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Effect of formaldehyde on some post-harvest qualities and shelf-life of selected fruits and vegetables

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Abstract

In Bangladesh, a lot of fruits and vegetables have been accused of having prolonged shelf-life by formaldehyde adulteration. So, an evaluation of the effect of formaldehyde was carried out by treating mango, litchi and oyster mushroom with different concentrations of formaldehyde and assessing their quality parameters. The three samples were dipped in 0%,1%, 5% and 10%formaldehyde solutions for 15 minutes and packed in a modified atmosphere package for observation. Changes in color, texture and weight loss were observed during storage at every alternate day. No significant increase in post-harvest quality and shelf-life was observed for mango and litchi treated with formaldehyde compared to control. Treated mushroom attained elastic texture and remained in this state up to the end of storage, whereas the control spoiled days after storage. Although formaldehyde-treated mushroom showed extended shelf-life, they lost their commercial freshness. The formaldehyde solutions did not have any significant effect on weight loss. So, formaldehyde is not a useful preservative to improve the post-harvest quality and shelf-life of fresh fruits and vegetables.

Introduction

Contamination and adulteration in foods have become an extreme situation in Bangladesh in the recent years. Numerous physical illness as well as deaths has been reported due to the consumption of adulterated foods (Ali, 2013a; Ali, 2013b). Various toxic chemicals and colorants are reported to use in foods to increase their stability, such as DDT (Dichloro Diphenyl Trichloroethane) in dried fish, textile colorants as a food coloring agent, urea fertilizer in puffed rice, which can cause cancer, reproductive problems, indigestions, allergies and other severe physical illness (Bhuiyan *et al*., 2008; Rahman & Alam, 1997; Khan, 2012a; Munim, 2011, Radomski, 1974; Khan 2012b). Weak regulatory controls, insufficient transportation facilities, increasing consumer demand, but inadequate storage and refrigeration conditions are resulting tendency of fraudulent of producers to increase the shelf life (UN, 2012). In Bangladesh and South-East Asian countries, there are reports that formalin, which is the 37-50% of an aqueous solution of formaldehyde (Kawamata & Kodera, 2004), is added to foods to increase its storage stability (Uddin *et al*., 2011). According to world health organization (WHO, 2006) and the Agency for Toxic Substances and Disease Registry (ATSDR, 1999), it is flammable, highly reactive and readily polymerized in gaseous form but stable over time in liquid form. Formaldehyde is mainly used in the production of wood products, papers, textile fibers, plastics, cosmetics, adhesives, nail hardeners, disinfectants, foaming insulators, etc. (WHO, 2006). It is recently classified as carcinogenic to humans (IARC, 2004).

The main route of exposure of this hazardous chemical is through the air (by occupational exposures, such as formaldehyde and resin production), dermal contact smoking (receiving about0.38 mg/day) and water (Mamun, 2014; Takahashi *et al*., 2007). According to some reports, formaldehyde can also be administrated in foods and drinking water naturally and artificially when used as a preservative (Restani *et al*., 1992; Tomkins *et al*., 1989). Formaldehyde accumulates in frozen food during storage and reacts with protein that causes protein denaturation and muscle toughness (Sotelo *et al*.,1995). Seafoods, crustaceans and fish proteins undergo biochemical and rheological changes due to high storage temperatures and prolonged storage time; these are reported to be due to the effect offormaldehyde produced from trim ethylamine oxide (TMAO) (Badii & Howel, 2003; Bianchi *et al*., 2007). In Bangladesh, producers as well as wholesalers are accused of adding formalin illegally to perishable fruits and vegetables, fishes and some other food products prolong their shelf-life. Tons of fruits have been destroyed in recent years based on the media reports to protect the consumers from taking the formalin-adulterated food, though there was no scientific evidence of the presence of formalin beyond the permitted level in those. Formaldehyde can naturally occur in various amounts:3-60 mg/kg in several fruits and vegetables,1 mg/kg in dairy product, 6-20 mg/kg in meat and fish and 1-100 mg/kg in shellfish(WHO, 2000). In Europe, the presence of formaldehyde is permitted to a maximum level of 25mg/kg as a breakdown product of hexamethylene tetramine in the production of cheese, and an amount up to 50mg/kg in gelling additives as a preservative (Wahed *et al*., 2016). The European Food Safety Authority (EFSA, 2014) has limited daily exposure to formaldehyde from food of both animal and plant origin to 100 mg/kg food per day. Dietary exposure is to be limited to about 11 mg/kg food per person per day on average (AFSSA, 2004). Though there are some reports of addition of formaldehyde in cheese, fish, milk and gelling additives, but other than the media reports, no scientific evidence is found till now that can scientifically prove the formalin addition to fruits and vegetables. As formaldehyde generally works on protein, it may not be effective on fruits and vegetables because they have a naturally lower amount of protein (Kiernan, 2000).

Based on aforementioned concerns of food adulteration in Bangladesh, this study was conducted to evaluate the effect of formaldehyde on post-harvest quality and shelf life of mango, litchi and mushroom (positive control). It is expected that the findings of the study will provide actual information to the consumers and researchers about the formalin adulteration rumors.

Materials and Methods

The effect of formaldehyde on quality and post-harvest shelf life of litchi, mango and oyster mushroom were studied under laboratory condition at the Department of Food Technology and Rural Industries, Bangladesh Agricultural University (BAU), Mymensingh. The experiment was carried out during September 2014 to May 2015.

Sample Selection:
Samples of litchi, mango and mushroom were used for treatment with formaldehyde. Matured uniform samples without any bruises and deformity were selected for treatment and common maturity parameters were observed in selecting maturity. The litchis were collected from the K.R. market at BAU, fresh mangoes were collected from BAU campus, and mushrooms were collected from the Horticulture Center adjacent to BAU campus. The samples were immediately transferred to the laboratory for performing the study. Formaldehyde solutions (37%), commonly known as formalin, and distilled water were used for the experiment.

Experimental Design:
The dipping method used for treating the samples in formaldehyde is a modified method of Brown and Dezman (1990). Four different concentrations of formaldehyde – 0%. 1%, 5% and 10% were prepared. Each solution of 1L was prepared in a 2L plastic containers. The containers with closed lids, were placed in laboratory under room temperature. Before soaking samples into the solution, the fruits and vegetables were cleaned carefully and delicately with clean and soft tissue paper so that the skin of the fruits and vegetable remain intact. All the samples were dipped in the prepared solutions for 15 minutes to allow formaldehyde enough time to penetrate the outer layer and reach inside the fruits and vegetable. Throughout the experiment same conditions (time, temperature and atmosphere) were maintained very carefully so that for all the three sample's physical appearances can compare with each other. After 15 minutes, the samples were taken out and dried at room temperature. The dried samples were packed into a modified packaging system with 1% perforated polyethylene bags. The bags were sealed mechanically. The samples that were kept without treatment were used as the control.

Evaluation of physical study

Shrinkage, freshness and change of color:
Visual observation on shrinkage, freshness and color changes were recorded. Observation was carried at an interval of 2 days except the first observation, which was assessed just on the next day. Samples were taken out of the package and the selected physical parameters were observed carefully. The type of twisting in the surface was taken as shrinkage of skin. Color changes were recorded by taking snaps with high resolution digital camera and freshness was assessed by comparing their appearance with the fresh samples.

Determination of Weight Loss:
Weight loss was measured as a reduction in weight of the treated samples. The weights of the treated samples treated were measured on an interval of one day. The weight loss was expressed in percentage. The samples of each treatment were individually weighed by using an electric balance and kept for observation. The percent total weight loss was calculated by using the following formula:

$$\%\ \text{Weight Loss} = \frac{\text{IW} - \text{FW}}{\text{IW}} \times 100$$

Where,

IW = initial weight of the samples, g
FW = final weight of samples, g

Statistical Analysis:
One-way analysis of variance (ANOVA), followed by t-test, was used to compare the difference between the means at 5% significance level. Data analysis was conducted by using statistical software IBM SPSS version 23.0 for Windows (SPSS, Inc., Chicago, II., USA).

Results

Effect of formaldehyde on postharvest quality of treated samples
No significant advantages on litchi (Table 1) in terms of physical changes were observed over the control after treated with various concentrations of formaldehyde. Rather, treated litchis went for faster deterioration. The higher the concentration of formaldehyde, the faster was

the deterioration of the color of litchis along with soft to glaireous in texture of flesh with increasing storage. Both the treated and untreated samples were found equally susceptible to microbial contamination during the last days of observation. Table 2 compares the physical changes of mango as influenced by formaldehyde treatment with different concentrations. The control samples were in acceptable condition during the entire storage time. The color of the treated samples deteriorated as the storage progressed. The color of the treated samples turned green to yellowish green with dark spots, and the texture grew soft into glaireous day by day. Microbial spoilage was observed in both the treated and untreated samples during the last days of observation. In fact, the pattern of physical changes of litichis and mangoes, due to the application of formaldehyde, was almost similar. In both the cases, the control samples remained better than the treated samples.

Table 3 presents the changes that occurred in mushroom treated with formaldehyde over the control sample. The color of the control sample became white to brown and acceptable up to two days of storage. The texture of the control sample became soft to glaireous. Significant changes in texture were observed in the treated samples over the control samples. The treated samples became elastic in texture and less brown in color with the increase in concentration of formaldehyde during the observation period. The changes in the treated samples versus control samples are clearly depicted in Plates 1-3.

Effect of formaldehyde on weight of the treated samples:

In case of litchi and mango, with varying concentration of formaldehyde, the change in mean weight loss was not significant (Table 4). But for mushroom at 5% formaldehyde concentration, mean weight loss differed significantly from the control. At 1% and 10% concentration, the mean weight loss differed in significantly. However, at 5% concentration, the difference in the mean weight loss of litchis, mango and mushroom was significant. But, varying results were obtained in control, 1% and 10% formaldehyde-treated samples, indicating that weight loss of fruits and vegetables is not dependent on formaldehyde application.

Table 1. Changes of physical parameters of formaldehyde treated Litchi

Strength of Formal-dehyde solution	*Observation*	Observation Period (Days) 0	1	3	5	7	Remarks
Control	***Color***	Greenish red	Greenish red	Not changed	Slight brown	Slight brown	Acceptable up to 2 days
	Texture	Soft	Not changed	Not changed	Dry peels	Dry peels	
1%	***Color***	Greenish red	Dark brown	Blackish	Black	Black	Not acceptable after treatment
	Texture	Soft	Soft	Glaireous	Glaireous	Glaireous	
5%	***Color***	Red with green hue	Brown	Brown	Dark brown	Dark brown	Not acceptable after treatment
	Texture	Soft	Soft	Soft & dry	Dry & soft	Dry & soft	
10%	***Color***	Red with green hue	Brown	Brown	Dark brown	Dark brown	Not acceptable aftertreatment
	Texture	Soft	Soft	Soft & dry	Dry & soft	Dry & soft	

Table 2. Changes of physical parameters of formaldehyde treated Mango

Strength of Formaldehyde solution	*Observation*	Observation Period (Days) 0	1	3	5	7	Remarks
Control	***Color***	Green	Not Changed	Not changed	Yellowish green	Yellowish Green	Acceptable
	Texture	Characteristic.	Not Changed	Slightly ripen	Ripen	Ripen	
1%	***Color***	Green	Green with black spots	Green with black spots	Yellowish green with black spots	Yellowish green with black spots	Not acceptable after treatment
	Texture	Characteristic.	Hard	Hard	Slight soft	Soft	
5%	***Color***	Green	Yellowish green with black spots	Yellowish green with black spots	Yellow with black spots	Burnt	Not acceptable after treatment
	Texture	Characteristic.	Hard	Slight soft	Soft	Glaerious	
10%	***Color***	Green	Yellow with black spots	Yellow with black spots	Burnt	Burnt	Not acceptable after treatment
	Texture	Characteristic.	Soft	Glaerious	Glaerious	Glaerious	

Table 3. Changes of physical parameters of formaldehyde treated Mushroom

Strength of Formaldehyde solution	*Observation*	Observation Period (Days) 0	1	3	5	7	Remarks
Control	Color	White	Not Changed	Brown Tint	Yellowish-brown	Brown	Acceptable up to 2 days
	Texture	Soft	Not Changed	Slightly glaireous	Glaireous	Slugde like appearance	
1%	Color	White	White	White	White with slight brown color in	White with light brown hue	Not acceptable after Treatment
	Texture	Soft	Elastic	Elastic	Elastic	Elastic	
5%	Color	White	White	White	White	White	Not acceptable after Treatment
	Texture	Soft	Elastic	Elastic	Elastic	Elastic	
10%	Color	White	White	White	White	White	Not acceptable after Treatment
	Texture	Soft	Elastic	Elastic	Elastic	Elastic	

Table 4. Mean weight loss of samples at different formaldehyde concentrations with standard error mean value

Samples	Formaldehyde concentration			
	0 %	1%	5%	10%
Litchi	5.21±2.42 (a)(A)	6.90±3.32 (a)(AB)	5.38±2.25(a)(A)	5.13±2.11(a)(A)
Mango	2.67±0.68(a)(A)	3.16±1.01(a)(A)	3.02±0.76(a)(A)	2.97±1.06(a)(A)
Mushroom	24.23±5.79(a)(B)	16.24±3.85(ab)(B)	8.63±2.48(b)(A)	13.77±3.63(ab)(B)

*Means in a same row with same small letter are not significantly different at 0.05% significance level. Means in same with same capital letter are not significantly different at 0.05% significance level.

Discussion

Several studies found that post-harvest quality of fruits and vegetables can be influenced by a large variety of pre-harvest and genetic factors (Weston & Barth, 1997). Generally, all phenomena (cutting, shock, loss of firmness) lead to the starting of physiological and biochemical mechanisms such as browning reactions, which induce losses or changes of flavor, odor and nutritional value (Toivonen & Brummell, 2008). During the whole storage period in our study, no significant advantages for any of the samples treated with various concentrations of formaldehyde were observed over the control. Rather, the treated litchis and mangoes went for faster deterioration. The higher the concentration of formaldehyde in the treated samples, the faster was the deterioration of color and texture. The texture of the samples, treated with higher concentration of formaldehyde, became soft just on the second day of storage. For litchi, the texture became dry and soft on the 3rd day for 5% and 10% formaldehyde-treated samples, while the samples treated with 1% formaldehyde became glaireous and the control sample remained unchanged up to 3rd day of storage. Note that the observation was continued only for 7 days because of spoilage of all treated samples. On the last day, all the samples treated with formaldehyde resulted in darker color on the skin with some fungal attacks on the peel, although formaldehyde itself is a fungicide. In case of weight loss, there was no significant changes in weight in the samples treated with formalin solutions. For litchi, 5% and 10% formaldehyde-treated samples had slower weight loss than the control and 1% formaldehyde-treated samples. Some studies, however, showed the opposite result for using chemical coating or growth hormone in increasing shelf-life of litchi (Sun *et al*., 2010). Especially, chitosan reduced weight loss by reducing water loss and acted as a defensive barrier against bacterial contamination to ensure a prolonged shelf-life (Hernández-Muñoz *et al*., 2008).

All the control samples were found still fresh compared to the formaldehyde-treated samples. Corrosive properties of formaldehyde, respiration and microbial attack might be the major reasons of faster color and texture deterioration of formaldehyde treated litchis compared to the control. The fluctuation of weight loss in litchi might happen due to the restriction of respiration of the treated samples and other chemical reactions within the samples.

For mango, the situation mostly similar. No significant changes were observed in the control. One day after the treatment, the control remained unchanged, whereas 1%, 5% and 10%formaldehyde-treated mangoes exhibited fresh texture, although color had changed slightly. On the 3rd day, the control remained unchanged, but the skin of 1%, 5% and 10% formaldehyde-treated mango turned into burnt color, and 5% and 10% formaldehyde-treated mangos were fully damaged. The skin became soft and flesh started to damage. Compared to control and 1% formaldehyde-treated mango, the condition of 5% and 10% formaldehyde-treated samples were too vulnerable, damaged and rotten. The skin became very dark, infected by microbes and the fleshes started to readily come out. At 7th day, the color of 5% and 10% formaldehyde-treated mangoes turned into completely burnt, and the texture became very glaireous. The control was completely ripened within this time. Although 1% formaldehyde-treated mango became soft in texture like the control, there were, however, black spots on the skin as shown in Plate 2. In mango samples, the control samples had a slightly slower rate of weight loss than the treated samples. But, there were no visible changes in weight loss pattern. Respiration, corrosive nature of formaldehyde and its reaction with the fruit components and microbial infection were the most possible causes of faster deterioration and stable weight loss pattern of mango.

Chitosan was proved to decrease the weight loss in mango by reducing the water loss (Chien *et al*., 2007). Combination of calcium chloride and gum arabic acid inhibited the decay incidence of mango. Treated fruits were delayed ripening and maintained overall quality. There were also other chemical agents, which helped to reduce the respiration rate, thus reducing the weight loss (Khaliq *et al*., 2016).

The case of mushroom was completely different from formaldehyde-treated litchi and mango samples. It is reported that the crude protein content of common mushroom is about 19–38 % (Braaksma & Schaap, 1996). On the 1stday of storage, the color of the control turned into light yellow, whereas the color of the other samples remained as fresh and did not show any sign of deterioration of color. With progressive storage, control went on further deterioration, and on day 3, this sample was spoiled. The samples treated with 1% formaldehyde also went on to slight color change and it was a yellowish tint on the stripe. The colors of the samples, treated with 5% and 10% formaldehyde, were found almost unchanged. As shown in Plate 3, the control samples became brown in color, completely damaged and there was a very unpleasant smell coming out of it. Though the samples treated with formaldehyde were not damaged but their texture became elastic and the characteristic fluffiness was completely vanished. So, these samples are also unacceptable for the consumers. As mushroom contains a significant amount of protein, fixation of formaldehyde with protein might be the cause of elastic texture. Browning and some other chemical reactions were the reason of development of unexpected brown color.

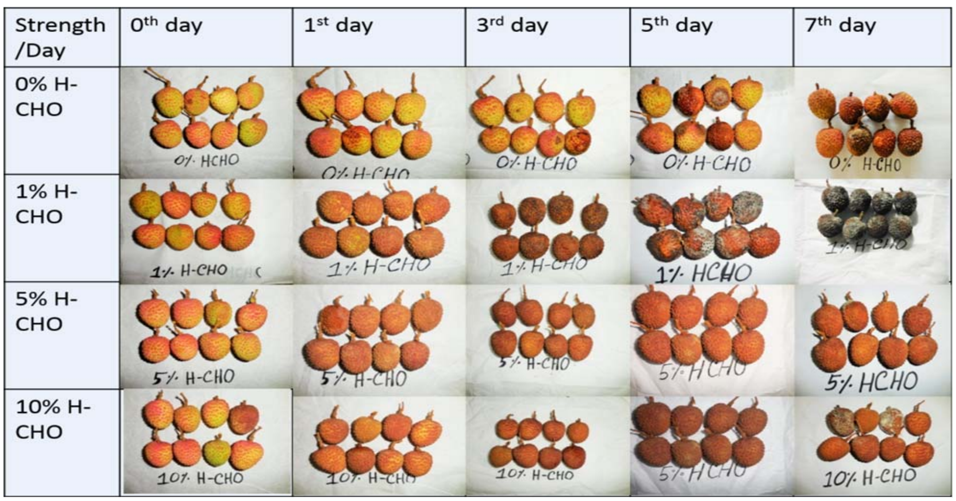

Plate 1. Effect of formaldehyde on storage quality of Litchi

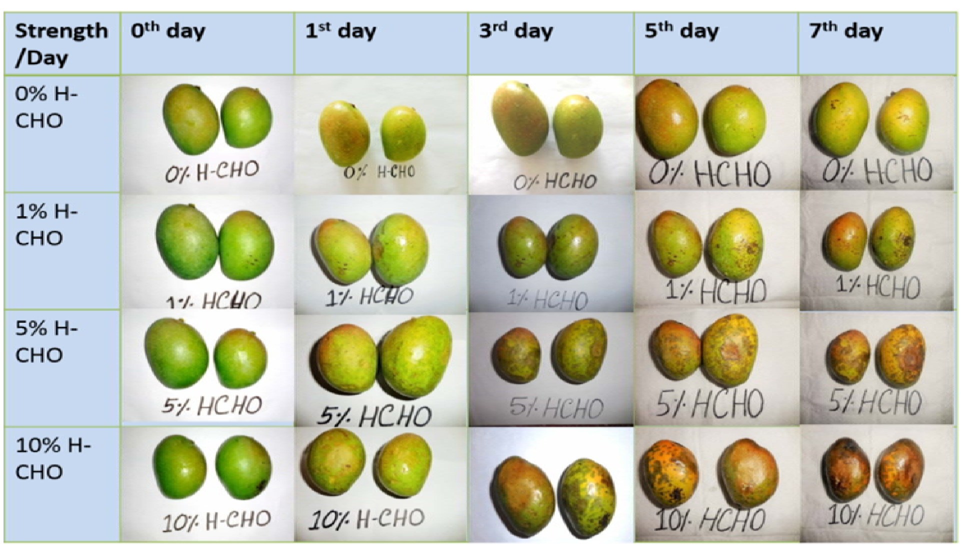

Plate 2. Effect of formaldehyde on storage quality of mango

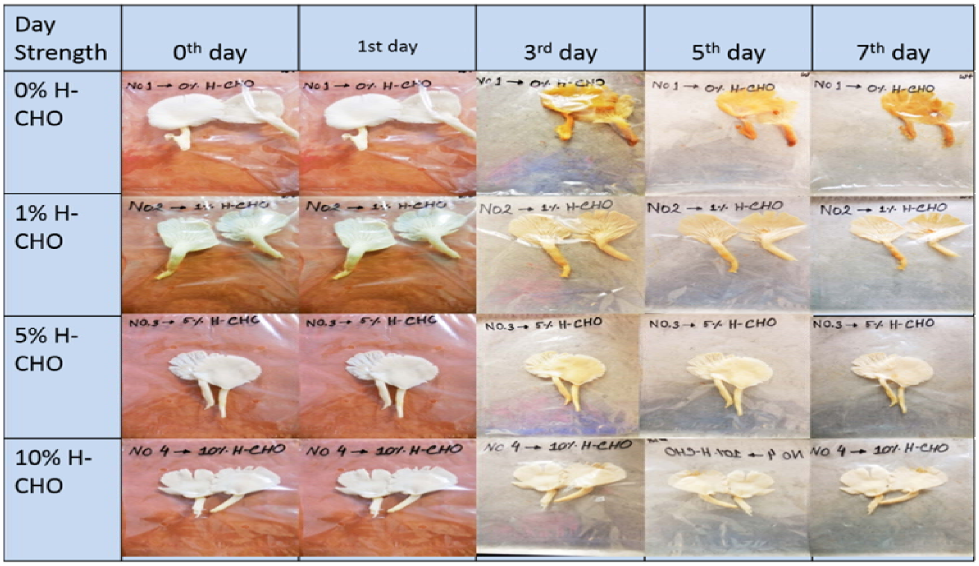

Plate 3. Effect of formaldehyde on storage quality of Mushroom

For mushroom, the result was quite different. The control sample lost weight faster than the treated samples. It is proved that formaldehyde is useful for rapid hardening of tissues as it creates fixation with protein or protenious substances (Puchtler & Meloan, 1985).The protein in the treated mushrooms reacted with formalin and made the outer layer rigid that can be justified with the basic mechanism of formaldehyde with proteins (Kiernan, 2000).

Limitations of this Study:

This study was done primarily to observe the effect of formaldehyde on fruits and vegetables. No quantitative study was performed to determine the amount of penetration of formalin to the samples. The study was done to be sure primarily that whether formalin is used in fruits and vegetables or not. Proximate analysis of the fresh and treated samples was not done to evaluate any difference in nutritional composition. No microbial study was done to identify the microbes that grew on the surface. This study solely focused on the physiological changes in fruits and vegetables after the addition of formalin.

Conclusion

No significant advantages were observed in formaldehyde-treated samples of litchi and mango over control with respect to shelf-life and quality during storage. Rather, the treated litchis and mangoes with elevated concentration of formaldehyde went for faster deterioration. The higher the concentration of formaldehyde in solution, the faster was the deterioration of color of litchis and mangoes. In case of mushroom, shelf-life increased with increasing formaldehyde concentration. There was no significant change in weight loss of the treated and untreated litchis and mangoes. So, it is concluded that formalin does not affect the weight loss. However, opposite phenomena was observed in case of mushroom. The weight loss of mushroom was relatively slow as formaldehyde binds with the protein in mushroom. The mushrooms were the indicator that shows that formalin only works on protein to increase the shelf-life. But, on fruits and vegetables, which mostly contain carbohydrates, formalin has no influence in increasing their shelf-life; rather it has a negative impact on their shelf-life. These findings are the opposite of the general perception of people of using formaldehyde in extending shelf-life of fruits and vegetables. For further research, the amount of penetration of formalin in fruits and vegetables, and the effect of formalin on the nutritional properties needs to be done in future research.

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