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Nano Zeolite-kmno$_4$ as Ethylene Adsorber in Active Packaging of Horticulture Products (*Musa Paradisiaca*)

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Abstract

Zeolite is high porous natural mining material and usually used as absorber. Particle size reduction of zeolite to nano-sized is expected improve absorption, because with the smaller particle size of materials, uptake extensive areas will increase. Nano zeolite-KMnO4 as ethylene absorber is expected better than existing commercial ethylene absorber. This study aims to determine the absorptive capability of nano zeolite-$KMnO_4$ as ethylene absorber and as an indicator of the shelf life of Ambon Banana (Musa paradisiaca). Nano zeolite -$KMnO_4$ from grinding for 40 minutes and chemical activation with KOH solution for 2 hours has the highest ability to oxidize ethylene than other treatments, namely 113 ppm/g/h. However, discoloration of the nano zeolite-KMnO4 during oxidizes ethylene is not too clear to be observed, thus difficult to make nano zeolites- KMnO4 as an indicator of the shelf life of fruit. Application of nano zeolite-KMnO4 as much as 3 grams packaged in cellulose paper (@ 1.5G) and attached to LDPE 0.04 mm packaging is able to extend the shelf life of banana at 25◦C temperature, RH 85% up to 23 days or 17 days longer than the control.

Keywords: nano zeolite; $KMnO_4$; ethilene.

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1. Introduction

One method to extend the shelf life of horticultural products, especially fruits and vegetables,is reducing ethylene gas produced. Ethylene is odorless compound whichproduced by fruits and vegetables when subjected to the ripening process [1]. An increase in ethylene production will be highly visible on climacteric fruits or vegetables, while for non-climacteric fruit increases in ethylene production was not seen significantly.

At certain concentrations (above 0.1 μl^1), ethylene may affect the shelf life of fruits and vegetables [2,3]. The first research on ethylene has been done by [4] on the effect of ethylene productionto the shelf life of apples. Further research on ethylene starting again around 1972, such as [5] using activated charcoal to absorb ethylene but still unsatisfied because ethylene is not fully absorbed. The use of a catalyst to improve active charcoal absorption has been carried out by [6]. Activated charcoal with palladium as catalyst and show better results than just using activated charcoal [5].

Potassium Permanganant or $KMnO_4$ is one of the ethylene absorber that has been extensively studied concerning the effectiveness and ability to absorb ethylene produced by a horticultural products during storage. . Similar research also has been carried out by [2, 7, 8], all of which examine the effect of $KMnO_4$ as ethylene absorber. However, it is not many studies evaluating the adsorption capacity of $KMnO_4$ to ethylene, especially effectiveness of $KMnO_4$ entrapped in the bonding matrix (zeolite) as ethylene absorber in nano-size. It opensa chance for further research, moreover [9] found surface area of a material will be higherin nano size, this will affect optical, catalytic and other properties of materials.

Many technologies have been used to extend the shelf life of horticultural products, including packaging technologies with CAP/MAP technique [10,11], active packaging technology [12] and smart packaging. Active packaging is one of packaging technology development. According to [13,14, 12], active packaging is one form of packaging in which the product, the packaging and the environment in the packaging actively interact so as to (1) extend the shelf life, (2) maintaining the organoleptic properties of materials and (3) ensure the safety of its food.

The use of ethylene absorber in active packaging of horticultural products, especially in climacteric fruits, is expected to be able to extend the shelf life of the product, so the quality can be maintained longer. The purpose of this study was to determine the ability of nano zeolite -KMnO4 as ethylene adsorber and as an indicator of the shelf life of Ambon bananaspacking.

2. Materials and methods

2.1 Time and Research's Location

Research was conducted at the Nanotechnology Laboratory and Chemical Laboratory, the Center for Post Harvest Agricultural Research in Bogor. The study began in April 2015- November 2015.

2.2 Materials And Tools

Nanozeolite -$KMnO_4$was obtained from previous studies, Ambon bananas from people's plantation in Bogor, glass chamber, Chromatography Gas, Chromameter and ethylene gas.

2.3 Method

2.3.1 The rate of respiration and ethylene production with GC

Preparation of ethylene production model begins by observing the rate of ethylene production of Ambon banana after harvested at the ripening level 1 until overripe. Production of ethylene in the fruit will be continuous observed periodically until overripe. Ethylene production was observed every 3 hours and expected have a regular pattern so that the data can be used to construct a model for ethylene production of Ambon banana.

An Ambon Bananas bunch with a weight of approximately 1000-1200 g put in a glass chamber with a size of 30x30x40cm. To prevent leakage, the connection on the chamber sealedby candles. Observations were made every 3 hours starting from the fruit put in a chamber. The research was conducted using 3 repetitions

Observations were carried out by taking 1 ml of gas in the chamber using a gas syringe and analyzed by GC. After observation, the chamber lid is opened until the next observation. Chamber closed again for 1 hour while being observed. After that, the chamber reopened. And so on. Observations were made for 8 times in 24 hours (3^{rd}, 6^{th}, 9^{th}, 12^{th} etc). Observations were made until the fruit reaches over climacteric phase (towards senescen). Observations of ethylene production rate was observed at a temperature around 18-20◦C. The data obtained will be used for developing the equations model of ethylene production for Ambon bananas. Total amount of ethylene produced by bananas for approximately 8 days of storage, will be used as guidelines in the calculation of the amount of nano zeolite-$KMnO_4$ powder required for Ambon bananas packing to have longer shelf life.

2.3.2 Maximum absorption capacity of the zeolite

Nano zeolite -$KMnO_4$ to be used is the best treatment results of previous research, namely nano zeolite-$KMnO_4$ were milled for 40 minutes and activated for 2 hours with maximum absorption capacity of 113 ppm ethylene/g.

2.3.3 The color change of zeolite

Visually, nano-zeolites KMnO4 is bright purple. Oxidation that occurs between KMnO4 and ethylene will cause color change on zeolite. The degree of the color change is closely linked to the level of oxidation. The higher the level of oxidation, the zeolite will change to be brown/dark. The color change was observed using chromatometer. Color measurement of each sample done 3 times. The obtained data was used as a basis in determining the shelf life of horticultural products.

2.3.4 Manufacture of ethylene adsorber packaging

Manufacture of nano zeolite -KMnO4packaging conducted with three techniques: (1) mixing, (2) coating and

(3) insertnano zeolite powder into sachet. In the mixing technique, there are two types of material tested, namely PVA (polyvinyl alcohol) and nano-cellulose. PVA 10 grams mixed with nano-zeolites as much as 1, 2.5, and 5 g. The mixing process is done by using ultrasound with a speed of 2000 rpm for 10 minutes. The same amount of zeolite used for mixing with 10g of nano cellulose, then blended using ultrasound with the same speed for 5 minutes.

The second, coating techniques, performedby sprinkling nano zeolite over the -adhesive material which further embedded inside of LDPE plastic packing. The last is technique is insert X g of nano zeolite-KMnO4 powder into a tea bag (cellulose paper) and attached on the inner surface of LDPE plastic packaging.

3. Results and discussion

3.1 Rate of Ambon Banana Ethylene Production

Ambon bananas harvested at optimal ripe about 65 days after the heart (banana flower) came out with a starch content of 23%. Complete data of proximate analysis for Ambon banana at harvest time and ripe are as shown in Table 1 below.

Table 1: Proximate analysis of Ambon banana

Banana	Water (%)	Protein (%)	Fat (%)	Ash (%)	Starch (%)
Just Harvested	73,4	1,07	1,36	1,2	23
Ripe	76,2	1,2	0,21	1	21,45

The banana as control is perfectly ripe at room temperature (29◦C) with a storage time of 8 days. Decreased levels of starch when the fruit ripe was caused by starch changes to sugars during ripening. Levels of total sugar when the banana is ripe is 15%. The pattern of Ambon banana respiration rate (with three replications) after 24 hours of harvesting is as shown in Figure 1.

Ethylene production reached the peak after 36-39 hours harvested. The peak of ethylene production reached an average of 26.93 ppm/kg fruit/h at 25◦C. The data is then used to construct equations model of ethylene production for Ambon banana as shown in the following equation (1):

$$Y = -5{,}462\ \mathrm{x}10^{2} + 4{,}462\ \mathrm{x}\ 10t^{1} - 1{,}256t^{2} + 1{,}491\mathrm{x}10^{-2}t^{3} - 6{,}406\ \mathrm{x}\ 10^{-5}t^{4} \qquad (1)$$

Each type of banana has different ethylene production profiles but in general, as climacteric fruit then after the harvest, the fruit will experience climacteric peak. Climacteric peak affected by observations temperature and the level of ripeness when harvested. Some studies suggest that if bananas harvested at the optimal age, climacteric peak will occur approximately 25-36 hours after harvest. After the climacteric peak, ethylene production will decrease close to 0 but usually will increase again during fruit decay.

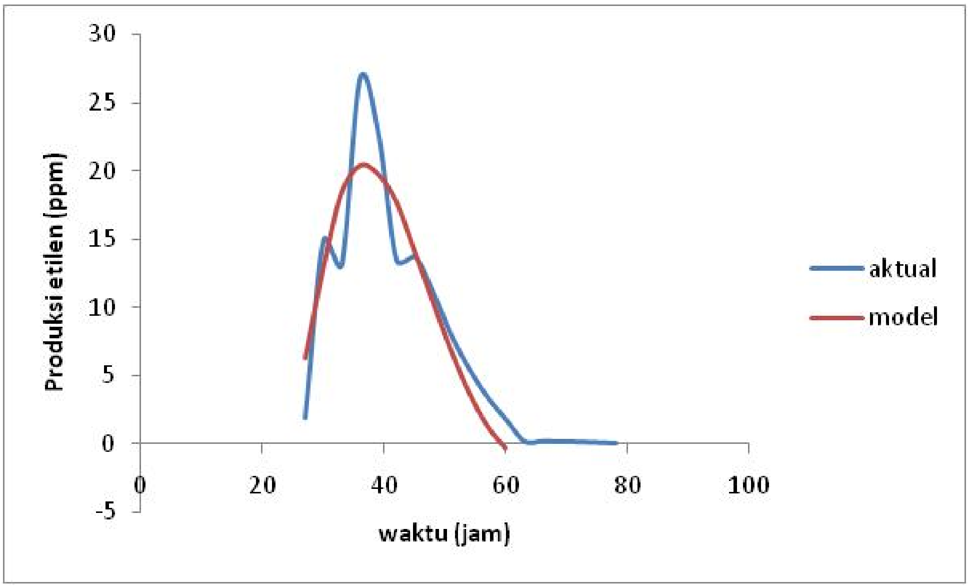


Figure 1: Profile of average ethylene production of Ambon bananas in 3 glass chamber

3.2 The ability of Nano zeolites- $KMnO_4$ to oxidizes ethylene

Previous studies have shown that the ability of nano zeolites-$KMnO_4$ to oxidizes ethylene is between 1 to 113 ppm/g. The treatment with the highest ethylene absorption capacity is nano zeolites-$KMnO_4$ milled for 40 and activated with 1 N KOH solution for 2 hours. As an illustration, pattern of ethylene oxidation by nanozeolites-$KMnO_4$ look like in Figure 2.

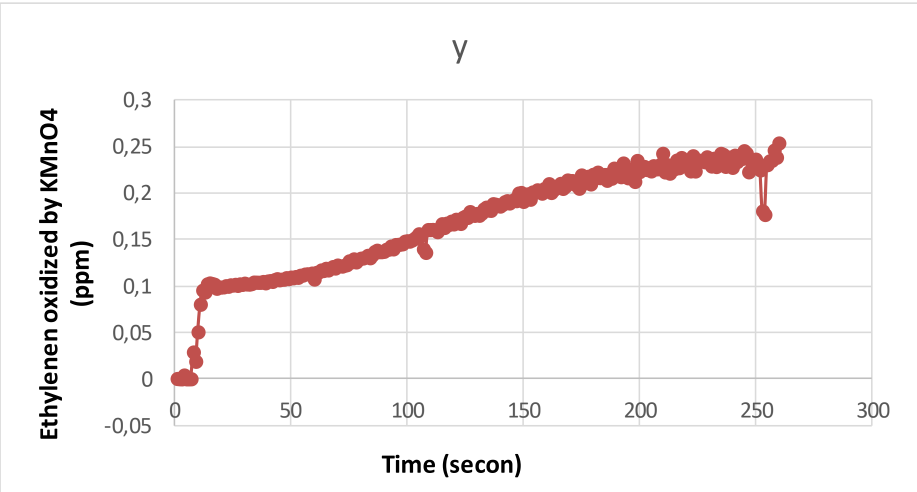


Figure 2: Profile of nano zeolite -$KMnO_4$ absorption pattern to ethylene

From the oxidation pattern, it was obtained the equations model as noted in the previous model of equation 2 :

$$Y = 5{,}03 \text{x } 10^{-2} + 1{,}160 \text{ x } 10^{-3} t^{1} - 7{,}05 \text{ x } 10^{-7} t^{2} - 3{,}895 \text{x } 10^{-9} t^{3} \qquad (2)$$

Indeed, ethylene absorption pattern does not follow a linear model but tend to quadratic. In line with observation time, the rate of ethylene absorption will be increased up to a certain point when absorptive capacity started to reduce and then relatively stable.

Figure 3 shows nano zeolite -$KMnO_4$ which has not undergone oxidation and has experienced the maximum oxidation ie nanozeolites-$KMnO_4$ with oxidation capacity of ethylene 113 ppm/g zeolite/hr. Visually, the color change is not very obvious. Efforts to make nano-zeolites $KMnO_4$ as oxidizer and indicators of the shelf life of horticulture is not yet possible. This is due to the difficulty of distinguishing the color change that occurs in zeolite based on the level of oxidation.

(a) (b)

Figure 3: Nanozeolite-$KMnO_4$ before (a) and (b) after oxidation with ethylene

3.3 Nano-$KMnO_4$ zeolite in a horticultural product packaging

Ethylene adsorber required by a horticultural products in packaging, will depend on several factors including the weight of stored products, permeability and surface area of plastic packaging as well as storage temperature. At lower temperatures, respirassi more slowly so that the ethylene product will be less and vice versa if the temperature gets higher, the rate of respiration and ethylene production will be higher.

As mentioned in the previous section, observations on the respiration rate were conducted for banana harvested at optimal maturity level, stored in temperature 25◦C and RH 85%. Ethylene production during the eight days of observation is 360 ppm. With the maximum absorption capacity of nano zeolite-$KMnO_4$ of 113 ppm/g/h,to reduce the functioning of ethylene as auto catalyst and extend the shelf life of banana 1kg, will require nano zeolite -$KMnO_4$ around 3 g.

If it is assumed that ethylene adsorber applied on the packaging at the time the product has not reached the climacteric phase, and taking into account the permeability of LDPE plastic, it is estimated that the accumulated amount of ethylene in the packaging will decrease and process to reach climacteric phase will be longer, so that the needs of nano zeolit- KMnO4 as ethylene adsorber will be less than 3 g. Therefore, in the application test on Ambon banana packaging, 1.5 g of nano zeolite inserted into each cellulose bags. If during storage nano zeolite-$KMnO_4$ have changed color to dark brown, it can be replaced with a new nano zeolite-$KMnO_4$ sachets.

3.4 Application of nano zeolites-$KMnO_4$ in packaging

Nanozeolite -KMnO4 is ethylene adsorber that reduce the content of ethylene in the air by oxidizing ethylene gas so it no longer functions as a compound that can accelerate the ripening of horticultural products. With the nano-sized particles and highly porous properties of zeolites, the application of zeolites in the packaging is done by mixing zeolite in the PVA resin, nano cellulose, sprinkled zeolite particles on adhesive surface and packed in tea bag (sachet). Appearance of the four treatments were as shown in Figure 4 below:

(a)

(b)

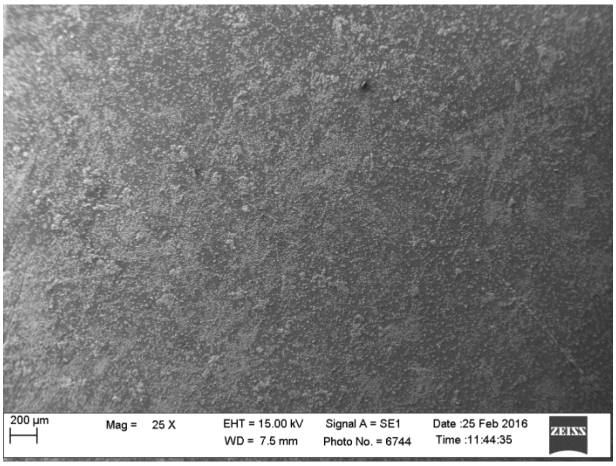
(c)

(d)

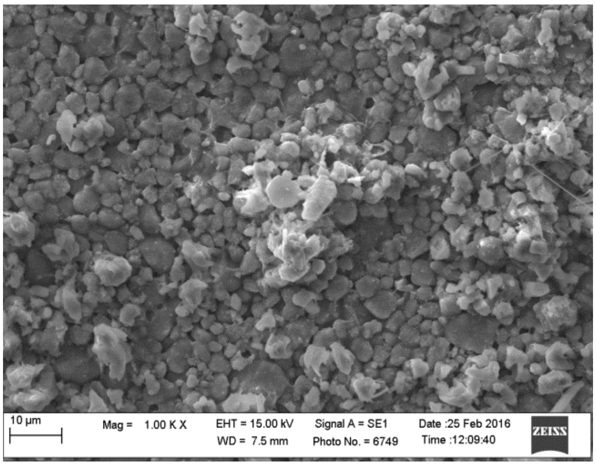
Figure 4: Nano Zeolite blended with PVA at different concentrations (a), nano zeolite dispersed in adhesive material (b), nano zeolite in nano cellulose and zeolite in a cellulose tea-bag (c)

SEM analysis (Figure 5) shows that the use of ultrasound in the mixing of PVA and nano zeolite does not produce a homogeneous mixture. Distribution of zeolite particles is uneven. Also, when zeolite is mixed with resin, the zeolite particles will be agglomerated, zeolite surface will be covered in resin. It is highly undesirable since the effectiveness of the zeolites are influenced by the porosity and its surface area. Closed-pore zeolite will cause the function of zeolite as adsorber is not met. Spreadingthe zeolite particles in adhesive material also reduces the surface area of zeolite. The use of a cellulose sachet is the best alternative in the use of nano zeolite-KMnO4 as ethylene adsorber because it does not affect the pore and surface area.

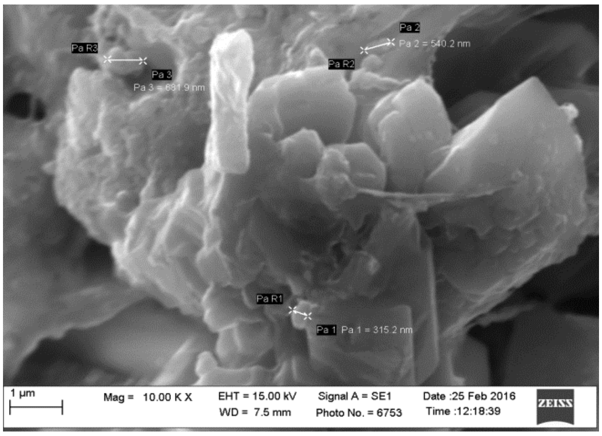
Ethylene absorbency ability of each treatment is done by inserting 100 ppm ethylene gas into the glass chamber 1.200 cm^3. Observations were made every one hour using GC. The results showed that the two treatments are not able to absorb the applied ethylene gas. This shows that nanozeolite on to two treatments are not capable of oxidizing ethylene.



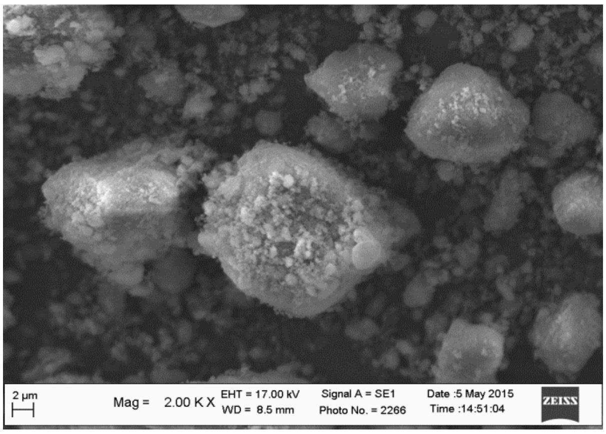
(a)



(b)



(c)



(d)

Figure 5: Appearance of nano-zeolites surface when mixed with PVA by magnification 25x to 10000x (clockwise) and zeolite with a magnification of 2000x

3.4 Application of nano zeolite-KMnO4 on Ambon Banana packaging

Sachet containing 1 gram of nano zeolite-$KMnO_4$ embedded on plastic bag 5 kg with 1 kg of bananas and stored at a temperature of 25◦C and RH 85% is able to maintain the shelf life of Ambon banana up to 23 days. Controls of banana ripe on shelf life of 8 days.

H0

H1

H2

(H3)

(H4)

(H5)

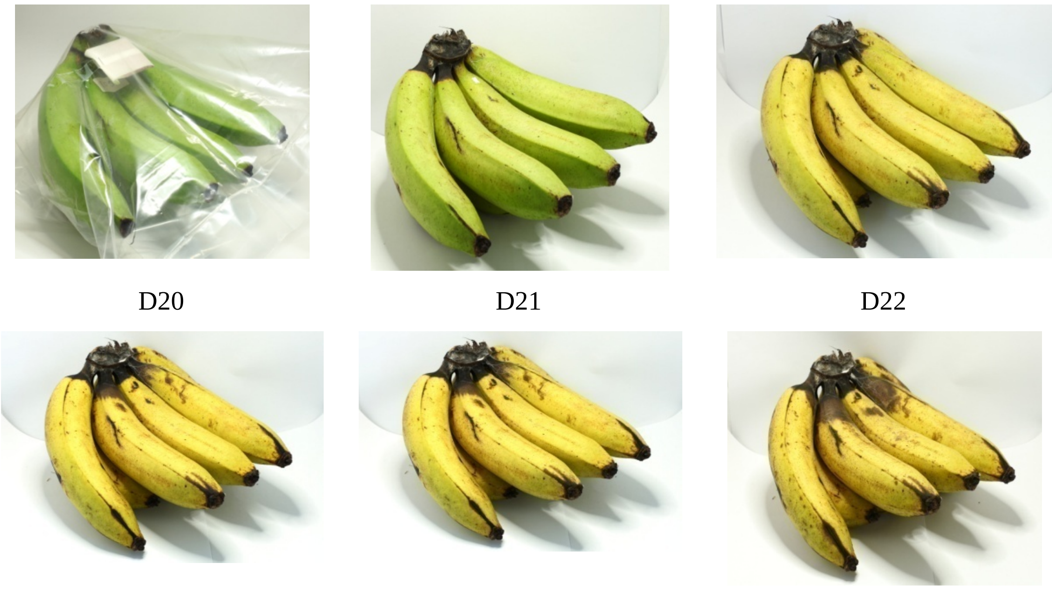
(H6)

(H7)

(H8)

Figure 6: Bananas control on day 8^{th}

Ambon bananas that packed using nano zeolite-$KMnO_4$ remain green and unripe up to the 16^{th} day of storage. To avoid physiological damage, on day 17^{th} the packaging is opened, the fruit can perfectly ripe without triggered by ethylene. Until the day of the 23^{rd}, bananas appearance is still fit for consumption as shown in Figure 7 below.



D20 D21 D22

D23 D24 D25

Figure 7: Banana storage for 25th days

4. Conclusions

1. Nano zeolite -$KMnO_4$ milled for 40 minutes and activated for 2 hours had the highest ethylene oxidation with absorption capability of 113 ppm/g/h
2. The color change on nano zeolite-KMnO4 during oxidizes ethylene showed no noticeable color change so it is very difficult to distinguish therefore nano zeolite-$KMnO_4$ is adsorber for ethylene but can not be used as an indicator of the shelf life of horticultural products
3. Nano Zeolite $KMnO_4$ able to maintain the shelf life of bananas for 23 days at a temperature of 25◦C with RH 85%

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