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THE CHLORINE REDUCTION IN EDAMAME BY WATER-OZONATED MINIMALLY PROCESS

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Abstract. The objective of this article was to study the effect of washing edamame using ozonated water to reduce residual chlorine contained in edamame through a continuous washing process. Chlorine residue in edamame was caused by the use of fertilizers and pesticides that contain chlorine compounds. The research method used was descriptive explanatory research consist of two treatment levels of ozonation time (0, 10, and 15 minutes) and ozone contact time (0, 12, 18, and 24 minutes) which were repeated twice. The residual chlorine and pesticide concentrations were calculated using the titration method. Based on research results, ozone can reduce chlorine in edamame. The lowest detected chlorine was in edamame which had been washed using ozone water with an ozonation time of 15 minutes with the amount of chlorine reduced by 56%. The longer the contact time, the greater the amount of reduced chlorine and the lower the concentration of ozone remaining in the washing water. Based on the research results, a brief conclusion that can be explained was ozone could reduce chlorine in edamame caused by fertilizer and disinfectant overuse until 50%.

Keywords: chlorine; edamame; fertilizer; pesticide; ozonated-water.

INTRODUCTION

The agricultural sector plays an important role in national development (Food Security Agency, 2018). Indonesia strives continuously to produce a quality agricultural sector. The wide market access provides economic benefits in agriculture development. Horticultural is one of the agricultural sectors that encouraged continuously to compete in the international market. horticultural products that are in great demand by foreign countries, one of which is edamame, which is a typical product of Jember.

The main export destinations of Jember edamame soybeans are Japan, Saudi Arabia and the Netherlands (Sukri et al., 2016). In these countries, on average, Indonesia occupies the fourth position out of edamame exporting countries. Based on this, the edamame export quantity increasing can still be increased. It's quantity of can be influenced by various things, including the availability of planting land, the availability of processing farmers, fertility and planting quality edamame, as well as safe and efficient processing to produce edamame according to the standards provided by the importing country (Purnama et al., 2018).

Currently edamame is preferred to be consumed fresh, so it is exported raw or undercooked, either with shell or without shell (K. C. Wang, 2018). Fresh or undercooked edamame, exported in a frozen state that has previously been minimally processed through a washing process. The washing process is critical control point in determining product safety, one of the reasons was because various export destination countries require the absent of pesticides, phosphate, and chlorine that were commonly used in the edamame planting process (Ali et al., 2018). Pesticides were used to prevent pest growth during the growing season to produce its quality according to the order of the importing country.

Now day, the chemical pesticides use with dangerous active ingredients such as diazinon, chlorpyrifos, and profenofos has been partially replaced by natural pesticides that are fermented from vegetable and fruit waste (Kendalpayak & Timur, 2017). While the use of chlorine is still unavoidable. The chlorine contained in edamame can come from pesticides, fertilizers containing chlorine with excessive use, and from washing water containing chlorine (Xu & Zhang, 2001). Chlorine commonly used as disinfectant to reduce spoilage microorganism. Many farmers often used chlorine to longer edamame shelf-life.

Chlorine reacts with water forming hypochlorous acid which can damage body cells, digestive disorders, stomach wall erosion, kidney disease, and cancers. chlorine reduction in edamame due to the use of pesticides, fertilizers and spoilage microorganism's removal can be carried out by oxidizing it using strong oxidizing agents (Bakri et al., 2018).

Ozone is powerful oxidizing agent with that can react 3000 times faster than chlorine (I. S Setiasih et al., 2015). Ozone on the other hand is nontoxic, has no residual, has no odor or taste, and no hydrocarbon byproducts. Excess ozone auto decomposes rapidly to produce oxygen

and leaving no residue in product. There were a number of agricultural commodities whose pesticide residues have been studied through ozone minimal washing process, but not edamame.

Ozone minimally process is affected by the ozonation time, ozone contact time and the design of the washing tank to distribute ozone into the washing water (Imas Siti Setiasih et al., 2020). The purpose of this study was to determine the effect of these three aspects in minimally process of edamame using ozonated water on the reduction of pesticide residues. ozone is expected to reduce chlorine levels in edamame. The novelty in this research is the variation of the ozonation time and the ozone contact time used for the design of the ozone washer (S. Yudiastuti & Wijaya, 2020).

METHODS

The research was conducted from May to November 2020, located at Metal and Wood Laboratory of Agricultural Technology Department, Politeknik Negeri Jember. Raw material used were edamame, KI 2%, H_2SO_4 0,1 N, $Na_2S_2O_3$ 0,2N, 2% of starch, Chlorine, Tap water, and destiled water. The tools used were continuous type ozone washer prototype (S. Yudiastuti & Wijaya, 2020), burette, Erlenmeyer, and crusher. The treatment consisted of two factors, namely ozonation time and ozone contact time.

The research combination is as follow :

Table 1. Reseach Combination

Contact Time (b)	**Ozonation Time (a)**		
	0 min	10 min	15 min
0 min	a_0b_0	a_1b_0	a_2b_0
12 min	a_0b_1	a_1b_1	a_2b_1
18 min	a_0b_2	a_1b_2	a_2b_2
24 min	a_0b_3	a_1b_3	a_2b_3

The replication of treatment was done two times. However, the assay was performed two times and the data were analyzed descriptively using Microsoft excel (2019) tool.

Edamame Ozonated Minimally Process

The edamame washing using ozone treatment was carried out using a continuous type ozone washer. The minimal washing process with ozone begins by filling the holding tank with 100 L of water, then the water pump was turned on until the water was circulated and the water in the washing tank shown a volume of 100 L. The washing tank was then closed and the ozone would flow into the washing tank for 15 minutes. Whole edamame that has been put in a nylon filter bag was then sink into the washing tank according to the ozonation time and the ozone contact time. (S. O. N. Yudiastuti & Wijaya, 2021)

Sampling and Preparation

Each treatment experiment was carried out using 500gr whole edamame. Edamame was put in a nylon net. After the washing process at a certain time of ozonation and contact time, the edamame was crushed along with the washing water in a 1:1 ratio of edamame: washing water. The sample was filtered, then the filtrate was titrated to determine the residual chlorine and ozone residue contained in the sample. The experiment was repeated two times and each test was performed in duplicate.

Chlorine Analysis

The edamame filtrate was pipetted as much as 5 mL and put in an Erlenmeyer flask and the blank solution was prepared using 5 mL of distilled water. Then 0.2 mL of each solution was added K_2CrO_4 indicator 5% w/v and stirred. The two solutions are titrated with $AgNO_3$ to the end point of the titration with repeated two times and recorded the volume of $AgNO_3$ used, then averaged and calculated chloride content in the sample. (SNI 6989.19.2009: Test Method for Chloride (Cl-) With Argentometry Method, 2009)

$$\text{ppm } Cl^- = \frac{(V_{Ag_{2NO_3}} \, x \, M_{Ag_{2NO_3}} \, x \, 5{,}84}{m_{sample}} \qquad (1)$$

Ozone Analysis

10mL of edamame filtrate was put in an Erlenmeyer, then 200mL of 2% KI was added. Immediately add 10 mL of 0.1 N H_2SO_4 to the mixture. Titrate with 0.2N $Na_2S_2O_3$ until pale yellow then add 0.5mL of 2% starch indicator into the Erlenmeyer, the solution will turn dark blue. Titrate again with 0.2N $Na_2S_2O_3$ until the solution is clear. (Masschelein et al., n.d.)

$$\text{ppm } O_3 = \frac{(V_{Na_2S_2O_3} \, x \, M_{Na_2S_2O_3} \, x \, 24}{m_{sample}} \qquad (2)$$

RESULTS AND DISCUSSION

From the result obtained as presented in figure 1, the average result of chlorine concentration in ozonated-water minimally process was decrease.

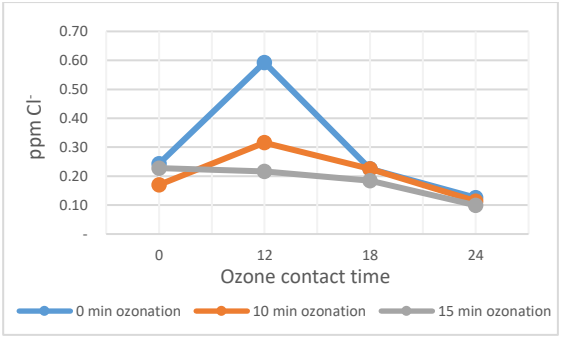

Figure. 1: Chloride concentration (ppm) after water-ozonated minimally process

Ozone is capable of oxidizing many organic compounds to carbon dioxide, water and other harmless compounds. Chlorine, upon contact with O_3, will break down and turn into CO_2, H_2O, and other harmless compounds (Batakliev et al., 2014). In the oxidation process, ozone can break chlorine and decompose it, turning chlorine into non-toxic substances. According to results had shown by figure above, the chlorine concentration reduction in edamame water-ozonated minimally process at 0 minutes ozonation drop from 0,24 ppm to 0,13 ppm, 10 minutes ozonation drop from 0,17 ppm t0 0,11 ppm, and 15 minutes ozonation drop from 0,23 ppm to 0,1 ppm.

The chlorine content in edamame was reduced the most in the ozonation treatment for 15 minutes and the ozone contact time for 24 minutes. Reduction of chlorin in the ozonation treatment of 0 minutes, 10 minutes, and 15 minutes, respectively, namely 48%, 33% and 56%. The chlorine percentage in the 10-minute ozonation treatment is smaller than the 0-minute ozonation treatment, because the amount of chlorine in the 0-minute washing was greater than the 10-minute washing, as shown in the graph in Figure 1,

the chlorine graph reduction in the 10-minute ozonation treatment is gentler than the 0 minutes ozonation treatment. In the treatment with an ozonation time of 0 minutes, the chlorine can still be reduced because the washing water has previously been induced with ozone gas for 15 minutes before the washing has started.

Based on the results of chlorine reduction from washing with ozone water at different ozonation time variations in this study, the increasing of chlorine reduction percentage was not linear with the increasing of ozonation time. This indicates that the rate of chlorine reduction by ozone is not only affected by the ozonation time and the ozone contact time. Based on observations in this study, other things that may affect the rate of chlorine reduction using ozone water are the initial induction time of ozone in washing water and the ozone induction method on water. the initial ozone induction time and the ozone induction method on water will affect the concentration of ozone in edamame washing water (Kying & Ali, 2016). The ozone concentration used in the study was measured using the titration method.

The ozon concentration measuring results in this study are presented in Figure 2.

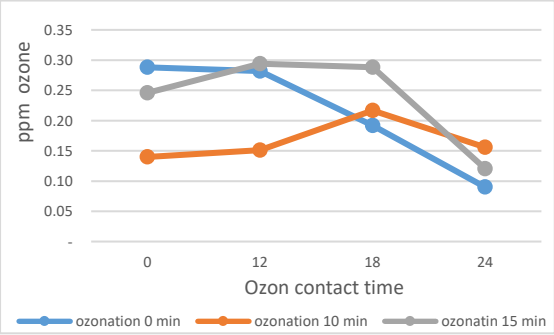

Figure. 2: Ozone concentration (ppm) after water-ozonated minimally process

From the graph presented in figure 2, the average ozone concentration in ozonated-water minimally process was decrease. The Initial ozone concentrations in water after ozone-induced for 15 minutes are shown in Table 2.

Table 2. Ozone concentration before and after water-ozonated minimally treatment

Ozonaton Time	**[Ozone] (ppm)**	
	Before	End
0 min	0,23	0,09
10 min	0,17	0,16
15 min	0,39	0,12

Both in Figure 2 and Table 2, it is shown that the ozone concentration was reduced during the ozone contact time. Ozone is a strong oxidizing agent, although it does not produce residues that are harmful to humans, direct exposure to high concentrations of ozone can cause body cells to oxidize (S. Wang et al., 2018). Although the oxidation of the body's cells is very mild, but it is better to avoid it by holding the edamame after washing for a sufficient duration of ozone contact time.

Based on ozone concentration results test in Figure 2, the initial ozone concentration increases with the time of ozonation increasing time on the washing water. while the decrease in ozone concentration during ozone contact time was influenced by the chlorine concentration degraded from edamame as a washed commodity in this study. the higher the chlorine concentration in the material, the more ozone reacts with the chlorine, thereby accelerating the half-life of ozone in washing water and edamame.

According to results had shown by

figure 2, the ozone concentration reduction in edamame water-ozonated minimally process at 0 minutes ozonation was 69%, 10 minutes ozonation was 43%, and 15 minutes ozonation was 51%. The greatest decrease in ozone concentration during the contact time of ozone in edamame was in the 0-minute treatment because ozone has no longer inducted into the water. In this study, the amount of chlorine in the edamame material cannot be uniformed, because the edamame used in the study was not injected with chlorine but the chlorine was contained in the edamame due to the use of fertilizers and pesticides containing chlorine that had been used by farmers during the planting process (Utami et al., 2020). This causes the amount of ozone that reacts with chlorine cannot be equalized during the contact time process. It also causes the increasing of ozonation time was not proportional to the chlorine concentration decreasing nor ozone concentration remains in edamame.

The end product of the reaction between chlorine and ozone is oxygen. The reaction equation for the reduction of chlorine in edamame in a minimal treatment process using ozone water proceeds through the following equation:

1. chlorine atoms react with ozone molecules to form chlorine monoxide and oxygen
$$Cl^- + O_3 \longrightarrow ClO^- + O_2$$
2. This reaction continues and the ClO radical can react further to produce chlorine radical.
$$ClO\cdot + O\cdot \longrightarrow Cl^- + O_2$$
3. In this reaction, the entire ozone decay reaction is catalyzed by chlorine, because the chlorine is ultimately unchanged. The overall reaction equation is
$$O\cdot + O_3 \longrightarrow 2O_2$$

The oxygen produced from the final reaction can be reused as free oxygen which will be the raw material for producing ozone in the minimal washing process with ozone (S. O. N. Yudiastuti & Wijaya, 2021). The ozone used in the minimal processing of edamame washing is not only environmentally friendly and non-toxic but also lower processing costs than washing using chlorinated water which requires more washing water and a larger washing area (S. Yudiastuti & Wijaya, 2021). The added value of the resulting edamame product will also increase through minimal processing using ozonation compared to the usual washing treatment process or washing using chlorinated water (S. O. N. Yudiastuti et al., 2021).

CONCLUSIONS

Ozone can be used to reduce and eliminate chlorine in edamame through a minimal washing process. The end result of the reaction process between chlorine and ozone is oxygen which can be reused as free air to produce ozone in a continuous washing process. Chlorine reduction in edamame using washing technique with ozone water is influenced by ozonation time, ozone contact time, ozone induction method into washing water, and ozone induction initial duration into washing water.

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