Kinetic studies of potassium permanganate adsorption by activated carbon and its ability as ethylene oxidation material

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Abstract. Generally, ethylene production in many horticultural products has been seen to be detrimental to the quality during storage and distribution process. For this reason, removing ethylene from storage or distribution atmosphere is needed to maintain the quality. One of the technologies that can be applied is the use of potassium permanganate (KMnO\textsubscript{4}). KMnO\textsubscript{4} is an active compound that can be used as an oxidizing agent on ethylene removal process. KMnO\textsubscript{4} is not recommended for direct used application. As the result, additional material is required to impregnate the potassium permanganate. The inert materials used are commercial activated carbon. Activated carbon is chosen because it has high surface area. The purpose of this research is to determine kinetics adsorption and oxidation model of ethylene removal material. The kinetics adsorption was determined using the pseudo-first and second-order kinetic models. The data on adsorption process show that the second-order equation is more suitable to express the adsorption process on this research. The analyzing of the ethylene oxidation capacity increased with time until it reach an optimal value. The ethylene oxidation rate is able to be estimated by the formula \( r = 0.1967 \left[ C_2H_4 \right]^{0.99} \left[ KMnO_4 \right]^{0.01} \); MSE = 0.44 %. The actual and estimation data of ethylene oxidation show that the model is fitted to describe the actual ethylene oxidation under same experimental conditions.

1. Introduction
Ethylene is a chemical compound that plays role in many physiological processes including undesirable ripening of fruits. Generally, ethylene production in many horticultural products has been seen to be detrimental to the quality during storage and distribution process. Horticultural products have different sensitivity to the presence of ethylene. A concentration of ethylene in the air of 0.1 μL L\textsuperscript{-1} is often quoted as the threshold level for physiological activity [1]. For this reason, good postharvest handling and removing ethylene from storage or distribution atmosphere are needed to maintain the quality. One of the technologies that can be applied is removing or reducing the level of ethylene in the atmosphere around horticultural products during storage and distribution process. The use of ethylene adsorber materials is one of the postharvest technology that can be used to maintain the horticultural product’s quality by removing or reducing the level of ethylene in the atmosphere. The materials that can remove ethylene have been identified and some have been succeeded in the commercial application, such as activated carbon [2], nano zeolite-KMnO\textsubscript{4} [3] and the used of potassium permanganate and alumina beads [4].
Potassium permanganate (KMnO₄) is an active compound that can be used as an oxidizing agent on ethylene removal process. However, potassium permanganate is not recommended for direct used application. As the result, additional material is required to impregnated the potassium permanganate. The inert materials that can be used are activated carbon, alumina, zeolite, and clay. Activated carbon from coconut shells is used in this research as inert material to adsorb potassium permanganate. Activated carbon has been chosen because it has high surface area and significant pore volumes which relatively large [5]. Nowadays, most published studies have been evaluated the effect of potassium permanganate on products, reporting the effect of potassium permanganate concentration, determining the effect of ethylene concentration but not determining the oxidation rate model of the absorber material itself.

This paper will evaluate the effect of corrugated cardboard ethylene absorber. The purpose of this research was to determine the ability of activated carbon to adsorb potassium permanganate (used kinetics adsorption models), determine the effect of impregnated activated carbon on the absorption of ethylene gas under some environmental conditions, and also to develop the ethylene oxidation rate model. The absorber materials will be applied on corrugated cardboard. This method will provide the undirected contact between the absorber and horticultural products. The corrugated cardboard ethylene absorber can be used as an inner on packaging box with high stability against mechanical effects and it may be easily recycled.

2. Materials and Methods

2.1. Kinetic Studies

The experiment was carried out using an untreated commercial activated carbon (coconut shells). First, activated carbon was washed with distilled water and dried overnight at 105°C. The kinetic studies were carried out by the modified method. The effect of contact time was determined by dipping 25 g of activated carbon in 100 mL of potassium permanganate solution (6.4 g of KMnO₄ on 100 mL water) under stirring [6]. The temperature of the solution was held constant at 20°C. After different time intervals (5-60 minutes), the volume of 1 mL supernatant was taken for spectrophotometrically measurements to determine the residual concentration of potassium permanganate. The solution was placed into a cuvette and determined with a spectrophotometer. The adsorption rate was analyzed using the pseudo-first-order [7]:

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  \hspace{1cm} (1)

\( q_e \) and \( q_t \) are the amount of potassium permanganate adsorbed (mg/g) at equilibrium and at time (min). The \( k_1 \) is the constant rate of adsorption. The values of \( k_1 \) were calculated between the graph of \( \ln (q_e - q_t) \) vs time. If the result showed the \( q_e \)-exp values have similarity with \( q_e \)-cal, it means the adsorption of potassium permanganate is the first-order reaction. However, if the value of \( q_e \)-exp does not match with the calculated one, the adsorption model is the second-order reaction. The second-order kinetic model is expressed as:

\[ \frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \]

(2)

\( k_2 \) is the constant rate of the second-order adsorption. If the second-order kinetic is acceptable, the graph of \( t/q_t \) vs t should show a linear relationship.

2.2. Corrugated Cardboard Ethylene Absorber-Making Procedures and It’s Ability as Ethylene Absorber
The corrugated cardboard ethylene absorber is made by glued 5 g of adsorbent on the surface of the corrugated paper (10 × 5 cm). The corrugated cardboard is glued to single paper ply. The fixing will holds the corrugation in shape and ethylene absorber materials are not visible to the end user. The glue is made from cassava starch and gelatin. Then, the corrugated cardboard ethylene absorber is applied as an inner box on the horticultural packaging. The evaluation of ethylene removal rate was determined by the modified method. The absorber (5 plies of corrugated cardboard ethylene absorber) was placed in 2.2 L of a glass jar and then sealed with a rubber stopper [8]. Gas containing 100 ppm (1 mL) of ethylene was injected into the jar. The ethylene concentration in the jar was determined by this formula:

\[ C_1, V_1 = C_2, V_2 \]  

\[ \text{C}_1, \text{V}_1 = \text{C}_2, \text{V}_2 \]  

\[ \text{V}_1 \text{ and } \text{V}_2 \text{ are the volume of ethylene injected and ethylene on the glass jar (mL), C}_1 \text{ and C}_2 \text{ are the concentration of ethylene injection and concentration of ethylene on a glass jar (ppm). During incubation at } 18^\circ \text{C, after different time intervals (15-75 minutes), 1 mL of sample gas from headspace was injected into a gas chromatograph (GC) to measure the residual ethylene concentration inside the glass jar.} \]

Jars with corrugated cardboard activated carbon were used as controls. The GC was equipped with FID (flame ionization detector). Ethylene concentration was measured by the following formula:

\[ \text{Ethylene concentration (ppm)} = \left( \frac{\text{peak sample}}{\text{peak standard}} \right) \times \text{concentration of ethylene standard} \]  

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The GC was equipped with FID, 8 ft unibead column with the permissible temperature at 85°C. The inlet temperature is set at 150°C and the outlet temperature is set at 200°C. Helium gas carrier resulting a total gas flow of 30 (mL/min) and the pressure maintained at 100 psi. The ethylene removal rate (mL/g.h) in the jar was calculated to determine the ethylene absorption rate [9].

2.3. The oxidation rate of Corrugated Cardboard Ethylene Absorber

The oxidation rate of corrugated cardboard ethylene absorber was processed into a model to estimate the rate of ethylene absorption. The actual data of absorption was analyzed to determine the oxidation rate model of corrugated cardboard ethylene absorber activated cardboard-KMnO₄. The oxidation process can be described by the following formula [10, 11]:

\[ A + B \rightarrow C \]  

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A and B are the two reactants that will react to produce C products. From the oxidation process, the A described the concentration of ethylene, B is the concentration of potassium permanganate and the products from oxidation process described with C.

3. Results and Discussions

3.1. Kinetic Study

The effects of dipping times of activated carbon on potassium permanganate are shown in Figure 1. Based on Figure 1, the residual concentration of potassium permanganate solution was decreased. This condition is supported by the increasing number of potassium permanganate accumulation on the surface and pore area of activated carbon (q̇). This process continues until reaches certain point which is no more potassium permanganate that is lost from the solution [5,12].
Figure 1. The effect of dipping time on residual concentration and the accumulation of KMnO$_4$ on the surface and pore area of activated carbon.

The amount of KMnO$_4$ on activated carbon (mg/g) has increased along with the addition of dipping time until it reaches certain point which is no more KMnO$_4$ that loss from the solution (10-15 minutes). The amount of KMnO$_4$ on activated carbon (mg/g) on 15 minutes of dipping time indicated the optimum capacity of KMnO$_4$ adsorption under this operating conditions. The results show that the amount of KMnO$_4$ adsorbed increases from 8.1555 mg (10 minutes of dipping time) to 19.3735 (15 minutes of dipping time) for each gram of activated carbon used on adsorption process.

The kinetic adsorption of KMnO$_4$ on activated carbon was analyzed with pseudo-first-order and pseudo-second-order. The value of $k_1$ on the pseudo-first-order kinetic model was obtained from the slopes of the linear graph between $\ln\left(q_e - q_t\right)$ vs times. According to pseudo-first-order kinetic models, the $q_e$ values did not match with the calculated values that were obtained from the linear graph (Table 1). This results indicated that the kinetic adsorption of KMnO$_4$ onto activated carbon did not follow the pseudo-first-order equation. If the pseudo-second-order kinetic model is acceptable, the graph of $t/q_t$ versus times should show a linear relationship. The relationship between $\ln\left(q_e - q_t\right)$ vs times and the linear graph of $t/q_t$ vs times are shown in Figure 2.

Figure 2. The graph model of first (a) and second (b) kinetic order of KMnO$_4$ adsorption.
According to Table 1, the calculation data show the pseudo-second-order model is more acceptable to describe the actual condition of KMnO₄ absorption on this experimental. This condition is supported by the higher coefficient correlation of calculated data on pseudo-second-order if it’s compared to coefficient correlation data on pseudo-first-order.

3.2. Efficiency of Corrugated Cardboard Ethylene Absorber

The coconut shell activated carbon was impregnated by the saturated solution of potassium permanganate for 15 minutes under stirring. Activated carbon then allowed to dry at 60 °C for 16 h. The corrugated cardboard ethylene absorber is made by glued 5 g of adsorbent on the surface of corrugated ply (10×5 cm) and then the surface was glued with the liner to holds the corrugated cardboard shape. The absorber (5 plies of corrugated cardboard) was placed in a glass jar and the ethylene absorption rate was determined. The ethylene absorption capacities of corrugated cardboard are shown in Figure 3.

![Figure 3](image.png)

Figure 3 shows the increasing number of ethylene absorption capacity from corrugated cardboard activated carbon and activated carbon-KMnO₄. This condition indicated the ability of corrugated cardboard ethylene absorber to reduce and even eliminated ethylene gas on the atmosphere packaging. The corrugated cardboard activated carbon-KMnO₄ has higher absorption capacity if compared with corrugated cardboard activated carbon. The absorption capacity on 15 minutes of absorption time was 87.41 % for corrugated cardboard activated carbon-KMnO₄ and 53.87 % for corrugated cardboard with activated carbon. The experimental data show that during an hour of absorption times, corrugated cardboard activated carbon-KMnO₄ is able to absorb 0.0745 ppm gas ethylene for each gram material ethylene absorber, while the ability of corrugated cardboard activated carbon is 0.0008 (ppm ethylene/g activated carbon).
3.3. The Oxidation Rate Model of Corrugated Cardboard Ethylene Absorber

The ethylene oxidation rate generally describes as a process of two reactants (ethylene and potassium permanganate) that produce some products (ethylene glycol, mangan dioxide and calcium hydroxide) which is influenced by a coefficient (k). The ethylene oxidation rate is calculated by the formula:

\[ r = -\frac{d[C_2H_4]}{dt} = -\frac{d[KMnO_4]}{dt} = k[C_2H_4]^x [KMnO_4]^y \]  \( (6) \)

where \( r \) is the oxidation rate (ppm/g.h), \([C_2H_4]\) and \([KMnO_4]\) are the concentration of ethylene and potassium permanganate (mg/L), \( x \) and also \( y \) are the kinetic order with respect to ethylene and potassium permanganate. Based on the experimental data, the ethylene oxidation rate model of corrugated cardboard activated carbon-KMnO_4 is given by the equation:

\[ r = 0.1967 [C_2H_4]^{0.99} [KMnO_4]^{0.01} \]  \( (7) \)

where \( r \) is the equation model to estimate the ethylene oxidation rate (ppm/g.h), \([C_2H_4]\) and \([KMnO_4]\) is the concentration of ethylene and potassium permanganate (mg/L) with the kinetic order for each component is 0.99 for ethylene and 0.01 for potassium permanganate.

The validation model was performed with mean square error (MSE) calculation from actual and estimation data. The advantage of validation model using MSE is to avoid the use of undesirable absolute data on mathematical calculations [14]. The validation models are shown in Figure 4.

![Figure 4. The ethylene oxidation rate, actual, and model estimation](image-url)

The validation data on Figure 4 show the similarities between actual and model estimation of the ethylene oxidation rate. According to Suryani [13], the model is valid to estimate the actual ethylene oxidation process with the value of MSE is under and equal to 5 %. From the calculation data on this experiment, the model is able to determine the ethylene oxidation rate with 0.44 % of MSE value. This condition indicated that the ethylene oxidation rate model is able to describe the actual ethylene oxidation process under same experimental conditions.
4. Conclusions
The results of this research reveal that the effect of dipping time on 10-15 minutes increased the amount of adsorbed from 8.1555 to 19.3735 (mg/g) which is fitted well to pseudo-second-order model. The analysis efficiency of corrugated cardboard ethylene absorber proves that the effect of corrugated cardboard ethylene absorber from treated activated carbon with KMnO₄ (AC-KMnO₄) has higher and faster ability to oxidizing the ethylene from the atmosphere of storage when it is compared with untreated activated carbon corrugated cardboard ethylene absorber (AC). The results show that the ethylene oxidation rate model can be estimated by formula $r = 0.1967\left[C_2\text{H}_4\right]^{0.99}\left[\text{KMnO}_4\right]^{0.01}$; MSE = 0.44% under same experimental conditions.

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