The effects of seaweed-based coating application on the respiration rate of shallots (*Allium cepa* L) during storage

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Abstract. In the postharvest handling of fresh products, coating is known as one of the preservation methods to lengthen shelf life. However, coating materials are still very difficult to find in Indonesia, more researches are still needed to explore indigenous materials to produce coating material. This research was intended to develop coating material based on seaweed flour (carrageenan) and to study the effect of its application on the respiration rate of shallot (*Allium cepa* L) during storage period. Coating material was produced in two different concentrations of carrageenan that were 0.5 and 0.75%. Fresh shallots as the samples were coated then loaded in the respirometer and stored at temperatures of 15°C and 28°C for 15 days storage periods. Uncoated shallots were also investigated as the control. Oxygen and carbon dioxide changes were monitored using O$_2$ and CO$_2$ Gas Analyzer (Quantek 902D) every day. It was found that the changes in gas composition inside the respirometer were found to vary for each coating materials and storage temperatures. Coated shallots showed lower respiration rates as compared to the control. Arrhenius equation could satisfactorily represent the effect of storage temperature on the respiration rate of the shallots.

1. Introduction

The decline in the quality of fresh fruit and vegetables generally occurs due to inadequate handling at harvest and post-harvest, causing various forms of damage. Short shelf life of fresh produce such as fruit and vegetable may occur due to physiological processes such as respiration, transpiration and ethylene production after harvest. Respiration has been known as the most important factor which accelerates deterioration of the agricultural products.

Various ways can be taken to reduce the rate of respiration, the use of low temperature storage such as controlled atmosphere storage and modified atmosphere storage (CAS) or modified atmosphere packaging (MAP) have been proven to be able to reduce respiration rate. Some other pretreatments have also been practiced such as precutting, coating, irradiating, blanching, and so on before the products are stored. Coating is one of the preservation methods which has large application in the field of postharvest of agricultural products. Edible coatings can provide an alternative to CA and MAP storage because they modify and control the internal atmosphere of individual fruit or vegetables [1]. Coating can be defined as a thin film material that is applied to the surface of a fresh product to extend its shelf life through controlled gas exchange of oxygen, carbon dioxide and ethylene [2]. However, to the date there is still very difficult to find coating material to be applied for agricultural products in Indonesia. As the tropical country, Indonesia has abundance agricultural products which can be used to produce edible coating. This means, many researches are still needed to explore the
indigenous materials to produce a good coating material, to provide a cheap and easy to create coating material for agricultural products. One of potential indigenous material to be used as edible coating is seaweed. Seaweeds are the natural marine algae that possesses permanent properties as a natural preservative to extend the shelf life of the perishable foods without causing any side effects [3]. From seaweed can be extracted a carrageenan flour. Carrageenan is a compound that belongs to the polysaccharide group, and carrageenan of kappa type can be used as a coating material. This research was intended to develop coating material based on carrageenan and to study the effect of its application on the respiration rate of shallot (*Allium cepa* L) during storage period.

2. Material and Methods

2.1. Material sample
In the following research, shallots were selected as samples to be coated. These samples were directly purchased from local farmers in Bantul, Yogyakarta, Indonesia. On the arrival at the laboratory, the samples were cleaned and sorted to find good and homogeneous samples. The others material to produce edible coatings were carrageenan, glycerol, and distilled water. The mass of each sample was taken before inserting it into a respirometer. The sample weight is 100 grams.

2.2. Edible coating production
Coating was produced in the following procedures. First carrageenan flour, distilled water and glycerol were mixed in a stainless-steel bucket. Then that mixture was heated at 70°C while agitated for 20 minutes. After that, that solution of coating material was cooled to room temperature and it was ready to use. In the following research coating materials were produced in two different concentrations of carrageenan that were 0.5% and 0.75%, while the concentration of glycerol was constant that was 1%.

2.3. Gas exchange measurement and respiration rate
Selected shallots to be use as the samples were measured for their weight and volume. The weight was measured using digital balance (Model MH-200, range of 0-200 g/0.01g), while the volume was measured using immersion method using water in a measuring cup. The samples were then wiped and coated using the produced coating materials, after that the samples were put in the basket in ambient room temperature to dry. After those samples dry, then they were loaded into the container of the respirometer. The respirometers were stored at 15°C and ambient room temperature (28°C) for 15 days. These two temperature levels were chosen to represent the refrigerator temperature and tropical room air conditions. The total respirometer used for this study was 18 respirometers, where three replications for each treatment with of 3 x 2 factorial completely randomized design. The changes in O$_2$ and CO$_2$ concentrations were measured periodically (every 6 hours for the first day, 24 hours for the second day and thereafter) for 15 days storage period. The measurement of O$_2$ and CO$_2$ were performed using an O$_2$ and CO$_2$ Gas Analyzer (Quantek 902D) and these values were used to calculate the respiration rate for each treatment. As the of comparison it was also investigated the shallots samples which were not coated but stored and measured in the same way as the coated shallot samples.

2.4. Modelling and data analysis
The respiration rate for each coated and uncoated shallot sample at a certain storage temperature were calculated from the change in O$_2$ and CO$_2$ concentrations, free volume, sample weight, and time difference using the following equations (1) and (2), for the respiration rates based on the oxygen consumption and carbon dioxide production, respectively.

\[
R_{O_2} = \frac{(y_{O_2}^{t_f} - y_{O_2}^{t_i}) \times V_f}{100 \, M \, (t_f - t_i)}
\]  

(1)
Where subscripts \( O_2 \) and \( CO_2 \) referred to \( O_2 \) and \( CO_2 \) gases, \( R \) = respiration rate, \((mlO_2/kg.h)\) or \((mlCO_2/kg.h)\), \( y \) = concentration of gas (%), \( V_f \) = free volume of respirometer (ml), \( M \) = mass of the product inside the container (kg), and \( t_i \) and \( t_f \) = initial time and final time or a certain period of time of measurement, respectively (hour).

2.5. Mathematics modelling

Based on the calculation of the respiration rate above, the effect of storage temperature on the respiration rate was determined using the Arrhenius equation (3).

\[
k = A \cdot e^{-\frac{E_a}{RT}}
\]

Where \( k \) = rate constant, where in this study \( k \) was the respiration rate of \( O_2 \) or \( CO_2 \) (ml/kg.h), \( A \) = frequency factor (ml/kg.h), \( E_a\) = activation energy (J/mol), \( R \) = universal gas constant, 8,314 J/mol K, \( T \) = temperature (K).

3. Results and Discussion

3.1. Change in gas concentration and respiration rate

The change in gas concentration for \( O_2 \) and \( CO_2 \) during storage was different for each observed coating concentration and temperature (Figure 1). Respiration can be defined as the metabolic process that provides energy for plant biochemical processes. It involves oxidative breakdown of organic reserves to simpler molecules, including \( CO_2 \) and water, with the release of energy. The significance of respiration in extending the shelf-life of fresh fruits and vegetables stems from the fact that there exists an inverse relationship between respiration rate and the shelf-life of the commodity. Respiration rate, which is commonly expressed as rate of \( O_2 \) consumption and \( CO_2 \) production per unit weight of the commodity, reflects the metabolic activity of the fruit tissue in the form of biochemical changes associated with ripening [4]. This process depends on the characteristics of the commodity, this is thought to be the cause of these differences.

In this study, it was found that at the same storage temperature, as the concentration of carrageenan in the coating material increase the decline of \( O_2 \) decreased and produced \( CO_2 \) increased, respectively. This suggested that the concentration of carrageenan in the coating material might have strong effect in the gas exchange between the shallots and the environment. As the concentration of the carrageenan increased, this might result in the increased in the thickness of the coating material and finally gave larger barrier against surrounding environmental gases. The edible coating material provides barrier properties against moisture and fresh produce gases during storage to slow down enzymatic oxidation, which provides protection from brown discoloration and softening of the texture [5]. Comparing between storage temperature of 15°C and 28°C indicated that at the storage temperature of 28°C or ambient air room storage, consistently produced larger decreased of \( O_2 \) and higher production of \( CO_2 \). At the end of storage day, the consumption of \( O_2 \) at the storage temperature 28°C was about 4 to 8 times larger than at storage temperature of 15°C, while \( CO_2 \) production at storage temperature of 28°C was about 2.5 to 4 times larger than the storage temperature of 15°C. Fonseca et al reported that the level of \( O_2 \) consumption was sixfold and the level of \( CO_2 \) production was fourfold increased with an increase in temperature from 4°C to 20°C using a closed system for diced shallots [6]. This meant that the storage temperature had profound effect on the change of \( O_2 \) and \( CO_2 \) between the product and surrounding environment. Lower temperature was known to inhibit products metabolism and as the result the change of \( O_2 \) and \( CO_2 \) would also decrease.
Figure 1. The changes of gases concentrations of O$_2$ and CO$_2$ (a and c) at storage temperature 15°C, (b and d) storage temperature 28°C.

Figure 2 depicts the respiration rate of shallot samples in different storage temperatures and coating conditions. As can be seen the respiration rates both RO$_2$ and RCO$_2$ decreased along with the storage time. However, it could be observed that those decreases differed in term of the storage temperature or carrageenan concentration in edible coating. For the same storage temperature, the same phenomenon as the depletion of O$_2$ was observed here, where as the carrageenan concentration in the coating material increased the rate of respiration would decrease. This meant that thicker edible coating would be more capable to suppress respiration rate of shallot samples. While, as compared between storage temperature it was clearly showed that the respiration rate at 28°C storage temperature considerably larger than at the storage temperature of 15°C. The values of the respiration rate at the storage temperature of 28°C were about 2 to 4 times larger than the respiration rate at the storage temperature of 15°C. Therefore cold storage is widely used to slow down the respiration rate and damage of fruit after harvest [7]. According to the Van't Hoff Rule, the velocity of a biological reaction (including respiration rate) increases two to threefold for every 10 rise in temperature [8]. A break of the cold chain can cause a sharp increase in the respiration rate of the fruit, which affects the oxygen and carbon dioxide levels in the package [9].
Figure 2. Respiration rate $RO_2$ and $RCO_2$ of shallots at different temperatures, (a and b) storage temperature 15°C (c and d) storage temperature 28°C.

3.2. Mathematical modelling

Respiration rate is known to depend on different product-related factors and atmosphere conditions. As stated by Cantarino et al, that the respiration rate models reported in the literature consider atmosphere composition and temperature effects [10]. One of the most important factors which affects respiration rate is the storage temperature. The effect of storage temperature on the respiration rate can be described using Arrhenius equation. By applying Arrhenius equation, the constants of frequency factor ($A$) and activation energy ($E_a$) could be found for each treatment combination of the shallot studied. Those new constants of $A$ and $E_a$ were then used to develop the equations of the respiration rate for both $RO_2$ and $RCO_2$ for each combination of storage temperature and carrageenan concentration (equations 4 – 9).

\[
RO_2 (0.5\%) = 4.568 \times 10^{15} \left( e^{-9694.3 \frac{1}{T}} \right)
\]

\[
RO_2 (0.75\%) = 5.175 \times 10^{15} \left( e^{-9167.1 \frac{1}{T}} \right)
\]
These equations were then used to develop prediction curves of the respiration rate RO₂ and RCO₂ for shallots with the concentrations of carrageenan in the coating material of 0.5%, 0.75% and control at different temperature ranged between 15°C to 28°C. Figure 3 illustrates those predicted respiration rate. Those curves showed that both RO₂ and RCO₂ increased as the temperature increased and decreased as the carrageenan concentration increased. It could also be seen that all the predicted respiration rates increased following the Van't Hoff Rule where, as the temperature increased 10°C the respiration rate increased two to three times. These findings suggested that Arrhenius equation clearly could be used to represent the effect of storage temperature on the respiration rate of shallot. It was also reported that the effect of temperature on respiration rate could be modeled using Arrhenius equation with satisfactory results for banana, mango, and guava [11].

\[
\begin{align*}
R_{O_2 (0.75\%)} & = 6.127 \times 10^{16} \left( e^{-10500 \frac{1}{T}} \right) \\
R_{CO_2 (0.75\%)} & = 1.253 \times 10^{16} \left( e^{-10149 \frac{1}{T}} \right) \\
R_{O_2 (control)} & = 4.622 \times 10^{12} \left( e^{-0.7569 \frac{1}{T}} \right) \\
R_{CO_2 (control)} & = 8.958 \times 10^{11} \left( e^{-7205.7 \frac{1}{T}} \right)
\end{align*}
\]

(6) (7) (8) (9)

Figure 3. Respiration rates prediction curves for concentrations of carrageenan in the coating material 0.5%, 0.75% and control (a) RO₂ and (b) RCO₂.

4. Conclusion
Concentration of carrageenan in the coating material and storage temperature were found to have strong influence on the gas exchange between shallots and the surrounding environment. The thicker the edible coating and the lower the storage temperature the slower would the gas exchange between product and surrounding environment. The consumption of O₂ at the storage temperature 28°C was about 4 to 8 times larger than at the storage temperature of 15°C, while CO₂ production at storage temperature of 28°C was about 2.5 to 4 times larger than at the storage temperature of 15°C. Respiration rate at 28°C storage temperature considerably larger than at the storage temperature of 15°C. The values of the respiration rate at the storage temperature of 28°C were about 2 to 4 times larger than the respiration rate at the storage temperature of 15°C. It was also known that Arrhenius equation clearly could be used to represent the effect of storage temperature on the respiration rate of shallot.
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