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"Green" Bleaching Process of Sugar Palm (*Arenga pinnata*) Flour by Using Sodium Salt and Ozone Technology

Wara Dyah Pita Rengga[1], Ria Wulansarie[1], Achmad Chafidz[2, a*], Tuasikal M. Amin[2], Prima A. Handayani[1], Hanif Abdillah[1], Mohammad Fariz Fauzan[1]

[1]Chemical Engineering Department, Universitas Negeri Semarang, Semarang 50229, Indonesia

[2]Chemical Engineering Department, Universitas Islam Indonesia, Yogyakarta 55584, Indonesia

[a]achmad.chafidz@uii.ac.id

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Abstract. Sugar palm (*Arenga pinnata*) is one of important commodities in Indonesia. One method that has been used to whiten sugar palm flour is by bleaching process using chlorine ($Ca(ClO)_2$). Unfortunately, the use of chlorine as a whitening agent is considered harmful to health and the environment. One of alternative methods that can be considered as "Green" bleaching process for sugar palm whitening is ozone technology. The effects of ozonation process and different concentrations of NaCl and Na_2SO_4 added in the ozonation process to the whiteness (i.e. L* and b* scale) and protein content of sugar palm flour were investigated. Suspension of sugar palm flour-water was contacted with ozone gas at rate of 325 mg/hour. The duration of ozonation process was varied for 30, 60, 90, 120, 150, and 180 minutes. The initial concentration or ratio of sugar palm and water was also varied, i.e. 1:2 (wt/wt); 1:3 (wt/wt); and 1:4 (wt/wt). To determine the effect of adding sodium salt; NaCl and Na_2SO_4 were added at different concentrations of 5, 10, and 15 g/L each. The test results showed that pH of the flour and b* value decreased, while L* value of sugar palm flour increased with the increasing ozonation time. The results also showed that the most significant increase of L* value was at the sample ratio (sugar palm:water) of 1:3 (wt/wt) and 30 minutes of ozonation time. The optimal NaCl addition concentration was 10 g/L with 150 minutes of ozonation time. Whereas, the optimal Na_2SO_4 addition concentration was 15 g/L with 150 minutes of ozonation time. The addition of Na_2SO_4 resulted in an increase of L* value greater than the NaCl. The protein content of sugar palm flour also decreased along with the increase of flour whiteness. A maximum decrease in protein content of 57% occurred in flour samples with initial concentration or ratio of 1:3 (wt/wt) and ozonation time of 30 minutes.

Introduction

Sugar palm (*Arenga pinnata*) is an important commodity in Indonesia due to the high starch content in the stem pith. Unfortunately, starch flour produced from sugar palm trees mostly has yellowish color. This is due to carotenoid content possessed [1]. Therefore, a method is needed to whiten the color of sugar palm flour before commercialized. One method that has been used to whiten sugar palm flour is by bleaching using chlorine ($Ca(ClO)_2$). Unfortunately, chlorine derivative is reactive and easily forms new compounds such as organochlorine compounds which are carcinogens [2]. Thus, the use of chlorine as a whitening agent is considered harmful to health as well as the environment. Therefore, other methods that are more environmentally friendly are needed. One of the newest, innovative, and environmentally friendly methods for bleaching/whitening of sugar palm is ozone technology [3].

Ozone (O_3) has been proven to be able to improve the whiteness of sago flour [4] where sago flour has characteristics that resemble sugar palm. The ozonation process is influenced by several factors including pH, temperature, ozone concentration, and the addition of additives in the form of sodium salt. Sodium salt, e.g. NaCl and Na_2SO_4 can increase the ability of ozone to degrade color because both are able to form radicals that act as oxidizer, which help in color fragmentation [5]. Therefore, the purpose of this study was to investigate the effect of suspension concentration of sugar palm flour and addition of NaCl and Na_2SO_4 (at different concentrations) to the whiteness properties of the sugar palm flour. Additionally, the changes in the protein content of sugar palm flour during the ozonation process was also investigated.

Experimental

Materials. The main ingredient used in this study, sugar palm flour (see Fig. 1b) was obtained from local producer in Ngabean District, Kendal Regency. Whereas, NaCl, Na_2SO_4, and distilled water were obtained from local chemical market, Semarang city.

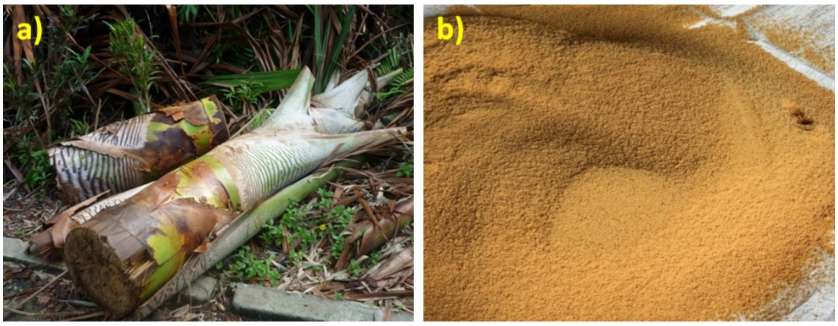

Fig. 1 Photographs of a) sugar palm stem, and b) sugar palm flour (from the stem pith).

Ozonation Process of Sugar Palm Flour. The instrument used in this study were AQUATIC ozone generator, IKA Eurostar 20 agitator with turbine stirrer type and BINDER brand incubator. The ozone produced by the ozon generator was contacted with the suspension of sugar palm flour/water at flow rate of 325 mg/hour. During the ozonation process, stirring was carried out using an agitator at speed of 400 rpm to avoid formation of precipitates during the ozonation process. The schematic design and appearance of ozonation reactor are shown in Figs. 2a and 2b, respectively. The variables examined in this study include the effect of suspension concentration of sugar palm and the addition of NaCl and Na_2SO_4 salts to the ozonation performance in whitening process of sugar palm. The ozonation performance was analyzed from the whiteness test of the treated sugar palm.

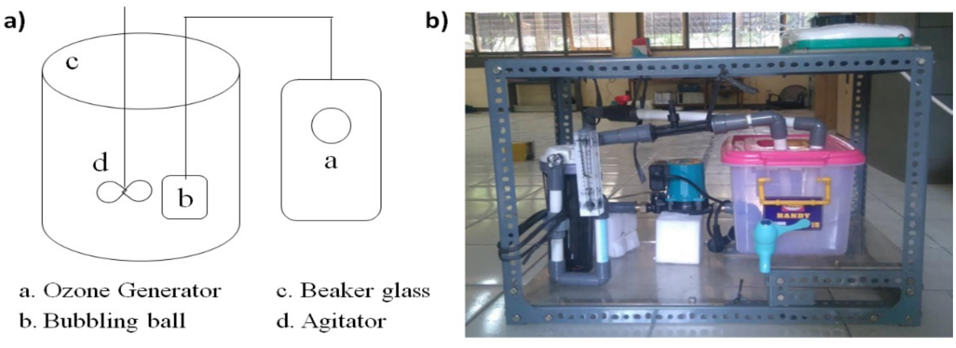

Fig. 2 a) Schematic design of ozonation reactor, and b) photo of ozonation reactor.

Ozonation with different ratios of sugar palm flour and water. The ratio of sugar palm flour and water were 1:3; 1:4; 1:2 (wt/wt). The ozonation process was carried out for 30, 60, 90, 120, and 150 minutes. Then the suspension of sugar palm flour was precipitated and dried using an incubator at temperature of 80°C for 1 hour. The sugar palm flour was then tested for its whiteness using chroma meters.

Ozonation with addition of NaCl and Na_2SO_4. The use of Na_2SO_4 and NaCl salts as additives and without using salt additives will be compared in the ozonation process. The concentrations of each sodium salt were 5, 10, and 15 g/L. The ozonation process was carried out for 30, 60, 90, 120, and 150 minutes. Then the suspension of sugar palm flour was precipitated and dried using an incubator at a temperature of 80°C for 1 hour. Sugar palm flour was then tested for whiteness using chroma meters.

Characterization of Sugar Palm Flour. The sugar palm flour before and after ozonation were characterized for their whiteness and protein content.

Whiteness of sugar palm flour. Measurement of the whiteness of flour can be done using a chroma meter with the Konica Minolta CR-400 brand. Chroma meter measurements include L*, a* and b*. The value of L* shows the brightness with a range of 0-100. The value of b* shows the color yellow-blue with the range of -100 - 100. The value of a* was not considered because it was unable to show the carotenoid color spectrum. This was because the carotenoids were yellow pigments while the a* value showed the green-red color range. Color measurement using a chroma meter showed a white tendency when the L* value is higher while the value b* is close to zero.

Protein content of sugar palm flour. The protein content of sugar palm flour was tested before and after the ozonation process. Testing of sugar palm flour protein was a quantitative method. This protein testing was carried out according to SNI 01-2891-1992.

Results and Discussion

Sugar Palm Flour Characterization. The flour used has the characteristic yellowish-brown color. The test results of the initial whiteness of sugar palm using chroma meter showed low L*. This indicates that sugar palm flour has a color that tends to be dark. A high b* value indicates that sugar palm flour has a yellow tendency. This is due to the carotenoid pigment content of the type of lutein found in sugar palm flour [6]. The characteristics of the whiteness in the initial sugar palm flour are presented in Table 1. In addition to color degree testing, it was also tested the initial protein content of sugar palm. The test results showed that the initial sugar content of sugar palm was 0.755%. The value of this protein is used as a reference during the ozonation process to examine the effect of ozonation on the protein content of sugar palm.

Table 1. The color testing of untreated sugar palm flour.

Chroma meter test	Values
L*	66.647
b*	9.643

Ozonation with different Ratio of Sugar Palm and Water. The graph of changes in L*value of the sugar palm flour after ozonation process is shown in Fig. 3a. The highest increase occurred in sugar palm flour with the ratio (sugar palm flour : water) of 1:3 (wt/wt). The L* value increased from 66.647 (initial L*) to 93.20. Flour with ratio of 1:2 (wt/wt) has L* value of 89.123, whereas ratio of 1:4 (wt/bwt) has L* value of 86.713. The L* value tend to decrease with increasing ozonation time. At the end of the ozonation process (i.e. 150 minutes), the highest L* value (i.e. 86.237) was obtained at ratio of 1:2 (wt/wt). This is because the higher the concentration of sugar palm flour, the higher the rate of oxidation by ozone [7]. Additionally, the L* value could also be related to the b* value, in which as the L* value increase, the yellow tendency (shown by b* value) will decrease [8].

The graph of changes in b* value of sugar palm flour at different ratios (sugar palm flour: water) is shown in Fig. 3b. As seen in the figure, the b* value decreased with increasing ozonation time for each variation of ratio. The decrease in b* indicated the degradation of the yellow pigment which was associated with a decrease in carotenoid levels in sugar palm. The decrease in b* value is possible because the oxidation of lutein which is the main carotenoid in the conjugate double bond in flour. Lutein has 11 conjugate double bonds that are susceptible to oxidation by ozone [6]. This is consistent with previous studies where b* decreased from 15.67 to 13.62 in the ozonation process for 30 minutes and reached the value of 13.39 for 60 minutes [9].

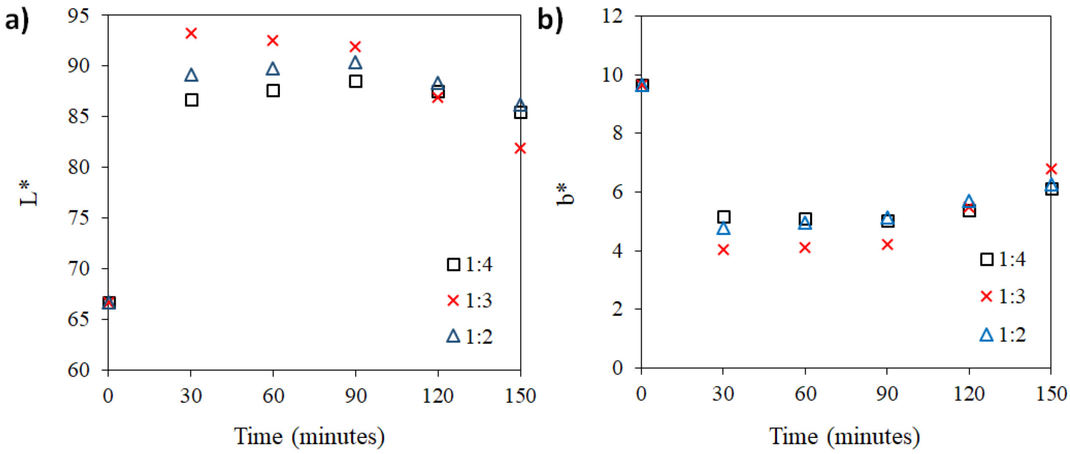

Fig. 3 Changes in a) L* value, and b) b* value of sugar palm flour at different ratios of sugar palm and water.

The most significant decrease of b* value occurred in the ozonation process with flour ratio of 1: 3 (wt/wt), which was from 9.643 (initial b* value) to b* value of 4.03. Based on the L* and b* values, the optimal ratio (sugar palm flour:water) was 1:3 (wt/wt) with ozonation period of 30 minutes. This was indicated by the highest increase in L* value accompanied by the lowest decrease in b* value. This was possible because ozone was able to diffuse maximally in the suspension of flour so that carotenoid degradation took place optimally. Ozone that reacts with carotenoid compounds can form new compounds with empirical formula of $C_{40}H_{56}O_3$ [10].

Ozonation with the Addition of NaCl. Addition of sodium chloride (NaCl) can affect the ozonation process. NaCl can bind well with ozone molecules and hydroxyl radicals, which then oxidize carotenoids contained in the sugar palm. The graph of changes in L*value at different at different NaCl concentrations shown in Fig. 4a. The L* value in the first 30 minutes of the ozonation process experienced a significant increase. Where the highest increase was experienced by the sample with the addition of NaCl of 10 g/L. The sugar palm flour added with NaCl had a higher L* value compared to that without the addition of NaCl. This is because in the presence of NaCl, ozone molecules that bind to Cl_2 become more reactive and faster to degrade carotenoids in sugar palm flour [11].

NaCl can react with ozone in both acidic and alkaline pH conditions. Under acidic conditions, the ozone molecule (O_3) will act with NaCl and oxidize organic compounds which in this case are carotenoids. The sodium chloride also reacted with ozone which turned into a hydroxyl radical at alkaline pH like a reaction at acidic pH with ozone molecules. The increase in L* value in the sample of sugar palm with the addition of NaCl was also inversely proportional to the value of b*. The higher the L* value, the lower the value of b*. The decrease in b* in the sample variation of the addition of NaCl was greater than the sample without the addition of NaCl. This was because the carotenoid compounds that are degraded by ozone have more binding to Cl_2. The change of b* value of sugar palm flour at different NaCl concentrations is shown in Fig. 4b.

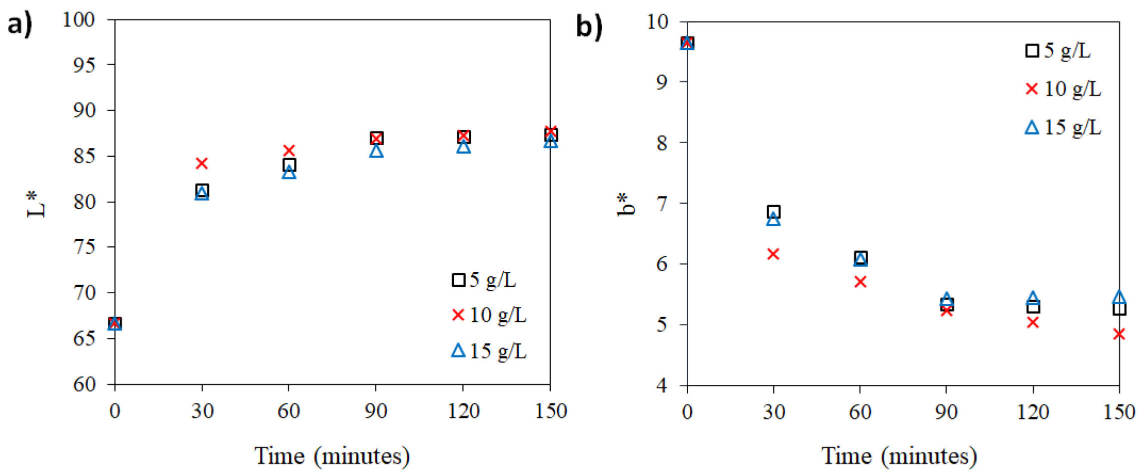

Fig. 4 Graph of changes in a) L* values, and b) b*values of sugar palm flour at different NaCl concentrations.

Based on the changes in L* and b* values in the ozonation process at different NaCl concentrations, the optimal NaCl concentration was 10 g/L with ozonation time for 150 minutes. This was shown in the samples with the addition of 10 g/L NaCl and ozonized for 150 minutes having the highest L* accompanied by the lowest decrease in b* (see Figs. 4a and 4b).

Ozonation with the Addition of Na_2SO_4. The sodium salt Na_2SO_4 only reacts at alkaline conditions. Therefore, the ozonation process with different of Na_2SO_4 concentrations was carried out at pH 10. The ozone decompose into hydroxyl radicals and cause sulfate ions to react with the hydroxyl radical. The graph of the increase in L* value of sugar palm flour during the ozonation process with variations in the addition of Na_2SO_4 is shown in Fig. 5a. At the same concentration of 15 g/L and 150 minutes of ozonation process, the increase in L* value with the addition of Na_2SO4 was greater than with the addition of NaCl. This was likely because Na_2SO_4 could form sulfate and peroxydisulfate radicals during the ozonation process [5]. The reaction between sulfate ions and hydroxyl radicals is as follows [11]:

$$SO_4^{2-} + OH^o \lozenge SO4^{o-} + OH^- \quad (1)$$

$$2SO_4^{o-} \lozenge S_2O_8^{2-} + 2^{e-} \quad (2)$$

Peroxydisulfate can help degrade carotenoids in sugar palm. However, this only applies when the pH conditions of ozonation are alkaline. It is because under acidic conditions, the sulfate does not react with ozone. At alkaline pH, ozone decomposes into OH^o hydroxyl radical, so it reacts with sulfate. The formation of sulfate radicals during the ozonation process can affect b* level of the sugar palm. This is because the oxidation potential of the sulfate and peroxydisulfate radicals is quite high, which is 2.01 V. This value is higher than the oxidation potential of hypochloric acid (1.5 V), hypolorate ion (0.89 V), chlorine dioxide (1.15 V) and chlorine (1.36 V) [11]. The formation of oxidant radicals of sulfate and peroxydisulfate which have greater oxidation potential can increase the ability of ozone in the process of carotenoid degradation of sugar palm.

The phenomenon of carotenoid degradation of sugar palm flour is shown in Fig. 5b, where b* value of the sugar palm flour decreased with increasing ozonation time. The lowest decrease in b* value of sugar palm flour was from 9.6433 to 5.6067, which occured at the addition of Na_2SO_4 15 g/L. This was likely because sulphate radicals were formed so that the carotenoid degradation process became optimal. Based on the changes in L* and b* values in the ozonation process with different Na_2SO_4 concentrations (see Figs. 5a and 5b), the optimal Na_2SO_4 concentration was 15 g/L with ozonation time of 150 minutes. As shown in those figures, the addition of 15 g/L of Na_2SO_4 and ozonation time of 150 minutes have resulted in highest L* value accompanied by the lowest decrease of b* value.

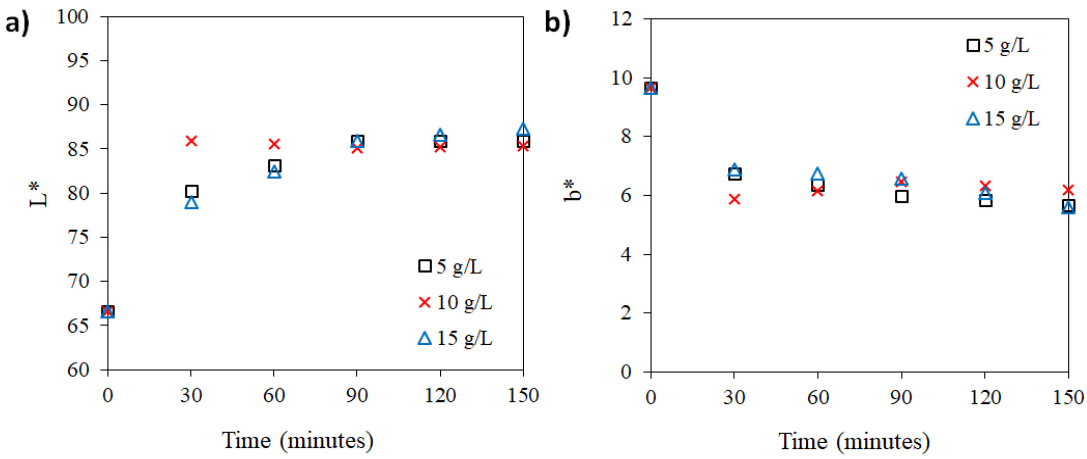

Fig. 5 Graph of changes in a) L* values, and b) b*values of sugar palm flour at different Na_2SO_4 concentrations.

Effect of Ozonation on Protein Content of Sugar Palm Flour. Protein testing results show that the ozone affected the protein content of the sugar palm. The protein content of sugar palm flour decreased during the ozonation process. The maximum decrease was from 0.755% to 0.480% (i.e. (57%), which occurred in the sample (flour:water) ratio of 1:3 (wt/wt) and ozonation time of 30 minutes. This results was consistent with the results of the whiteness test where the sample has the highest L* value and the lowest b* value. The decrease in protein content of sugar palm was also shown in the sample with the addition of NaCl and Na_2SO_4. The decrease in protein content in the sample with the addition of 10 g/L NaCl was approx. 42.85%. This decrease was greater if compared to the sample with the addition of 15 g/L Na_2SO_4, which was 35.71%. This results were supported by the results of whiteness test of flour, where the sample with the addition of 10 g/L NaCl had a greater L* value and smaller b* value than the sample with the addition of 15 g/L Na_2SO_4. Based on the explanation above, it can be seen that the increase in the whiteness of flour w accompanied by a decrease in the protein content. This indicates that ozone can also destroy protein compounds contained in sugar palm flour [12].

Conclusion

The use of ozone has successfully whiten the sugar palm flour, where the ozone molecules acted as oxidants to degrade the carotenoids contained in the sugar palm flour. The optimal conditions were initial concentration or ratio (sugar palm flour:water) 1:3 (wt/wt) with ozonation period of 30 minutes. The addition of NaCl in the ozonation process could increase the L* value and decrease b* value of the flour, which indicated carotenoid degradation. The optimal NaCl addition concentration was 10 g/L with 150 minutes of ozonation time. The addition of Na_2SO_4 resulted in an increase of L* value greater than the NaCl. Whereas, the optimal Na_2SO_4 addition concentration was 15 g/L with 150 minutes of ozonation time. The protein content of sugar palm flour also decreased with increasing the whiteness of sugar palm. The decrease in protein content by 57% occurred in samples of sugar palm flour with the sample ratio of 1: 3 (wt/wt) and ozonation time of 30 minutes.

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