYUNG WISNU BRATA[2], RENDRA EFENDI[1] AND MOONDRA ZUBIR[1]*

[1]Chemistry Department, [2] Biology Department,
Faculty of Mathematics and Natural Science, Universitas Negeri Medan,
Jl. Willem Iskandar Pasar V, Medan Estate, Medan, North Sumatera 20221, Indonesia

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ABSTRACT

***Jatropha curcas* L. leaves was prepared as bio-sorbents and activated carbon for the purification of used cooking oil in reducing the value of FFA and PV. It compared the differences of the effect of functional group presence on bio-sorbents and pore frameworks on activated carbon can affect in decreasing of FFA and PV values of used cooking oil. XRD pattern and FTIR spectrum were observed the different of bio-sorbent and activated carbon properties of *Jatropha curcas* L. Leaves. The decrease in the lowest free fatty acid levels using bio-sorbent occurs at the optimum bio-sorbent mass of 8 g in 120 minutes with free fatty acid levels of 0.83% and activated carbon by 10 g in 150 minutes with free fatty acid levels is 0.79%. The optimum reduction of peroxide number using bio-sorbent is found in the mass of adsorbent 10 g for 150 minutes with a peroxide number is 9.87 mek O_2/kg and activated carbon is optimum in 10 grams for 90 minutes with a peroxide number is 13.99 mek O_2/kg. Bio-sorbent is more effective to reduce the PV value of used cooking oil while activated carbon have more potential to reduce its FFA value.**

KEY WORDS : Bio-sorbent, Activated carbon, *Jatropha leaves*, Adsorption, Used cooking oil

INTRODUCTION

Cooking oil is one of the basic human needs that is used as a food processing media. The need for cooking oil will enhance with the increasing population and in 2013 cooking oil consumption in Indonesia is 4.2 million tons and in 2015 it increased to 5.2 million tons. Some people, both of the household or industry, use cooking oil were repeatedly used for economic reasons. When it used repeatedly, the cooking oil will damage and affect to the quality and nutritional value of fried foods. During the frying process, degradation process reaction occurred due to the heat, air and water then produce oxidation, hydrolysis and polymerization reaction (Bhattacharya *et al.*, 2008). It also changes its physicochemical properties (oil damage) such as color, odor, increased peroxide number (PV) and free fatty acids (FFA). The major damage is due to the oxidation reaction, because of the formation of peroxide and aldehydes. It can cause serious health hazards, such as liver damage, potential gastrointestinal disorders, cancer and mutagenesis in the human body (Man *et al*., 2010).

For this reason, proper handling is needed to propose the used cooking oil can be beneficial and not cause harm in terms of human health and the environment. Improving the quality of used cooking oil can be done with the refining process. Its purification is the separation of degradation reaction products (water, peroxide, free fatty acids, aldehydes and ketones) from oil (Méndez *et al.*, 2014; Contran *et al.*, 2013). Several ways for that are the extraction membrane using supercritical fluid, or

using various types of adsorbents. Purification process with membrane or extraction using supercritical fluid requires investment and operational costs which are relatively higher than the adsorption process using adsorbents. Purifying used cooking oil with adsorbents is a simple and efficient process. The surface of the adsorbent will adsorb dye, colloidal suspension, and oil degradation products (Baseri *et al.*, 2012).

The adsorption method is expected to improve the quality of used cooking oil. Various types of adsorbents have been developed, such as adsorbents from natural materials. Adsorbents from biomaterials or bio-sorbents can be used to restore the quality of used cooking oil. Bio-sorbents produced from carbon-containing materials is the function of purification or separators of components in the gas or liquid phase, which is solids used to adsorb certain components of a fluid or adsorbate phase. Then, this bio-sorbent can also be a continued processing with high temperatures to be activated carbon. The prepared activated carbon can also be used for refining used cooking oil by utilizing the pore structure of the activated carbon.

In general, adsorbents can be produced from all natural materials that contain carbon, both organic and inorganic which has a porous structure, such as *Jatropha curcas* L. leaves. The chemical content of jatropha leaves are a carbohydrate (45.4%), fat (3.2%), protein (28.0%), ash (23.4%) (Yakout *et al*., 2016; Kaouah *et al.*, 2013). The high amount of carbohydrate content of Jatropha leaves is very possible to be used as bio-sorbent and activated carbon. Some reports informed that organic matter is effective for the preparation of activated carbon with a very porous structure (Chennouf-Abdellatif *et al*., 2015; Lin *et al.*, 2016). Activated carbon has great potential in removing dyes, odors, flavors and contaminants, in water purification and other decontamination processes (Mekonnen *et al.,* 2018; Kembaren *et al*., 2018).

Utilization of *Jatropha curcas* L. leaves have prepared biosorbents to remove the metals content in the water. But, no reports it used to reduce the value of FFA and PV from used cooking oil. In this study we compared *Jatropha curcas* L. leaves prepared as a bio-sorbent and activated carbon for the purification of used cooking oil in reducing the value of FFA and PV. We compared the differences in the effect of functional group presence on bio-sorbents and pore frameworks on activated carbon can affect the decreasing of FFA and PV values in used cooking oil (Minyu *et al*., 1993).

MATERIALS AND METHODS

The used cooking oil samples taken from several fried food sellers, in Medan Area Selatan, Jalan Sutrisno Street and Halat Street, Medan City which had been used 3-6 times. *Jatropha leaves* were collected from Durian village Pantai Labu Deli Serdang, Ethanol 96%, Glacial Acetic Acid (CH_3COOH), Chloroform ($CHCl_3$), Potassium Iodide (KI), Amylum Indicator, Sodium Thiosulfate ($Na_2S_2O_3$), Phenolphthalein (pp) Indicator, Potassium Hydroxide (KOH), Phosphoric Acid (H_3PO_4) and Aquades (H_2O).

Bio-sorbent Preparation of *Jatropha curcas* L. Leaves

10 g *Jatropha curcas* L. leaves were cleaned with distilled water to remove dust from the leaf surface and dried for 24 hours. The dried leaves were put into the oven at 105 ^oC for 4 hours to remove the water content. Then mashed using an electric blender and sieved with a size of 100 mesh to get a uniform bio-sorbent size.

Activated Carbon Preparation of *Jatropha curcas* L.Leaves

Jatropha curcas L. leaves were cleaned with running water then dried for 24 hours. The dried *Jatropha* leaves were put into the furnace at 200 ^oC for 30 minutes. After becoming carbon, the leaves were blended and sieved to be 100 mesh. Then activated it using 5% H_3PO_4 with a ratio of activated carbon : H_3PO_4 (1: 2) for 24 hours at room temperature. After activation, it was filtered and washed with distilled water to neutral pH. Then it was dried using an oven at 105 ^oC for 3 hours and cooled.

Characterization of Bio-sorbent and Activated Carbon of *Jatropha* Leaves

Crystalinity of *Jatropha curcas* L. leaves which prepared as bio-sorbent and activated carbon were characterized by using XRD (X-ray difractometer), morphological analysis with SEM (Scanning Electron Microscope), and analysis of functional groups cotent with FTIR (Fourier Transform Infra red).

Used Cooking Oil Preparation

Samples of used cooking oil was mixed and filtered to remove solids or remnants of the frying pan.

Then, free fatty acids and peroxide numbers were measured and its composition was also measured by gas chromatography.

Adsorbents Weight Effect of Used Cooking Oil Adsorption

Adsorbents were prepared with various weight are 2, 4, 6, 8 and 10 g and put into the beaker glass, then added 100 grams of used cooking oil at room temperature. The system was stirred using a magnetic stirrer for 90 minutes. After finish the adsorption process, filtered and collected the filtrate then analyzed its free fatty acids and peroxide numbers.

Contact Time Effect of Used Cooking Oil Adsorption

The adsorbent weight at the optimum conditions were put into the beaker glass, then added 100 g of used cooking oil at room temperature, then stirred using a magnetic stirrer with variations in contact time for 60, 90, 120 and 150 minutes. After finish the adsorption process, filtered and collected the filtrate then analyzed its free fatty acids and peroxide numbers.

RESULTS AND DISCUSSION

XRD pattern as Figure 1 observed the diffraction patterns of bio-sorbent samples and activated carbon of *Jatropha curcas* L. leaves. It detected that bio-sorbent have a major peak at 18.1° and other supported peaks at 14.96°, 24.339° and 64.27°. Insteed, XRD characterization of activated carbon of *Jatropha curcas* L. leaves shown 2 °C around 24.28° and supported peak at 14.89° and 38.41°. It indicates the difference in crystallinity between the *Jatropha curcas* L. leaves bio-sorbent and activated carbon-based on a shift of 2 °C and the resulting peak intensity. It confirm the crystallinity of *Jatropha curcas* L. leaves bio-sorbents is greater than of activated carbon which is closer to form as amorphous state of carbon.

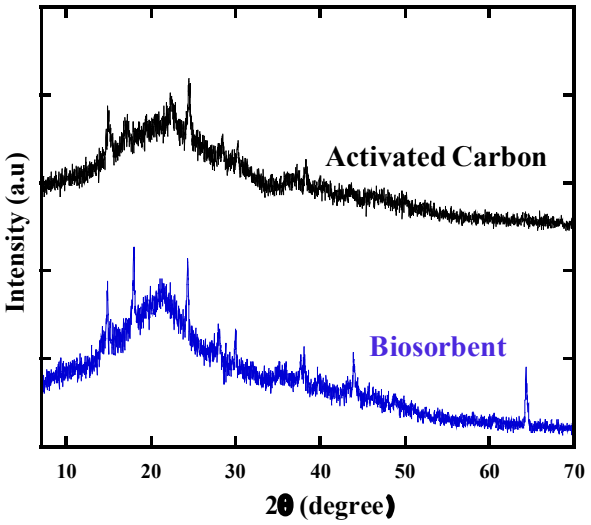

Fig. 1. XRD patterns of *Jatropha curcas* L. leaves were prepared as bio-sorbent and activated carbon

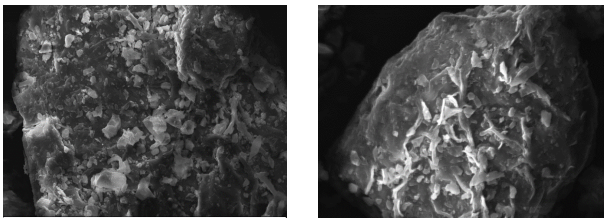

Fig. 2. SEM image of *Jatropha curcas* L. leaves were prepared as bio-sorbent and activated carbon

SEM images were observed both of bio-sorbent and activated carbon and indicate the surface of the bio-sorbent is uneven and there are still many impurities attached to its surface. While the surface of activated carbon looks more evenly which possibility caused by high temperature prepared. Characterization using FTIR was intended to compare the functional groups found between bio-sorbents and activated carbon. The functional groups contained in the adsorbent need to determine because it is related to the ability of the adsorption process in used cooking oil (Figure 3). It observed some functional group of bio-sorbent which the appearance of wave number absorption bands 1041.96 cm^{-1} and 1049.79 cm^{-1} indicate the presence of CO groups, absorption at 1618.01 cm^{-1} and 1616.01 cm^{-1} in the presence of C = O groups. Then -CH groups formed at absorption at 2918,71 cm^{-1} and 2917,98 cm^{-1}, and the presence of -OH groups in absorption at 3276.42 cm^{-1} and 3270.52 cm^{-1}. The -OH group indicates that bio-sorbents have polar properties. Whereas activated carbon has a very significant change in absorption of wave numbers, this is due to the breaking bonds of organic compounds contained in the *Jatropha curcas* L. leaves so that its remaining carbon frameworks.

The effect of the mass of adsorbent on the measurement results of the free fatty acid content of used cooking oil after the adsorption process using bio-sorbent and activated carbon from *Jatropha curcas* L. leaves observed the decreasing of free fatty acid value of oil by using bio-sorbents and activated

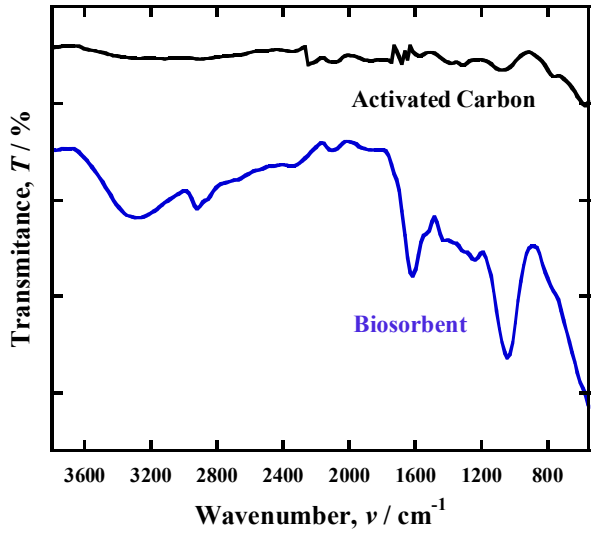

Fig. 3. FTIR spectrum of *Jatropha curcas* L. leaves were prepared as bio-sorbent and activated carbon.

carbon from *Jatropha curcas* L. leaves (Figure 4). The decrease of the lowest free fatty acid levels using bio-sorbent occurs at the optimum bio-sorbent mass is 8 g with free fatty acid levels of 0.89%. While the reduction in free fatty acid levels using optimum activated carbon by 10 g with free fatty acid levels of 0.83%. The addition of mass of adsorbent using bio-sorbent and activated carbon of jatropha leaves influence the reduction of fatty acid levels, indicating the tendency of more adsorbent mass to be used, the higher the reduction of free fatty acid levels in oil. However, the use of *Jatropha* leave mass is not significant effect, because it can trigger the formation of free fatty acid compounds. It is possible because the adsorption process between bio-sorbent

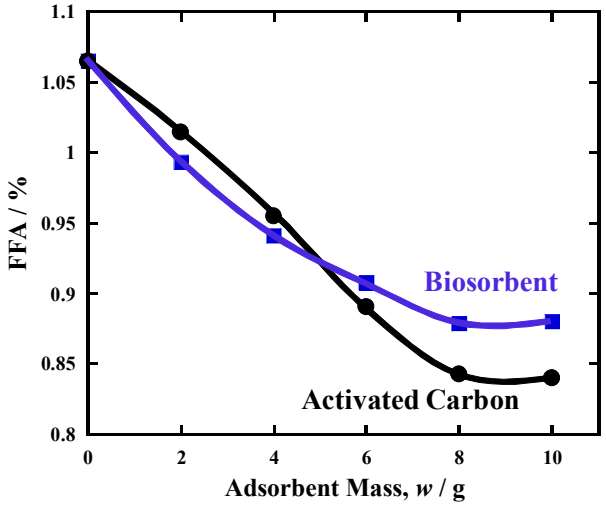

Fig. 4. Adsorbents Weight Effect on reduce FFA content of Used Cooking Oil

and cooking oil has already saturated so that the desorption process of free fatty acids is needed.

Decreasing of free fatty acid levels using bio-sorbents and activated carbon *Jatropha curcas* L. leaves along with increasing contact time were measured as shown in Figure 5. It was optimum at the contact time of 120 minutes with free fatty acid levels of 0.83% for bio-sorbent. Whereas carbon active was optimum at 150 minutes contact time with free fatty acid levels of 0.79%. It shows that the longer contact time of the adsorption process, induce higher the free fatty acid levels absorbed by adsorbents used.

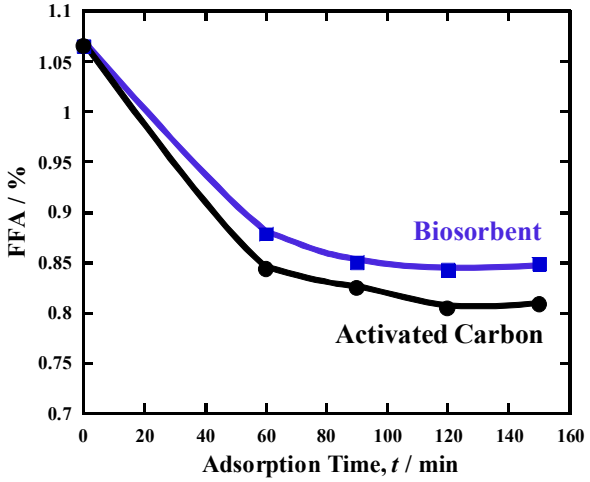

Fig. 5. Adsorption Time Effect on reduce FFA content of Used Cooking Oil

The adsorption process between adsorbents and free fatty acids is due to the difference in potential energy between the surface of the adsorbent and the adsorbed substances, which include both physical and chemical forces. Physical adsorption includes intermolecular forces (Van der Waals forces or hydrogen bonds). The functional groups contained in the bio-sorbent of *Jatropha curcas* leaves play a very important role in reducing the levels of free fatty acids in oil. Electronegative -OH groups in bio-sorbents cause polar properties, so bio-sorbents can absorb polar compounds better than non polar compounds. Free fatty acids are polar compounds with carboxylic acid groups (-COOH), induce FFA contained in cooking oil can be absorbed by hydrogen bonds by the bio-sorbent surface (Kaur *et al*., 2012).

While the decrease in free fatty acid levels with *Jatropha curcas* L. leaves activated carbon is due to the adsorption process between the surface of

activated carbon and free fatty acids contained in used cooking oil. Acidic organic compounds will be adsorbed well with polar adsorbents. Activated carbon with phosphoric acid is expected to have polar properties to reduce levels of free fatty acids in used cooking oil, in this case carboxylic acids in free fatty acids. This can be reinforced by the results of research conducted by Ozgul and Turkay (Ozgul *et al*., 2003), the percentage reduction in free fatty acid content is greater than the percentage reduction in methyl ester content in the same treatment, that is the adsorption process with rice husk ash as an adsorbent. Where the adsorption affinity properties of carboxylic acid compounds are greater when compared to ester compounds (Lam *et al*., 2010).

The use of bio-sorbent and activated carbon of *Jatropha curcas* L. leaves can reduce levels of free fatty acids, but activated carbon has a greater absorption of free fatty acids. It ossible because its surface area and its morphology are better than bio-sorbents based on SEM data. It caused through physical adsorption between the surface of activated carbon and free fatty acids in used cooking oil.

The measurement of peroxide number of used cooking oil after the adsorption process using bio-sorbents and activated carbon from *Jatropha curcas* L. leaves can be seen in Figures 6 and 7. The peroxide number is the most important value for determining the degree of oil or fat damage based on the reaction between alkali iodide in acidic solution with peroxide bonds. Based on Figure 6 the decrease in peroxide number using bio-sorbent and activated carbon of *Jatropha curcas* L. leaves increases with the amount of adsorbent added. The optimum reduction of peroxide number using bio-sorbent is found in the mass of adsorbent 10 g with a peroxide number is 11.80 mek O_2 / kg which higher than using activated carbon is found in 10 g of adsorbents with a peroxide number is 13.99 mek O_2 / kg.

Jatropha leave bio-sorbent can reduce the peroxide number in used cooking oil, because it contains saponins, flavonoids, tannins and polyphenol compounds which possible to capture free radicals in used cooking oil, and also prevent the next oxidation reactions (Kaouah *et al.*, 2013). On the other hand, ability of activated carbon to absorb peroxide numbers in used cooking oil is due to it activated with phosphoric acid which is polar so that it has a great affinity for polar solutes. The peroxide compound contained in cooking oil contains a polar peroxide group so that it is easily absorbed by the polar carbonative surface (Ma *et al*., 2013).

Based on Figure 7 the reduction in peroxide number using bio-sorbent and activated carbon of leaves increases with the increasing contact time. The decrease in optimum peroxide number using bio-sorbent occurs at the contact time of 150 minutes with a peroxide number is 9.87 mek O_2/kg and by using activated carbon occurs at the contact time of 90 minutes with a peroxide number of 13.73%. The polar carbonative surface of activated carbon is faster to reach saturated if compare than interaction of functional groups in bio-sorbent shows strong contribution to reduce this peroxide value. The longer contact time causes the active substance contained in jatropha leaves to effectively prevent oxidation reactions that occur, so the decrease in peroxide number will also be higher.

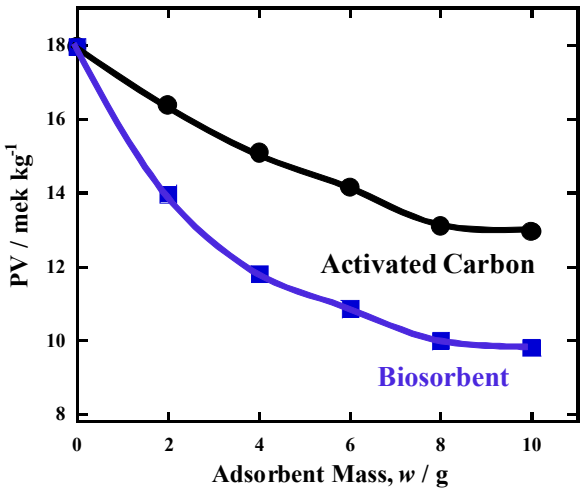

Fig. 6. Adsorbents weight effect on reduce Peroxide value (PV) of used cooking oil

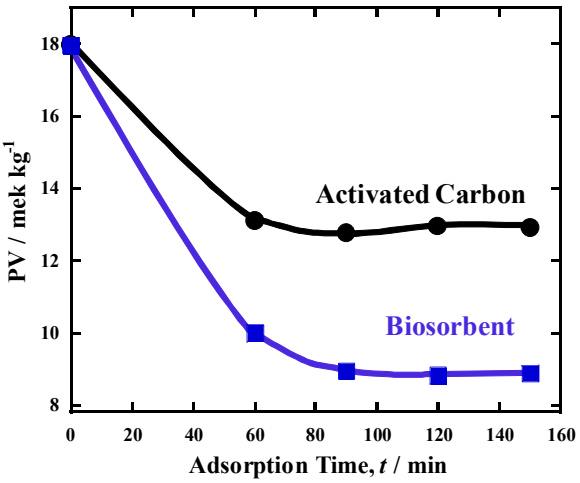

Fig. 7. Adsorption time effect on reduce Peroxide value (PV) of Used Cooking Oil

Table 1. Fatty acid composition of cooking oil sample

Fatty Acid	Oil Sample (%)			
	New	Used	After Bio-sorbent Adsorption	After Activated Carbon Adsorption
Laurat Acid (C:12)	0.32	0.32	0.32	0.315
Miristat Acid (C:14)	1.02	1.04	1.04	1.09
Palmitat Acid (C:16)	38.12	42.11	40.18	39.96
Palmitoleat Acid (C16:1)	0.20	0.21	0.21	0.20
Stearat Acid (C:18)	4.33	4.34	4.36	4.36
Oleat Acid (C18:1)	42.68	40.66	41.50	41.61
Linoleat Acid (C18:2)	10.07	8.09	9.03	9.06
Linolenat Acid (C18:3)	0.19	0.15	0.18	0.18
Arachidat Acid (C:20)	0.37	0.38	0.40	0.37
Eicosenoat Acid (C20:1)	0.15	0.13	0.13	0.14

The composition of fatty acids in new cooking oil, used cooking oil, used cooking oil after adsorption with bio-sorbent and used cooking oil after adsorption with activated carbon were determined as Table 1. Oil or fat consists of two main components are fatty acids and glycerol. Based on the presence or absence of a double bond in its molecular structure, cooking oil is divided into oils with saturated fatty acids, mono-unsaturated fatty acids (MUFA) and compounds (polyunsaturated fatty acids / PUFA). Saturated fatty acids are fatty acids that contain a single bond on the hydrocarbon chain. This oil is stable and does not easily react or turn into other types of fatty acids. Saturated fatty acids contained in cooking oil generally consist of octanoic acid, decanoic acid, lauric acid, myristic acid, palmitic acid and stearic acid.

There are not a significant decrease in saturated fatty acids namely Palmitic acid (C16) from new cooking oil to used cooking oil which was originally 40.12% to 40.11% and there was a change after adsorption with bio-sorbents and activated carbon respectively 40.18% and 39.96%. Unsaturated of oleic acid (C18: 1) from new cooking oil to used cooking oil which was changed from 42.68% to 40.66% and after adsorption with bio-sorbents and activated carbon are slightly increased respectively 41.50% and 41.61 % due to the decreasing of Palmitic acid (C16). Linolenic acid (C18: 3) content of new cooking oil to used cooking oil which was reduce from 0.19% to 0.15% and increased after adsorption with bio-sorbent and activated carbon respectively by 0.18 % and 0.18%. It indicates the formation of linolenic acid in the adsorption process but the addition is not too significant. Because no significant change in the composition of fatty acids in excess of 1%, it confirm bio-sorbents and activated carbon from *Jatropha curcas* L. leaves do not affect the fatty acid content of cooking oil.

We found different functions of two adsorbents prepared from *Jatropha curcas* L. leaves as bio-sorbent and activated carbon. The decrease in the lowest free fatty acid levels using bio-sorbent is 8 g in 120 minutes with free fatty acid levels of 0.83% and activated carbon by 10 g in 150 minutes with free fatty acid levels is 0.79%. Peroxide number using bio-sorbent is adsorbent used 10 g for150 minutes with a peroxide number is 9.87 mek O_2/kg. and activated carbon when 10 g for 900 minutes with a peroxide number is 13.99 mek O_2/kg. It confirm that bio-sorbent is more effective to reduce the PV value of used cooking oil while activated carbon have more potential to reduce its FFA value.

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