Application of ethylene adsorber by active charcoal for extending the banana shelf life

[Penggunaan etilen adsorber yang terbuat dari arang aktif untuk memperpanjang umur simpan buah pisang]

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Received: 23 February 2023, Accepted: 26 October 2023, DOI: 10.23960/jtihp.v29i1.44-55

ABSTRACT

Bananas is a tropical fruit that is quite popular because of their freshness and can be consumed directly or processed as a snack. Banana cultivation is increasing along with the increasing demand for bananas in the market. As a climacteric fruit, bananas ripen quickly so they spoil quickly and have a low shelf life. To extend shelf life, ethylene gas in the surrounding environment must be controlled, for example, using active packaging made from ethylene gas absorbent. Several studies used activated carbon from coconut shells, chitosan, and teak leaves as ethylene absorbent material to extend the shelf life of climacteric fruit (e.g., guava, avocado, and tomato) with various types of packaging and doses of absorbent materials. This study examines the shelf life of bananas packaged in active packaging that absorbs ethylene using activated charcoal from coconut shells. As a result, activated charcoal with the addition of KMnO₄ to absorb ethylene could extend the shelf life of bananas for 6 days longer than without activated charcoal.

Keywords: activated charcoal; active packaging; banana; ethylene; shelf life

ABSTRAK

Pisang merupakan salah satu buah tropis yang cukup digemari karena kesegarannya dan dapat dikonsumsi langsung maupun diolah sebagai camilan. Budidaya pisang semakin meningkat seiring dengan meningkatnya permintaan pisang di pasaran. Sebagai buah klimakterik, pisang cepat matang sehingga cepat rusak dan mempunyai umur simpan yang rendah. Untuk memperpanjang umur simpan, gas etilen di lingkungan sekitar harus dikontrol, misalnya dengan menggunakan kemasan aktif berbahan penyerap gas etilen. Beberapa penelitian menggunakan karbon aktif dari tempurung kelapa, kitosan, dan daun jati sebagai bahan penyerap etilen untuk memperpanjang umur simpan buah klimakterik (misalnya jambu biji, alpukat, dan tomat) dengan berbagai jenis kemasan dan dosis bahan penyerap. Penelitian ini mengkaji umur simpan buah pisang yang dikemas dalam kemasan aktif yang menyerap etilen menggunakan arang aktif dari tempurung kelapa. Hasilnya, arang aktif dengan penambahan KMnO₄ untuk menyerap etilen mampu memperpanjang umur simpan pisang 6 hari lebih lama dibandingkan tanpa arang aktif.

Kata Kunci: arang aktif; kemasan aktif; pisang; etilen; umur simpan

Introduction

Banana is a tropical fruit that is often found in Indonesia. Banana cultivation is increasing along with the increasing demand for bananas in the market (Sulistyowarni et al., 2020). Based on data from the Badan Pusat Statistik (BPS) from 1995-2015, banana production in Indonesia is the largest compared to other local fruits. So it is reasonable that bananas are the most consumed by the Indonesian population (Ni'matir Roudloh et al.,2021). In addition, the shelf life of bananas tends to be relatively short, thus reducing the turnover of sellers of bananas that can be eaten directly or processed into snacks (Widodo et al., 2019).

Active packaging is a technological concept that adds specific components that can absorb substances in the product into the surrounding environment to extend the shelf life, for example, using an ethylene gas absorber (Widayanti et al., 2016). Ethylene is the result of the metabolism of horticultural products,

especially fruit, and is one of the compounds that stimulate the ripening process of fruit so that fruit has a limited shelf life (Arti & Manurung, 2018). As much as 0.1 ppm ethylene can affect the ripening process of fruit, so the presence of ethylene in the fruit storage process needs to be controlled (Sholihati et al., 2015). The principle of absorption is that the double bond of ethylene makes it a very reactive component, so it is very easily degraded (Novita et al., 2015). Ethylene can be absorbed by several substances, such as activated charcoal, crystalline aluminosilicates, silica gel, aluminum oxide, and some ceramic materials, such as cristobalite, oya stone, and zeolite. Ethylene gas absorption by absorbent materials such as activated charcoal is beneficial for delaying fruit ripening and can extend the shelf life (Arini et al., 2015).

Previous research to extend the shelf life of fruit by absorbing ethylene gas that comes out of the fruit was carried out by (Warsiki et al., 2020). The research using activated charcoal applied to cardboard to delay the ripening of mango fruit. In this research, In addition to utilizing waste in value-added products, coconut shell-activated charcoal is also beneficial in improving the quality of climacteric fruit to extend the shelf life of fresh fruit. The purpose in this study to designed an active packaging technology as an ethylene absorber in bananas using activated charcoal with the addition of KMnO4 from coconut shells and to obtain the best treatment.

Materials and Methods

Materials

The main ingredients are bananas with 80% ripeness, activated charcoal from coconut shells, aquadest, KMnO₄, and tea bags. The tools used in this research include analytical balance, refractometer, and low-density polyethylene (LDPE).

Water and ash content

The water content and ash content refer to (Aprilliani et al., 2018). The sample used is 2g which is weighed in a cup whose weight has previously been known. The samples were then dried in an oven at 105°C for 3 hours. Samples that have been oven cooled in a desiccator for 15 minutes and then weighed. Drying and weighing were repeated every hour until a constant weight was obtained. For the ash content, the test was carried out on a sample of 2 g which was weighed and put into a porcelain cup whose weight was known. The sample was then heated in a furnace at 750°C for 6 hours. The heated sample is cooled in a desiccator and weighed. Drying and weighing were repeated until a constant weight was obtained.

Measurement of ethylene content

Measurement of ethylene gas in bananas was carried out using gas chromatography (GC). The purpose of this measurement is to determine the production of banana ethylene gas during the storage process. The measurement procedure was carried out by storing bananas in a sealed jar and a sampling hole was provided on the lid. Gas sampling was carried out once a day. Sample measurements were carried out for 10 days. The amount of ethylene gas produced is expressed in the number of ppm ethylene gas/kg day, this method refers to (Putri et al., 2019).

Active packaging

Activated charcoal is made from coconut shells of 1-2 mm. The activated charcoal sample was washed first with distilled water and dried at 105 $^{\circ}$ C for 24 hours before being used in the absorption stage (Rahmah et al., 2020). Drying is done to open the pores of the activated charcoal so that it can absorb KMnO₄.

Color change kinetic

The °hue value is used to determine the reaction order kinetics from the color change on the label. Banana color change response was measured using a colorimeter. The measurement results obtained the

value of L. a. and b. Then calculate the chroma value with the formula \sqrt{a} 2+ b2 and the oHue value with the formula oHue = tan-1 (b/a).

From this data a relationship between color change and ethylene concentration will be obtained to determine a color map that will facilitate the application of banana storage. Color changes can follow the zero or first order depending on the model's suitability from the observation data. Equations 1 and 2 show the fundamental equations of reaction kinetics of zero and first order, respectively (Mashitoh et al. 2013).

$$Q = Qo - k.t \tag{1}$$

$$Q/Qo = e^{-kt}$$
 (2)

A zero-order reaction is a constant degradation. A chemical reaction is said to have zero order if the reaction rate is not affected by the reactant concentration (Yuda, Reza Critian Prihatiningtyas, 2017). No matter how much the concentration of the reactants increases, it will not affect the reaction rate. This type of zero-order reaction is not very common. Types of damage following zero-order reaction kinetics include enzymatic breakdown, browning, and oxidation reactions. Other zero-order reactions are gas reactions on metal surfaces, reactions with enzyme catalysts at high substrate concentrations, photosynthetic reactions on green leaves during the day, and reactions of glucose with hemoglobin in the blood. Equation 2 shows the fundamental equation of zero-order reaction kinetics (Masithoh et al., 2013). A chemical reaction is said to have first order if the rate of reaction is directly proportional to the concentration of the reactants. If the concentration of the reactants is increased, the reaction rate will also double

Results and discussion

Water and ash content

Activated charcoal is made from coconut shells, so it has an economical price for active packaging (Sa'diyah & Baga, 2017). In addition, the coconut shell has a density, high purity, and minimal impurities (Nustini & Allwar, 2019). Activated charcoal containing water content is characterized by agglomerated physical form and is the main parameter in food products (Hidayati et al., 2020). Activated charcoal samples were tested based on moisture content and ash content. The characteristics of activated charcoal are then compared to the Indonesian National Standard (SNI) 06-3730-1995 can be seen in Table 1.

Table 1. Moisture and ash content of activated charcoal

Sample	Water Content (%)	Ash Content (%)
Activated charcoal	4.43±0.66	2.190±1.39
Activated charcoal – KMnO ₄	3.5±0.14	2.015±0.82

Each number was an average of three replications and standard deviation

Table 1 shows the characteristics of activated charcoal on the moisture and ash content compared to the SNI 06-3730-1995. The test uses 2 samples, namely activated charcoal and activated charcoal – KmnO $_4$. The moisture content of activated charcoal samples is 4.43%, more significantly higher than activated charcoal - KmnO $_4$, which was 3.5%. However, these two samples still meet the standards set by SNI 06-3730-1995, which requires that the water content of activated charcoal should not be more than 4.5%. Ash content is a mineral element left in a material. The ash content of activated charcoal is 2.190%, and the ash content of activated charcoal - KMnO $_4$ is 2.015%. The ash content value obtained still meets the standards set by SNI, which is still below 2.5%.

Banana fruit ethylene

Bananas are climacteric agricultural commodities easily damaged and have a short shelf life at room temperature, so they must be appropriately handled to improve quality and minimize farmer losses (Praja

et al., 2021). Bananas have high postharvest losses (Basel et al., 2002; Decosta & Erabadupitiya. 2005). Meanwhile, ethylene is an odorless compound produced by fruits and vegetables when they undergo a ripening process (Putri et al., 2019). At concentrations >0.1, activated charcoal is ethylene can affect the shelf life of commodities (Azrita et al., 2020).

Measurement of ethylene production of bananas refers to the research by Rahmah (2021) by placing 1000 g of Ambon bananas with a maturity level of 85% with green color in a closed 3L container stored at room temperature. Measurement of banana fruit ethylene gas production for 10 days of observation with the pattern in Figure 1.

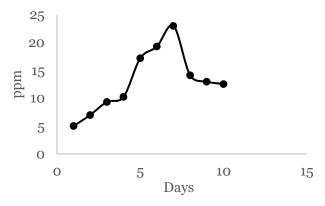


Figure 1. Banana ethylene production

Based on Figure 1, it can be seen that the production of ethylene gas after the harvesting process continued to increase, and the peak production on day 7 was 22 mg/kg and continued to experience a decrease in ethylene production until day 10. The value was used as a reference for packing bananas by knowing the gas ethylene produced so that the performance of activated charcoal and the ratio of the amount of activated charcoal used would be more effective and optimum.

Application banana fruit storage

One indicator of banana ripeness is indicated by color changes that occur daily. The yellower the color of the banana, the more ripe the banana is. The samples used were bananas without the addition of active packaging or called controls, then stored at room temperature. The changing color of bananas can be observed visually on both bananas using activated charcoal packaging, KMnO₄ activated charcoal, and control. Bananas with the active packaging in them have a slower color change when compared to the control. Bananas with the addition of activated charcoal – KMnO₄ have a longer shelf life of 2 days compared to activated charcoal alone. In Table 2 it can be seen that the bananas experienced a color change on days 5-7 for control bananas. Meanwhile, bananas with the addition of activated charcoal changed color on day 9, and bananas with activated charcoal-KMnO₄ changed color on day 11. Visual color changes can be seen in Table 2. Based on this data, bananas continue to ripen and end in the process of decay as storage time increases due to the ethylene gas in bananas. Ethylene is an odorless compound produced by fruits and vegetables when they undergo a ripening process (Rahmah et al., 2020). At specific concentrations (above 0.1 l), ethylene can affect the shelf life of fruits and vegetables (Azrita et al., 2020). Therefore, controlling storage conditions has become one of the drivers of the development of packaging technology. Active packaging technology and intelligent packaging are examples of developing technologies expected to overcome the damage to horticultural products during storage, primarily due to ethylene

Table 2. The appearance of banana color changes.

Days	Control	Activated Charcoal	Activated Charcoal – KMnO ₄
1			
3			
5			
7			
9			
11			
13			

Bananas treated with activated charcoal-based charcoal – KMnO₄ were slower to change color. This mechanism is because potassium or potassium permanganate is an inorganic chemical compound as a potent oxidizing agent, so KMnO₄ can be used as an ingredient to oxidize ethylene. Ethylene can be oxidized by potassium permanganate to manganese dioxide, potassium hydroxide, and carbon dioxide (Novita et al., 2015). The reaction of the breakdown of ethylene by potassium permanganate can be seen from the following equation:

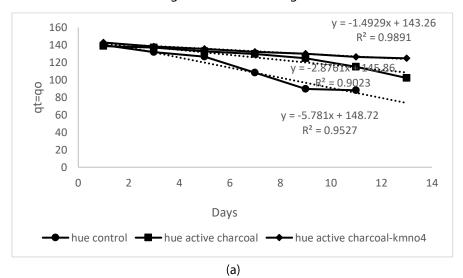
$$3C_2H_{12} + 12KMnO_4 - - \rightarrow 12Mn_2 + 12KOH + 6CO_2$$

Ethylene + Potassium Permanganate → Manganese Oxide + Potassium Hydroxide + Carbon Dioxide

In its application, KMnO₄ will be more effective if it is made into a solution and then added KMnO₄ absorbent material or media in the form of activated charcoal. Currently, KMnO₄ is still considered the most widely used ethylene adsorber worldwide. Many studies have been conducted to extend the shelf life of horticultural products, both fruits, and vegetables, using KMnO₄ as the active ingredient. Thus, adding KMnO₄ to activated charcoal can delay the ripening of bananas longer than other treatments. Giving ethylene adsorber in fruit storage is an effort to extend the shelf life of fruit, because absorption is affected by surface area (Artioli & Bullard, 2013).

Color change kinetics

The banana color change was calculated as the °hue to determine the kinetics of the reaction order. The order was determined using (equations 1 and 2) by plotting the °hue against the storage time, which resulted in the equation value and the correlation coefficient (R²) (Putri et al., 2019). Furthermore, the comparison of the R² of zero and the first order is selected based on the R² value closest to 1. The mathematical model of banana color change can be seen in Figure 2.



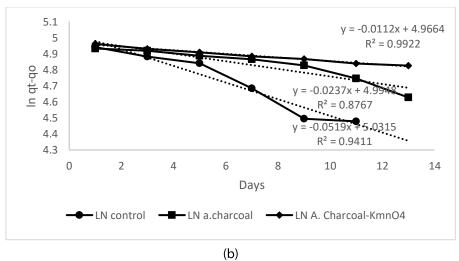


Figure 2. Mathematical model of banana color change (a) °hue. (b) LN °hue

Based on Figure 2, the value of °hue on banana storage time using activated charcoal – KMnO₄ produces a linear line with the equation Qt = Q0 - 1.49t, and the correlation coefficient R^2 is 0.9891. Furthermore, plotting the natural logarithm (ln) °hue data on the storage time of bananas using activated charcoal –

 $KMnO_4$ resulted in an $R^2 = 0.9922$. The same thing was also done to the storage time for controlling bananas and bananas using activated charcoal.

•	•		•			
Samples	Zero-order		First Order			
Treatment	$Q_t = Q_0 \text{-} k.t$	k (°hue/Days)	R ²	$Q_t = Q_0 e^{-kt}$	k (°hue/Days)	R ²
Control	$Q_t = Q_0 - 5.78t$	5.78	0.9527	$Q_t = Q_0 e^{-0.0519t}$	0.0519	0.9411
Activated charcoal	$Q_t = Q_0 - 2.87t$	2.87	0.9023	$Q_t = Q_0 e^{-0.0237t}$	0.0237	0.8767
Activated charcoal - KMnO ₄	$Q_t = Q_0 - 1.49t$	1.49	0.9891	$Q_t = Q_0 e^{-0.0112t}$	0.0112	0.9922

Table 3 Equation of the rate of change of Ohue in various active packaging

Based on the data, the rate and R^2 of color change in various treatments (°Hue/time) can be seen in Table 3. Ambon banana storage using activated charcoal - KMnO₄ is better than other treatments because the R^2 is close to 1, and the kinetics of change in banana °hue can follow a first-order reaction. This mechanism is because the R^2 of first order 1 is higher than zero order.

First-order reactions are characterized by an exponential increase in the rate of color change. That is, the rate of color change is getting faster at the same time. This phenomenon was also observed by (Aidila Fitria et al., 2017) regarding the change in the color of the chlorophyll indicator label of cassava leaves following the zero order and the first order. (Masithoh et al., 2013) stated that the decrease in carotene, citric acid, and vitamin C levels in tomatoes was approached by linear regression of order 1. Color degradation, vitamin C, and drip loss in broccoli also followed the Arrhenius equation with order 1 (Widayanti et al., 2016). Thus, the mathematical equation model (Table 3) can be used to predict the color of bananas to determine the ripeness of Ambon bananas.

Based on the color change model, the value of k is used to predict the color change of bananas if stored for a long time to determine the level of ripeness of bananas that were not tested in this study. Table 3 shows the reaction rate constant (k) and the R² of each banana storage packaging treatment on order 0 and order 1. The color change of bananas in this study can use order 1. Based on (Aidila Fitria et al., 2017), a quality determination is selected based on parameters that have a reasonably significant correlation coefficient (R2) (>0.75). The results of plotting the values of 1/T and ln k in each order can be seen in Figure 3. Based on Figure 3, the banana color degradation followed an order 1 reaction based on the increase in the Hue value. The value of the correlation coefficient (R2) on order 1 is 0.904, while the correlation coefficient (R2) of order zero is 0.0232, so the banana color change rate uses a mathematical model of order 1.

Based on the study results, the storage of bananas produced was more stable using activated charcoal - KMnO4 than activated charcoal. Bananas stored without active packaging will start to rot on day 7, while bananas stored with activated charcoal start to rot on day 11, and bananas stored with activated charcoal – KMnO4 rot on day 13. Therefore, active packaging made from activated charcoal – KMnO4 can be recommended to be applied as active packaging for the storage of Ambon bananas in order to extend their shelf life.

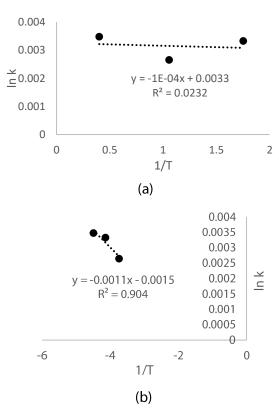


Figure 3. Plot of the mathematical model (a) of zero order (b) of first order.uses a mathematical model of order 1.

Chromameter change value

Measurement of the color change of banana samples was carried out using the color system proposed by Munsell for the parameters of lightness (L*), Chroma (C*), and Hue (H°). The effect of storage with multi absorbers on changes in the parameters of lightness (L*), Chroma (C*), and Hue (H°) can be seen in Table 4.

Table 4 Parameters of chromameter change value.

Samples –	L*			C*		
	Day 1	Last Day	Day 1	Last Day	Day	Last Day
Control	60.33	53.33±9.15	70.53	49.66±27.22	139.9	126.6±22.16
Activated charcoal	59.02	42.31±7.96	51.17	45.85±7.16	138.7	124.9±13.08
Activated charcoal – KMnO4	59.65	53.38±3.27	50.29	42.76±4.58	142.8	126.4±6.48

Each number was an average of three replications and standard deviation

Table 4 shows that the treatment given active charcoal packaging and activated charcoal - KMnO₄ did not affect the color change of bananas during storage, but the room temperature treatment experienced a color change of ohue value on the 7th day. Storage with control treatment, bananas changed color on the 7th day and continued to experience maturity and fruit damage marked by changes in the color of bananas to yellowish and brown on the part of the banana attached to the stem. The chroma value measurement results did not affect each treatment because this condition showed a similar color change for the entire banana storage treatment. The results of mapping the oHue value on the color map can be seen in Figure 4. The color map according to Munsell where the banana sample changed from green to yellow, bananas packaged without multi absorbers changed color faster, compared to bananas stored using activated charcoal and activated charcoal - KMnO₄ packaging. Storage of bananas using active packaging of activated charcoal and activated charcoal – KMnO₄ is one way to delay fruit ripening. Bananas with storage using activated charcoal packaging – KMnO₄ can delay banana ripeness for 6 days.

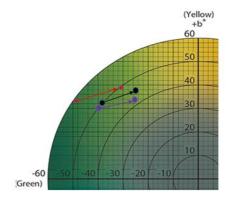


Figure 4. Diagram of changes in chroma value in banana storage (Control, activated charcoal, and activated charcoal − KMnO₄)

Weight loss

Weight loss during storage is one indicator of a commodity's quality caused by water's evaporation through the skin (Wibowo, 2018). The longer the storage time, the more weight loss will increase. The results of weight loss of bananas for 13 days of storage can be seen in Figure 6.

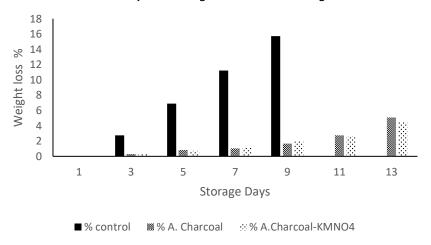


Figure 5. Weight loss of bananas during storage

Figure 5 shows the percentage of weight loss in banana samples. The presentation of the weight loss value of bananas without activated charcoal packaging was higher with a presentation value of 15.73% on the 9th day of storage when compared to bananas packaged using activated charcoal packaging with a presentation value of 5.07% on day 13 and the weight loss of activated charcoal – KMnO₄ was 4.48% on the 13th day of storage.

Treatment with active packaging is known to suppress the occurrence of weight loss of bananas during storage. This occurs because of the ethylene absorption process, which can reduce the ability of ethylene to stimulate ATPase, this causes the banana metabolism process to be disrupted, which causes minimal product water loss so that the weight loss is relatively small (Aprilliani et al., 2018). The main factor causing weight loss is moisture that occurs during the storage period. According to Vázquez-Celestino et al., (2016), weight loss in fruit is related to water vapor loss, and the withering process is closely related to the high metabolic rate.

Total dissolved solids

Total dissolved solids are measured using a reading scale expressed in °Brix. The °Brix scale will increase during the maturation process because of the reshuffle of carbohydrates into sucrose, glucose, and fructose in fruits(Leksikowati, 2013). The total dissolved solids test can be seen in Figure 7.

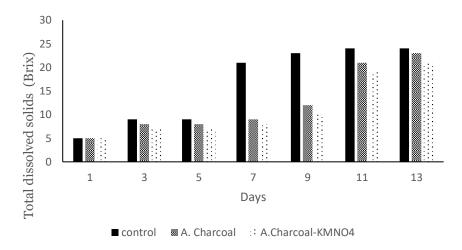


Figure 6. Total soluble solids of banana during storage

Based on Figure 6, the total dissolved solids increased during storage, as indicated by an increase in the $^{\circ}$ Brix scale. On day 1 the total dissolved solids value of control, activated charcoal, and activated charcoal – KMnO₄ was 5°Brix, while on the control ripe fruit on day 7 the total value of soluble solids was 21 °Brix, and on rotten fruit on day 9 the total of solids dissolved by 23 °Brix.

Packaged bananas using activated charcoal ripen on the 9th day with a total dissolved solid of 12 °Brix, and while packaging bananas using activated charcoal – KMnO₄ ripen on day 11, the total dissolved solids value is 21 °Brix. In rotten bananas, on the 13th day, the total solids value dissolved by 23 °Brix. Based on the results of this study it can be seen that the addition of KMnO4 in delaying the ripeness of bananas makes the process of overhauling the substrate optimal. This is indicated by the increasing value of °Brix in bananas. The increase in °Brix occurs due to a metabolic process that facilitates the conversion of carbohydrates into sugar during fruit ripening. In rotten fruit, the oBrix value continues to increase because, during the ripening process. These results are supported by Putri et al., (2019) research, that the avocado produces ethylene gas that accumulates in storage, resulting in a continuous metabolic process. Thus, the breakdown of starch into glucose takes place quickly, causing an increase in the °Brix scale, leading to ripening and spoilage of the sample. The increased °Brix value was also caused by the high water content of the banana due to spoilage.

Conclusion

The analysis of active packaging applications using activated charcoal derived from coconut shells as an ethylene gas absorber or absorber was able to delay the ripening of bananas for 4 days longer when compared to bananas without the addition of active packaging. Activated charcoal with the addition of potassium permanganate (KMnO₄) was able to delay the ripening of bananas even longer, which is 6 days longer when compared to bananas without the addition of active packaging during storage.

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