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PREPARATION OF ETHYLENE SCAVENGER BASED ON $KMnO_4$ TO THE EXTENSION OF THE STORAGE TIME OF TOMATOES

Abstract: Ethylene is one of the simplest plant growth regulators and is known to play a role in many physiological processes in fruit and vegetables. It helps to accelerate ripening in fruit, followed by aging and ultimately death. It is known that much fresh produce emits relatively large amounts of ethylene and smaller amounts of alcohol, aldehyde, and ester vapours in addition to carbon dioxide. The effect on the respiration rate depends primarily on the relative concentration compared to the ethylene emission of the plant, rather than on the absolute ethylene concentration. The removal of ethylene gas from the package headspace slows senescence and prolongs shelf life. Various methods of ethylene control are offered commercially, including several based on ethylene adsorption/oxidation.

The aim of this study was to prepare an ethylene scavenger with the use of potassium permanganate. The prepared ethylene scavenger was used extend the storage time of fresh tomatoes. The storage conditions were similar to tomato vegetable storage conditions at home and on shop shelves. This test used three equal groups (five replicates per group) and placed them in commercial plastic packaging. The first group of tomatoes was placed in packaging without any ethylene absorber, while the other two groups were placed in packaging with any ethylene absorber. The sachets placed in the packaging contained respectively 1 and 2 grams of previously prepared ethylene absorber. The first mold on the tomatoes in the packaging with ethylene absorber occurred on the ninth day of the experiment. In the two remaining packets, mold appeared after nearly fifty days. There were differences in the first group of stored tomatoes. Also, the obtained results confirmed the possibility of using ethylene absorber with zeolite for food storage.

Keywords: ethylene scavengers, fruits, vegetables, storage.

JEL classification: L79, L89.

OPRACOWANIE POCHŁANIACZA ETYLENU NA BAZIE $KMnO_4$ DO OCENY CZASU PRZECHOWYWANIA POMIDORÓW

Streszczenie: Etylen jest jednym z najprostszych regulatorów wzrostu roślin. Odgrywa bardzo istotną rolę w wielu procesach fizjologicznych owoców i warzyw. Jest jednym z czynników przyspieszających dojrzewanie owoców, prowadząc do ich starzenia, a w efekcie do zepsucia. Wiele produktów świeżych emituje stosunkowo duże ilości etylenu, mniejsze ilości alkoholu, aldehydu i estru oraz dwutlenku węgla. Wpływ etylenu na szybkość oddychania zależy przede wszystkim od względnego stężenia emisji etylenu przez rośliny. Nie zależy natomiast od bezwzględnego stężenia etylenu. Usunięcie etylenu z przestrzeni opakowania spowalnia starzenie i wydłuża okres przydatności do spożycia. Na rynku dostępne są różne metody kontroli emisji etylenu, między innymi oparte na adsorpcji.

Głównym celem niniejszych badań było opracowanie pochłaniacza etylenu na zeolicie z wykorzystaniem nadmanganianu potasu. Opracowany pochłaniacz etylenu został wykorzystany do przedłużenia czasu przechowywania świeżych pomidorów. Warunki przechowywania pomidorów były podobne to warunków sklepowych. Badane pomidory zostały podzielone na trzy równe grupy (pięć powtórzeń na grupę) i umieszczone w komercyjnych opakowaniach z tworzywa sztucznego. Pierwsza grupa pomidorów umieszczona została w opakowaniu bez pochłaniacza etylenu, podczas gdy pozostałe dwie grupy były umieszczone w opakowaniu z pochłaniaczem etylenu. Saszetki zawierały odpowiednio 1 i 2 g wcześniej przygotowanego pochłaniacza. Pierwsze objawy psucia na pomidorach pojawiły się w dziewiątym dniu eksperymentu. W dwóch pozostałych próbach pleśń pojawiła się po prawie pięćdziesięciu dniach. Uzyskane wyniki potwierdzają zatem możliwość wykorzystania pochłaniacza etylenu na bazie zeolitu do przechowywania żywności.

Słowa kluczowe: pochłaniacz etylenu, owoce, warzywa, przechowywanie.

Introduction

Active packaging is a system that involves interactions between package or package components and food or internal gas atmosphere and complies with consumer demands for high quality, fresh-like, and safe products. Important examples of active packaging include oxygen scavengers, carbon dioxide emitters/absorbers, moisture absorbers, ethylene absorbers, ethanol emitters, flavour releasing/absorbing systems, time-temperature indicators, and antimicrobial containing films [Ozdemir and Floros 2004]. Ethylene is a growth-stimulating hormone that accelerates ripening and senescence by increasing the respiration rate of climacteric fruits and vegetables, thereby decreasing shelf life. Ethylene also accelerates the rate of chlorophyll degradation in leafy vegetables and fruits. Hence, the removal of ethylene gas from the package headspace slows senescence and prolongs shelf life [Knee 1990; Blindi et al. 1993].

In the literature, a number of ethylene sorbing substances are described. Most of these are supplied as sachets or integrated into films. Many of the claims for ethylene adsorbing or absorbing capacity have been poorly documented so the efficacy of these materials is difficult to substantiate [Vermeiren et al. 1999; Zagory 1995]. Ethylene scavengers have been proven to be effective in the storage of packaged fruits, including kiwi fruit, bananas, avocados, and persimmons [Sacharow 1998]. An ethylene scavenging system, containing active carbon and palladium(II) chloride as a catalyst, effectively reduced the rate of softening of minimally processed kiwi fruits and bananas and decreased the loss of chlorophyll in spinach leaves stored at 20°C by absorbing ethylene from the medium [Abe and Watada 1991]. For example, activated charcoal, used to adsorb ethylene, has been impregnated with bromine or with 15% $KBrO_3$ and 0.5 M H_2SO_4 to eliminate the activity of ethylene. A number of catalytic oxidizers have been combined with adsorbents to remove the adsorbed ethylene such as potassium dichromate, potassium permanganate, iodine pentoxide, each respectively embedded on silica gel. Such compounds can be embedded in permeable plastic bags or printing inks to remove ethylene from the packages of plant produce [Holland 1992]. Moreover, one of the most effective materials to remove ethylene is potassium permanganate.

Wills and Warton [2004] conducted a detailed study on the ability of potassium permanganate absorbent to remove low levels of ethylene from the atmosphere. The conducted experiments and calculations showed that at 20°C and 90% RH, use of a potassium permanganate-alumina absorbent would be beneficial with produce having a low level of ethylene generation but for larger packages of produce generating higher ethylene levels can be unsuitable. Bailén et al. [2006] developed an active packaging on the basis of the combination of modified atmosphere packaging and the addition of activated carbon alone or impregnated with palladium as a catalyst. They studied the impact of packaging on the active life and shelf life of tomatoes. As a result, the higher scores in terms of sweetness, firmness, juiciness, colour, odour, and flavour of tomatoes treated with GAC-Pd were received. Palladium supported on activated carbon increases the removal rate of ethylene in comparison to the activated carbon even at the at low concentrations but requires a large amount of a mixture of adsorbent and catalyst, which is related to the absorption of other environmental gases and associated loss of efficiency [Martínez-Romero et al. 2009]. Also, zeolite was used to prepared ethylene absorber [Brody, Strupinsky and Kline 2001; Lasris 1990]. In recent years, new formulations of ethylene scavenger based on palladium coated on the zeolite were proposed. The obtained results shows that these products are effective adsorbents of ethylene and has a significant ethylene adsorption capacity at 20°C and a humidity of about 100% RH. Under these conditions such formulation exceeds absorbers based on $KMnO_4$ [Terry et al. 2007]. This formulation has several advantages and can be used to protect the freshest agricultural products and flowering in both low and high humidity and despite the high cost of palladium it has a chance to become a business practice [Smith et al. 2009]. The presented ethylene absorbers that used palladium are rather expensive. Potassium permanganate seems to be a cheaper solution. Magargee et al. [2006] proposed the use of sodium permanganate to remove ethylene from the gases. Also, we offer the advantage of this solution compared to the potassium permanganate is the better solubility of the sodium equivalent in water and as a result a much higher absorption on the substrate is achieved.

In this study, we prepared an ethylene scavenger using potassium permanganate ($KMnO_4$). The prepared ethylene scavenger was used to extend the storage time of fresh tomatoes. Potassium permanganate is a stable purple solid that is a strong oxidizing agent and readily oxidizes ethylene. Moreover, for potassium permanganate to be effective in oxidizing quite small concentrations of ethylene from the atmosphere around produce where natural convection and diffusion are the only driving forces giving contact between ethylene and the oxidant, the potassium permanganate needs to have a high surface area exposed to the atmosphere. In this experiment, lima tomatoes were used. Based on the literature, tomato, cucumber and broccoli are, from the morphological point of view, 'fruits' which are responsive to ethylene [Jacxsens 2000; Oh et al. 1996; Picon et al. 1993; Wills et al. 2001]. These vegetables can benefit from the removal of ethylene, as ethylene detrimentally affects their colour, by yellowing, and texture, by promoting unwanted softening in cucumbers and peppers or toughening in asparagus and sweet potatoes [Saltveit 1999]. Moreover, the reduction in ethylene affected by the addition of potassium permanganate was subsequently found to delay the ripening of many climacteric fruits such as banana, kiwi fruit, mango and avocado [Wills and Warton 2004].

1. Materials and methods

1.1 Preparation of ethylene scavenger

Ethylene scavenger was prepared by dipping activated zeolite in the saturated solution of potassium permanganate (6.4 g/100 mL) at 20°C for varying times, between 3 min and 6 h, allowing it to dry in air for 30 min, and repeating the dipping and drying process for up to 6 times. The final drying of the impregnated zeolite was achieved by allowing zeolite to dry in ambient air at 20°C for 24 h. The concentration of potassium permanganate was determined using spectrophotometer.

1.2. Materials

The efficacy of obtained ethylene scavenger to retard ripening in tomatoes were tested. Tomato fruits were harvested from a commercial farm near Kalisz (Wielkopolska, Poland). The tomatoes were put in polyethylene terephtalate (PET) boxes (volume 500 cm^3).

1.3. The storage condition

In this study, storage conditions were similar to tomato vegetable storage conditions at home and on shop shelves. The temperature of storage was maintained in the range of 22°C to 24°C. This test used three equal groups (five replicates per group) and placed them in polystyrene boxes. The first group of tomatoes was placed in packaging without ethylene absorber, while the other two groups were placed in packaging with ethylene absorber. The sachets placed in the packaging contained respectively 1 and 2 grams of previously prepared ethylene absorber.

1.4. The colour measurement

These studies used the colour measurement system model colorimetric colour space L*a*b*. This is a space extending between opposite colours forming the following dimensions: L – brightness of the range of 0 (black) to 100 (white), and the dimensions a and b are negative or positive, determining variation from green to red (a) and from blue to yellow (b). Scales a and b axis extend from –150 and +100 and –100 and +150, regardless of the fact that some values do not have an equivalent colour. The colour values were recorded as the mean values of 10 measurements. Minolta CR 200 containing pulsed xenon arc lamp built into a measuring head as a light source was used.

1.5. Statistical analysis

Student's t-test was used to determine the differences in the studied values. The p-values < 0.05. All analyses were performed with Excel.

2. Results and discussion

2.1. The concentration of potassium permanganate

The concentration of potassium permanganate absorbed by zeolite was determined by grinding a sample of zeolite (2 g). For this purpose 0.2 g powered zeolite was immersed in a solution of potassium permanganate. The solution was placed into a cuvette and the absorbance at 528 nm was determined with a spectrophotometer. Table 1 presents potassium permanganate uptake and the colour of zeolite dipped in potassium permanganate solution after many times.

Table 1. Potassium permanganate uptake and the colour of zeolite dipped in potassium permanganate solution at 20°C after many times

Time of measurement [min.]	$KMnO_4$ [g/ml]	Visual
0 min.	0	White
3 min.	0.5	Pale pink
30 min.	0.8	Dark pink
60 min.	1.8	Purple
90 min.	2.0	Purple
120 min.	2.0	Purple
180 min.	2.0	Purple
240 min.	2.0	Purple
360 min.	2.0	Purple

The uptake of potassium permanganate in zeolite increased with the increasing dip time up to 90 min. when a concentration of about 2 g/100 g was achieved.

2.2. The colour measurement of lime tomatoes

Table 2 presents the average values of L*, a* and b* parameters before storage and after 5 weeks storage of tomatoes. One can observe the changes in each value.

Table 2. Tomatoe colour change during storage at room temperature

Storage, week	Packaging without ethylene absorber			Packaging with 1 g of ethylene absorber			Packaging with 1 g of ethylene absorber		
	L*	a*	b*	L*	a*	b*	L*	a*	b*
0	38.40	25.69	17.23	38.26	25.62	17.32	38.36	25.94	17.34
5	36.72	21.96	13.73	37.90	24.79	15.11	37.05	23.63	15.26

Figure 1a presents tomatoes (a) in packaging without absorber, Figure 1b presents tomatoes with a sachet of 1g ethylene absorber, Figure 1c presents tomatoes with a sachet of 2 g ethylene absorber.

a) b) c)

Figure 1. Tomatoes on the first day of the study

On the 9th day of the study, there appeared visible signs of spoilage of the tomatoes in the first packaging. The most noticeable organoleptic changes were those in the structure of the vegetables, such as skin wrinkling, the loss of firmness, and even the appearance of mold. In the two other packets, no significant changes were observed.

a) b) c)

Figure 2. Tomatoes on the 9th day of the study

On the 13th day of the study, there began to appear visual changes in the tomatoes from the second and third group. Individual tomatoes significantly darkened and lost their firmness but no signs of mold were noted in any of these groups. However, in the first group, in the packaging without ethylene absorber, the mold was constantly developing and transferring to other tomatoes. The visual condition of the whole group strongly deteriorated.

a) b) c)

Figure 3. Tomatoes on the 18th day of the study

The observation on the 18th day of storage showed that the process of deterioration in packaging 1 was accelerating. It was noted that the mold developed further, there was juice coming out from the inside of the tomatoes, and an accompanying strong, unpleasant, pungent odour. The structure of some of the tomatoes in this group deteriorated to such an extent that it prevented the colorimetric study of the individual units. In the second and third group, there was no significant change as compared to the study conducted on the thirteenth day. Still there were no traces of mold, juice leak or perceptible odour. The products in the second and third group remained similar to each level of freshness.

On the twenty-second day of the experiment, there could be seen organoleptic changes in each group of vegetables. There were differences in the appearance of the tomatoes stored in the packaging with ethylene absorber (both with 1 g and with 2 g) and without the absorber. Thirty six days from the start, the tomatoes in the first group were in the process of deep spoilage. In the packaging without ethylene absorber, the research material was completely damaged.

2.3. Statistical analysis

The student's t-test was used to determine the differences in the values L a*b* for tomatoes stored in three types of packaging. The study was conducted under the assumptions: schedules of the two groups are close to normal, the sizes of the two groups are similar, the variances in the two groups are similar, and the variances in the two groups were similar. To study changes in the parameters, two hypotheses were made: a) hypothesis H_0 – L values obtained for the groups at the beginning of each experiment did not differ in a statistically significant way, b) hypothesis H_1 – L values obtained for the individual groups differed in a statistically significant way.

Similar hypotheses were made for the other studied parameters (a* and b*). The first hypothesis was a determination of no statistically significant differences for the evaluated parameters. Moreover, the opposite hypothesis was to find a statistically significant difference. Table 3 shows the statistical comparison of the tomato products in the individual packaging.

Table 3. The absolute values t calculated and $t_{0.05}$ for a comparison of parameters at the start of the experiment

Tested parameter	Comparison of the samples with and without ethylene absorber		Packaging with 1 g of ethylene absorber		Packaging with 2 g of ethylene absorber	
	$t_{calculated}$	$t_{0.05}$	$t_{calculated}$	$t_{0.05}$	$t_{calculated}$	$t_{0.05}$
L	0.3144	2.1009	0.7351	2.1009	0.4402	2.1009
a*	0.0793	2.1009	−0.2408	2.1009	0.3735	2.1009
b*	0.1645	2.1009	0.1645	2.1009	0.2890	2.1009

The next step involved the analysis of the changes after five weeks of storing the tomatoes. The tests were performed with the hypotheses as described above. The analysis was performed for the significance level of 0.05. Two hypotheses were prepared for the study:

a) hypothesis H_0 – the value L of the individual groups at the beginning of the experiment and after five weeks of storage do not differ from each other in a statistically significant way;

b) hypothesis H_1 – the value L of each group at the start of the experiment and after five weeks of storage differed from each other in a statistically significant way. Similar hypotheses were formulated for the other tested parameters (a*b*). The results were presented in Table 4.

The colour of the tomatoes from the first group of packaging underwent a statistically significant change after five weeks of storage. For the tomatoes stored in the packaging with ethylene absorber, the obtained results showed that the change of at least one parameter was statistically significant. This may

Table 4. The absolute values t calculated and $t_{0.05}$ to test the parameter changes of tomatoes at the beginning of the experiment and after five weeks of storage (test student's t-distribution)

Tested parameter	Comparison of the samples with and without ethylene absorber		Packaging with 1 g of ethylene absorber		Packaging with 2 g of ethylene absorber	
	$t_{calculated}$	$t_{0.05}$	$t_{calculated}$	$t_{0.05}$	$t_{calculated}$	$t_{calculated}$
L	4.2872	2.1199	0.8800	2.1098	2.5542	2.1448
a*	4.1074	2.1199	1.4152	2.1098	1.6385	2.1448
b*	6.8639	2.1199	4.0425	2.1098	2.7941	2.1448

indicate that the tomatoes in the packaging with ethylene absorber undergo the aging process. On the other hand, this process was not as clear as in the case of the tomatoes which were stored in the packaging without ethylene absorber.

Conclusions

This study confirmed the effect of ethylene on the ripening and spoilage of tomatoes. The first mold on the tomatoes in the packaging with ethylene absorber occurred on the ninth day of the experiment. In the two remaining packets, mold appeared after nearly fifty days. There were differences in the first group of stored tomatoes. Moreover, there were small differences between the tomatoes from the second and third group. The uptake of potassium permanganate in zeolite increased with the increasing dip time up to 90 min. when the concentration of about 2 g/100 g was achieved. To sum up, this study confirms the possibility of using ethylene absorber with zeolite for food storage. This corresponds to the question why the search for other materials with ethylene removal capability and with fewer precautions has focused so much attention on zeolite.

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