Assessment of the impact of formalin treatment on the quality and shelf life of mango

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Abstract: This study was conducted to observe the effect of formalin application on the post-harvest quality and shelf life of mango. Mango samples were treated with different concentrations of formalin solutions (10, 100 and 1000 mg/L) in two different modes (dipping and spraying) and stored for seven days at ambient condition. Physical characteristics, such as weight loss, color, texture and shrinkage and residual formalin content were observed at every alternate day during storage period. Formalin treatment (dipping and spraying) did not bring up any positive effect in increasing the shelf life of mango. Rather treated with higher concentration of formalin solution (10<100<1000 mg/L) caused internal and external deterioration which is explained in discussions section. Residual formalin content of mangoes for the both treatments decreased readily according to the treatment mode. The overall study indicates that the post-harvest quality and shelf life of mango could not be improved treating with any concentration of formalin either spraying or dipping mode. **Keywords:** Formalin; adulteration, post-harvest quality, shelf-life, mango

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1 Introduction

Mango (*Mangiferaindica* L.) belongs to the family Anacardiaceae and the most popular fruit around the world due to its excellent flavor, delicious taste and high nutritive value. It is also most preferable fruit in the sub-continent (Hussain et al., 2002). Nowadays, mango is established as a pre-eminent place among the fruit crops grown in Bangladesh (Sarker and Rahim, 2013) with 2.2% contribution to the total production (FAOSTAT, 2013). For being a popular fruit around the world, shelf life of mango is an important factor in case of processing, long distance transportation and marketing. Shelf life of mango can be extended by applying several methods including edible coating, controlled atmosphere (CA) storage system (Ravindra and Goswami, 2007) and ethanol application (Plotto et al., 2006). A rumor of using formalin to improve the shelf life of fruits or vegetables is a matter of concern in Bangladesh.

Typically, formalin is a colorless gas at room temperature (McNary and Jackson, 2007) and marketed as formalin in the form of aqueous solutions containing 37% H-CHO (w/w) in which 10%-12% methanol is added to suppress oxidation and polymerization. Formalin can be applied in many industries with the primary function of ceasing spoilage by microbial contamination (Norliana et al., 2009).

Formalin is used to preserve and maintain the freshness of fish and other seafood from pathogens while it causes cross linking of protein and produces rubbery texture, which is unable to decompose by microbes and other spoilage organisms (Bianchi et al., 2007). On the other hand, formalin is used as food additive in processing seafood, such as herring and caviar in some countries (Liteplo et al., 2002).

Chemistry of formalin indicates that it protects spoilage of only proteinous materials. Since most of the

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fruits and vegetables are low in protein content, treatment of fresh fruits and vegetables with formalin may not be effective in extending the shelf-life. Thus formalin always has the tendency to be stable by reacting with others. Such as if there is no protein to react with, and then formalin absorbs Carbon dioxide from air and be stable by forming other compound. In spite of having no proper scientific evidence about the effectiveness of formalin in extending shelf-life and quality of fresh fruits and vegetables, regulatory bodies in Bangladesh is used to carry out mobile court and destroy huge amount of seasonal fruits and vegetables claiming them contaminated with formalin. Keeping views above in mind, this study has been undertaken for the following objectives:

I. To assess the effectiveness of formalin in extending shelf-life and post-harvest quality of mango, and

II. To quantify the residual amount of formalin in treated mango samples.

2 Materials and methods

2.1 Sample collection and formalin treatment methods

Fresh and Matured mangoes (Amrapali) were collected from the Germplasm center, BAU, Mymensingh. Collected samples were sorted and cleaned very carefully for subjecting to different formalin concentrations (10, 100 and 1000 mg L^{-1}) for 15 minutes. Two different treatment methods, namely dipping and spraying were applied. Control and treated samples were stored in ambient condition and observed till seven days.

2.2 Parameters studied

2.2.1 Physical appearance

Some changes in physical parameters such as shrinkage, texture, freshness and color changes of treated samples compared to the control samples were recorded with an interval of two days.

2.2.2 Total weight loss

Weight loss of samples was measured according to the following formula:

% Weight loss = <u>Initial weight – Weight at the day of observation</u> <u>Initial weight</u> ×100

2.2.3 Internal color change

Internal color change of samples was measured in terms of a, b and L values using Chroma meter (CR-400/410, KONICA MINOLTA, Japan). h-value and C-value were further calculated by using the formula:

Hue angle, $h = \tan^{-(b/a)}$; Chroma, $C = \sqrt{(a^2 + b^2)}$

2.2.4 Residual formalin analysis

Formalin content in treated samples was measured with acetonitrile and derivatization with dinitrophenylhydrazine (DNPH) by high-performance liquid chromatography (HPLC) with ultra violet-diode array detection according to the modified method of Claeys et al. (2009). Residual formalin content (RFC) was measured by subtracting formalin content in treated sample from formalin content in control sample.

3 Results

3.1 Physical changes

The overview of physical changes of mango treated with different concentrations of formalin solutions with two different modes (dipping and spraying) observed for 7 days at ambient storage condition are shown in Figure 1 (a) and (b).

In both cases, the changes in external color of mango are clearly visible. Following the day 3, surface color of mangoes treated with 10, 100 and 1000 mg L^{-1} formalin solutions were started to turn away with visible dark spots. The color gradually became worse and shrinkage of skin was observed. The treated samples (both dipped and sprayed) were vulnerable, damaged and rotten after the five days of storage were occurred compared with control.

3.2 Total weight loss

The total weight loss of formalin treated (both dipped and sprayed) mangoes during storage at room temperature are shown in Figure 2 (a) and (b), the trend of weight loss for treated mango samples were quite different compared to the control sample.

For both treatment modes (dipping and spraying) the changes in weight loss were found almost same throughout the storage period. In case of formalin treated samples the weight loss trend was the same as control up to the third day of storage and right after the weight loss of treated samples started to decrease and came towards static up to the day three. For both treatment modes, the trends of weight loss dropped to a certain level on the fifth day and suddenly raised on the last day of observation. Weight loss drop observed on the fifth day on the sprayed samples were almost same for different formalin concentrations. On the other hand, the rate of weight loss in samples dipped in formalin was decreased with increasing the concentration of formalin.

3.3 Internal color (pulp color) change

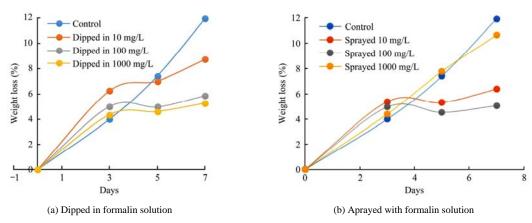
The internal color changes (Hunter color lab test) of mango samples treated with formalin stored in room temperature are illustrated in Figure 3 (a) and (b).

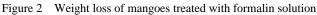
Concentrations	Days					
(mg/L)	Oth	3 rd	5 th	$7^{\rm th}$		
Control	control	eontrol	control	control		
	Samples	surples	Samples	Samples		
10	IO PPM	10-ppm	lo ppm	10 PFM		
	K-EHO Dipped	H-CKO Dipped	H-EHO Dipped	K- EKO Dipped		
	Samples	Samples	Samples	Samples		
100	Looppin	Icoppm	Icop pm	Icoppin		
	H-cHo Dipped	H-EHO Dipped	H-cho Dipped	H-CHO Dipped		
	Samples	Samples	Samples	Samples		
1000	IOOSPAT	1000 Ppm	1000 PPM	1000 Ppm		
	H-CHO Dipped	H-CHO Dipped	H-eHO Dipped	H-CHO Dipped		
	Stamples	Sumples	Samples	Samples		

(a) Dipped in formalin

Concentrations	Days					
(mg/L)	Oth	3 rd	5 th	7 th		
Control	control samples	control samples	eontrol Samples	eontrol samples		
10	ID PPM-Spray H-CHO Samples	IO PPM Sproy H-CHO Sample	IO PPM Sprot H-eHO Samples	LO PPM Sproy H-elio Samples		
100	H-CHO Samples	H-Sto Samples	IDO PPM Spray H-CHO Samples	looppm Spray H-CHO Samples		
1000	IDOO PPH Spray H-EHO Sumples	HIBO PPH Sport	LOGO PERS Spray H-EHO Samples	1000 ppm Spray H-CHO Samples		

(b) Sprayed with formalin Figure 1 External color change for mangoes dipped and sprayed with formalin





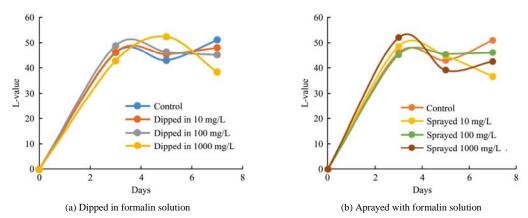


Figure 3 Changes in L-value of mango samples treated with formalin solution

Samples dipped in 1000 mg L⁻¹ formalin solution and sprayed with 10 mg L⁻¹ formalin solution showed unusual changes in L-value compared to control samples. Pulp color of samples dipped in 1000 mg L⁻¹ formalin solution grew lighter on the fifth day and suddenly grew darker on the last day. On the other hand, 10 mg L⁻¹ sprayed samples became darker throughout the storage. Change in L-values for other treatment concentrations (dipped and sprayed) was almost same in pattern. In both treatments pulp color became slightly darker on the fifth day of storage and became lighter on the seventh day.

The change in h-value (Hue angle) was also observed for all treated samples are presented in Table 1. For 10 mg L⁻¹ dipping treatment h-value raised suddenly on the mid of the observation and dropped slightly on the final observation. On the other hand, in 10 mg L⁻¹ sprayed samples h-value raised day by day. Samples treated with 100 and 1000 mg L⁻¹ concentration of formalin showed same type change for different treatment modes. The h-value increased on fifth day and dropped on the seventh day. In every case, the changes in h-value were within the range of red to yellow hue region (0°-90°).

Table 1	Change in h-value of different mango sample for
	different treatment modes

a 1	Treatment	Storage period (day)			
Sample	(mg L ⁻¹)	3 rd	5 th	7 th	
Control	0	51.18°	55.49°	61.34°	
	10	51.36°	61.16°	58.25°	
Dipped samples	100	57.29°	60.51°	62.17°	
I III	1000	51.39°	60.70°	57.30°	
	10	53.34°	63.24°	64.36°	
Sprayed samples	100	48.73°	60.27°	62.85°	
r	1000	52.16°	58.59°	54.48°	

Differences in C-values (Chroma) found in each treated sample are clearly shown in Table 2. For 10 mg L⁻¹ dipped sample, C-value decreased on the fifth day than the value found on the third day. In samples sprayed with 10 mg L⁻¹ formalin, C-value decreased with the proceeding storage. Samples treated with 100 mg L⁻¹ concentration C- value decreased day by day. C-value increased slightly during mid of the observation and suddenly dropped for the samples dipped in 1000 mg L⁻¹ formalin. On the other hand, 1000 mg L⁻¹ sprayed sample C- value decreased to a certain level on the fifth day and increased on the last day of storage.

G 1	Treatment concentration - (mg L ⁻¹)	Storage period (day)		
Sample		3 rd	5 th	7 th
Control	0	27.79	29.44	27.32
	10	33.45	29.25	31.16
Dipped samples	100	33.51	29.86	27.07
sampies	1000	30.66	32.29	17.16
	10 ppm	34.35	29.59	21.24
Sprayed samples	100 ppm	34.57	29.72	28.84
samples	1000 ppm	31.37	25.06	27.68

 Table 2
 Change in C-value of different mango sample for different treatment modes

3.4 Comparison of residual formalin concentration found in treated samples

The differences in residual formaldehyde content in each treated (dipped and sprayed) samples are clearly shown in Table 3. For both treatment mode with different concentrations of formalin solutions showed fluctuating results. Only 100 mg L^{-1} formalin treatment, residual formalin content decreased as the days proceed.

 Table 3
 Comparison of residual formalin content

Treatment Conc. (mg/L)	Residual H-CHO in dipped samples (mg L ⁻¹)		Residual H-CHO in sprayed samples (mg L ⁻¹)			
	3 rd Day	5 th Day	7 th Day	3 rd Day	5 th Day	7 th Day
10	0.91	0.90	0.89	0.88	0.93	0.89
100	1.38	1.20	1.06	0.99	0.98	0.97
1000	1.45	1.29	1.47	1.08	1.04	1.02

4 Discussion

Treated samples exhibited noticeable physical changes in their external color, skin condition and texture against the control samples shown in Figure 1 (a) and (b). Control samples were more stable than the treated ones and acceptable until the fifth day. High rate of respiration, enzymatic reactions and microbial infection could be the most possible causes of deterioration. Postharvest quality of fruits and vegetables can be influenced by a large variety of pre-harvest and genetic factors. Some studies revealed that pre-harvest stress reduce the postharvest quality of fruits (Calderon-Lopez et al., 2005; Galvis-S´anchez et al., 2004; Weston and Barth, 1997). In case of both treatment methods (dipping and spraying) samples became yellowish green to yellow with dark spots right after the treatment. Color grew darker and texture grew gloomier along with increasing Formalin concentrations. It may be caused by the reaction of formalin with organic matters on the mango surfaces that

produces extra pigment. The physical changes occurred in samples treated with both manners might be due to the presence of Formalin, respiration of fruit samples and microbial attack. Though Formalin acts as an antimicrobial agent, the cause of microbes in treated (dipped and sprayed) fruits was unknown. EPA Office of Pesticide Programs described Formalin as a fungicide and micro biocide (Anonymous, 2008).

In each treatment modes (dipping or spraying), the trend of weight loss decreased suddenly at the middle of the storage, and then increased on the last day of storage period shown in Figure 2 (a) and (b). While weight loss in the control samples increased gradually with the storage period. The weight loss stability trend indicated the freshness of the untreated sample and the fluctuation of weight loss happened due to the end of respiration of treated samples and other chemical reactions within the samples. However, storage temperature and relative humidity had significant effect on the weight loss of both control and treated samples.

Significant changes in internal pulp color in terms of L, h and C- values was measured by Hunter color Lab shown in Figure 3 (a) and (b) were assessed during the study. Unusual changes were observed in case of 1000 mg L⁻¹ dipped samples and 10 mg L⁻¹ sprayed samples. Pulp color became darker to lighter during the middle of the storage period and then suddenly became darker on 1000 mg L⁻¹dipped samples and 10 mg L⁻¹ spray treated samples. The unstable changes in color accrued due the respiratory reactions during the storage and the change in color contrast can also be changed with verity and individuality of the sample. In addition, similar changes in L-values of both samples were observed throughout the storage period.

10 mg L⁻¹ concentration showed different pattern for two different treatment modes where 100 and 1000 mg L⁻¹ concentrations showed same type of change for two different treatment modes within the specific hue region (0°-90°) (Table 1). The most probable cause of finding difference in hue region for 10 mg L⁻¹ formalin treatment was sample difference, as in each observation day an individual sample was examined and due to the level of microbial attack. Fluctuations in Chroma were observed in case of 10 and 1000 mg L⁻¹ Formalin treated samples for both treatment methods (Table 2). On the other hand, 100 mg L⁻¹ concentration showed decreased value of Chroma. The probable causes of increasing darkness might be due to raise in the solid content in the pulp and the cause of lightness might be possibly for destruction of the pigments of pulp due to action of corrosive Formalin on pigment compounds. The cause of fluctuation in Hue angle might be due to error occurred from replicated mango samples and decrease in Chroma possibly happen due to some physico-chemical changes within the fruit pulp.

Fruits and vegetables naturally produce formaldehyde where mango contains $1.22-3.08 \text{ mg } \text{L}^{-1}$ formaldehyde itself. The differences in residual Formalin content in each treated (dipped and sprayed) samples are clearly shown in Table 3. For each concentration and each treatment modes, the residual Formalin content decreased gradually except 10 mg L⁻¹ sprayed and 1000 mg L⁻¹ dipped samples. The amount of residual Formalin content was slightly higher in dipped samples than the sprayed ones. Residual amount of different chemicals such as pesticide or preservative generally depends on treatment modes. According to FAO (2013), mango dipped in fludioxonil at 52°C for a minimum of 30 seconds to a maximum of 5 minutes at the maximum rate of 34.5 g $h^{-1} L^{-1}$. Corresponding residues in pulp, in rank order were (n = 14): <0.01 (6), <0.02(4), 0.02, 0.04(2), and 0.09 $mg kg^{-1}$.

Again Bhattacherjee (2013) analyzed persistence behavior of imidacloprid and carbosulfan in mango through spraying mode. The initial residues of imidacloprid, after 30 days of spraying, were 1.21, 0.56 and 1.77 mg kg⁻¹ in peel, pulp and whole fruit, respectively. On the other hand, Carbosulfan residue in pulp was very low (0.08 mg kg-1) after 1 hr of spraying, which increased gradually to 0.90 mg kg⁻¹ after 10 days and finally came down to 0.04 mg kg⁻¹ after 26 days of spraying.

5 Conclusions

The effect of formalin either in any concentrations (10 , 100 and 1000 mg L^{-1}) or in mode of application

(dipping and spraying) has no significant advantages over control with respect to shelf life and quality during storage. Rather treated mangoes with elevated concentration of formalin went for faster deterioration in overall physical changes (external color, texture, shelf life etc.) and changes were all most same for dipped and sprayed samples. Some significant changes were observed in weight loss of treated (dipped and sprayed) mango samples over the untreated samples but those changes did not responsible for any makeable variation in shelf life of mango. The internal color (pulp color) changes of mango samples were easily visible throughout the study. Analyzing different color parameters differences were observed for each concentration treatment and two different treatment methods. The changes in pulp color clearly indicated the deterioration of mango during entire storage. Residual formalin content of treated mango sample was analyzed for both modes of treatments (dipping and spraying). Samples dipped in formalin contained more trace formalin than the sprayed ones. Some negligible variations were also observed. The residual content decreased as the storage proceeded and the condition of fruit became worse as well.

From analyzing the overall results of this experiment, it is concluded that formalin at any concentration and in mode of application had no effect in increasing the postharvest shelf life of mango used in this study. This finding is the opposite of the general perception of people of using formalin in extending shelf life of fruits and vegetables. Usually the shelf-life of mango is around seven days depending on storage conditions. Even, fresh mangoes are available in marketing channel with a range of five to seven days. However, further research with longer storage can be suggested to evaluate the physico-chemical changes in mango with formalin treatment. Finally, it is expected that the study will bring confidence of mango producers, traders and consumers against unscientific hearsay of contaminating mango with formalin to extend shelf-life and improve quality.

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