CHAPTER 5

RESULTS AND DISCUSSION: EFFECT OF WASHING ON REMOVAL OF PESTICIDES RESIDUE FROM DATE FRUITS

5.1 Introduction

The effect of washing treatments on the removal the three pesticidal residues (dimethoate, carbendazim and chlorpyrifos) in the date fruits were studied by using HPLC-DAD. The washing solutions were described in section 3.6.4.

The concentrations of pesticides residue decreased dramatically as washing duration increased when the fruits were treated with different washing solutions. There were also significant differences between all the treatments tested and control (unwashed sample) regarding their ability to remove pesticides within allocated times and temperature, as well as significant variations between most treatments when contact time was 2, 5, and 10 min.

5.2 Results and Discussion

5.2.1 Effect of Tap Water on Pesticides Residue Removal

The result of washing by soaking in tap water for 2 and 5 min at 25°C and 37°C is shown in Table 5.1. The tabulated values indicate that the washing duration and the temperature shows a significant effect in the water ability on removing the pesticide residue. furthermore, the type of pesticide also seemed to affect the % removal. Water washing showed the highest % removal of chlorpyrifos among of the group ranged from 18.22 % - 79.17 %, while dimethoate removal ranged from 10.89 - 44.42 %. However, carbendazim % removal was the lowest among the examined pesticides and ranged from 5.38 - 31.54 % compared with the control sample. The result also shows that there was a significant difference ($P< 0.05$) between the % removal at 25°C and 37 °C and between the % removal at washing durations of 2 and 5 min, indicated that temperature and time has a positive effect on pesticides' % removal. Temperature and pH can also affect the % removal of various pesticides from fruits and vegetables via enhancing the solubility and hydrolysis. When the water temperature rises, the solubility of pesticides in water increases resulting in more pesticide residue being removed. Hydrolysis increasing with temperature, and the acidity also strongly influences this process (Burchat et al.1998). It can be noted that the % removal of the pesticides by water washing in this study was greater than those reported by Abou-Arab (1999) and Cengiz et al., (2006) who reported pesticide reduction rates of 9 – 23 % compared to pesticide levels of control sample by washing fruits using tap water and that may refer to difference in the pesticides and the fruits being washed. The results also differed to those reported by Karol et al., (2000) who observed that soaking fruits and vegetables with tap water for 15–30 min achieved significant reductions in residue levels of pesticides namely, malathion, iprodione and other pesticides this may be referred to washing for longer duration and their high solubilities in water (1mg/mL and 12.2 mg/mL) respectively. But the results are close to the % removal of chlorpyrifos and dimethoate in cucumber reported by Liang et al., 2012 (62.9 % and 32.6 %) respectively, when washed by tap water for 10 min. The results also agree with that observed by Osman et al., 2014 who reported that washing date fruits with running tap water achieved 37.08 %, 42.46 %, 51.77 % and 51.93 % removal of chlorpyrifos in 5, 15, 30 and 60 min at room temperature, respectively. Washing rice grains with water, on the other hand, eliminated around 60% of the chlorpyrifos residues from the grains (Lee et al., 1991). Xia et al., (2016) reported removal rate for carbendazim above 70 %

from mushroom by rinsing under running tap water for 5 min and removing rate of 53.64 % by washing in tap water for 10 min. According to literature and the result of the present study it is clear that the effect of water washing on % removal of pesticides depends on pesticide types, washed matrix, temperature, and washing duration.

Table 5.1: Removal (%) of Pesticides in Dates by Washing with Water for Duration of 2 and 5 Min at 25 and 37°C

Tap water	**2 min**		**5 min**	
	25°C	**37°C**	**25°C**	**37°C**
Pesticide	Removal %	Removal %	Removal %	Removal %
Dimethoate	10.89 ± 1.23*	12.42 ± 0.78*	26.89 ± 1.23*	44.42 ± 2.78*
Carbendazim	5.38 ±0.4 *	14.14 ± 0.52*	14.38 ± 2.18*	31.54 ± 0.32*
Chlorpyrifos	18.22 ± 2.03*	24 .48 ± 2.84*	62.22 ± 2.03*	79.17 ± 2.53*

Note: Values with * are statistically different values ($p < 0.05$).

5.2.2 Effect of Dishwashing Detergent Solution on Pesticides Residue Removal

The effect of Detergent DWD (1% w/v) in removing three types of pesticides from date fruits through washing for duration of 5 min at 25 and 37°C was studied. The tabulated data in Table 5.2 showed that detergent solution achieved % removal of 91.23 ± 0.88 %, 19.28 ± 0.84 % and 68.97 ± 3.11 % for dimethoate, carbendazim and chlorpyrifos, respectively at 25°C. While at 37 °C the % removal was improved to 95.48 ± 2.32 %, 22.94 ± 0.35 % and 71.15 ± 6.9 % respectively, comparing with control sample. The effect of increasing the temperature from 25°C to 37°C did not show any significant difference ($P > 0.05$). This could be interpreted as due to the ability of detergent to dissolve waxes and therefore pesticides within epicuticolar waxes (Chung, 2018). However, due to their lipophilic properties, some pesticides cannot penetrate the fruit because of its polar composition. Similarly, Sheikh et al. (2012) reported that the solubility of pesticides in both tap water and detergent's solutions were a significant factor in soaking. Soaking with detergent solution improves the solubility and thus reduce pesticides residues.

Table 5.2: Removal (%) of Pesticides in Dates by Detergent (1%) Solution for 5 Mins at 25 and 37°C

Detergent 1% Solution	Temperature	
	25°C	**37°C**
Dimethoate	91.23± 0.88 ⁕	95.48 ± 2.32 ⁕
Carbendazim	19.28 ± 0.84 ⁕	22.94 ± 0.35 ⁕
Chlorpyriphos	68.97± 3.11 ⁕	71.15 ± 6.9 ⁕

Note: Values with (⁕) are significantly different (P<0.05)

5.2.3 Effect of Sodium Chloride Solutions on Pesticides Residue Removal

The effect of NaCl solutions on % removal of the pesticide's residue is shown in Table 5.3. Washing by 1 %, 2 % and 3 % (w/v) sodium chloride solutions in tap water at 25°C for time duration of 5 min, showed high % removal of dimethoate ranging from 97.75 % - 98.43 % and relatively low % removal of carbendazim ranged from 17.42 - 22.39 %. While chlorpyrifos % removal was ranged between 67.39 % - 68.35 %. The result of current study is in agreement with those reported in the literature regarding the efficiency of NaCl in removing the pesticide residues from fruits and vegetables. Kumar et al., (2000) reported that 91% and 67 % of cypermethrin residues were removed from green chili after dipping into 20 g/kg salt solution in duration of 10 min followed by washing in water. Similarly, Harinathareddy et al., (2014) found that % removal of pesticide residues in tomatoes after being soaked in 20 g/kg salt solution for 10 minutes were higher than that of samples washed with tap water. Furthermore, Liang et al., (2012) reported that sodium chloride 2 % and 5 % achieved dimethoate % removal of 41.3 %, 47.3 % and 50.0 % in washing duration of 5, 10 and 20 min respectively from cucumber while chlorpyrifos % removed was 53.1 %, 52.2 % and 66.7 % for same time intervals, respectively. The viscosity of NaCl saturated aqueous solution (1.93 mPa-s) and its pH may be increasing the ability of water in removing the pesticides. However, temperature and concentration both affect the kinematic viscosity of an aqueous NaCl solution. The kinematic viscosity of the NaCl solution decreases as the temperature of the solution rises. Alternatively, increasing the concentration of NaCl will result in an increase in viscosity (Akoulov & Wiens, 2018).

Table 5.3: Removal (%) of Pesticides in Dates by washing in Different Concentrations of NaCl for 5 Min at 25°C

Concentration (w/v)	**1 %**	**2 %**	**3 %**
Pesticide	**Pesticide % removal**		
Dimethoate	97.75±1.23 ⁎	98.1±1.15 ⁎	98.43±2.99 ⁎
Carbendazim	17.42 ±1.5 ⁎	22.39±1.64⁎	22.04±1.46 ⁎
Chlorpyriphos	68.35±1.56 ⁎	67.97 ± 1.20 ⁎	67.39±2.56 ⁎

Note: (⁎) Numbers in columns are significantly different values ($P<0.05$).

5.2.4 Effect of Sodium Bicarbonate Solutions on Pesticides Residue Removal

Effect of different concentrations, washing time and temperature of sodium bicarbonate ($NaHCO_3$) solutions on % removal of pesticide residues is shown in Table 5.4. High % of dimethoate, carbendazim and chlorpyrifos residues which ranged from 94.89 ± 0.73 % to 98.96 ± 0.012 %, 13.5 ± 5.6 % to 27.5 ± 8.06 % and 73.11 ± 0.95 to 100 % were removed. It was observed that increasing in temperature and concentration at 1 % and 2 %, $NaHCO_3$ exerted significant effect ($P<0.05$) on improving the removal of pesticide residues. While at of concentration 3%, the effect of solution concentration became the dominant factor so, the increasing of temperature and contact time did not show significant effect on % removal of pesticides' residues. By washing with $NaHCO_3$ 3 % solution, almost 100 % of chlorpyrifos was removed at all time intervals and no residue was detected in the filtrate. Although % removal of carbendazim were found to be the lowest among the group and not exceeding 27 %, increasing the concentration of $NaHCO_3$ solution from 1 %, 2 % and 3 % generally showed a positive effect on the %

removal of carbendazim. These findings agree with that revealed by Liang et al., (2012) who stated that both carbonate and bicarbonate solutions at concentration 2 % and 5 % (w/v), had contributed to the greatest loss in organophosphorus pesticides namely, chlorpyrifos as 75.3 %, 77.8 % and 81.5 % at 2-, 10- and 20-min soaking, respectively. In addition, the study concluded that the soaking with detergent solutions has also been shown to be more efficient than tap water. Pesticides that are normally stable at acidic pH can be hydrolyzed by the alkaline solution treatment. It is well known that sodium bicarbonate and sodium hydroxide solutions are effective at dissolving insecticides. Yang et al., (2017), reported 99 % reduction in thiabendazole and phosmet residues were removed from apples after 15 min treatment in sodium bicarbonate.

Table 5.4: Removal (%) of Dimethoate, Carbendazim, and Chlorpyrifos Pesticide by Sodium Bicarbonate Solutions at Different Concentrations (1 %, 2 % and 3 %), Temperature (25°C and 37°C), and Time Intervals of 2, 5, 10 minutes (Mean ± SD)

$NaHCO_3$ concentrations	**Removal %**		
	Dimethoate	**Carbendazim**	**Chlorpyrifos**
1 %, 2 min, 25 °C	94.89 ± 1.73	13.5±5.6	73.11± 0.9
1 %, 5 min, 25 °C	96.35 ± 0.50	15.9 ± 0.06	82.21± 8.40
1 %,10 min, 25 °C	97.88 ± 2.74	21± 6.41	87.48 ± 5.1
1 %, 2 min, 37 °C	95.90 ± 0.59	16.5±3.88	74.87 ± 1.11
1 %, 5 min, 37 °C	98.09 ± 3.88	18.5±1.79	83.32 ± 2.9
1 %, 10 min, 37 °C	98.31 ± 1.34	24.9 ±10.3	88.43 ± 3.69
2 %, 2 min, 25 °C	96.2 ± 2.28	17.2 ± 1.51	83.70 ± 4.45
2 %, 5 min, 25 °C	97.12 ± 0.51	21.8 ±1.07	86.02 ± 3.9
2 %, 10 min, 25 °C	98.13 ± 3.05	24.5 ±10.50	88.26 ± 3.44
2 %, 2 min, 37 °C	98.04 ± 5.16	18.6 ± 5.78	85.69 ± 3.64
2 %, 5 min, 37 °C	97.46 ± 0.95	23.6 ± 1.39	88.78 ± 0.66
2 %, 10 min, 37 °C	98.37 ± 1.25	23.8 ± 12.18	89.95 ± 0.78
3 %, 2 min, 25 °C	98.96 ± 0.012	21.5 ± 10.55	100
3 %, 5 min, 25 °C	98.38 ± 0.04	23.6 ± 8.12	100
3 %, 10 min, 25 °C	98.79 ± 3.23	25.3 ± 2.85	100
3 %, 2 min, 37 °C	98.67 ± 1.52	23.2 ± 10.64	100
3 %, 5 min, 37 °C	98.34 ± 2.45	25.4 ± 7.77	100
3 %, 10 min, 37 °C	98.44 ± 4.42	27.5 ± 8.06	100

5.2.5 Effect of Acetic Acid (AA) Solutions on Pesticides Residue Removal

The effect of acetic acid solutions on pesticides removal at different concentrations temperature and time intervals was studied. Result demonstrated in Table 5.5, showed that the % removal of the three pesticides were gradually and significantly ($P<0.05$) increasing according to solution concentration, temperature and washing duration. Dimethoate % removal was the highest and ranged from: 73.49 - 96.74 %, while the % removal of carbendazim was the lowest and ranged from 12.3 - 31.9 %. Chlorpyrifos % removal ranged from 75.88 - 97.25 %. Changing in solution concentration, temperature or contact time exerted a significant increasing in % removal of the examined pesticides ($P > 0.05$). The efficiency of acetic acid in removal of pesticides residues was previously reported by Radwan et al., (2005) who revealed that the residue of profenofos was completely removed from eggplant when soaked with 1% soap solution or 2 % acetic acid solution. Study conducted by Chai and Tan (2010), concluded that acetic acid was the most effective reagent in the removal of residues of the pesticides under investigation, with 44 –70 % removal of residues from the samples compared by 30–50% removal caused by sodium carbonate and 23–40 % removal caused by salt. Similarly, Osman et al., 2014 reported rinsing date fruits by 1% acetic acid solution at room temperature removed 81.12, 88.91, 91.93 and 98.42 % of chlorpyrifos residue at duration 5, 15, 30 and 60 min respectively, while rinsing at concentrations of 2 % acetic acid improved the efficiency of pesticide removal rates to 87.23 %, 93.36 %, 99.17 % and 99.5 % for the same time duration, respectively. As, residues of pesticides undergo hydrolysis in presence of water, the acidity and temperature are strongly influencing this process (Burchat et al.,1998) and that could explain the activity of acetic acid solutions in pesticide removal.

Table 5.5: Removal (%) of Dimethoate, Carbendazim, and Chlorpyrifos Pesticide by Acetic Acid Solutions at Different Concentrations (1 %, 2 % and 3 %), Temperature (25°C and 37°C), and Time Intervals of 2, 5, 10 minutes (Mean ± SD)

Acetic acid concentration	Removal %		
	Dimethoate	Carbendazim	Chlorpyrifos
1 %, 2 min, 25 °C	73.49 ±1.53	8.15 ± 0.33	75.88 ± 2.47
1 %, 5 min, 25 °C	81.89 ± 2.98	10.95 ± 1.35	78.03 ± 1.87
1 %, 10 min, 25 °C	85.15 ± 3.49	11.37 ± 1.36	80.93 ± 1.22
1 %, 2 min, 37 °C	86.74 ± 5.87	11.22 ± 0.46	85.63± 4.74
1 %, 5 min, 37 °C	86.29 ± 5.67	12.3 ± 2.35	79.85 ± 0.44
1 %, 10 min, 37 °C	88.98 ± 1.23	15.28 ± 0.56	82.68 ± 2.17
2 %, 2 min, 25 °C	83.85 ± 3.81	17.83 ± 2.59	83.09 ± 3.16
2 %, 5 min, 25 °C	86.21 ± 1.32	20.15 ± 3.50	86.82 ± 5.48
2 %, 10 min, 25 °C	91.33 ± 1.05	20.38 ± 5.43	87.87 ± 1.75
2 %, 2 min, 37 °C	92.23 ± 1.95	20.50 ± 7.91	86.25 ± 0.45
2 %, 5 min, 37 °C	91.01 ± 0.73	22.53 ± 7.42	87.13 ± 0.63
2 %, 10 min, 37 °C	93.57 ± 1.47	23.11 ± 3.78	88.54 ± 0.98
3 %, 2 min, 25 °C	94.94 ± 4.52	20.3 ± 7.45	88.72 ± 1.73
3 %, 5 min, 25 °C	95.14 ± 5.68	24.25 ± 4.30	89.63 ± 0.37
3 %, 10 min, 25 °C	96.42 ± 2.12	25.96 ± 7.57	91.48 ± 3.31
3 %, 2 min, 37 °C	96.45 ± 1.8	23.01 ± 9.7	92.53 ± 3.09
3 %, 5 min, 37 °C	96.28 ± 2.11	25.3 ± 6.10	94.45 ± 3.35
3 %, 10 min, 37 °C	96.74 ± 2.42	31.9 ± 1.27	97.25 ± 2.45

5.2.6 Effect of Hydrogen Peroxide Solutions on Pesticides Residue Removal

The effect Hydrogen peroxide (H_2O_2) solutions on pesticide residues removal is shown in Table 5.6. The behavior of pesticides with hydrogen peroxide differed from the pattern of the previous solutions. The results show that % removal of pesticide residues decreased with increasing temperature at fixed concentration of H_2O_2, and this may be explained by the nature of the exothermic oxidative activity of H_2O_2 as heat slow down the exothermic reaction and may reverse it. However, when both concentration and temperature are fixed, increasing the washing duration leads to a positive effect on the % removal of the pesticides. The highest % removal of dimethoate was 98.76 ± 3.01 achieved using 3 % H_2O_2, 10 min washing at 25°C. While the lowest

% removal was 95.97 ± 1.05 at 1% H_2O_2, 2 min washing at 37°C. The % removal rates of the other pesticides showed similar trend regarding the temperature effect. The highest % removal of carbendazim was 35.20 ± 3.73 when the H_2O_2 concentration was 1 %, at 25°C for duration of 2 min, while the lowest % removal was 21.68 ± 4.64 at 37°C in the same solution concentration (1 %) and washing duration of 10 min. The result indicates that the washing temperature is the most dominant factor on pesticide’s removal. Similarly, the lowest % removal for chlorpyrifos was 64.67 ± 5.75 when the H_2O_2 concentration was 1% at 25°C for 2 min soaking duration, while the maximum % removal was 84.0 2 ± 1.97 when the H_2O_2 concentration was 2 % at 25°C for washing duration of 10 min.

The result agrees with the findings of the study carried out by Osman et al., (2014) which reported that when the date fruits contaminated with 2 mg/L of chlorpyrifos solution and washed by 1 % H_2O_2 solution, the % removal of chlorpyrifos were 47.33, 73.79, 76.30 and 77.80 %, while at 2 % H_2O_2 solution achieved % chlorpyrifos removal of 59.82, 79.55, 81.56 and 84.13 % when the contact time was 5, 15, 30 and 60 minutes, respectively.

Table 5.6: Removal (%) of Dimethoate, Carbendazim, and Chlorpyrifos Pesticide by H_2O_2 Solutions at Different Concentrations (1 %, 2 % and 3 %), Temperature (25 and 37°C), and Time Intervals of 2, 5, 10 Minutes (Mean ± SD)

H_2O_2 concentrations	Removal %		
	Dimethoate	**Carbendazim**	**Chlorpyrifos**
1 %, 2 min, 25 °C	96.5 ± 1.05	23.34 ± 1.59	64.67 ± 5.75
1 %, 5 min, 25 °C	98.31 ± 1.11	29.88 ±1.45	75.46 ± 3.13
1 %, 10 min, 25 °C	98.45 ± 0.82	35.20 ± 3.73	82.55 ± 1.25
1 %, 2 min, 37 °C	95.97±1.26	21.68 ± 4.64	73.24 ± 0.49
1 %, 5 min, 37 °C	96.96 ± 0.61	30.16 ± 7.79	69.42 ± 2.51
1 %, 10 min, 37 °C	97.62 ± 0.45	32.55 ± 3.63	81.83 ± 3.31
2 %, 2 min, 25 °C	97.58 ± 0.45	25.41±1.06	76.39 ± 5.85
2 %, 5 min, 25 °C	97.68 ± 0.19	30.07± 1.70	77.6 ± 0.003
2 %, 10 min, 25 °C	98.39 ± 0.06	33.70 ± 6.61	84.0 2 ± 1.97
2 %, 2 min, 37 °C	96.42 ± 1.04	24.57 ± 1.63	75.82 ± 3.46
2 %, 5 min, 37 °C	97.19 ± 0.90	30.12 ± 1.38	72.45 ± 8.21
2 %, 10 min, 37 °C	97.2 3 ± 0.76	30.83 ± 1.02	78.61 ± 1.80
3 %, 2 min, 25 °C	96.83 ± 0.59	25.62 ± 0.75	77.27 ± 2.56
3 %, 5 min, 25 °C	97.05 ±0.32	28.91± 2.40	79.48 ± 0.18
3 %, 10 min, 25 °C	98.76 ± 3.01	31.07 ± 0.31	88.06 ± 3.15
3 %, 2 min, 37 °C	96.27 ± 3.49	23.39 ± 4.13	78.02±0.63
3 %, 5 min, 37 °C	92.9 7 ± 2.79	28.63 ± 3.89	75.03 ± 0.41
3 %, 10 min, 37 °C	94.5 ± 4.31	29.06 ± 3.77	86.05 ± 5.33

5.2.7 Effect of Potassium Permanganate Solutions on Pesticides Residue Removal

The effect potassium permanganate ($KMnO_4$) solutions on pesticide residues removal is shown in Table 5.7. The behavior of pesticides in potassium permanganate solutions was similar to that of hydrogen peroxide. Increasing in temperature when the concentration of the solution and the washing duration were constant, resulted in decreasing in the pesticides % removal. This may be explained by the exothermic nature of the oxidative activity of $KMnO_4$. But when the concentration and temperature are fixed, the washing duration exerted a positive effect on the rate of pesticides % removal. Percentage removal of dimethoate was ranged from 96.54 ± 1.06 % which was achieved when 1 % $KMnO_4$ at 25 °C for duration of 2 min to 98.75 ± 3.12 % which was achieved when 3 % $KMnO_4$ at 25 °C washing duration of 10 min. Percentage removal of carbendazim was ranged from 22.19 ± 5.78 % by 1% solution at 37 °C for duration of 5 min to 35.14 ± 2.19 % which was achieved by 3 % solution $KMnO_4$ at 37 °C for duration of 10 min. % of chlorpyrifos removal was ranged from 61.49 ± 1.49 % to 86.38 ± 4.49 % .The highest removal (86.38 ± 4.49 %) was achieved using 3 % solution at 25 °C for duration of 10 min.

The result revealed that the % removal of pesticides by soaking in $KMnO_4$ solution was increases with the concentration of $KMnO_4$ solution and soaking time while increasing the temperature from 25 °C to 37° C resulted in decreasing the % removal of the examined pesticides which may be attributed to the effect of the exothermic nature of $KMnO_4$ reaction with the pesticides.

The result of the present study agrees with those obtained by Osman et al., (2014) who reported that about 64 % of chlorpyrifos residue in date fruits was removed by soaking date fruits in 1 % $KMnO_4$ within 5 min and 70-75 % within 15-60 min while 2 % $KMnO_4$ removed 69-73 % within 15 min and 84 % within 30 - 60 min. In kinetic research done by Osman and colleagues (2014), it was reported that chlorpyrifos was more easily removed from date fruit after being treated with the various chemical solutions when compared to running water. Their findings demonstrated that the removal of chlorpyrifos increased in the following order: acetic acid > citric acid > hydrogen peroxide (H_2O_2) > potassium permanganate ($KMnO_4$) > running water, and that the percent of pesticide residue removed from date fruit depended on the concentration of tested chemical and the length of time the fruit was submerged in the solution. Furthermore, washing with water or soaking in salt solutions, as well as the use of certain chemicals (e.g., chlorine, chlorine oxide, ozone, H_2O_2, acetate, hydroxyl peracetic acid), have been shown to be quite effective in lowering pesticide levels (Bajwa and Sandhu. 2014). In the present study dimethoate removal rates is higher than that of chlorpyrifos that may refers to its solubility in water >1000 µg/L at 20°C while solubility of chlorpyrifos is < 10 µg/L which considered very poor. But the solubility rule is not working with carbendazim which have solubility 29 mg/L and showed the lowest removing rates with all examined chemicals (mostly <40%). The low % removal of carbendazim may attributed to being penetrating very fast to deep date's tissues and could not be removed within the applied washing time as it is systematic pesticide and readily mobile in plants (Croucher & Jewess, 2007. Based on this result, it is clear that the pesticide solubility is not always a dominant factor in pesticide removal but also the type of the pesticide and the matrix being treated. These findings agree with those observed by Angioni et al. (2004) who concluded that there was no relationship between the solubility of pesticides in water and their reduction rates after washing. The pesticide behavior varies not only depending on the pesticide applied, but also depending on the crop under research (Burchat et al.,1998). There is worry regarding the use of reagents with redox characteristics such as $KMnO_4$ and H_2O_2, which may change the chemical structure of selected pesticides, resulting in the production of a derivative that may be more dangerous than the original pesticide. When it comes to pesticide residue levels in fruits, such chemicals should not be utilized, unless necessary. Certain organophosphorus pesticides containing P = S bonds, such as chlorpyrifos, when they encounter oxidative reagents may produce their respective oxygen analogues, such as chlorpyrifos-oxone, which are more potent mammalian acetylcholinesterase inhibitors than the original parent pesticide (Amdur et al., 1991).

Osman et al., (2014) explored the formation of harmful by-products using either $KMnO_4$ or H_2O_2 as oxidative reagents by tracking m/z ions: 109, 197, 242, 270, and 298 for chlorpyrifos oxone, using gas chromatography (GC-MS). In the GC-MS chromatogram, only a single peak of RT 12.14 min belonged to chlorpyrifos, and no intermediate or dead-end product was found under the experimental conditions. Furthermore, no hazardous by-products such as chlorpyrifos-oxone, malaoxone, methidaoxone, or methyl paraoxone were detected in the washed sample extracts for the time duration and the concentrations used. There are numerous parameters that influence the action of oxidative reagents in the development of oxons, including the solvent, pH, pesticide identity, type of reagent and their concentration, reaction time, temperature, as well as the composition of the matrix used in the process (Pugliese et al., 2004). However, washing with oxidative reagents to minimize the amounts of pesticide residues or to achieve other technical advantages (delaying maturation) must therefore be used with caution, as derivatives can be developed under some conditions.

Table 5.7: Removal (%) of Dimethoate, Carbendazim, and Chlorpyrifos Pesticide by Potassium Permanganate Solutions At Different Concentrations (1 %, 2 % and 3 %), Temperature (25°C and 37°C), and Time Intervals of 2, 5, 10 Minutes (Mean ± SD)

Washing solution $KMnO_4$	Removal %		
	Dimethoate	**Carbendazim**	**Chlorpyrifos**
1 %, 2 min, 25 °C	96.54 ± 1.06	25.07±1.55	62.50 ± 3.63
1 %, 5 min, 25 °C	98.30 ± 1.1	26.32 ± 4.53	73.5 ± 2.12
1 %, 10 min, 25 °C	98.44 ± 0.82	29.49 ± 4.11	81.57 ± 1.51
1 %, 2 min, 37°C	96.95 ± 1.27	22.19 ± 5.78	61.49 ± 1.49
1 %, 5 min, 37 °C	96.94 ± 2.61	24.17 ± 3.59	67.51± 2.51
1 %, 10 min, 37 °C	97.61 ± 0.45	27.95 ±1.11	79.85 ± 3.60
2 %, 2 min, 25°C	97.56± 5.46	27.09 ± 1.04	75.42 ± 3.35
2 %, 5 min, 25°C	97.67± 0.19	28.07 ±1.93	77.84 ± 1.33
2 %, 10 min, 25°C	98.38 ± 1.6	32.19 ± 0.07	82.3 ± 2.31
2 %, 2 min, 37°C	96.41±1.05	26.28 ±1.59	73.97 ± 3.53
2 %, 5 min, 37 °C	97.18 ± 0.91	27.53 ± 0.59	71.63 ± 7.47
2 %,10 min, 37°C	97.2 ± 0.77	35.14 ± 2.19	76.8 ± 2.46
3 %, 2 min, 25 °C	96.82 ± 4.60	27.30 ± 0.73	75.29 ± 2.6
3 %, 5 min, 25 °C	97.03 ± 1.34	29.60 ±1.06	77.50 ± 2.24
3 %, 10 min, 25°C	98.75 ± 3.12	30.12 ± 1.19	86.38 ± 4.49
3 %, 2 min, 37 °C	96.25 ± 3.5	25.12± 4.03	75.94 ±1.63
3 %, 5 min, 37 °C	97.44 ± 3.80	25.91± 5.23	73.06 ± 2.4
3 %, 10 min, 37 °C	97.50 ± 2.31	28.16 ± 3.69	84.42 ± 5.32

5.3 Conclusion

The results of this study revealed that the removal of dimethoate and chlorpyrifos from date fruits is dependent on the concentrations of tested chemical solutions, temperature, and contact times. The efficiency of solution seems to be in order $NaHCO_3$ >acetic acid > NaCl > detergent > H_2O_2 >$KMnO_4$ > tap water. In case of H_2O_2 and $KMnO_4$ the temperature showed a negative effect on pesticides removal rates which may attributed to the exothermic nature of those oxidizing agents. The obtained results agree with the findings of Abou-Arab (1999), who revealed that the loss of HCB, lindane, p, p'-DDT, dimethoate, profenofos, and pirimiphos-methyl is dependent on the concentrations of acetic acid and NaCl. Furthermore, the amount of pesticide removed by washings is proportional to its water solubility and the octanol–water partition coefficient (Pugliese et al., 2004), with the exception of carbendazim behavior in this study, which showed a lower removal rate and less effect when the optimization factors (concentration, contact time, and temperature) were changed, which may be due to carbendazim's ability to penetrate through date fruit tissues. This phenomenon should be investigated in future study.