Chiang Mai J. Sci. 2018; 45(5) : 2152-2167
http://epg.science.cmu.ac.th/ejournal/
Contributed Paper

Preparation and Evaluation of Ethylene Absorbers from Zeolite A/$KMnO_4$ Composite for Monitoring of Silk Banana (*Musa sapientum* L.) Ripening

Saral Yimmongkol [a], Patcharee Pratumpong [b], Supakorn Boonyuen [c] and Chiravoot Pechyen* [a]

[a] Department of Materials and Textile Technology, Faculty of Science and Technology, Thammasat University, Patumtani 12120, Thailand.

[b] Department of Physics, Faculty of Science and Technology, Thammasat University, Patumtani 12120, Thailand.

[c] Department of Chemistry, Faculty of Science and Technology, Thammasat University, Patumtani 12120, Thailand.

* Author for correspondence; e-mail: chiravoot.p@gmail.com

Received: 1 November 2017
Accepted: 30 April 2018

ABSTRACT

Ethylene absorptive properties of zeolite A were improved by strong bases and potassium permanganate ($KMnO_4$). The zeolite surface was activated with a solution of potassium hydroxide (KOH) and sodium hydroxide (NaOH) at concentrations of 1, 2 and 3M. Activated zeolites were soaked in a 5 w/v% solution of $KMnO_4$ for 5 hours, with powder collected after freeze-drying. The effects of ethylene absorbers with zeolite-$KMnO_4$ and without as control on Silk bananas during storage at room temperature were investigated. Silk bananas and zeolite-$KMnO_4$ tablets were evaluated daily for changes in total sugar content and peel and tablet color. Silk bananas without zeolite-$KMnO_4$ tablets were ripe after 2 days and total sugar content increased rapidly after 4 days. Contrarily, Silk bananas with zeolite-$KMnO_4$ tablets delayed the development of the yellow color of banana peel for 5 days and total sugar content slowly increased after 5 days. On the other hand, the color of zeolite-$KMnO_4$ tablets stored with banana changed from light violet to deep blue. °Bx of bananas without zeolite-$KMnO_4$ tablet significantly increased after 5 days while bananas with zeolite-$KMnO_4$ tablet remained comparatively lower for up to one week.

Keywords: zeolite, potassium permanganate, ethylene absorber, color changing sensor, ripening retardation, postharvest conservation

1. INTRODUCTION

Silk banana (*Musa sapientum L.*) is one of the most popular fruits in the world because of its availability to growth, low cost, various use, rich nutritive content with a sweet aroma, soft texture and ease to peel and eat [1]. Banana is a climacteric fruit with poor storage characteristics of the high rate of respiration and ethylene production after harvest relatively short shelf-life [2, 3].

Commercially, bananas are harvested mature green, stored in the low-temperature room during transportation and then treated with ethylene gas before marketing [4]. The ethylene treatment is known to provide identically ripened climacteric fruit within a few days. The color-changing of banana peel during ripening concerns with a replacement of chlorophyll, green pigment, by other pigments such as carotenoids [5] and a conversion of starch to sugars, resulting in flesh softening and aroma [6, 7] and a change in peel color from green to yellow as shown in Figure 1. Bananas are marketable as long as the peel color mostly green or yellow. Harvested bananas go from marketable mature green to unmarketable ripened banana within a week [8].

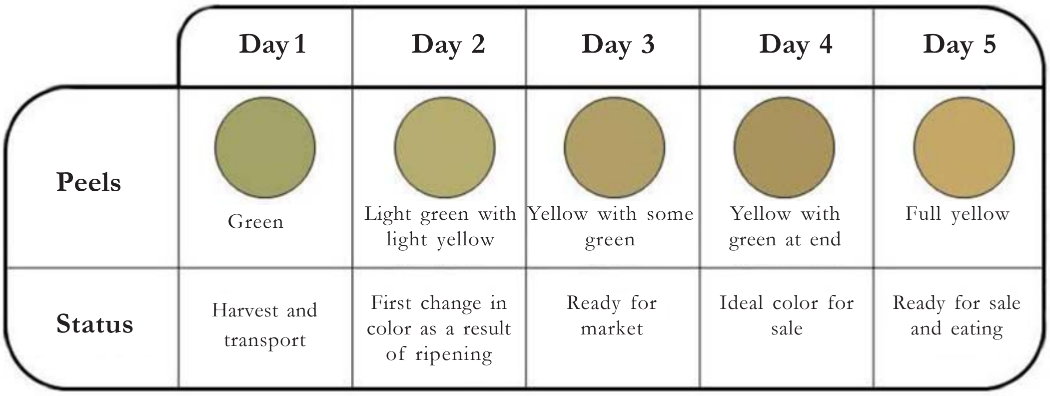


Figure 1. The banana ripening chart.

The global banana exports reached up to 18.8 million tonnes. Latin America and the Caribbean are the major banana exporters with 75 percent of bananas selling in the world market. The top five banana export destinations are Europe, USA, Russia, Japan and China [9]. The distance between harvest and consumption is complicated by post-harvest losses, both in quantity and quality [10]. The postharvest losses in fruits during transportation ranging from 25 to 50 percent are due to poor packaging, storage facilities, lack of transportation and physiology of fruit ripening [11]. Consequently, ripening retardation of banana during transportation by a few days can gain significant commercial value.

The ripening of climacteric fruits controlled by the releasing ethylene from fruit during ripening process [12] and its effects on quality attributes such as fruit nutritive value, flavor, texture and external appearance have been extensively reported [13]. Several postharvest storage techniques have been applied in the banana ripening retardation by restraining ethylene gas with an absorber. Ethylene absorbers such as alumina beads [14], Al_2O_3-SiO_2 [15], marls [16], clinoptilolite [17] and zeolite [13, 18] composite with potassium permanganate as an oxidizing agent were tested. Potassium permanganate is a powerful oxidant that neutralizes the ethylene by oxidizing into carbon dioxide and water with MnO_2 as a side product, leading to the complex color change from violet of $KMnO_4$ to brown of MnO_2 [19]. Moreover, the amount of ethylene release from fruits, which is related to fruit ripeness, can be determined by using gas chromatographic system [20], carbon nanotube-based chemoresistive sensor [21] or color changing sensor from molybdenum [22] and infrared based sensor [23]. Therefore, the ripeness of banana can be monitored by determining the ethylene gas in the storage atmosphere.

The purpose of this work is to prepare the activated zeolite composite with potassium permanganate, to study the effect of the application of this ethylene absorber on ripening retardation and to monitor the characteristic ripeness of banana.

2. MATERIALS AND METHODS

2.1 Materials, Preparations and Storage Conditions

Zeolite A with particle size less than 10 microns and pore size of 5-angstrom in diameter (Sigma Aldrich, Germany) was employed. The surfaces of zeolites, after soaking 5g of zeolite in a 200mL solution of potassium hydroxide (KOH) and sodium hydroxide (NaOH) prepared from dry pellet (Vectec, Scientific Promotion Co., Ltd, Thailand) at concentrations of 1, 2 and 3M, were compared. Activated zeolites were soaked in 100 mL of 5 w/v% $KMnO_4$ solution prepared from dry powder (Univar, USA) for 5 hours; all solutions were prepared using de-ionized water. The powder of ethylene absorber was collected and pressed into a 0.2g tablet after freeze-drying.

Silk bananas (*Musa sapientum L.*), with the average mass of 53±5 g, were purchased from a local trader (Pathumthani, Thailand) and used for the analysis of their ripening. Each fruit was stored separately in a plastic box at room temperature (28±3 °C). The samples were divided into two groups, those with and those without ethylene absorber tablet.

2.2 Characterization of Ethylene Absorbers

FTIR measurements were performed using a Perkin Elmer USA spectrophotometer. All FTIR absorption spectra were recorded in the range of 400 cm^{-1} to 4000 cm^{-1} and at a resolution of 4 cm^{-1}. Before testing, all samples were freeze-dried and prepared by KBr disc technique.

2.3 Physical Appearances

The microstructure of ethylene absorber was investigated using Leica Microsystems LEICA ICC50 HD optical microscopy at a resolution X50. Samples were spread and articulated between glass slides. The color values of ethylene absorbers and banana peels were measured using the color matching machine (GretagMacbeth Color i5). The color values range from 0 to 100 for L* and -120 to 120 for a* and b*. Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS) was performed using a JEOL JSM-5410LV with OXFORD EDS operating at 20 kV for 7500X images.

2.4 Total Soluble Solids

Total soluble solids content of banana, which is related to sugar content, in degrees Brix was prepared by mashing 1g of banana in 10 mL of de-ionized water and measured by using an Atago Hand-held Refractometer (Atago Co., Ltd, Japan), with the values ranging from 0.0 to 32.0 degrees Brix.

2.5 Color Profile of $KMnO_4$ Solution

Effects of the bases on color profile of 0.01g of $KMnO_4$ in 0.0075M 400mL of different base solutions (NaOH and KOH) reduced by adding 0.1mL of 4 w/v% sucrose solution each were determined absorption over a wavelength range of 200 to 800 nm using PerkinElmer Lambda 25 spectrophotometer.

2.6 Statistical Analysis

All data were expressed as the mean without including the standard deviation. Data were subjected to one-way analysis of variance (ANOVA) and then independent-sample t-test (SPSS 19.0, Chicago, U.S.A.). A p-value ≤ 0.05 was considered as statistically significant.

3. RESULTS AND DISCUSSION

3.1 Characterization of Ethylene Absorbers

The FTIR spectra of zeolite and zeolite with surface modification by base solutions were shown in Figure 2 and those after soaking in $KMnO_4$ solution in Figure 3. The FTIR data for related functional group were shown in Table 1. According to Table 1, the spectra between 3700-3000 cm^{-1} could be due to hydroxyl (-OH) and silanol (Si-OH) group on the surface of zeolite [24]. The peaks appear at 1650 cm^{-1} could be due to hydroxyl group bending, indicating trapped water molecules inside the pore of zeolite [25, 26]. The specific transmittance peaks at 1100-1050 cm^{-1} may be assigned to asymmetric stretching vibrations of Si-O-Si. The peaks at 465 cm^{-1} in Figure 2 may be assigned to bending vibrations of Al-O and Si-O in AlO_4/SiO_4 [27].

Figure 2A shows FTIR spectra of zeolite after modification of the surface by potassium hydroxide solution for 2 hours. The significant increase in transmittance intensity of OH band at 3700-3000 cm^{-1} of the hydroxyl group on the zeolite with surface modification by 3M KOH compared to unmodified zeolite [24]. The slight change of peaks at 800-600 cm^{-1} was assigned to the ion balance from base solution and AlO_4 from zeolite surface [25]. From Figure 2B, FTIR spectra of zeolite after surface modification by sodium hydroxide solution are similar to those of zeolite modified by potassium hydroxide. The significant increase in the intensity of OH band of the hydroxyl group on the zeolite surface modification by 2M and 3M KOH compared to unmodified zeolite. After soaked in $KMnO_4$ solution, the intensity of broad peak at 3000-3700 cm^{-1} of hydroxyl were decreased and broad peak at 1100-1050 cm^{-1} of Si-O-Si were shielded by sharp peak of MnO_4 at 1110 cm^{-1} due to the coating of $KMnO_4$ on the zeolite surface (Figure 3) [28].

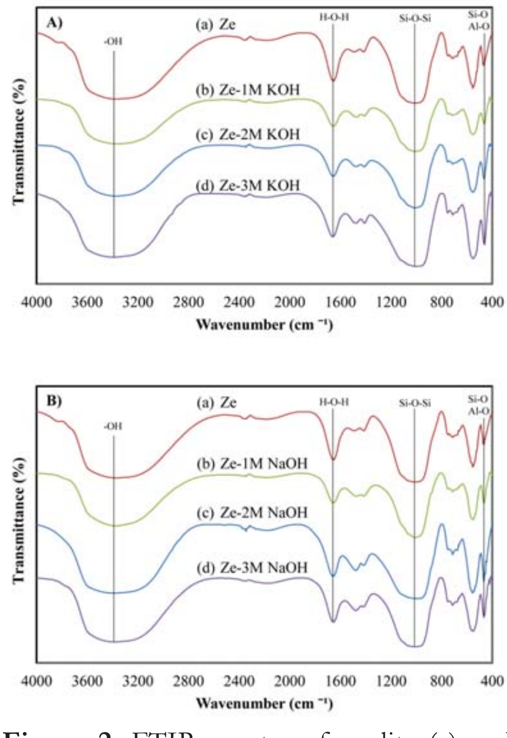


Figure 2. FTIR spectra of zeolite (a) and zeolite with surface modification (b) to (d) by A) KOH solution and B) NaOH solution.

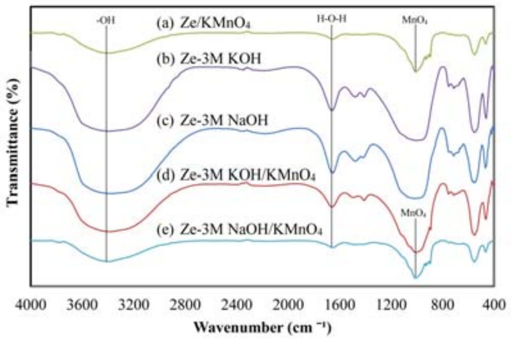


Figure 3. FTIR spectra of zeolite after soaked in $KMnO_4$ solution (a) and zeolite with surface modification by 3M KOH (b) and 3M NaOH (c) and zeolite with surface modification by (d) 3M KOH and (e) 3M NaOH after soaked in $KMnO_4$.

Table 1. FTIR data of zeolite and differently modified zeolite.

Functional groups	Wavenumber (cm^{-1})	Reference
Si-OH, -OH	3700-3000	[24]
H-O-H	1650	[25]
MnO_4	1110	[28]
Si-O-Si	1100-1050	
Si-O, Al-O	465	[27]

3.1 Physical Appearance

The microstructure (50X) of zeolite-$KMnO_4$ activated by various bases at different concentrations was shown in Figure 4. As can be seen in Figure 4 (a), the microstructure of the pure zeolite is in various forms. There was a different character, sizes, and shapes. The white crystal of zeolite was highly dispersed from each other. After activated with base and soaked in the $KMnO_4$ solution, the zeolite particles were of similar size and shape after cleaning the surface by base solution [27, 29] and packed with zeolite and $KMnO_4$ crystals. The color of the zeolite changed from clear white to deep violet (Figure 4 (b), (c), (e), (g)) or light violet (Figure 4 (d), (f), (h)), which is assigned to the $KMnO_4$ inserted into zeolite pore and surface. The excessive of $KMnO_4$ was crystallized to form a violet crystal. The base-activated zeolite-$KMnO_4$ as ethylene absorber that eliminates the content of ethylene gas in the atmosphere by oxidizing ethylene to H_2O and CO_2 follows the below chemical equations [19, 30]. With the highly porous properties of zeolite, the ethylene gas in storage atmosphere can be trapped inside the porous and easily oxidized by $KMnO_4$ coated on the zeolite surface.

$$3C_2H_4 + 2KMnO_4 + H_2O \rightarrow 2MnO_2 + 3CH_3CHO + 2KOH \quad (1)$$

$$3CH_3CHO + 2KMnO_4 + H_2O \rightarrow 3CH_3COOH + 2MnO_2 + 2KOH \quad (2)$$

$$3CH_3COOH + 8KMnO_4 \rightarrow 6CO_2 + 8MnO_2 + 2H_2O + 8KOH \quad (3)$$

Shape and size of zeolite particles improved by different concentration of strong bases and potassium permanganate were studied by SEM and images with a scale bar of 10 μm were displayed in Figure 5. The SEM images (Figure 5 (a)-(h)) show the solid particle contained a mixture of different particle diameter cube crystals of zeolite along with needle-rod shape of $KMnO_4$ crystals. Since some particles apparently connected with other particles, the particle size distribution was expected to be large. The SEM images of zeolite (Figure 5 (a)) samples indicate the formation of some cube crystals with sharp edges, smooth surface and large sizes. After soaked in the KMnO4 solution (Figure 5 (b)), the cube crystals of zeolite packed together with rod crystals of $KMnO_4$ but still smooth and clear surface. After zeolite was activated with strong bases solution, some zeolite crystals were broken down into smaller particles and rougher surface by increasing base concentration. The needle-rod shape of $KMnO_4$ crystals decreased and disappeared at high concentration of strong base solution respectively, indicating that there were surface interaction between zeolite surface and $KMnO_4$. It can generally be suggested that activated zeolite with strong bases solution can induce $KMnO_4$ to coat on the zeolite surface.

EDS analysis can provide the elemental analysis (e.g. Al, Si, O, Na, etc) on the selected spots located on the external surface of a crystal. EDS allows one to identify what those particular elements are and their relative proportions in the sample. The output of an EDS analysis of zeolite, zeolite-$KMnO_4$ and base activated zeolite-$KMnO_4$ were shown in EDS spectra in Figure 5. EDS spectra of the zeolite show strong elemental signal of oxygen, silicon, aluminum and calcium with low signal of sodium. After soaked in the KMnO4 solution, the signals from EDS analysis on zeolite surface show strong peak of potassium and weak peak of manganese. Figure 5 shows that signals of potassium and manganese are higher for the zeolite activated with strong base than for non-activated zeolite

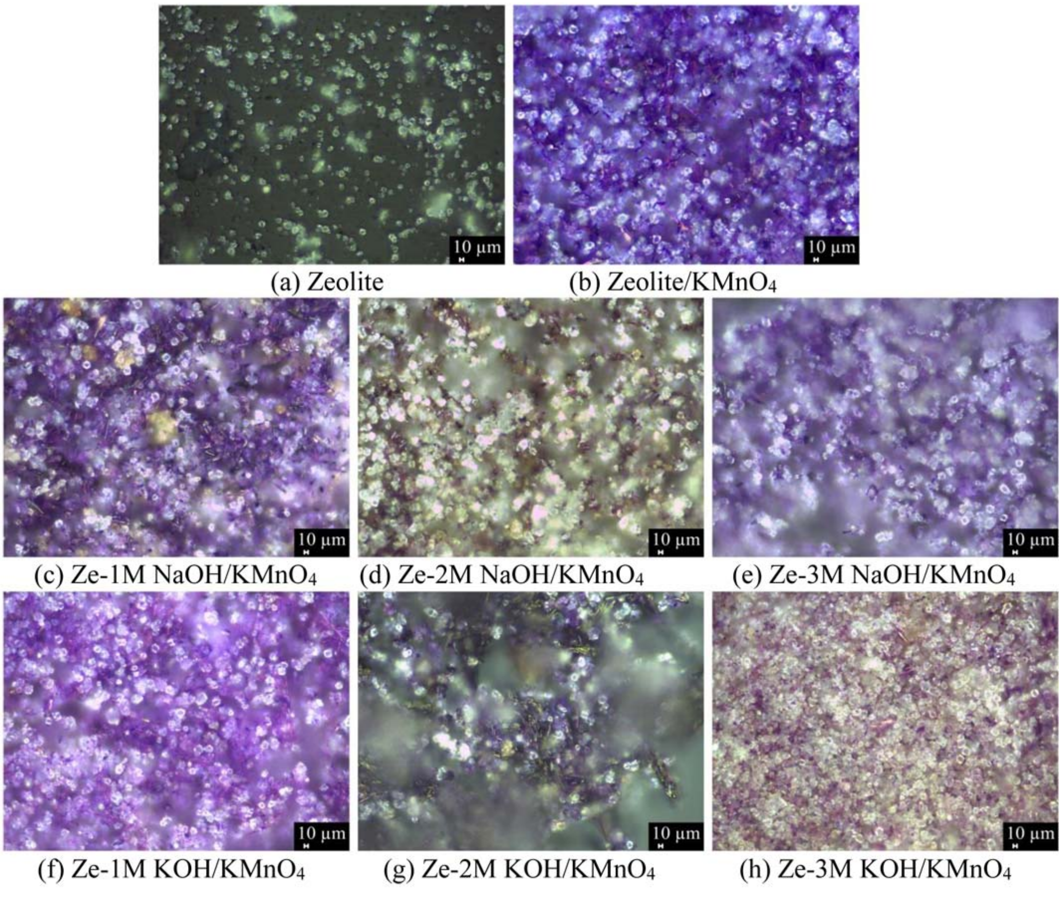
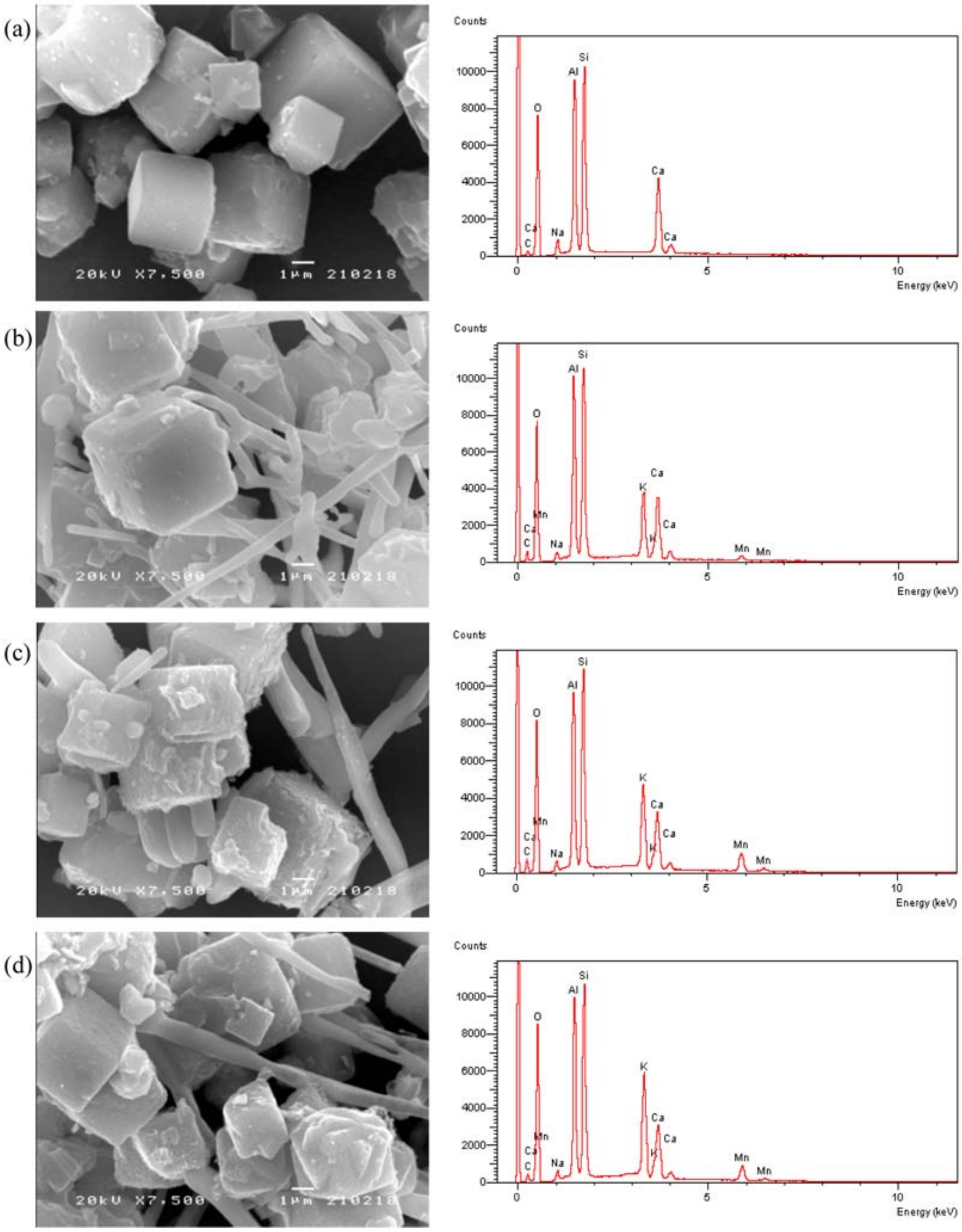


Figure 4. The microstructure (50X) of zeolite (a), zeolite after soaked in $KMnO_4$ (b) and zeolite activated by solution of 1M NaOH (c), 2M NaOH (d), 3M NaOH (e), 1M KOH (f), 2M KOH (g) and 3M KOH (h) after soaked in $KMnO_4$.


(a)
20kV X7,500 1μm 210218
Counts
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20kV X7,500 1μm 210218
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20kV X7,500 1μm 210218
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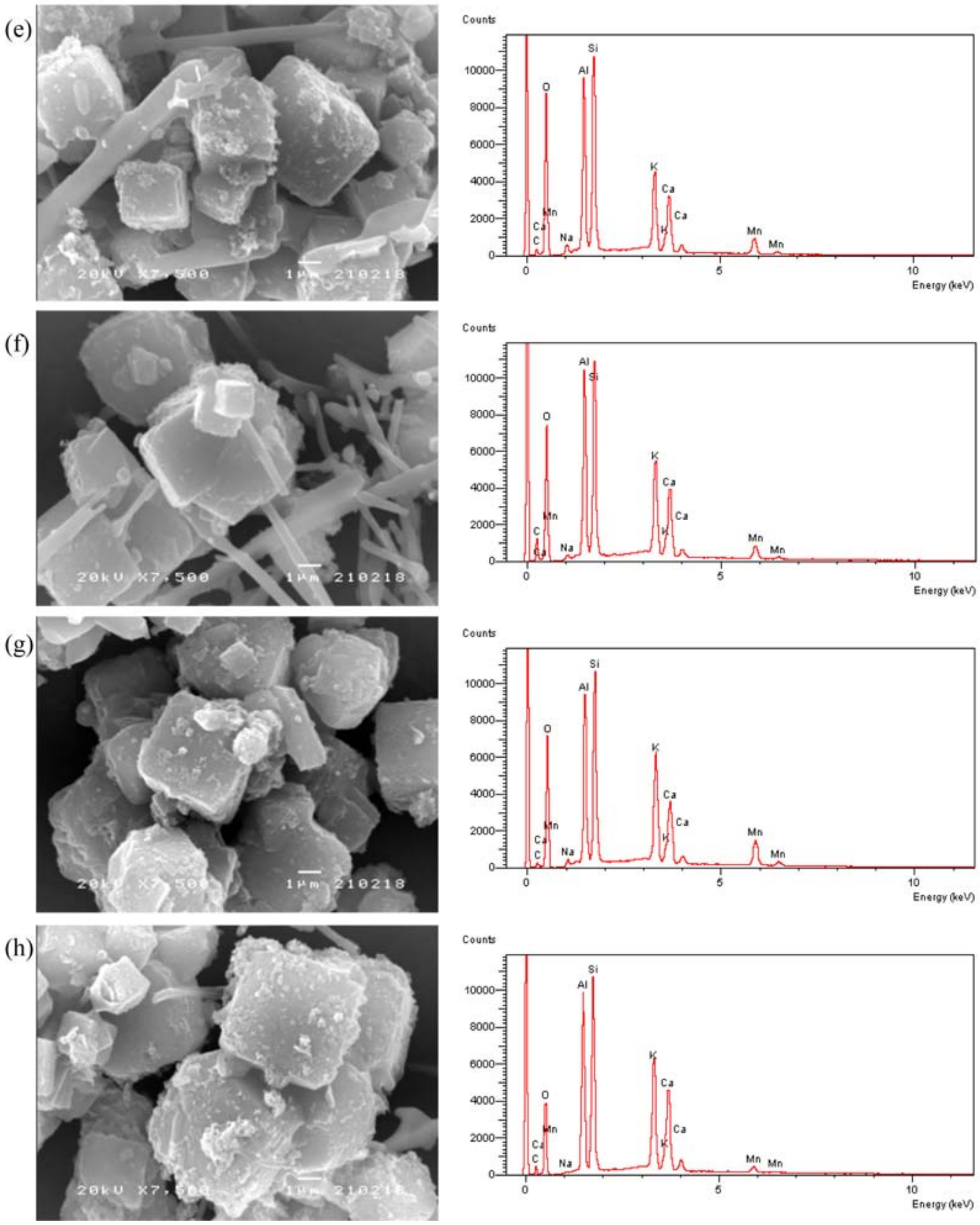

Figure 5. SEM images (Left) and EDS patterns (Right) of (a) zeolite, (b) zeolite soaked in $KMnO_4$ and zeolite soaked in $KMnO_4$ after activated by (c) 1M NaOH, (d) 2M NaOH, (e) 3M NaOH and (f) 1M KOH, (g) 2M KOH, (h) 3M KOH solution.

3.3 Color Profile of Ethylene Absorber

The color change of ethylene absorber were monitoring by color-matching machine in L*, a* and b*, where L* is the lightness or luminance component ranging from 0 to 100, and parameters a*(green to red) and b*(blue to yellow) are the two chromatic components, which range from -120 to 120 [31]. For ethylene absorbers on control condition (stored without banana), the average L*, a* and b* values and the images of ethylene absorber color were shown in Table 2 while for ethylene absorbers stored with banana, the average L*, a* and b* values and the images of ethylene absorber color were shown in Table 3.

Table 2. The average L*, a* and b* values and color image of ethylene absorber without banana.

	Color value	Day 0	Day 1	Day 2	Day 3	Day 4	Day 5
Ze/$KMnO_4$	L*	32.19	38.76	45.91	40.99	44.19	44.96
	a*	13.09	3.41	0.18	2.13	-0.13	-0.45
	b*	-6.16	-7.08	-4.36	-5.99	-4.56	-4.26
Ze-1M NaOH/$KMnO_4$	L*	32.83	43.66	45.59	43.81	43.26	42.32
	a*	11.31	1.66	1.72	1.35	0.76	2.11
	b*	-4.52	-8.08	-7.93	-7.42	-7.52	-8.23
Ze-2M NaOH/$KMnO_4$	L*	37.89	37.04	39.32	37.23	37.15	37.89
	a*	3.27	2.80	2.76	2.79	2.61	2.53
	b*	3.14	-0.83	-1.00	-0.29	-0.81	-0.74
Ze-3M NaOH/$KMnO_4$	L*	36.08	46.10	48.35	46.48	45.89	47.38
	a*	12.11	-0.14	-0.20	-0.39	-0.44	-0.99
	b*	-4.95	-1.61	-0.30	-0.37	-0.48	-0.31
Ze-1M KOH/$KMnO_4$	L*	33.92	42.89	42.22	39.56	42.30	42.85
	a*	130.22	0.85	2.61	2.75	0.85	0.75
	b*	-5.50	-4.18	-6.85	-4.89	-4.37	-3.76
Ze-2M KOH/$KMnO_4$	L*	34.07	43.94	47.50	43.20	42.38	46.49
	a*	7.80	2.02	0.74	2.18	1.85	-0.11
	b*	0.29	-9.32	-8.18	-8.58	-8.54	-7.71
Ze-3M KOH/$KMnO_4$	L*	40.34	39.37	44.03	42.46	43.55	43.13
	a*	13.14	3.82	2.18	1.54	0.87	1.52
	b*	-3.63	-2.66	-3.04	-2.68	-1.47	-3.06

Table 3. The average L*, a* and b* values and color image of ethylene absorber with banana.

	Color value	Day 0	Day 1	Day 2	Day 3	Day 4	Day 5
$Ze/KMnO_4$	L*	32.19	29.98	30.02	26.79	25.99	26.02
	a*	13.09	5.06	-8.3	2.89	2.78	2.33
	b*	-6.16	-4.6	-1.38	-1.5	-1.14	0.75
Ze-1M $NaOH/KMnO_4$	L*	32.83	30.21	31.46	27.98	27.04	26.24
	a*	11.31	4.21	3.9	2.72	2.5	2.82
	b*	-4.52	-5.22	-2.47	-1.57	-0.45	-0.1
Ze-2M $NaOH/KMnO_4$	L*	37.89	37.05	38.13	35.84	35.06	35.54
	a*	3.27	3.19	3.16	3.35	3.4	3.43
	b*	3.14	3.76	4.38	3.74	3.32	3.31
Ze-3M $NaOH/KMnO_4$	L*	36.08	32.3	34.37	31.75	30.2	30.62
	a*	12.11	6.2	5.35	5.06	4.5	4.42
	b*	-4.95	-0.84	-1.14	-0.52	-0.03	0.1
Ze-1M $KOH/KMnO_4$	L*	33.92	31.09	31.24	26.17	26.28	24.59
	a*	13.22	7.22	7.72	2.07	4.94	3.65
	b*	-5.5	-0.3	0.15	-2.55	-2.55	4.25
Ze-2M $KOH/KMnO_4$	L*	34.07	29.88	30.93	29.74	30.42	34.5
	a*	7.8	3.32	3.74	1.78	1.46	0.89
	b*	0.29	-4.93	-1.31	-3.61	-0.59	-2.54
Ze-3M $KOH/KMnO_4$	L*	40.34	34.73	32.56	24.73	34.88	31.17
	a*	13.14	10.19	8.3	3.63	1.26	5.62
	b*	-3.63	0.15	0.45	1.65	-2.7	-0.24

At the beginning, the color of ethylene absorbers appeared in deep or light violet with the range from 32.19 to 40.34 for L*, 3.27 to 13.22 for a* and -6.16 to 3.14 for b* (Table 2). The color of ethylene absorbers from zeolite activated with 2M NaOH appeared in grey-brown color with the values of 37.89, 3.27 and 3.14 for L*, a* and b*, respectively. The color of ethylene absorber on control condition for all activated conditions changed to range from 37.04 to 48.35 of L*, -0.99 to -3.82 for a* and -9.32 to -0.30 for b* (Table 2). Essentially the average L* value increased while the color slightly changed during 5-day period.

In the cases of ethylene absorber stored with banana (Table 3), the average L*, a* and b* values of each ethylene absorber changed differently. After 5 days, the color of the ethylene absorbers changed to range from 24.59 to 35.54 for L*, 0.89 to 5.62 for a* and -2.54 to 3.31 for b*. Generally the average L* value decreased during 5-day period. The color appearance of ethylene absorbers changed from violet to brown by the oxidation reaction between $KMnO_4$ and ethylene to give brown solid of manganese dioxide (MnO_2) that would stick and sealed on the ethylene absorber, zeolite porous and $KMnO_4$ crystal surface, so ethylene gas could no longer be absorbed [12, 19]. It is highly undesirable since the effectiveness to reduce the ethylene gas from the storage atmosphere of the zeolite-$KMnO_4$ absorber are influenced by the remaining of $KMnO_4$, zeolite porosity and its surface area. In application, $KMnO_4$ could be more effective in solution form than in solid form. The $KMnO_4$ solution can still react with the ethylene gas as long as $KMnO_4$ remains in the solution, which may undergo a color change representing the remaining absorption capacity. The violet solution of $KMnO_4$ turned brown once the absorption rate was decreased [32].

3.4 Color Profile of Banana Peels

The average L*, a*, b* value and color image of banana peels before storage were shown in Table 4. The color of banana peel was still green from chlorophyll pigment on the mature age of banana fruit [6]. The average L*, a* and b* values of banana peels stored for 5 days with and without ethylene absorber and the images of banana peel color were shown in Table 5.

The physiology of banana ripening, changing of peel color, is involved with a breakdown of chlorophyll (green pigment) and a replacement by other yellow pigments such as carotenoid [5]. The peel color of bananas stored without ethylene absorber changed from deep green at the beginning (Table 4) to light green after 2 days and continuously changed to yellow after 3 days while the peel color of bananas stored with ethylene absorber from zeolite activated by 2M KOH, 3M KOH and 3M NaOH changed from green to yellow after 5 days. On the other hand, the peel color of bananas stored with absorber from non-activated zeolite and zeolite activated by 1M KOH and 2M NaOH changed from deep green to light green with increasing L* value. In contrast, the peel color of bananas stored with absorber from zeolite activated by 1M NaOH slightly changed from deep green to light green with insignificantly change of L* value. The relationship between color changing of fruit, ethylene gas releasing while ripening and storage duration have been reported in many studies [33-36]. In case of banana, the color of banana peel changes from green to yellow on ripening and the ethylene release during ripening reach its highest value within a day [23]. Reducing ethylene in the storage atmosphere by transforming into CO_2 and H_2O may delay the ripeness of bananas up to 3 days before banana peel starts to turn yellow.

Table 4. The average L*, a*, b* value and color image of banana peels before storage.

Color	value	Color
L*	59.91	
a*	-10.30	
b*	30.95	

Table 5. The average L*, a*, b* values and color image of banana peels.

	Color value	Day 1	Day 2	Day 3	Day 4	Day 5
Ze/$KMnO_4$	L*	59.84	67.92	63.45	63.8	64.67
	a*	-7.35	-8.3	-7.36	-6.48	-3.64
	b*	29.58	31.14	29.84	29.73	30.42
Ze-1M NaOH/$KMnO_4$	L*	64.48	63.68	63.51	61.9	62.22
	a*	-9.13	-6.7	-7.03	-6.84	-8.15
	b*	30.83	29	29.36	28.75	30.6
Ze-2M NaOH/$KMnO_4$	L*	62.72	66.24	62.76	63.4	64.15
	a*	-7.94	-7.69	-6.66	-5.77	-7.03
	b*	30.45	30.58	28.37	27.98	30.79
Ze-3M NaOH/$KMnO_4$	L*	62.38	64.88	65.3	64.9	69.54
	a*	-8.69	-8.14	-7.31	-7.99	0.14
	b*	30.67	30.74	28.98	31.05	33.94
Ze-1M KOH/$KMnO_4$	L*	64.43	69.55	65.77	64.89	69.27
	a*	-6.53	-7.97	-6.06	-4.8	-5.73
	b*	29.64	31.55	27.74	27.73	30.29
Ze-2M KOH/$KMnO_4$	L*	64.93	69.99	65.88	62.27	70.38
	a*	-8.81	-7.06	-2.37	0.6	1.58
	b*	31.34	34.21	31.97	31.81	37.18
Ze-3M KOH/$KMnO_4$	L*	62.37	64.67	66.03	63.95	70.2
	a*	-9.62	-8.7	-4.5	-6.42	0.68
	b*	31.24	31.59	33.21	29.48	36.74
Without absorber	L*	63.50	67.08	61.59	65.34	67.14
	a*	-7.85	-5.90	-3.17	-2.62	-1.24
	b*	31.17	34.66	31.68	34.36	34.43

3.5 Total Soluble Solid Contents

The total soluble solids, related to sugar content, of banana in degrees Brix (°Bx), measured by hand-held refractometer, is shown in Table 6. The sweetness of fruit depends on the ratio of total solid content to acidity. This indicator is commercially used to determine the quality of the fruits [37]. During the ripening process, bananas turn carbohydrate to sugar and thus bananas became sweeter [38].

Table 6. Total soluble solids content of bananas from difference storage conditions in degrees Brix (°Bx).

Days	0	1	2	3	4	5	6	7
Control	1.15	1.00	1.30	1.20	1.50	4.50	4.60	4.60
With absorber								
Ze/$KMnO_4$	1.15	0.90	1.00	0.80	3.20	1.80	1.80	3.80
Ze-1M KOH/$KMnO_4$	1.15	1.00	1.10	1.10	1.20	1.70	3.00	4.00
Ze-2M KOH/$KMnO_4$	1.15	0.90	1.20	0.80	1.00	1.80	2.50	4.00
Ze-3M KOH/$KMnO_4$	1.15	1.00	1.30	0.60	1.20	1.50	1.80	1.80
Ze-1M NaOH/$KMnO_4$	1.15	1.00	1.10	1.00	1.20	1.60	1.80	1.90
Ze-2M NaOH/$KMnO_4$	1.15	0.80	1.00	0.80	1.50	1.50	2.00	4.00
Ze-3M NaOH/$KMnO_4$	1.15	1.00	1.30	0.90	1.10	1.60	1.60	2.00

The degrees Brix of bananas stored without ethylene absorber (control) increased rapidly after 4 days and reached above 4.50 degrees Brix after 7 days. The bananas stored with ethylene absorber from non-activated zeolite and zeolite activated by 1M KOH, 2M KOH, 2M NaOH showed the increase in degrees Brix were start after 5 days and reach to 4.00 degree brix after 7 days while the bananas stored with ethylene absorber from zeolite activated by 1M NaOH, 3M NaOH, and 3M KOH slightly increased the sugar content reach up to only 1.50 after 7 days. The slowly increasing of total soluble solid content in banana represent to the retardation of banana ripening by ethylene absorber. Ripening of bananas is accompanied by the green pigment was replaced by yellow pigment and the banana peel start changed from green to yellow and the conversion of starch to sugars [39]. Climacteric fruit ripening is known to be controlled by the plant hormone ethylene. The slowly increasing in the accumulation of sugars, low starch consume rate, corresponding to the retardation of banana ripeness cause the ethylene insufficiency [4]. The oxidation reaction of $KMnO_4$ oxidizes ethylene gas released from bananas into storage atmosphere to CO_2 and H_2O.

3.6 Color Profile of $KMnO_4$ Solution

The change in absorbance shows the amount of sucrose, represents ethylene, which affects the color change of the KOH/$KMnO_4$ (Figure 6) and NaOH/ $KMnO_4$ (Figure 7) solution. From sucrose added into the KOH/$KMnO_4$ solution, the color changes from violet to blue-green and finally yellow. Observe the peak start in the wavelength range 500-580 nm. Peaks then gradually lower and move the peaks to another wavelength respectively. Show that color changes ultimately result in overlapping peaks in the wavelength range of 325-380 nm. In addition, the graph of the amount of sucrose that affects the color change of the NaOH/$KMnO_4$, the peak occurs in the wavelength range of potassium hydroxide. But the graph line is in disorder, there is overlap or it leaves the space at some wavelengths. Which corresponds to color changes of the solution and effect of difference counter-ion of K^+ and Na^+ that disturbed the MnO_4^- absorption has been observed [40]. When increasing of sucrose content up to 0.132 to 0.140 g, the constant of absorbance was observed. The color of the solution remains the same, or do not appear certain colors to be seen assigned to $KMnO_4$was completely reduced to MnO_2 by sucrose in solution. Moreover, the base-$KMnO_4$ solution can be reacted with ethylene, undergo a color that responds to the changing of oxidation state from Mn^{7+} of $KMnO_4$ (violet) to Mn^{4+} of MnO_2 (brown) complex in the solution [41].

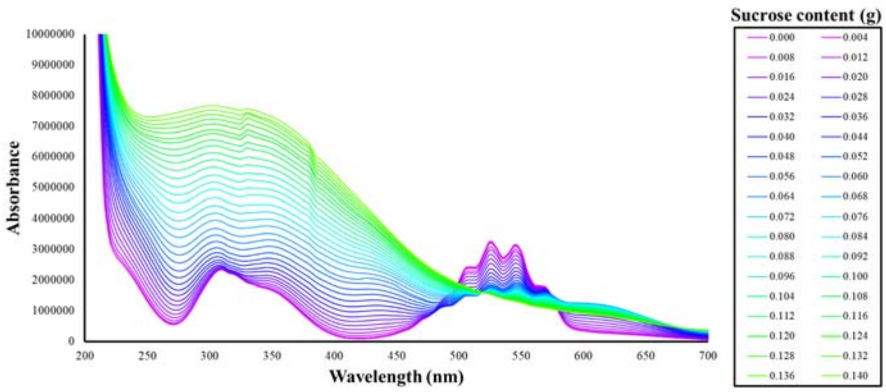

Figure 6. The absorbance of the KOH/$KMnO_4$ solution reduced by adding 0.1 mL of 4 w/v% sucrose solution each (0.00 to 0.140g of sucrose content).

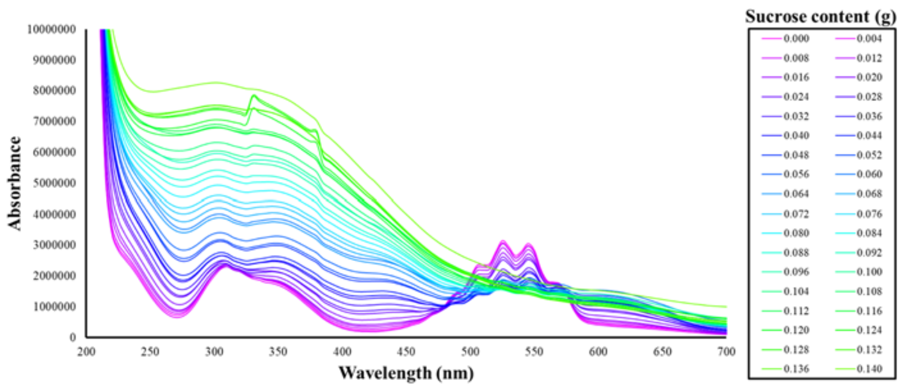

Figure 7. The absorbance of the NaOH/$KMnO_4$ solution reduced by adding 0.1 mL of 4 w/v% sucrose solution each (0.00 to 0.140 g of sucrose content).

4. Conclusions

After activated with base and soaked in the $KMnO_4$ solution, the zeolite particles were similar size and shape after cleaning the surface by base solution and packed with zeolite and $KMnO_4$ crystals. The color of control ethylene absorber stored without banana appeared in grey-blue on the first day and slightly changed during 5 days. The color appearance of ethylene absorber stored with banana changed from violet to brown ranging from 24.59 to 35.54 for L*, 0.89 to 5.62 for a* and -2.54 to 3.31 for b* by the oxidation reaction between $KMnO_4$ and ethylene. The peel color of bananas stored without ethylene absorber changed from deep green to yellow after 3 days (L*= 67.14, a*= -1.24, b*=34.43), while the peel color of the bananas stored with ethylene absorber changed from deep green to light green after 4 days (L* = 62.22 to 70.38, a*= -8.15 to 1.58, b*= 30.29 to 37.18). The sugar content in brix percentage of control banana increased rapidly after 4 days and reached the maximum sugar content after 5 days while the bananas stored with ethylene absorber from zeolite activated by 1M NaOH (1.90), 3M NaOH (2.00) and 3M KOH (1.80) had only slight increase in the sugar content during 7-day period. In case of $KMnO_4$ dissolved in the base solution, the color change of the solution can be seen by the naked eye, from purple to blue, green and finally yellow with increasing content of sucrose instead of ethylene.

The active packaged fruits presented higher acceptance, lower weight loss rate during the storage time and an extended shelf life, as compared to the control bananas. It is clear from these studies that ethylene absorber filters containing zeolite coated with potassium permanganate should be used in all climacteric fruit storage areas in order to ensure maximum shelf life at an affordable cost [12-18].

Acknowledgements

The authors gratefully acknowledge the financial support provided by Thammasat University Research Fund under the TU Innovative Scholar, Contact No. 5/2560 and the National Research Council of Thailand. We also acknowledge Department of Materials Technology and Textile and Department of Chemistry, Faculty of Science and Technology, Thammasat University.

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