

EFFECTIVENESS BLEACHING OF WASTE COOKING OIL CLEANING USING NANO-MONTMORILLONITE ADSORBENT

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Abstract: Waste cooking oil contains carcinogenic compounds which are formed during the frying process. The content change makes it is not worth for reuse cooking oil. One of the damages to cooking oil is caused by heating. The quality of useable oil refers to SNI 01-3741-2013. The sample used in this research is waste cooking oil that is used for 5 times of frying. The quality of the oil can be improved using Nano-Montmorillonite adsorbent. Based on the results of PSA and FTIR characterization, it shows that Nano-Montmorillonite has a nano-scale particle size of 15.3 nm with a percentage of 6%, and the rest are particles that have a size >100 nm with a total percentage of 94% with a respective size of 383.9 nm with a percentage of 59% and 6647.1 nm with a percentage of 35% and have functional groups, namely hydroxyl (-OH), Si-O-Si and Al-Al-OH. Testing of waste cooking oil quality includes organoleptics, acid numbers, peroxide numbers and saponification numbers using Nano-Montmorillonite. Based on the results, the more Nano-Montmorillonite adsorbent was added, the lower numbers of acid, peroxide and saponification in waste cooking oil and the quality of flavor and colour are better. Based on this analysis, Nano-Montmorillonite adsorbent can improve the quality of waste cooking oil.

Keywords: Waste cooking oil; Bentonite; Nano-montmorillonite; Adsorbent

Abstrak: Minyak jelantah mengandung senyawa yang bersifat karsinogenik yang terbentuk selama proses penggorengan. Perubahan sifat ini menjadikan minyak goreng tersebut tidak layak digunakan kembali sebagai bahan makanan. Salah satu kerusakan pada minyak goreng disebabkan oleh pemanasan. Kualitas minyak layak pakai merujuk pada SNI 01-3741-2013. Sampel minyak yang digunakan dalam penelitian ini adalah minyak jelantah dengan 5 kali penggorengan. Kualitas minyak tersebut dapat ditingkatkan menggunakan adsorben Nano-Montmorillonit. Berdasarkan hasil karakterisasi PSA dan FTIR menunjukkan bahwa Nano-Montmorillonit memiliki ukuran partikel berskala nano yaitu 15,3 nm dengan persentase sebesar 6% dan sisanya merupakan partikel yang memiliki ukuran > 100 nm dengan total persentase 94% dengan ukuran masing-masing sebesar 383,9 nm dengan persentase 59% dan 6647,1 nm dengan persentase 35%serta memiliki gugus-gugus fungsional yaitu hidroksil (-OH), Si-O-Si dan Al-Al-OH. Pengujian kualitas minyak jelantah meliputi organoleptik, bilangan asam, bilangan peroksida dan bilangan penyabunan menggunakan Nano-Montmorillonit. Berdasarkan hasil pengujian maka semakin banyak jumlah adsorben Nano-Montmorillonit yang ditambahkan maka bilangan asam, bilangan peroksida, bilangan penyabunan mengalami penurunan serta kualitas aroma dan warna pada

minyak jelantah menjadi lebih baik. Berdasarkan analisis tersebut adsorben Nano-Montmorillonit dapat meningkatkan kualitas minyak jelantah.

Kata kunci: Minyak Jelantah; Bentonit; Nano-Montmorillonit; Adsorben

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Introduction

Cooking oil is one of the basic needs that is often consumed by the community. Cooking oil comes from vegetable oil that has been refined and can be used as food. Oil functions as a medium for processing food ingredients and can add the greatest nutrition and caloric value among other nutrients, besides that oil can also provide a savory taste, texture and appearance of foodstuffs to be more attractive and a dry surface (Mardiah and Darwis, 2019; Oko *et al.*, 2020; Sopianti *et al.*, 2017; Alamsyah *et al.*, 2021; Santriwati *et al.*, 2020; Sinurat and Ramlan, 2021; Muhammad *et al.*, 2020). The use of cooking oil repeatedly can cause a decrease in the quality of the oil. Cooking oil heating at high temperatures for a long time will cause the double bonds to be oxidized, forming cyclic monomer and peroxide groups. In addition, oil also undergoes chemical changes such as hydrolysis, oxidation, polymerization, and browning reactions. So as to produce oil degradation compounds such as ketones, aldehydes, and polymers that are detrimental to human health. The process of oxidation and polymerization can destroy some of the vitamins and essential fatty acids in the oil so that it can cause poisoning in the body and lead to various diseases such as diarrhea, deposition of fat in blood vessels, and cancer which is harmful to the health of consumers. Therefore, several attempts have been made to purify waste cooking oil with the aim of saving but not endangering the health and easy to do (Erlita, 2017; Krismaya *et al.*, 2016; Nurani *et al.*, 2016; Sopianti *et al.*, 2017).

One of the efforts that can be made to overcome the problem of using waste cooking oil is by bleaching it to produce oil that is suitable for reuse. The bleaching can be done through the adsorption process. Adsorbents that are commonly used in the bleaching process consist of bleaching earth, bleaching carbon, and fiber. The mechanism of action of the adsorption process is to absorb colloid suspensions (gum or resin) and the results of soil degradation (e.g. peroxides) on the adsorbent surface (Prasetyowati *et al.*, 2011; Andhiarto and Santi, 2018). In addition, the material that can be used for refining waste cooking oil is montmorillonite (MMT), which is the main component found in clay minerals (Triandhani *et al.*, 2021).

This type of mineral is widely used in the manufacture of various products, one of which is as a catalyst, catalyst support, and reinforcement (Saputra *et al.*, 2018). Montmorillonite has a considerable swelling ability. This swelling ability

makes montmorillonite an adsorbent with a greater adsorption capacity than other adsorbents (Wahyuningsih *et al.*, 2020). To increase the activity of montmorillonite as an adsorbent, materials engineering was carried out by modifying the particle size of montmorillonite into nanoparticles. The engineering of montmorillonite materials in nano-scale sizes has the advantage of large porosity and a larger surface area so that it can increase the activity of montmorillonite as an adsorbent in refining waste cooking oil. Based on this background, it is very important to purify waste cooking oil using Nano-Montmorillonite adsorbent. The parameters used to determine the quality before and after the adsorption process were the organoleptic test, including odor and colour, acid number, peroxide number and saponification number. The oil parameters obtained will be compared with the oil quality parameters according to SNI 01- 3741-2013.

Material and Methods

Manufacture of Nano-Montmorillonite

It weighed as much as 50 grams of bentonite, was put in ultrasonic batches filled with 2 L of distilled water, and given ultrasonic waves for 15 minutes. The precipitate is taken. This precipitate is called Fraction 1. The filtrate is stirred 10 times, left for 3 days, and the sediment is taken. The precipitate is called Fraction 2. Then the filtrate is stirred 10 times, left for 7 days, and the sediment is taken. The precipitate is called Fraction 3. The filtrate is evaporated to completely remove the moisture content (Fraction 4) (Gea *et al.*, 2018). The manufacture of montmorillonite into nano-montmorillonite was carried out using a High Energy Milling (HEM) for 20 hours then analyzed by Fourier Transform Infrared (FTIR) (Shimadzu), *X-Ray Diffraction* (XRD) (PanAnalytical, Type E'xpert pro) and Particle Size Analyzer (PSA) (Horiba Scattering Light Intensity) to prove that Montmorillonite was nano-sized.

Bleaching the Waste Cooking Oil

Put 120 mL of waste cooking oil and add nano-montmorillonite, and stir for 20 minutes at a speed of 500 rpm. It was filtered using Whatman 42. A test is carried out to determine the quality of the oil, including color, odor, peroxide number, acid number, and soaping number (Dewi and Nurul, 2012).

Results and Discussion

XRD (X-Ray Diffraction)

The identification of Aceh Tamiang natural bentonite with XRD in figure 1 shows that it contains montmorillonite. The peaks that indicate the presence of montmorillonite are found at the $2\theta = 19.7^\circ$ and 20.7° and 26.5° peaks, which are the peaks of the mineral quartz (SiO_2), which has a high diffraction intensity. Therefore, bentonite has constituent minerals in the form of montmorillonite and

other natural minerals derived from the SiO_2 structure in the main component of montmorillonite and impurities in very small amounts. XRD analysis data shows that Nano-Montmorillonite contains the main components of montmorillonite and quartz (SiO_2).

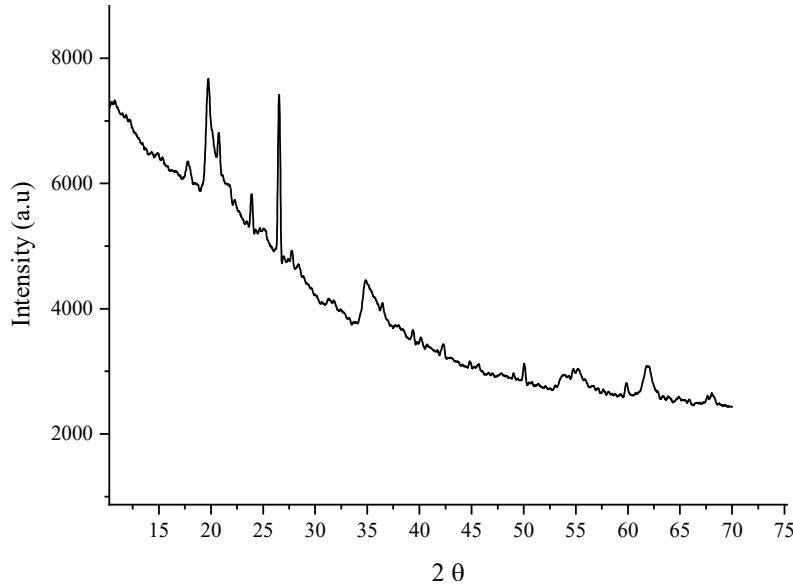


Figure1. Nano-Montmorillonite XRD

PSA (Particle Size Analyzer)

Nano-Montmorillonite particles produced by milling for 20 hours using High Energy Milling (HEM) have had nano-size through testing the size distribution using a Particle Size Analyzer (PSA). The particle size of Nano-Montmorillonite can be shown in figure 2.

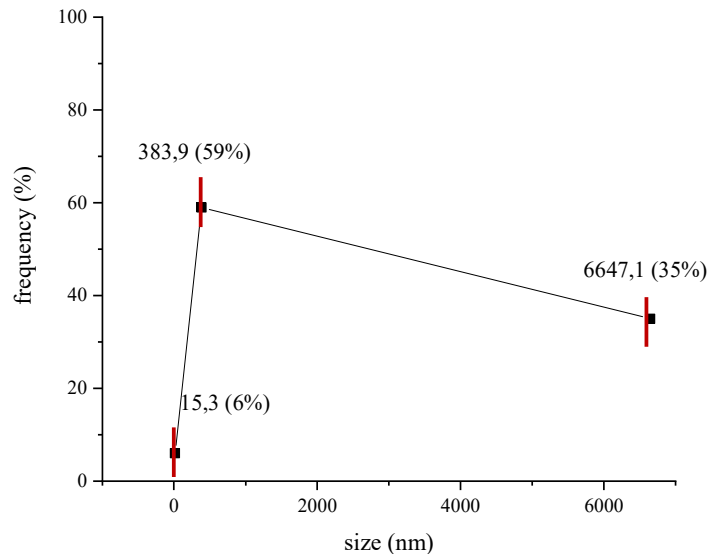


Figure 2. Graph of Nano-Montmorillonite Particle Size Distribution using PSA

Based on figure 2, it can be seen that Nano-Montmorillonite has a nano-scale particle size of 15.3 nm with a percentage of 6%, and the rest are particles that have a size > 100 nm with a total percentage of 94% with a size of 383.9 nm each with a percentage of 59% and 6647.1 nm with a percentage of 35%. According to Aisyah *et al.*, 2017, nanoparticles are particles that are dispersed at the nanometer size or the thousandth of a micron-scale and are classified as nanoparticles if they have a size of 1-100 nm.

FTIR (Fourier Transform Infrared)

Infrared spectra of the Nano-Montmorillonite sample provide information about the presence of functional groups present in the sample. The FTIR spectrum of Nano-Montmorillonite in figure 3 shows that the absorption peak in the region of wave numbers 3645.46 and 3606.89 cm^{-1} shows the -OH group attached to the cation on the octahedral sheet and the bond between the -OH group and the Al^{+3} cation (Caccamo *et al.*, 2020). The peak vibration at wave number 466.77 cm^{-1} is the Si-O-Si bending vibration (Soleman, 2011). Based on these results, it is known that Nano-Montmorillonite has functional groups such as -OH derived from the montmorillonite framework and water molecules, Si-O, and Al-Al-OH, which are the structures on the octahedral and tetrahedral sheets of Nano-Montmorillonite.

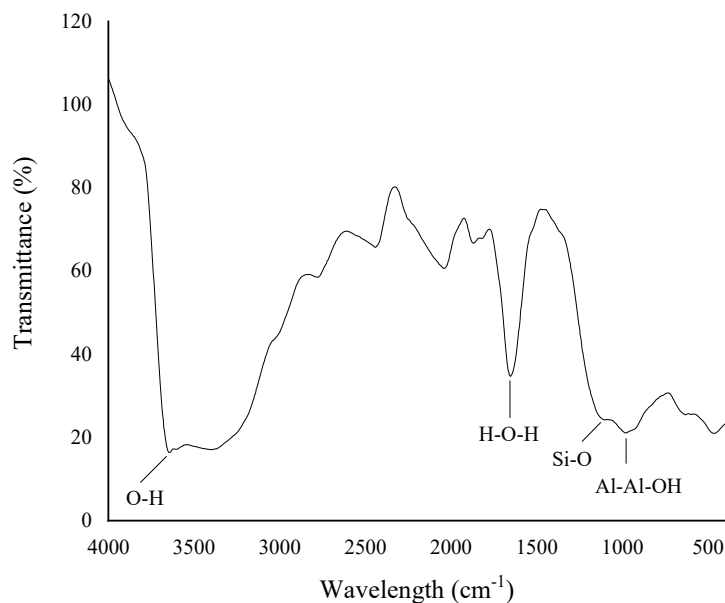


Figure 3. Nano-Montmorillonit Infrared Spectra

Quality Of Waste Cooking Oil

The colour and smell of cooking oil are one of the requirements for good quality cooking oil. According to SNI 2013, the good colour of cooking oil is a pale yellow to yellow and has a distinctive smell of cooking oil. The organoleptic

test results of used cooking oil using Nano-Montmorillonite before and after adsorption can be seen in figure 4 and table 1.

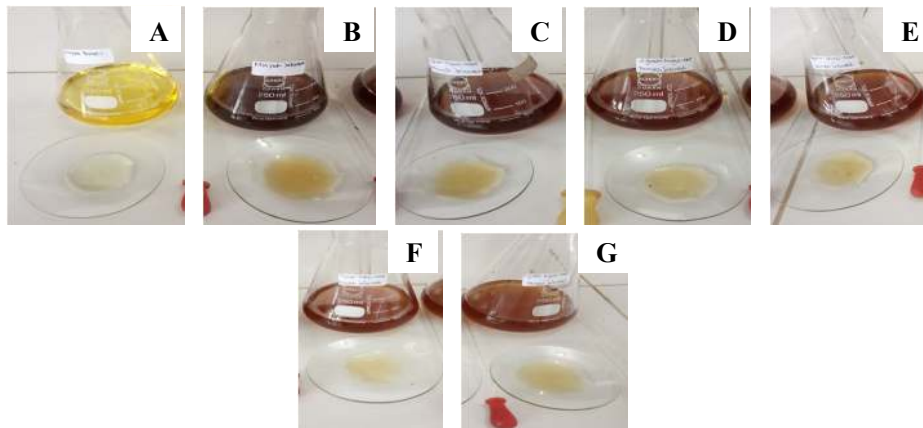


Figure 4. Waste Cooking Oil Before and After Adsorption

Table 1. Organoleptic Test on Waste Cooking Oil before and after adsorption using Nano-Montmorillonite.

Test Sample	Scale	
	Flavour	Colour
Sample A	3	3
Sample B	0	1
Sample C	2	2
Sample D	2	2
Sample E	3	2
Sample F	3	3
Sample G	3	3

Information:

Sample A = Bimoli Oil

Sample B = Waste Cooking Oil (MJ)

Sample C = MJ + 1 gram Nano-Montmorillonite

Sample D = MJ + 2 grams of Nano-Montmorillonite

Sample E = MJ + 3 grams of Nano-Montmorillonite

Sample F = MJ + 4 grams of Nano-Montmorillonite

Sample G = MJ + 5 grams of Nano-Montmorillonite

0 = Very rancid; black

1 = rancid; brownish black

2 = Slightly rancid; brownish yellow

3 = The characteristic smell of oil; clear yellow

Based on table 1, it can be seen that the addition of Nano-Montmorillonite in the bleaching process has a significant effect on the colour quality and odor of waste cooking oil. The oil colour's brightness increases as the amount of Nano-Montmorillonite is added to waste cooking oil. The increase in oil impurities also causes a decrease in brightness level. The more Nano-Montmorillonite adsorbent

used, the lighter the oil's colour (yellow). The smell of cooking oil has different characteristics. The smell of waste cooking oil is different from the smell of hydrolyzed oil and generally depends on the smell of the ingredients in contact with the cooking oil. After being adsorbed using Nano-Montmorillonite, the smell of waste cooking oil underwent a significant change with the increase in the amount of Nano-Montmorillonite added to the waste cooking oil.

The addition of 1 and 2 grams of Nano-Montmorillonite still smells slightly rancid from waste cooking oil. The addition of 3. 4 reduced the rancid odor of used cooking oil. And 5 grams of Nano-Montmorillonite become a distinctive smell of cooking oil. The results of the organoleptic analysis showed that the colour change produced after the bleaching process using Nano-Montmorillonite had met the requirements of SNI 3741-2013.

The acid number indicates the number of milligrams of KOH needed to neutralize 1 gram of cooking oil sample. Free fatty acids are fatty acids that are released due to the hydrolysis process. The results of the acid number of the oil before and after being adsorbed by Nano-Montmorillonite are shown in figure 4.

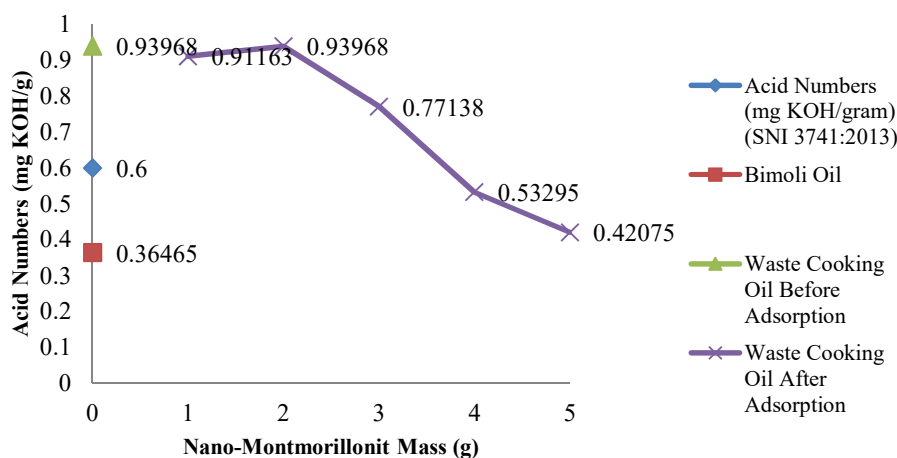


Figure 4.The Effect of Adsorbent Mass Variation on Decreasing Acid Numbers

The acid number in waste cooking oil after adsorption using Nano-Montmorillonite decreased as the mass of the adsorbent used increased. This is due to a large number of adsorbents used. The more free fatty acids that are adsorbed, the better the quality of the oil produced when adsorbed. In addition, the absorption of free fatty acids in waste cooking oil is influenced by the size of the adsorbent particles. The smaller size of the adsorbent particles can increase the surface area of the adsorbent (Sera *et al.*, 2019). This means that the smaller the particle size, the larger the surface area, so more substance will be adsorbed.

The peroxide number is the most important value to determine the level of damage that has been done to oil or grease caused by the oxidation process that occurs when oxygen comes in contact with the oil. The results of determining the

peroxide number in used cooking oil before and after adsorption using Nano-Montmorillonite with various mass variations can be seen in figure 5.

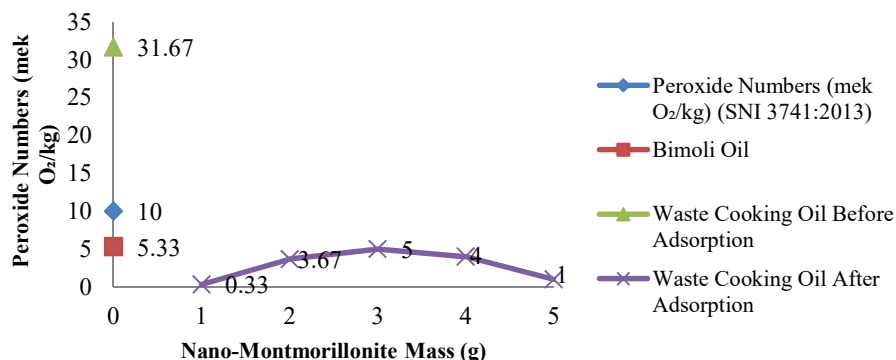


Figure 5. The effect of adsorbent mass variation on decreasing peroxide numbers

Based on figure 5, it is known that the addition of Nano-Montmorillonite with various mass variations as an adsorbent in used cooking oil resulted in a decrease in the value of the peroxide number. The decrease in the number of peroxide in used cooking oil after adding the Nano-Montmorillonite adsorbent is because the peroxides that have been in the used cooking oil before being processed with the adsorbent have active properties. The interaction that occurs between peroxides and Nano-Montmorillonite is in the form of an ionic bond between the oxygen group on the negatively charged peroxide and metal cations such as Al^{+3} , which are found between the octahedral and tetrahedral sheets on Nano-Montmorillonite. During the bleaching process, the formation of peroxides as a result of oil oxidation is reduced. The higher the adsorbent concentration used in the refining process of used cooking oil, the greater the absorption of the peroxide number content. This happens because the higher the adsorbent concentration, the more adsorbent molecules can bind (contact) and absorb the peroxide compounds in the oil.

The saponification number is determined to determine the properties of the oil or fat and to distinguish the oil from other oils. The results of saponation numbers in used cooking oil before and after adsorption using Nano-Montmorillonite with various mass variations can be seen in figure 6.

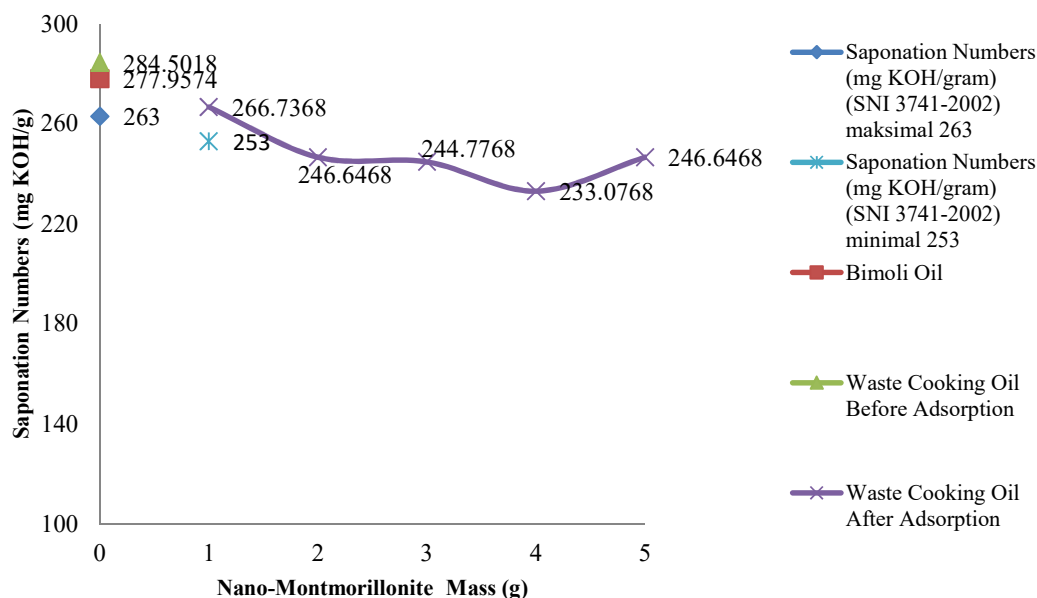


Figure 6. The Effect of Adsorbent Mass Variation on the Decrease in Sapling Number

Based on figure 6, it can be seen that there is a decrease in the saponation number as the mass of Nano-Montmorillonite used increases. The more the number of Nano-Montmorillonite added, the smaller the saponation number. This is because the particle size of the Nano-Montmorillonite is getting smaller the wider the surface area so that the adsorption capacity of Nano-Montmorillonite is getting bigger. This maximum adsorption power can help reduce the soaping number of waste cooking oil. The low saponation number produced after the adsorption process is because the oil is so saturated that the particle size and mass of the addition of Nano-Montmorillonite do not affect the adsorption power of Nano-Montmorillonite and the change in the soaping number. In addition, Nano-Montmorillonite has a main component, namely SiO_2 is polar, so it can bind the fatty acids found in used cooking oil, which are also polar.

Conclusion

Based on the results of research on improving the quality of waste cooking oil with Nano-Montmorillonite adsorbent, it can be concluded that Nano-Montmorillonite is very effective in the process of refining waste cooking oil because Nano-Montmorillonite has a nano-scale particle size of 15.3 nm with a percentage of 6% classified as a nanomaterial and the rest is particles which have a size > 100 nm with a percentage of 94% and has functional groups namely hydroxyl (-OH), Si-O-Si and Al-Al-OH. The more the amount of Nano-Montmorillonite adsorbent is added, the acid number, peroxide number, and saponation number decrease. The smell and colour quality of waste cooking oil becomes better. The quality of cooking oil with the addition of Nano-Montmorillonite adsorbent has increased in terms of colour, odor, acid number,

peroxide number and saponification number, and meeting the quality requirements for packaged cooking oil based on SNI 01-3741-2013.

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