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Utilization of Coffee Waste as Active Charcoal For Purification of Waste Cooking Oil

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ABSTRACT

This research aims to find the comparison of the chemical-physical characters of coffee waste activated charcoal using $ZnCl_2$ with HCl, to calculate the highest adsorption efficiency, and to determine the quality of waste cooking oil after purification. The washed and dried of coffee waste are carbonized by the temperature 700°C and chemically activated using $ZnCl_2$ 5% and HCl 5%. The adsorption process used by batch system. The object of this research is the character of activated charcoal from coffee waste such as water content, ash content, iodine adsorption capacity of activated charcoal, peroxide number and free fatty acid (FFA) number of waste cooking oil before and after purification. Morphological analysis of activated charcoal was carried out using Scanning Electron Microscope (SEM). Analysis of the number of peroxide and FFA were carried out respectively using the titration method. The results of the characterization of activated charcoal showed that the activated charcoal with $ZnCl_2$ 5% activator had a water content of 6.55%, an ash content of 6.046%, adsorption of iodine 1039.5 mg/g, and had clean and wide pores. Activated charcoal with HCl 5% activator has a water content of 7.25%, an ash content of 7.55%, and 1008 mg/g of iodine adsorption. The highest adsorption efficiency of activated charcoal was 49.9749% in reducing the peroxide number and 50.1113% for reducing FFA, these results were obtained at 3 hours contact time with 3 g adsorbent mass. The peroxide number in the waste cooking oil that has been purified has not qualitified the standard SNI 01-3741-2013, but the FFA at 3 hours contact time with 3 g adsorbent mass qualitified the standard.

Keyword: *: activated charcoal, adsorption, coffee waste, waste cooking oil*

1. INTRODUCTION

Along with the times, drinking coffee has become a global phenomenon, especially among young people. The wider lifestyle in drinking coffee can be proven by the presentation of Dewi (2019) which states that the increase in coffee business growth until 2019 has increased 15% -20% higher than the increase in the coffee business in 2018. One of the coffee sellers in Yogyakarta is the Pak Lik Man angkringan which is located around the Tugu Yogyakarta station. Based on the results of interviews conducted by Purwanto (2020) with the coffee seller at the angkringan, the average coffee grounds waste produced per angkringan is between 4-5 kg per night. The increase in coffee consumption in Indonesia can lead to the accumulation of waste in the form of skin and coffee grounds. Coffee grounds

waste contains tannins, caffeine, alkaloids, and polyphenols which can poison the environment if the waste is disposed of carelessly (Zainuddin, et al., 1995). Another impact is that the high water content in coffee waste can cause the growth of spoilage microbes (Simanihuruk, et al., 2010). In addition, coffee waste can be overgrown by pathogenic bacteria that can cause disease outbreaks if carried by the wind or infested by flies. Therefore, it is necessary to treat coffee waste.

So far, the coffee waste has been processed into biodegradable interior products and is expected to be used as a substitute for particle wood (Anam, 2019), and composite materials as an alternative basic material for making wallet products (Purwanto, et al., 2020). The number of studies to utilize coffee waste will be very useful in this era to balance business growth and coffee consumption, especially in Yogyakarta. Activated charcoal is one type of adsorbent that can be made from natural materials so that it can increase the economic value. Natural ingredients that have been used as activated charcoal include coconut shells (Suhartana, 2006), corn cobs (Suhendra et al., 2010), sea pandan (Kristianingrum et al., 2014), coffee grounds (Tomi Mukhtar, 2014) and rice husks. (Rahman et al., 2012). Charcoal activation process can be done by physical, chemical, and chemical-physical methods. According to Hendra (2019), the chemical activation process on charcoal can be done by adding certain chemical compounds.

Research conducted by Tomi Mukhtar (2014) showed that activated charcoal from ZnCl2 activated coffee grounds had a greater absorption capacity than activated charcoal H_3PO_4 and KOH. In the study of Kristianingrum, et al. (2014), a solution of 5% HCl and 5% H_2SO_4 can open the pores of activated charcoal from sea pandan leaves so as to allow the adsorption process to run optimally. Based on SNI 06-3730-1995, the parameters used in determining the quality of activated charcoal are ash content, water content, absorption of iodine, volatile content and carbon content. Analysis using a Scanning Electron Microscope (SEM) can also be used to see the surface of the activated charcoal that will be used.

Cooking oil is oil produced from animal or plant fat that is purified and in liquid form. In general, cooking oil is used as a means of processing food ingredients. According to Siti Aminah (2010), heating cooking oil at high temperatures (during frying) can reduce the quality of cooking oil. It can also lead to degradation of cooking oil and discoloration of cooking oil. Parameters that determine the quality of cooking oil based on SNI 01-3741-2013 are odor, color, moisture content, free fatty acid (ALB) number, peroxide number, linolenic acid and metal contamination. Degradation of cooking oil can reduce the quality of cooking oil, so it cannot be reused (Maskan, 2003). The decline in the quality of cooking oil can affect the quality of foodstuffs that are processed using the oil so that it can cause health problems (Lee, et al., 2002). Therefore, efforts are needed to process used cooking oil so that it can be reused. The results of research from Siti Aisyah, et al. (2010) showed that activated charcoal from Moringa fruit pods was very effective in reducing the number of peroxides and free fatty acids (ALB) in used cooking oil.

This article reported the utilization of coffee grounds waste as activated charcoal to reduce the peroxide value and free fatty acid number of used cooking oil. Charcoal from coffee grounds was chemically activated by using a variety of activators in the form of a 5% $ZnCl_2$ solution with 5% HCl. Several parameters that affect the efficiency of coffee grounds activated charcoal adsorption in refining used cooking oil will be studied, i.e. variations in adsorbent mass and contact time in the adsorption process.

2. RESEARCH METHOD

2.1 Materials

The materials used in this research are coffee grounds waste, $ZnCl_2$ 5% solution, HCl 5%solution, 1% starch solution, demineralized water, 0.1 N iodine solution, 0.1 N $Na_2S_2O_3$ solution, used cooking oil, ethanol, phenolphthalein indicator, 0.1 N KOH solution, Acetate-Chloroform (3:2), 0.1 N saturated KI solution, demineralized water, and 0.1 N iodine solution.

2.2 Preparation activated charcoal from coffee grounds waste

The coffee grounds are brewed with hot distilled water and then allowed to stand for 10 minutes and filtered. The filtered coffee grounds were dried in an oven for 5 hours at a temperature of 105 ^{o}C and carbonated at a temperature of 700 ^{o}C for 2 hours, then sieved through a 100 mesh sieve. 150 g of coffee grounds charcoal was soaked with 500 mL of 5% $ZnCl_2$ solution for 48 hours and filtered. Activated charcoal was washed with demineralized water to a constant pH (neutral), then dried in an oven at 110 oC for 3 hours. Repeat the procedure by replacing the 5% $ZnCl_2$ solution with 5% HCl. The resulted activated charcoal was characterized (Imawati, et al., 2015) by analyzing the water content, ash content, and adsorption toward yodium. As control, the procedure also applied to inactivated charcoal.

2.3 Purification of used cooking oil

20 mL of used cooking oil was put into a 250 mL erlenmeyer and mixed with activated charcoal with variations in weight of 1 g, 2 g, 3 g and contact time variations of 1 hour, 2 hours, and 3 hours. The mixture was stirred for 1 hour at 180 rpm, then filtered. The quality of purified cooking oil was measured as peroxide number (SNI 01-3555-1998) and free fatty acid (SNI 01-3555-1998)

3. RESULTS AND DISCUSSION

Activation of Ground Coffee Waste Charcoal

Coffee grounds are brewed with hot distilled water in order to dissolve the ingredients that are still attached to the coffee. The coffee grounds obtained were dried in an oven at a temperature of 105 oC for 5 hours so that the water vapor in the coffee evaporated. Furthermore, the clean coffee grounds are carbonized at a temperature of 700 oC for 4 hours so that the material decomposition process occurs and produces a material that has absorption and a neat structure (Atmoko et al., 2012). The resulting coffee grounds charcoal was ground and sieved with a size of 100 mesh so that the charcoal size obtained was uniform. Then the charcoal is chemically activated so that the charcoal pores that are covered during carbonization can be opened and reduce the water in the pores so that the adsorption power is maximized (Alfiany et al., 2013). The activator used is a solution of $ZnCl_2$ and HCl with a concentration of 5%. The selection of $ZnCl_2$ activator was based on research by Tomi Mukhtar (2014) which showed that activated charcoal from coffee grounds activated $ZnCl_2$ had a greater absorption capacity than activated charcoal activated by H_3PO_4 and KOH. Meanwhile, the selection of HCl activator and 5% concentration was based on the research of Susila Kristenngrum et al., (2014), that 5% HCl and 5% H_2SO_4 solution can open the pores of activated charcoal from sea pandan leaves so as to allow the adsorption process to run optimally. Furthermore, the activated charcoal of the pulp is washed with demineralized water to a constant pH, this effort is made to remove the remaining $ZnCl_2$ and HCl that are still present in the activated charcoal of the coffee grounds. Then dried in the oven at 110 ^{o}C for 3 hours.

Characterization of activated charcoal

The water content shows the amount of water that covers the pores of the activated charcoal. The smaller the value of the water content, the more space in the pores that can be occupied by the adsorbate so that the adsorption process can take place optimally (Mu'jizah, 2010). Ash content is determined to determine the remaining mineral content in activated charcoal that is not lost in the carbonization and activation process. These minerals can clog the pores of activated charcoal so that it affects the adsorption process (Herlandien, 2013). Iodine absorption is used to determine the ability of activated charcoal to adsorb adsorbate with a small size (10 Angstrom). The value of iodine absorption in activated charcoal can be seen from the iodine number obtained. This figure shows the amount of iodine (mg) that can be absorbed by 1 gram of activated charcoal. The results of determining the characterization of activated coffee grounds charcoal waste ZnCl2 and HCl on the parameters of water content, ash content, and iodine absorption are presented in Table 1.

Table 1. Charcoal character before and after activation

charcoal	Water content (%)	Ash content (%)	Iod absorption (mg/g)
Before activation	6,65	6,91	970,2
Activated using $ZnCl_2$	6,55	6,05	1039,5
Activated using HCl	7,25	7,55	1008
SNI 06-3730-1995	Maks. 15	Maks. 10	Min 750

The water content of activated charcoal $ZnCl_2$ has the lowest value. The water content of activated charcoal depends on the activator used. The low water content is caused by the ability of the activator to bind water in activated charcoal well (Budiono et al., 2006). The water content of the three charcoals has met the Indonesian National Standard so that activated charcoal from coffee grounds waste can be used as an adsorbent. The ash content obtained showed that activated charcoal $ZnCl_2$ had the lowest value. The value of ash content is influenced by the ability of the activator to dissolve inorganic minerals in activated charcoal (Budiono, 2006). The ash content of the three activated charcoals has met the Indonesian National Standard.

Table 1 showed that activated charcoal $ZnCl_2$ has the highest absorption value for iodine. This value shows the number of micropores formed on activated charcoal ZnCl2 has more micropores and is better able to dissolve impurities that cover the pores optimally compared to activated charcoal HCl. Analysis using Scanning Electron Microscope (SEM) was used to determine the morphology and topography of activated charcoal. The analysis was carried out using four magnifications, namely 500X, 1000X, 3000X, 5000X. Images or analysis results from SEM are called micrographs. The micrograph that most clearly depicts the pores on the surface of the charcoal from coffee grounds waste is at 1000X magnification, while the micrograph can be seen in Figure 1, which showed that the coffee grounds charcoal before being purified has pores that have small lumps which are assumed to be impurities. After activation using ZnCl2, the impurities contained in the charcoal are lost. The loss of impurities indicates that the pores in the activated charcoal become cleaner and wider, so that the adsorption process can take place optimally.

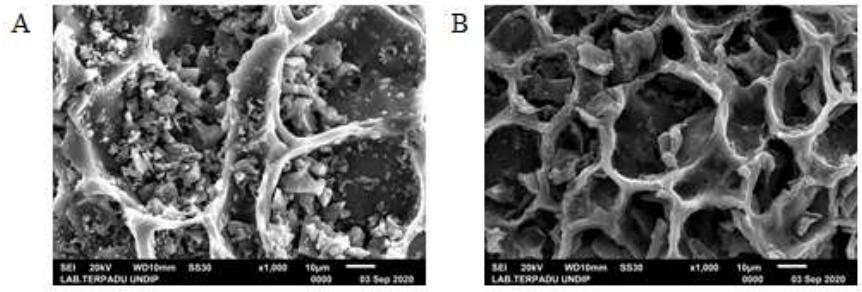

Figure 1. Micrograph of the charcoal before (A) and after activated with $ZnCl_2$ (B)

Analysis of cooking oil quality

This purification was carried out by varying the weight of the adsorbent as much as 1 g, 2 g, and 3 g and the box time for 1 hour, 2 hours, 3 hours. The parameters used to determine the quality of the cooking oil in this study were the peroxide number and the free fatty acid number. The purification process in this study uses activated charcoal from ZnCl2 activated coffee grounds which has clean and wide pores, so that it can bind and absorb peroxide compounds and free fatty acids. According to the National Standardization Agency (BSN) in SNI 01-3741-2013 regarding cooking oil, the quality requirements of cooking oil can be observed in Table 2.

Table 2. Standard Quality of Cooking Oil based on SNI 01-3741-2013

No.	Criteria	Unit	Standard
1	Condition		
1.1	Smell	-	Normal
1.2	Colour	-	
2	Water and volatile content	%(b/b)	max 0.15
3	Acid number	mg KOH/g	max 0.6
4	Peroxide number	mek O_2/kg	min 10
5	Pelican oil	-	Negative
6	Linolenat acid (C18:3)	%	max 2
7	Metal		
7.1	Cadmium (Cd)	mg/kg	max 0.2
7.2	Lead (Pb)	mg/kg	max 0.1
7.3	Timah (Sn)	mg/kg	max 40.0/250.0
7.4	Mercury (Hg)	mg/kg	max 0.05
8	Arsenic (As)	mg/kg	max 0.1

The variation of the adsorbent mass was carried out to determine the amount of activated charcoal needed to reduce the peroxide number and free fatty acid number in used cooking oil to the maximum. The variation of contact time in the used cooking oil refining process was carried out to find out how long it took for activated charcoal to reduce the peroxide number and free fatty acid number in used cooking oil to the maximum. Peroxides are a group of compounds that have a single bond of oxygen with oxygen (Anonymous, 2016). The peroxide value is one of the most important parameters in determining the degree of damage to an oil or fat. The formation of peroxides is caused by heating which causes damage to the oil or fat. The formation of hydrogen peroxide in oil can be seen in Figure 2.

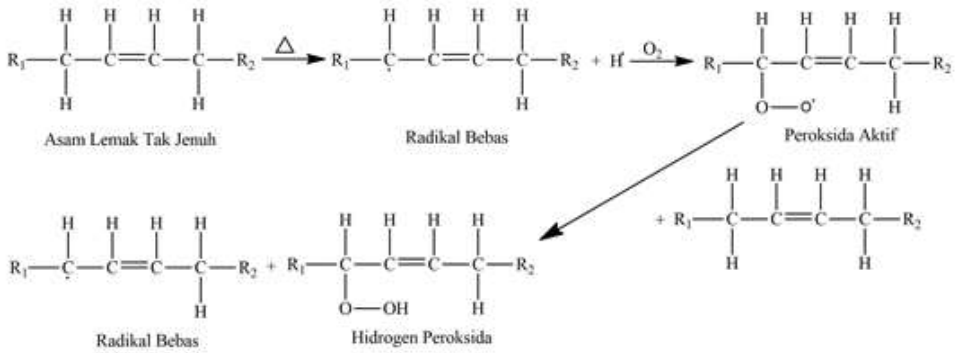

Figure 2. Reaction of hydrogen peroxide in oil

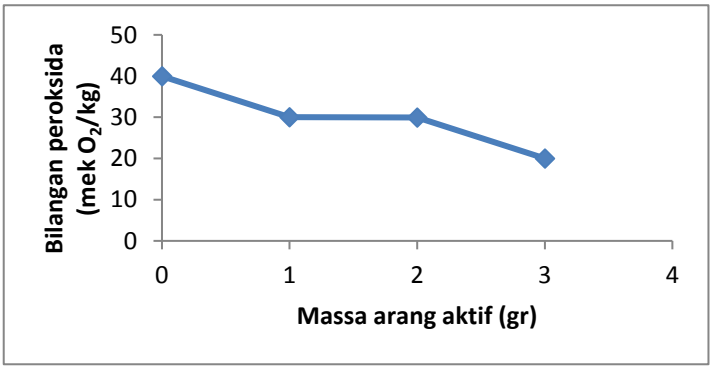

Figure 3. Adsorben mass variation at the measurement of peroxide number

Based on Figure 3. the maximum adsorption of activated charcoal ZnCl2 occurs at a mass of 3 gr adsorbent with a peroxide number of 20.016 mek O2/kg. The mass of activated charcoal affects the decrease in the peroxide number. The greater the mass of activated charcoal, the greater the decrease in peroxide value in used cooking oil. The more adsorbents, the more surface area that can absorb peroxide compounds in used cooking oil. However, if too much activated charcoal is added, the deposition process will take longer, making it difficult to extract the purified oil. The peroxide value in used cooking oil after being purified with a mass variation of 1 g, 2 g and 3 g still does not meet the quality standard of cooking oil based on SNI 01-3741-2013. The possibility that occurs is the lack of activated charcoal mass and contact time used in the purification process. The best adsorption efficiency is found in the mass variation of 3 g, which is 49,9099%.

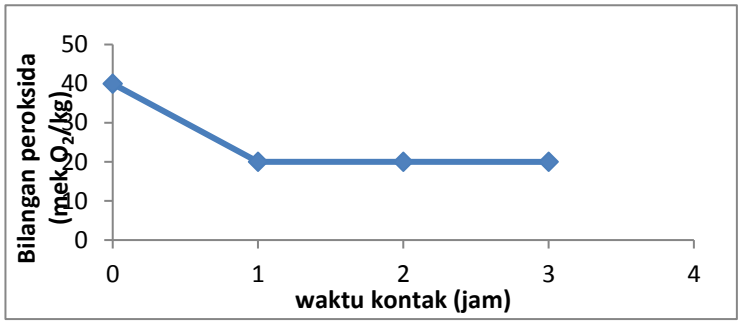

Figure 4. Contact time variation at peroxide number determination

The results of the analysis of the peroxide number in used cooking oil with variations in adsorption contact time are presented in Figure 4, indicating that the maximum adsorption of activated charcoal $ZnCl_2$ occurred at an adsorption contact time of 3 hours with a peroxide number of 19.99 mek O_2/kg. The longer the contact time of activated charcoal with used cooking oil, the lower the peroxide value in the oil. However, the peroxide value of used cooking oil after being purified with variations in contact time of 1 hour, 2 hours and 3 hours did not meet the standards of SNI 01-3741-2013. The cause of this may be the lack of contact time during the purification process and the unobserved volume of titrant (less than 0.05 mL) required during the titration. The best adsorption efficiency is found in the 3-hour contact time variation, which is 49.9749%. Free fatty acids (ALB) are types of fatty acids that are not bound as triglycerides and are produced by hydrolysis and oxidation processes. ALB is the amount of acid that can be neutralized by a base, so it can be used to measure the amount of free fatty acids in the oil. In the process of hydrolysis of palm oil, the products obtained are glycerol and free fatty acids. Things that can affect the speed of this reaction are water, acidity, heat and catalysts (enzymes). The longer this reaction lasts, the higher the levels of fatty acids, causing an unpleasant taste and odor in palm oil (Henny Nurhasnawati, 2015).

Based on SNI 01-3555-1998, the principle in the analysis of free fatty acids is that the sample in the form of oil or fat is dissolved in an organic solvent in the form of 95% neutral alcohol and then titrated using a base (KOH or NaOH). The reaction that occurs is as follows (SNI 01-3555-1998) as shown in Figure 7.

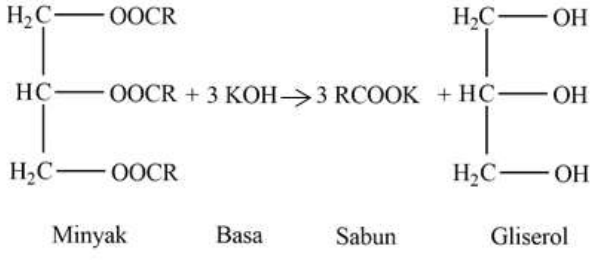

Figure 5. Reaction of ALB analysis

The results of the analysis of the number of free fatty acids in used cooking oil with variations in the mass of activated charcoal are presented in Figure 6, which shows that the maximum adsorption of activated charcoal $ZnCl_2$ occurs at a mass of 3 g of activated charcoal with an ALB number of 0.8407 mg KOH/gr. showed that the more mass of activated charcoal used in the adsorption process, the greater the decrease in free fatty acids. The greater the mass of activated charcoal, the greater the decrease in free fatty acids in used cooking oil. The more adsorbents, the more surface area that can absorb free fatty acids in used cooking oil. However, if too much activated charcoal is added, the deposition process will take longer, making it difficult to extract the purified oil.

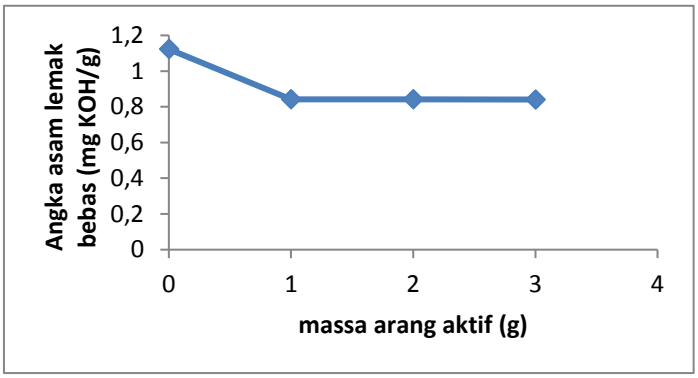

Figure 6. Mass adsorbent variation at free fatty acid determination

The number of free fatty acids after purification with a mass variation of activated charcoal was more than 0.6 mg KOH/gr, so that the quality of the oil did not meet the requirements of the quality standard of SNI 01-3741-2013. This is possible due to the lack of mass of activated charcoal used in the purification process. The best fatty acid adsorption efficiency was found in the mass variation of activated charcoal as much as 3 g with a value of 25.1278%. The results of the analysis of the number of free fatty acids in used cooking oil with variations in adsorption contact time are presented in Figure 9, which shows that the maximum adsorption of activated charcoal ZnCl2 occurred at an adsorption contact time of 3 hours with an ALB number of 0.5602 mg KOH/gr. The variation of the contact time of 3 hours has met the provisions of the quality standard of SNI 01-3741-2013 for free fatty acid parameters, while at the time variation of 1 hour and 2 hours it has not met the standard. This is because the volume of KOH required (less than 0.05 mL) is not observed in the titration process. So that the best adsorption efficiency is found in the 3-hour contact time variation with a value of 50.1113%.

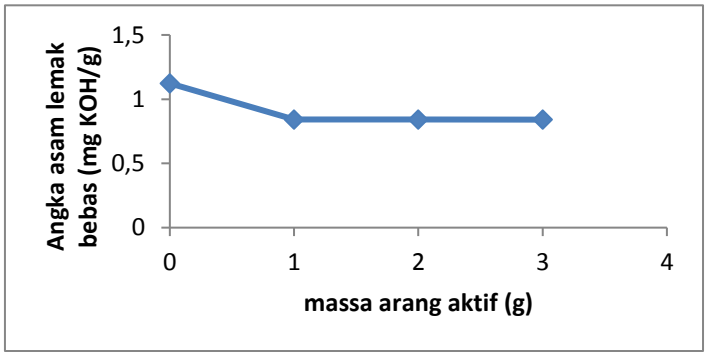

Figure 7. The variation of charcoal mass into number of free fatty acids

4. CONCLUSION

Activated charcoal from $ZnCl_2$ 5% activated coffee grounds has a water content of 6.55%, an ash content of 6.046%, an absorption capacity of 1039.5 mg/g of iodine, and has clean and wide pores. Activated charcoal with 5% HCl activator has 7.25% moisture content, 7.55% ash content, and 1008 mg/g iodine absorption. The highest adsorption efficiency of activated charcoal from coffee grounds was 49.9749% in reducing peroxide value and 50.1113% for reducing free fatty acids, the results were obtained at a contact time of 3 hours with an adsorbent mass of 3 g. The quality of used cooking oil on the peroxide number parameter in used cooking oil that has been purified has not met the provisions of the SNI 01-3741-2013 standard. The parameter of free fatty acid number at contact time variation of 3 hours with adsorbent mass of 3 g has met the standard

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