

Original article

Determination of peroxide by spectrophotometry in waste cooking oil using adsorbents from banana midrib and water hyacinth

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Abstract

Waste cooking oil is cooking oil that has been used as fry food ingredients repeatedly. Cooking oil heated at high temperatures will be decomposed and produced peroxide compounds that accelerate the process of developing a rancid odor, reducing the quality of the oil and the nutritional value of fried foods. The research was conducted by the spectrophotometric method using a wavelength of 200-300 nm. Based on the results of the study, the addition of 0.5 g, 1.0 g, 1.5 g and 2.0 g of banana midrib adsorbents obtained peroxide concentrations of 0.031%, 0.033%, 0.034%, and 0.034% respectively. The addition of water hyacinth adsorbent successively obtained peroxide concentrations of 0.035%; 0.038%, 0.039%, and 0.038%, respectively. The largest percentage decrease was found in the addition of banana midrib adsorbents, namely 38% and water hyacinth 30%. From the independent T-test statistical test obtained $p < 0.05$, so it can be concluded that there is a significant decrease in peroxide value to the adsorbent of banana midrib and water hyacinth in waste cooking oil.

INTRODUCTION

Cooking oil is one of the basic human needs as a food processor which is generally used for frying (Pakpahan, et al., 2013). Cooking oil functions as a heat conductor, a savory taste enhancer, and an increase in the calorific value of pagan ingredients (Winarno, 1995). The cooking oil is generally rarely used once but is often used repeatedly, especially for street vendors or sellers of fried food ingredients (Yazid & Ningsih, 2019). The use of oil that is done repeatedly is often known as waste cooking oil.

The repeated use of cooking oil at high temperatures accompanied by air and water in the frying process will cause a complex degradation reaction so that the quality of the oil decreases (Maskan, M., 2003). Oil heated at high temperatures produces peroxide compounds that can accelerate the process of developing a rancid odor and unwanted flavor. The high

number of peroxides in the oil indicates that the degree of damage to the oil is getting higher (Rohman, 2015).

Waste cooking oil is cooking oil that has been decomposed so that there is a change in the physicochemical properties of the oil. Decomposition of cooking oil will reduce the quality and nutritional value of fried foods, remove some vitamins and essential fatty acids. The peroxide content in used cooking oil is unstable, easily decomposed by the polymerization process to produce free radical compounds that have the potential to trigger cancer, narrowing of blood vessels, and itching in the throat (Ketaren, 2005). The high number of peroxides in the oil absorb degradation products such as free radicals which gives a negative impact for health. In the long term, it will trigger oxidative damage, causing various chronic and degenerative diseases (Thadeus, 2015).

Waste cooking oil can be reused by processing and refining to get better oil quality. Efforts to improve the quality of used cooking oil have been carried out in several different studies, including the addition of alkaline chemicals (Nagasaku, et al., 2002), membranes (Wulyoadi, 2004), using adsorbents from activated charcoal from Moringa fruit pods (Aisyah, et al., 2010), bagasse (Ramdja, 2010), rice husk (Wahjuni & Kostradiyanti, 2008), banana peel (Nasir, et al., 2014), salak seeds (Girsang, et al., 2015), keluwak shell (Puspita & Tjahjani, 2018), the paper used newspapers (Yazid & Ningsih, 2019) and water hyacinth (Abdullah & Yustinah, (2020).

The method of adding adsorbent is a processing technique, often used to improve the quality of waste cooking oil. The use of adsorbents has several advantages that are more economical, easy to obtain, and more effective. Adsorbent materials can be obtained from natural materials or agricultural product wastes such as straw, peanut shells, bagasse, rice husks, salak seeds, cotton seeds, banana peels, and water hyacinth (Nasir, et al., 2014; Adam, 2017; Nurhilal, et al., 2020). These natural materials are generally rich in cellulose and hemicellulose as well as lignin, so they can potentially be used as adsorbents (Yazid & Ningsih, 2019). According to Elizabeth (2001), banana stems contain 35.2% cellulose; lignin 17.8%. Meanwhile, according to Chen, et al., (2008), water hyacinth has 60% cellulose content, hemicellulose 8%, and lignin 17%.

Most Indonesians plant banana trees because it is known as delicious fruit. Generally, banana stems in the community are underutilized and thrown away as a waste (Elizabeth, 2001). Meanwhile, water hyacinth is commonly found in waters and is considered as a weed (Putera, 2012).

This study aims utilized banana midrib and water hyacinth as adsorbents to reduce the peroxide content in waste cooking oil by spectrophotometric methods. Banana midrib and water hyacinth are materials that are easily obtained, can be used as adsorbents to absorb dyes and degradation products from cooking oil such as peroxide so that it is expected to improve the quality of waste cooking oil.

MATERIALS AND METHODS

Materials and Instruments

The basic ingredients used in this study were banana midrib, water hyacinth, waste cooking oil taken from fried food vendors in the city of Gresik. Other ingredients are distilled water, nitric acid (HNO_3), peroxide solution (H_2O_2 30%). The equipment used was a UV-1600PC spectrophotometer with 1.0 cm quartz cell cuvette, analytical balance, oven, vacuum pump,

magnetic stirrer, volume pipette, microburette, Whatman filter paper (No. 42), and 50 mesh sieve.

Research methods

This research was conducted experimentally with spectrophotometric methods. The waste cooking oil before being analyzed was filtered using Whatman filter paper (No. 42) and a vacuum pump. The filtering results were treated with the addition of adsorbent from banana midrib and water hyacinth with a concentration of 0.0 g; 0.5 g; 1.0 g, 1.5 g, and 2.0 g per 100 ml of cooking oil. The adsorption process was carried out at room temperature with a time variation of 15 minutes each, stirred using a magnetic stirrer on a scale of 4. Each treatment was repeated three times, then analyzed by means of the peroxide content parameter.

Adsorbent preparation

Banana midrib and water hyacinth are cut into small pieces uniformly. The material was cleaned and washed using distilled water and then dried in an oven at 105 °C for 4 hours. Furthermore, the dry adsorbent material is activated to get better adsorbent properties.

Adsorbent activation

The dried banana midrib and water hyacinth stems were soaked in 4.0 N nitric acid in a ratio of 1:2 (w/v) for 2 hours at 80 °C. After soaking, the mixture was filtered and washed with distilled water at pH 6.5 – 7.0, then dried in an oven at 130 °C for 2 hours. The resulting adsorbent material was mashed using a blender until a fine powder was obtained and sieved using a 50 mesh sieve.

Peroxide Adsorption on Cooking Oil

The waste cooking oil obtained from the seller was filtered to remove solid impurities or seasonings contained in the oil. The oil obtained is taken 100 mL into a 250 mL beaker that has been prepared. Furthermore, oil adsorbents from banana midrib and water hyacinth were added as much as 0.0 g; 0.5 g, 1.0 g, 1.5 g, and 2.0 were then allowed to stand at room temperature while stirring with a magnetic stirrer for 15 minutes. The mixture was filtered through Whatman filter paper (No. 42) using a vacuum pump. Each treatment was repeated three times. The filtering results are in the form of oil samples for peroxide analysis. Results are in the form of oil samples for peroxide analysis.

Maximum wavelength.

Determination of the maximum wavelength was made by taking 2.0 mL of freshly prepared 3% peroxide solution, put into a 50 mL volumetric flask, diluted with distilled water to the mark, and shaken until

homogeneous. The absorbance of the solution was read with a UV-1600PC spectrophotometer at a wavelength of 200-300 nm. The maximum wavelength obtained was then used to determine the absorption of the standard solution and peroxide in the used cooking oil sample.

Calibration curve

Serial concentrations of peroxide standard solution were made with a concentration of 0.03%-0.15%. Taken a solution of peroxide (H₂O₂ 3%) using a microburette sequentially is 0.5 mL; 1.0 mL; 1.5 mL; 2.0 mL; and 2.5 mL, were put into a 50 ml volumetric flask to obtain a concentration of peroxide solution of 0.03%, 0.06%, 0.09%, 0.125 and 0.15%. The solution was diluted with distilled water to the limit mark and shaken until homogeneous then read the absorption using a solvent blank at the maximum wavelength.

RESULT AND DISCUSSION

Experimental Stages

There are three stages in this research, the first is the manufacture of adsorbents from banana midrib and water hyacinth which have been cut into small pieces uniformly and then washed with distilled water and dried in an oven to obtain a clean and dry material. In the second stage, the adsorbent material produced from the first stage is activated using chemicals by immersing it in a 4.0 N HNO₃ solution. The purpose of this activation process is to remove residual impurities from the remaining fibers and improve the structure of the adsorbent material to increase the absorption ability. The third stage is the treatment part which is carried out by contacting the adsorbent material from banana midrib and water hyacinth stems with a sample of waste cooking oil that has been filtered so that the adsorption process of peroxide and other materials occurs.

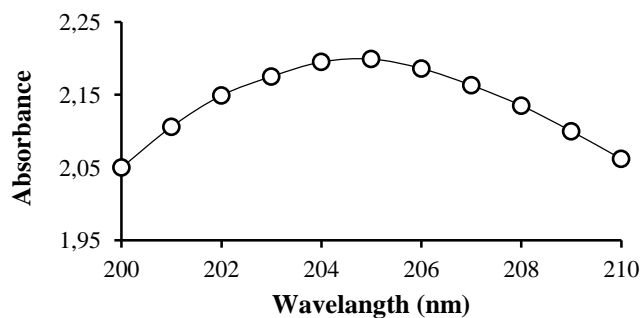


Fig 1. Maximum wavelength curve

Maximum Wavelength

Before the waste cooking oil was analyzed, the maximum wavelength was measured using a spectrophotometer at a wavelength of 200-400 nm. The measurement results obtained a maximum wavelength of 205 nm (Figure 1). The wavelength is then used to determine the absorbance of the standard solution of peroxide and waste cooking oil samples.

Calibration Curve

Based on the standard curve of the peroxide solution, good linearity was obtained and it complied with the Lambert-Beer law with a concentration range of 0.03%-0.15%. Figure 2 shows that a linear regression equation $y = 15.78x + 0.1872$ is obtained with a correlation coefficient of $r = 0.991$. The value of r close to 1.0 indicates good linearity, which means that there is a linear relationship between peroxide concentration and absorbance.

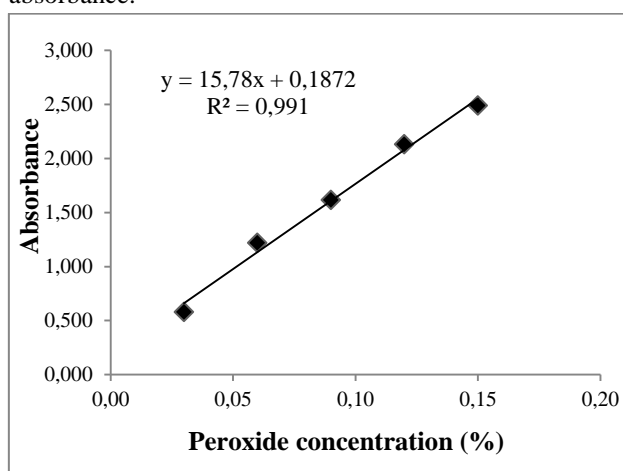


Fig 2. Peroxide solution calibration curve

Determination of Peroxide

Cooking oil that has been damaged will experience changes in physicochemical properties marked by the appearance of dark color, taste, and a rancid odor. The presence of rancidity indicates a very high peroxide content in the oil (Ketaren, 2005). The occurrence of rancidity is caused by autoxidation of cooking oil to form peroxide and hydroperoxide compounds which are unstable and easily decomposed to produce free radicals, aldehydes, ketones, and free fatty acids (Yazid and Lisda, 2015). Autoxidation begins with the formation of free radicals that are accelerated in the presence of light, heat, oil peroxides or hydroperoxides, and metal catalysts such as Cu, Fe, Co, and Mn (Winarno, 1995). In general, the formation of peroxides can be shown as in Figure 3.

The results of the determination of peroxides in waste cooking oil before and after the addition of adsorbents from banana midrib and water hyacinth are listed in Table 1. Before adding the adsorbent, the concentration of peroxide in waste cooking oil was 0.05%. After the addition of the adsorbent from the banana midrib each 0.5 g, 1.0 g, 1.5 g, and 2.0 g in 100 ml of waste cooking oil with a contact time of 15 minutes, the average peroxide content was found respectively 0.031%, 0.033%, 0.034%, and 0.034%. Meanwhile, for the addition of water hyacinth adsorbent, the peroxide content was found at 0.035%, 0.038%, 0.039%, 0.038% and respectively.

Table 1. Peroxide content in waste cooking oil

| No. | Adsorbent weight (g) | Peroxide (%) | |
|-----|----------------------|-----------------------------|------------------------------|
| | | Banana midrib ^{*)} | Water hyacinth ^{*)} |
| 1. | 0.0 | 0.050 | 0,050 |
| 2. | 0.5 | 0.031 | 0,035 |
| 3. | 1.0 | 0.033 | 0,038 |
| 4. | 1.5 | 0.034 | 0,039 |
| 5. | 2.0 | 0.034 | 0,038 |

^{*)} Average repetition three times

Based on the peroxide content obtained, it can be seen that the addition of banana midrib and water hyacinth adsorbents can provide a significant reduction. This was proven after the Independent T-test was carried out, it was obtained significantly 0.000 ($p < 0.05$), so it can be concluded that there was a significant decrease in the peroxide content of the adsorbent of banana midrib and water hyacinth in used cooking oil.

The occurrence of a decrease in peroxide in waste cooking oil after contact with the adsorbent was due to the adsorption process that occurred between the peroxide compound by the adsorbent forming a layer on the surface of the adsorbent. The nature of the molecule being adsorbed, in this case the peroxide cannot move freely or be bound by the adsorbent. When separated from waste cooking oil, peroxide compounds and other components in the oil are carried along with the adsorbent.

According to Asip, et al., (2008), the factors that influence the adsorption process are the stirring process and the solubility of the adsorbent. If the stirring process is relatively small, it is difficult for the adsorbent to penetrate the film layer between the adsorbent surface and the diffusion film layer, which is a limiting factor that reduces the absorption rate. If the agitation is appropriate it will increase the film diffusion layer to the point of pore diffusion. The solubility of the adsorbent is the property of the dissolved element having a stronger attractive force for the liquid when compared to the insoluble element. Thus the dissolved elements will be more difficult to absorb than the insoluble elements. Meanwhile, according to Mardina, et al., (2012), the effectiveness of adsorption is also influenced by the capacity of the adsorbent and the length of contact time between the adsorbent and the adsorbate.

In this study, the decrease in peroxide content occurred in the addition of 0.5 g of banana midrib and water hyacinth adsorbent. The addition of the next adsorbent with a concentration of 1.0 g to 2,0 g tends to decrease constantly. The occurrence of differences in the decrease in peroxide levels in the type of adsorbent can be seen in Figure 4.

The highest percentage decrease in the amount of peroxide was found in the addition of banana midrib adsorbent with a concentration of 0.5 g of 38%. Meanwhile, with the addition of water hyacinth adsorbent, the decrease was slightly smaller with a concentration of 0.5 g, which was 30%.

Table 2. Percentage of peroxide reduction in waste cooking oil

| No. | Adsorbent weight (g) | Percentage of peroxide reduction (%) | |
|-----|----------------------|--------------------------------------|----------------|
| | | Banana midrib | Water hyacinth |
| 1. | 0,5 | 38 | 30 |
| 2. | 1,0 | 34 | 24 |
| 3. | 1,5 | 32 | 22 |
| 4. | 2,0 | 32 | 24 |

The addition of banana midrib adsorbent with a weight of 1.0 g to 2.0 g decreased slightly and tended to be constant at 34% and 32%, respectively. Meanwhile, the water hyacinth adsorbent each decreased with a smaller percentage and also tended to be constant, namely 24% and 22% (Table 2). According to Mardina, et al., (2012), contact time is very influential on the absorption process. The longer the contact time, the more absorption will also increase until a certain time reaches a maximum, after which it will decrease again.

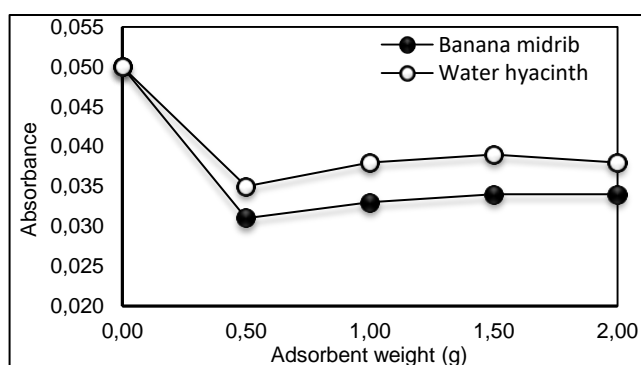
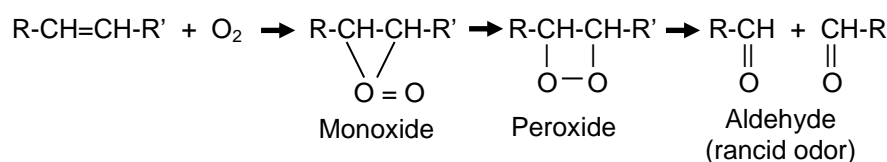


Fig 4. Graph of the decrease in peroxide content

Peroxide formation reaction (Ketaren, 2005)



The relatively short contact time can result in the amount of adsorbent not being able to significantly increase the adsorption capacity, so desorption is suspected. According to Mandasari & Purnomo (2016), desorption is the release of adsorbate (peroxide) from the surface of the adsorbent. This phenomenon occurs due to the saturation of the adsorbent surface so that the peroxide compounds that have been absorbed are released back into the oil. In the saturated state, the adsorption rate is reduced, so it does not increase the peroxide absorption. In addition to the contact time, it is suspected that the mass of the adsorbent also affects the instability of the peroxide absorption. The variation in the mass of the adsorbent used is too close, resulting in an increase in peroxide absorption after the addition of 0.5 g of adsorbent, and then tends to be constant or slightly decreased.

The adsorption process is influenced by the physical and chemical properties of the adsorbent, such as particle size, surface area, and chemical composition. The smaller the particle size of the adsorbent, the greater the surface area so that more substances are adsorbed (Hasyim, et al., 2019). The occurrence of the adsorption process between the adsorbent compound of banana midrib and water hyacinth with peroxide in waste cooking oil is due to the attraction between the peroxide molecule and the surface of the adsorbent. According to Palar (2008), the interaction that occurs in the adsorbate molecule with the surface of the adsorbent may be followed by more than one interaction, depending on the chemical structure of each component. Meanwhile, according to Suryandari (2016), the occurrence of adsorption is caused by the difference in potential energy between the surface of the adsorbent and the adsorbed substance. Based on this, the adsorption that occurs can be in the form of electrical adsorption, mechanical adsorption, chemical adsorption, and thermal adsorption.

CONCLUSION

The addition of adsorbents from banana midrib and water hyacinth can reduce peroxides in waste cooking oil. Both can be used as alternative bio-sorbents to improve the quality of waste cooking oil through a parameter of reducing the amount of peroxide

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