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Improvement in Quality of Used Palm Oil by Rice Husk Ash.

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ABSTRACT

The objective of this study is to improve the quality of used cooking oil by rice husk ash(RHA). Several variabels that will effect of recovery used cooking oil such as of weight and contact time variation of RHA. Subsequently, the used cooking oil was filtered to analysis the change of colour intensity, free fatty acids (FFA), peroxide value (PV), cholesterol, triglycerides, LDL and MDA were observed.RHA adsorbent surface characteristic were analyzed with SEM, functional groups Si-O-Si with FTIR and the content of silica in RHA by XRF. The results showed that the variation of the optimum recovery condition in weight of RHA is 20 g and contact time for 4 weeks it could reduce the value of the absorbent colour is 69.80,%, FFA is 74.42%, PV is 69.22%, cholesterol is 17.09% , triglycerides is 46.63 %, LDL is 33.24%, and MDA is 24.02% respectively. Based on the data obtained, it can be concluded that all the parameter tests under the requirements of SNI and the US National Cholesterol Education Program (NCP) -E2001 (maximum) and adsorbent RHA can improve the quality of used cooking oil.

Keywords: Rice husk ash(RHA), used cooking oil, FFA, PV, Cholesterol, Triglycerides, LDL, MDA.

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INTRODUCTION

Used cooking oil is derived from several repetitions cooking, repeated use of oilis not good for health such as narrowing of the arteries that can lead to stroke, and hypertension (Ghidurus,.et al. 2010). Several researchers said that RHA containing silica oxide dominant could used as adsorbent for the adsorption of heavy metals (Pb, Hg, Cu, Cd and Zn) from waste water and for purified of used cooking oil as resources of biodiesel [Qingge,et al. 2004; G, Doner.,S.Akman.2003; Manique, C.M, et al. 2004).Furthermore RHA has a good adsorbent properties that can adsorb FFA and PV in used cooking oil, If RHA unwashed, washed with HCl and washed with HNO3 could reduce the level of FFA 63.91% PV 45.64% , and FFA 53.60%), PV(21.37%), and FFA 52.58%, PV 13.95% respectively (Nattaporn, S and Porjai, T. 2015). According(Kalapathy, U and Proctor. 2000) a silica film from RHA can reduce FFA 20.70% and PV 12.5%, silica compounds synthesis could reduce levels FFA59%, PV93%(Yuliana, dkk.2005). The aim of this research were to study the ability of RHA as adsorbent for reduce the colour, FFA, PV, cholesterol, triglycerides, LDL and MDA in used cooking oil.

EXPERIMENTAL SECTION

Chemicals and Equipments

All chemicals used in this experiment AR analytical grade and obtained from Merck (Germany). Distilled water obtained from laboratory made, analytical balance (Kern & Sohn, GmbH), UV-Vis (Thermo Insight), FTIR (Nicolet iS 10 with KBr), SEM(Hitachi S-3400N) and PAN alytical XRF were used in this experiment, MICRO LAB 300(MRK Diagnostic), Diagnostic Reagent(Diasys).

Used Cooking Oil

Used cooking oil was prepared from cooking of from restaurant is Padang City, the new cooking oil was considered as a standard.

Adsorbent preparation of RHA

RHA taken from a rice mill in the village of Padang Siteba Nanggalo. RHA is stored in a glass bottle.

Determination of Optimum Condition

Effect of weight various RHA

RHA 5, 10, 15, and 20 g soaked with 50 ml of used cooking oil for 2 weeks in 250 mL glass beaker. Closed with aluminium foil then stored at room temperature for two weeks. Filtered with filter paper. The quality of oil were analyzed (colour, free fatty acid (FFA), peroxide value (PV), lipid profile(total cholesterol, triglycerides, Low Density Lipoprotein) and MDA.

Effect optimum of contact time various RHA

Optimum weight of RHA used to searching the optimum contact time (1,2,3 and 4 weeks) with 50 mL of used cooking oil in 250 mL glass beaker, closed with aluminium foil and filtered with filter paper the quality of oil were analyzed (colour, free fatty acid (FFA), peroxide value (PV), lipid profile(total cholesterol, triglycerides, Low Density Lipoprotein) and MDA.

Oil Quality Testing

Colour Analysis

1 mL of sample was taken. Put in the volumetric flask 10 mL and diluted with n-hexane then was measured with spectrophotometer.

FFA (%)

5 g of oil sample was weighted in flask 250 mL. Added 50 mL hot ethanol and 2 mL pp indicator then was titrated with 0.1 N KOH which was standardized until pink colour and constant for 30 seconds. FFA was measured as % FFA.

$$\% \text{ FFA} = \frac{\text{mL KOH x N x Molecular weight of fatty acid}}{\text{Sample weight x 1000}} \text{ x } 100\% \quad \text{.....(1)}$$

PV (meq/kg)

5 g of oil sample was weighted in flask 250 mL and added 30 mL of acetate acid-chloroform solution (3:2) then was homogenized. Saturated solution of KI was added and allowed for 1 min then was added 30 ml of distilled water. It was titrated with 0.01 N $Na_2S_2O_3$ until colorless of yellow colour. Then it was added 0.5 mL starch solution 1% and was continuous until colorless of blue colour.

$$\text{PV} = \frac{\text{(S-B)mL x N thio x 1000}}{\text{sample weinght (g)}} \quad \text{.....(2)}$$

Cholesterol

Prepared 3 tube containing blank (aquadest), Sample (oil), Standard 10 (mL). Added to each tube 1000 (mL) reagent cholesterol. Mix using homogeneous, incubation 20 minutes at room temperature or 10 minutes 37^{o}C. Red using MicroLab 300 at a wavelength of 546 nm.

Triglycerides

Prepared 3 tube containing blank (aquadest), Sample (oil), Standard 10 (mL). Added to each tube 1000 (mL) reagent triglycerides. Mix using homogeneous, incubation 20 minutes at room temperature or 10 minutes 37^{o}C. Red using MicroLab 300 at a wavelength of 546 nm.

LDL (low density lipoprotein)

Filter LDL

Prepared 3 tube containing blank (Aquadest), Sample(oil), Standard 10 (mL). Added to each tube 1000 (mL) reagent LDL. Vortex by using a vortex mixer until homogeneous. Incubation 30 minutes. Centrifuget to get filtarte and preciprate.

Measurement

Supplied 3 tube containing blank (Aquadest), Sample (oil), Standard 10 (mL). Added to each tube 1000 (mL) reagent colesterol. Mix using homogeneus, incubation 20 minutes at room temperature or 10 minutes 37^{o}C. Red using Microlab 300 at a wavelenght of 546 nm.

MDA (malondialdehide)

Supplied 3 tube containing blank, standard, oil 0.5 mL. Added each 2.5 TCA 5%. Mixed using a vortex mixer. Centrifuge for 10 minutes, at a speed of 2000 rpm. Pipette each 1.5 mL of the filtrate, put into labeling tube. Added each 1.5 mL Na. Thio acid Barbituric. Mixed with less using a vortex mixer. Heated in boiling water for 30 minutes and chilled. Determined absorbent with Spectrophotometer at a wavelength of 530 nm.

FTIR, XRF and SEM analysis

The sample is before and after contacting with the used cooking oil were analyzed by using FTIR, XRF and SEM.

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RESULTS AND DISCUSSION

Effect weight variation of RHA on colour used palm cooking oil

The efficiency of adsorbent depends on the polarity, surface active sites, surface area, porosity, particle size, pH and moisture content (Zhu, Z, Y, et al.1994).Analysis of colour used palm cooking oil was done by using a spectrophotometer, with new palm cooking oil as a blank. The increase in absorbance values greater shows that the darker colour of oil means the degradation products of used palm cooking oil more in the oil. The analyzed colour of used palm cooking oil were obtained as follow (figure 1). Colour development is an indication of oxidation, polymerization and formation of carbonyl compounds. It increases dramatically during frying and is influenced by frying temperature, although the quantitative amount of chemicals causing the increase in color is small(Paul, S, et al. 1997).

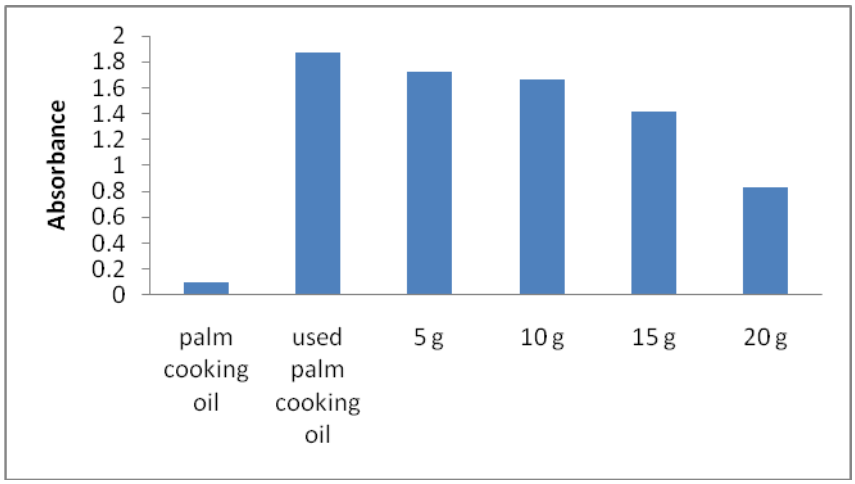

Figure 1: Effect of weight variation of rice husk ash to changes in value Absorbant colour with 50mL of used cooking oil and contact time for 2 weeks

Effect on the Free Fatty Acid

RHA has good adsorbent properties due to the high silica content [11] could reduce the value of FFA.

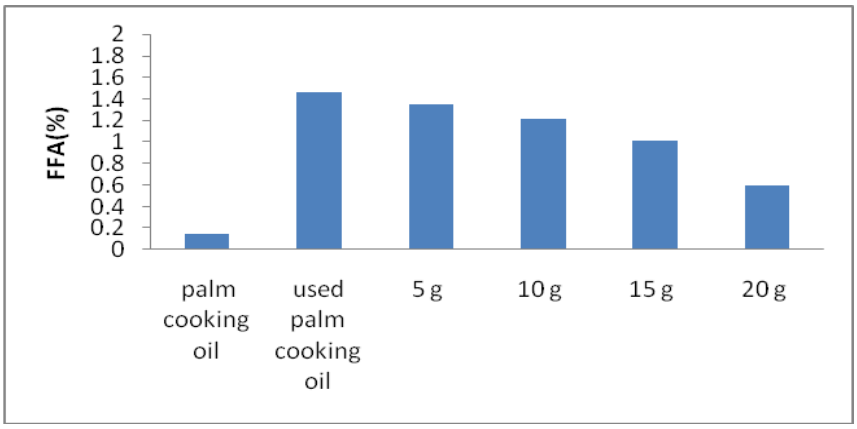

Figure 2: Effect of various RHA weight towards FFA number from used palm cooking oil contact for 2 weeks.

FFA value from new palm cooking oil (before used) is 0.1349% and used palm cooking oil was 1.462%. FFA value of increased significantly during frying and were strongly. By adding RHA adsorbent from 5-20 g used palm cooking oil, causing FFA value decreased to 59%. According to research (Yuliana, et al. 2005), the greater concentration of calcium silicate and magnesium silicate are added, obtained free fatty acid content is getting smaller. Meanwhile, according to (Paul, S, et al. 1997), rice husk ash has good adsorbent properties due to the

high silica content. Besides, magnesium silicate has a large active surface area and has a good ability to adsorb acids and polar compounds (Maskan, M and H,I.Baggci.2003).

Effect on the Peroxide value

Peroxide value is the number mol equivalents of active oxygen contained in 1000 grams of oil or fat (Apriantono, A.et al. 1989). Peroxide value is the value important to know the level of damage that have occurred in the oil or fat caused by the oxidation process takes place when there is contact between oxygen with oil. Unsaturated fatty acids constituent a triglyceride can bind oxygen to carbon double bond, so that form peroxides (Ketaren, S. 1986).Increasingly great peroxide value show more the greater the degree of damage to oil (Figure 3).

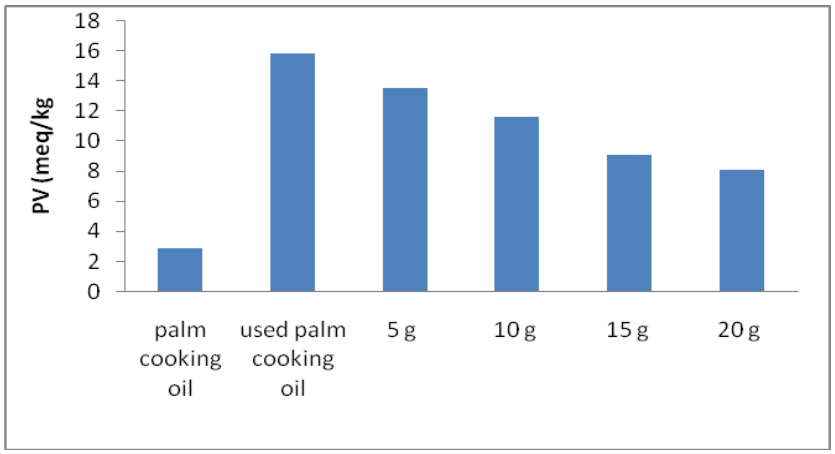

Figure 3: Effect of various RHA weight towards PV from used palm cooking oil contact time 2 weeks.

PV new palm cooking oil (before used) is 2,821 Meq/Kg, PV of used palm cooking oil was 15.85 Meq/Kg. The increasing the number of adsorbent massa from 5-20 g PV value of increased significantly during frying and were strongly. the PV value will decreased to 45%.

Effect of Lipid profile (total cholesterol, triglycerides and LDL) on RHA

The number of cholesterol in vegetable oil (Coconut oil, palm oil), also contain significant dietary cholesterol. To reduce the number of cholesterol level in used palm oil was used ram but as seen as adsorbent. Triglycerides are the main constituents of vegetable oils. Triglycerides have lower densities than water (they float on water), and at normal room temperatures may be solid or liquid. When solid, they are called "fats" or "butters" and when liquid they are called "oils".

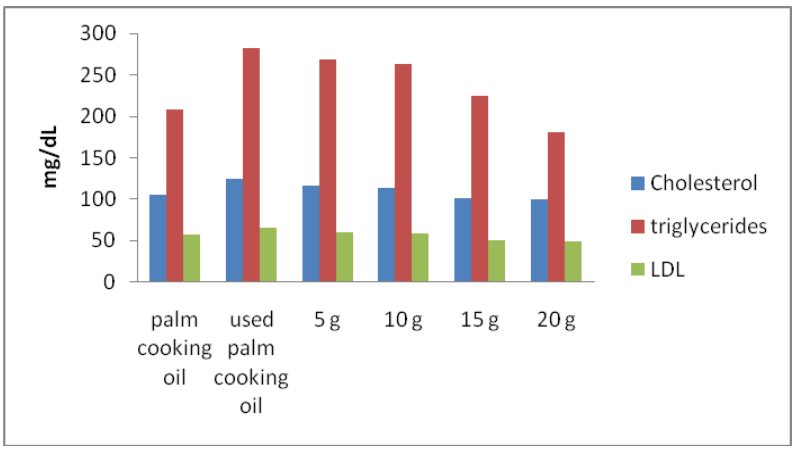

Figure 4: Effect of weight variation of rice husk ash to changes in valuecholesterol, triglycerides and LDL with 50mL of used cooking oil and contact time for 2weeks.

LDL is low-density lipoprotein, or the "bad" cholesterol. Higher LDL levels put you at greater risk for a heart attack from a sudden blood clot that forms there. In this study we were analyzed the concentration of cholesterol, triglycerides, LDL in the used palm cooking oil after remove by RHA (Figure 4).

Total cholesterol in new palm cooking oil (before used) is 105,14 mg/dL, total cholesterol of used palm cooking oil was 124,90 mg/dL. The increasing the value of adsorbent mass a from 5-20 g the total cholesterol value will decreased from 116,21, 100,4 mg/dL .

Triglycerides new palm cooking oil (before used) is 208,63 mg/dL, triglycerides of used palm cooking oil was 262,59 mg/dL. The increasing the value of adsorbent massa from 5-20 g the triglycerides value will decreased from 255,81, 80,58 mg/dL .

LDL new palm cooking oil (before used) is 57,13 mg/dL, LDL of used palm cooking oil was 65.31 mg/dL. The increasing the value of adsorbent massa from 5-20 g the LDL value will decreased from 60,10, 48,97 mg/dL .

The decrease in total cholesterol, triglycerides, high LDL seen on absorbent RHA treatment at 20g. The more absorbent added to the greater power of absorbs of RHA, this is because the silanol group which adsorbs organic compounds(Yang, R.T. et al 2003).

Effect of MDA on RHA

MDA new palm cooking oil (before used) is 4.85 nmol/L, MDA of used palm cooking oil was 6.91 nmol/L. The increasing the value of adsorbent mass from 5-20 g the MDA value will decreased from 6,25, 5,55 nmol/L

High levels of MDA is influenced by the levels of lipid peroxidation, which indirectly also showed a high number of free radicals. To reduce the number of MDA level in used palm oil was RHA as adsorbent. The result was showed in fig 5.

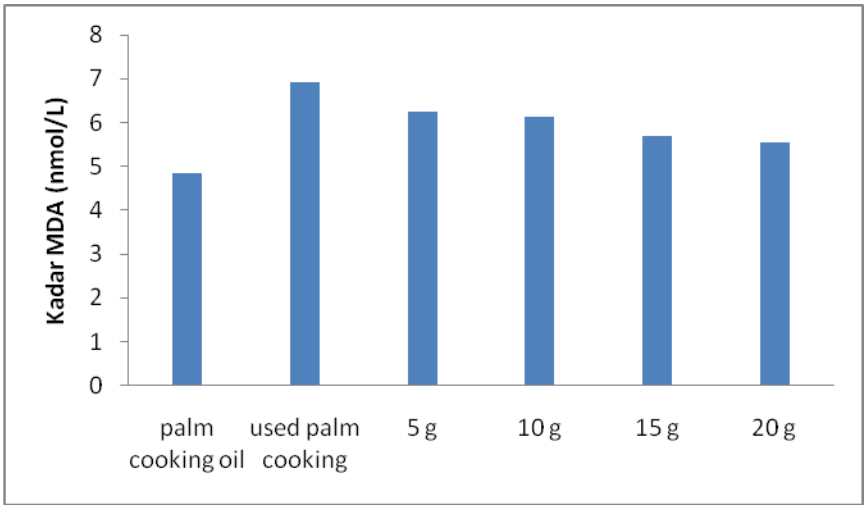

Figure 5: Effect of various RHA weight towards MDA value to 50 mL and the time used palm cooking oil contact for 2 week

The Effect of variation Time Contact Rice Husk Ash.

Colour analysis

The increasing the value of adsorbent contact time from 1-4 week the absorbance value will decrease to 69.80% (Figure 6).

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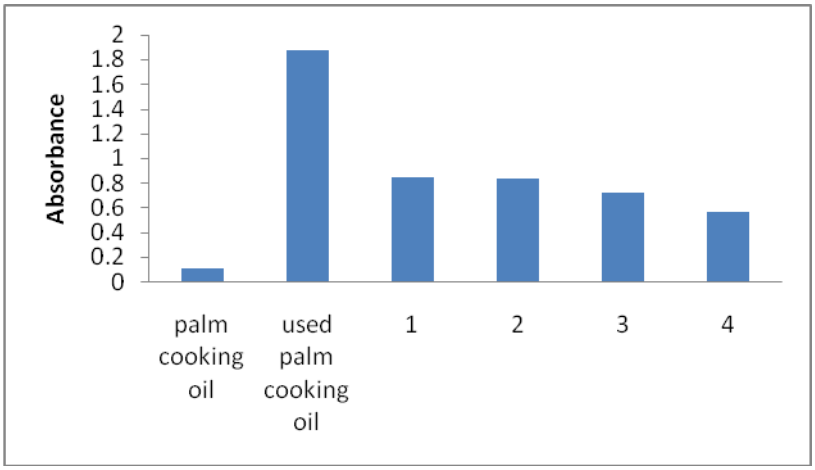

Figure 6: Effect contact time RHA and used palm cooking oil towards colour.

Effect on the Free fatty acids

FFA value of increased significantly during frying and were strongly. The increasing the value of adsorbent contact time from 1-4 week the FFA value will decreased to 74.42%. The value of FFA from the experiment is based on the Indonesian Standard 0.6 mg KOH/g.

Silicate compounds ability to reduce levels of free fatty acids due to the silanol (Si-OH) on the surface of the absorbent silica, because the silica surface chemistry dominated by hydroxyl or silanol (Si-OH). Silanol is what plays a role in the adsorption of water, organic compounds and other compounds. Silanol also plays a role in chemical modification (Yang, R.T. et al. 2003).Carbonyl oxygen group on free fatty acids react with hydrogen silanol, so that free fatty acid molecules adsorbed on the surface of the absorbent by forming hydrogen bonds with silanol hydrogen. The result was showed in Figure 7.

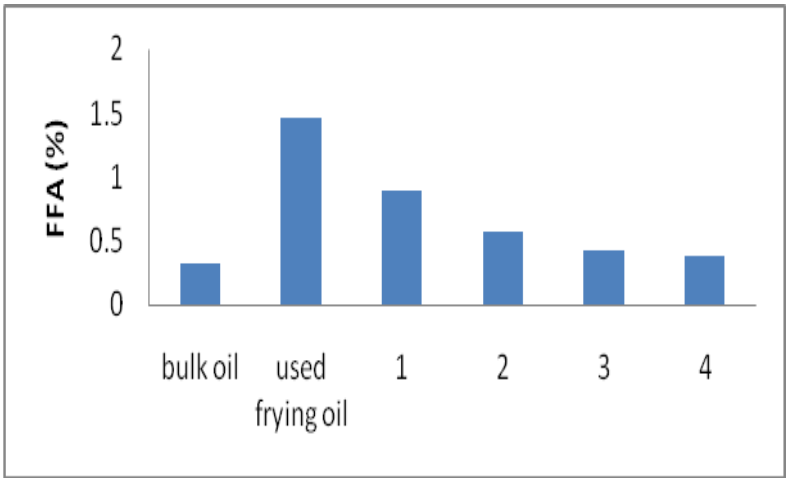

Figure 7: Effect contact time RHA and used palm cooking oil towards FFA value.

Effect on the Peroxide value

The percentage of rice husk ash capability in lowering levels of peroxide, the optimum conditions of 4 weeks, weight 20g (Figure 8). Meet the requirements of peroxide levels according to ISO 3741 - 2013(10). The increasing top vare influenced by the presence of silanol groups on the surface of the absorbent, the silanol groups adsorb organic compounds(Yang, R.T. et al. 2003).

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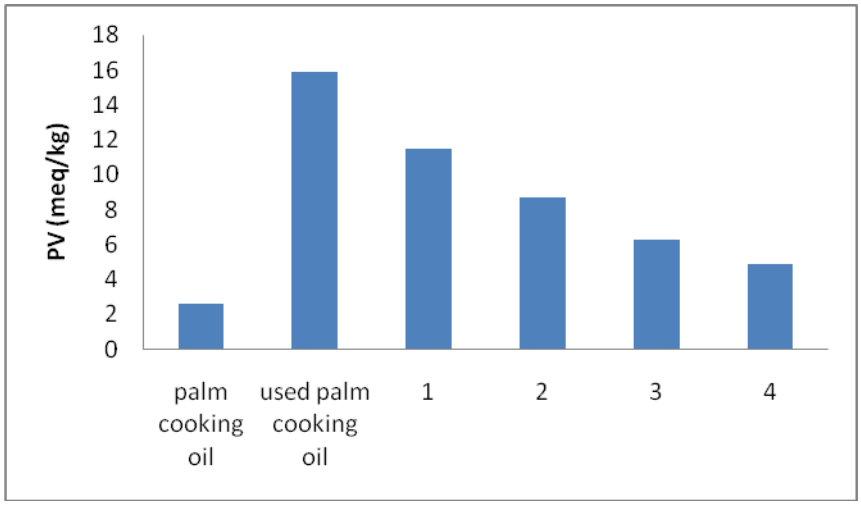

Figure 8: Effect contact time RHA and used palm cooking oil towards PV value. oil.

Effect on the Total cholesterol, triglycerides, LDL

The percentage of RHA capability in lowering total cholesterol (17.01%) triglycerides(46.63%), and LDL(56.77%) in optimum condition 4 weeks with a weight of 20grams absorbance levels of total cholesterol (.250 mak mg/dL), triglycerides (max200mg/dL) and LDL(max. <60 mg/ dl) is to meet the requirements according to the US National Cholesterol Education Program (NCEP) - 2001. The longer the absorbent is contacted, the greater the power absobrsi of rice husk ash (Figure 9).

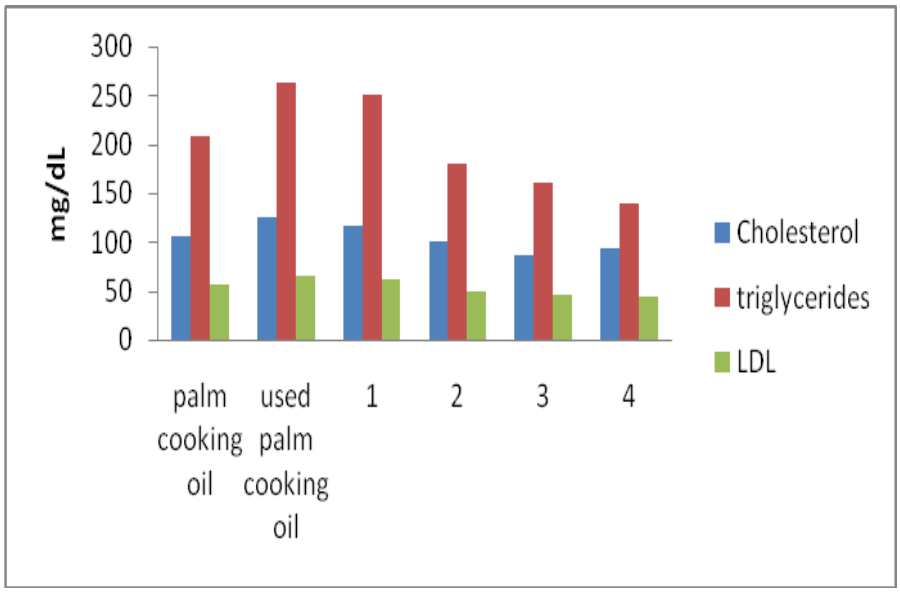

Figure 9: Effect contact time RHA and used palm cooking oil towards cholesterol, triglycerides and LDL value.

Effect on the MDA

The increasing the value of adsorbent contact time from 1-4 week the MDA value will decreased to 24.02% (Figure 10).

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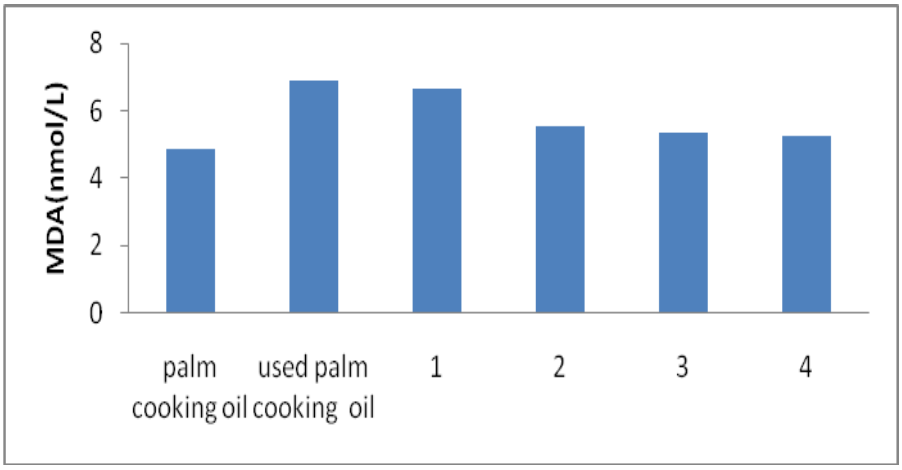

Figure 10: Effect contact time RHA and used palm cooking oil towards MDA value.

FTIR Analysis

Based on FTIR spectra as shown in Figure 11a and 11b, we obtained the common peaks of –OH and functional groups silanol 722,28 cm^{-1} dan 792,62 cm^{-1} and siloxane Si-O-Si 1162,32 cm^{-1}

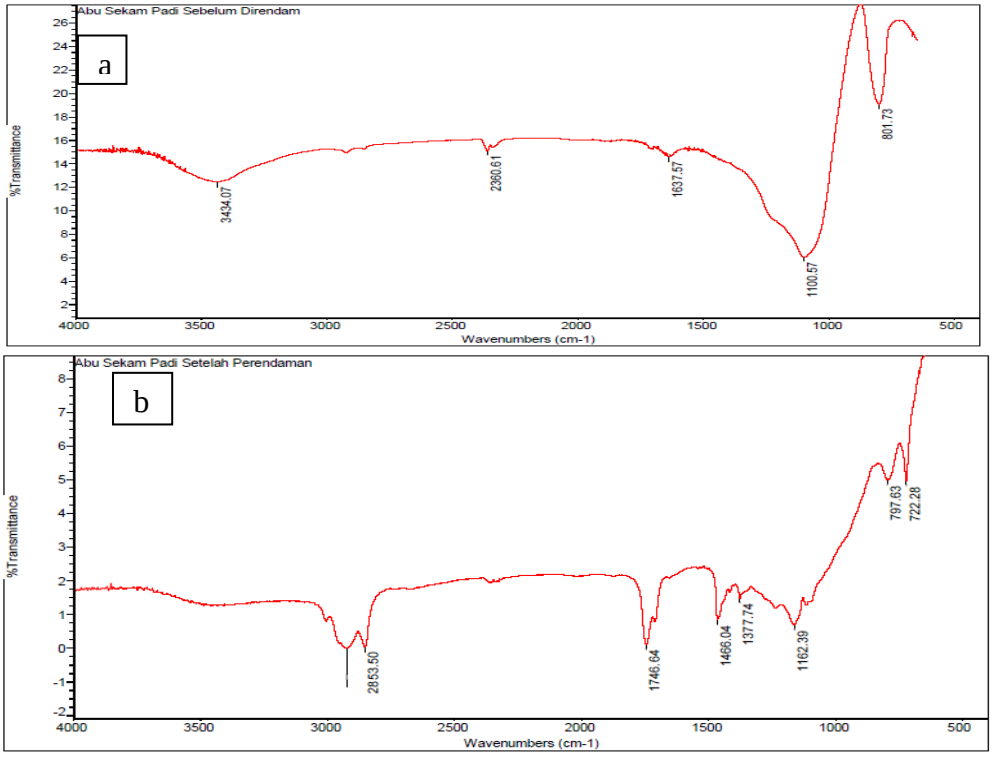

Figure 11: FTIRRHA (a) That has not been treated; (b) that have been treated with used palm cooking oil.

XRF Analysis

XRF was used to determine the qualitative and quantitative elemental composition of RHA. Silica content derived from RHA before used cooking oil treated with a higher(94.12%) compared with the silica content of RHA after contacted with used palm cooking oil (90.70%), it mean that silica content in the RHA reduce 3.4%.This suggests that silica formed compound Si-OH (silanol) and Si-O-Si [11].

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SEM Analysis

The surface morphology of the RHA before and after contacted with used palm cooking oil adsorption was observed using SEM analysis. There are significant changes to the surface morphology of the RHA, as well as the formation of discrete aggregates on their surfaces following chemical compounds, in adsorption. Fig12 (a) is RHA before contacted with used palm cooking oil was showed that so many pores on the RHA surface, fig 12 (b) is RHA after contacted with used palm cooking oil.

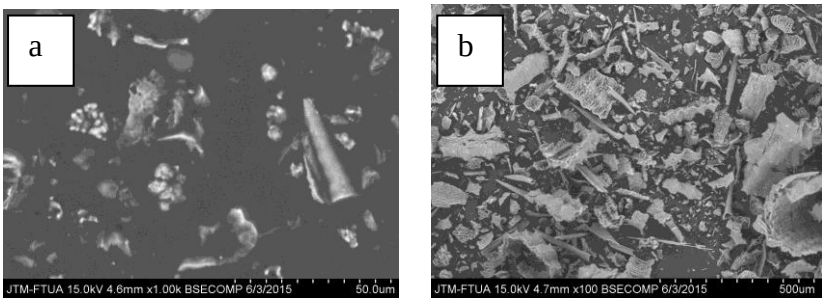

Figure 12 (a) SEM image of RHA before batch treatment (b) SEM image of RHA after batch treatment.

CONCLUSION

RHA can be used as an adsorbent to reduce the values of colour, free fatty acids, peroxide value, cholesterol, triglycerides, LDL and MDA. In this absorption were compound of groups OH silanol and siloxane Si-O-Si, at optimum conditions was 20 g and contact time 4 weeks.

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