Production of date palm fruits free of acaricides residues by ozone technology as post-harvest treatment

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Abstract Distilled water and ozonated water as postharvest wash treatments for 15–60 min as dipping times were tested to remove two acaricides namely, dicofol and amitraz from different varieties of date fruits. Recovered amount of the acaricides was extracted using solid phase extraction (SPE) and then analyzed by gas chromatography–mass spectrometry (GC-MS). Dicofol removal percentages in the presence of ozone increased in the order of Nabtet Aly>Nabout Seif>Khalas>Sakay, while amitraz removal increased in the order of Nabtet Aly>Nabout Seif>Sakay>Khalas, respectively, and the percentages of residues on date fruits depended on the dipping time. Kinetic studies revealed that dicofol and amitraz were easily removable from date fruits treated with ozonated water. Ozone-treated date palm fruits were not associated with significant changes in antioxidant capacity, and phenolic and sugar contents. Due to the large amount of dates consumed by Saudi residents, a higher risk of exposure to pesticides, especially in children and other vulnerable individuals may occur and the search for safety methods to remove pesticides with negligible residual deposits has always been preferred. Therefore, the present study validated that ozone technology as wash treatments is safe and promising processes for the removal of acaricides from date fruits surface under domestic conditions to reduce the impact over consumer's health.

Keywords Acaricides · Date fruit · Ozone · Antioxidant capacity

Introduction

Pesticides are used globally for the protection of food, fiber, human health and comfort (Schreinemachers and Tipraqsa 2012). However, their excessive use/misuse especially in the developing countries, their volatility, long-distance transports eventually results in widespread environmental contamination. In addition non-patented, more toxic, environmentally persistent and inexpensive chemicals are used extensively in developing nations, creating serious acute health problems and global environmental impacts (Ecobichon 2001). Further while remarkable progress has been made in the development of effective pesticides, the fact remains that a very small fraction of all applied pesticides is directly involved in the pesticidal mechanism. This implies that most of the applied pesticides find their way as ‘residue’ in the environment into the terrestrial and aquatic food chains where they undergo concentration and exert potential, long term, adverse health effects (Ekström et al. 1996; Osman and Al-Rehiayan 2003; Osman 2011; Schreinemachers and Tipraqsa 2012).

Residue of organochlorine pesticides in the environment is still a world-wide problem although the use of chlorinated hydrocarbon insecticides has been sharply curtailed or banned, but they are still the active ingredients of some pest control products (Moore 1986). Dicofol (DCF) is an organochlorine pesticide, used world-wide as a pre-harvest non-systemic miticide on cotton, citrus, vegetable, nuts, date palm and other crops (Mourer et al. 1990; Tomlin 2002; Kitajama et al. 2003; Al-Rehiayani and Osman 2003). DCF is structurally similar to DDT, which is used as the starting material for synthesis for DCF (Wiemeyer et al. 2001) and more easily degradable than DDT and other organochlorine insecticides showing the lowest accumulation hazard (Van Dijck and Van De Voorde 1976). Indeed, the trichloromethyl group of DCF is extraordinary susceptible to carbon-carbon bond cleavage to

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form 4,4'-dichlorobenzophenone (Van Dijck and Van De Voorde 1976; Walsh and Hites 1979). The US-EPA became concerned about the continued use products containing DCF because they also contained DDT and related compounds (Moore 1986).

Amitraz (AMZ) is a formamidine insecticide and acaricide used primarily to control pear psylla, whiteflies and mites on cotton, pears, apples, fruits and date palm (Environmental Protection Agency EPA 1996; Tomlin 2002; Al-Rehiyani and Osman 2003), livestock ticks, lice, and mange mites on beef and dairy products (Queiroz-Neto et al. 1994; Yaramis et al. 2000) and currently employed by beekeepers in Europe to control *Varroa jacoboni* in hives (Martel, and Zeggane 2002).

AMZ is unstable under moist conditions (The Royal Society of Chemistry 1988) with $t_{1/2}$ disappearance of 18.9 days in date fruits (Al-Rehiyani and Osman 2003) and 95 % of it is degraded within a relatively short time (FAO/WHO 1985; Kamel et al. 2007). Amitraz degraded to 95 % on date palm after 21 days of application (Kamel et al. 2007). With a 14-day interval between the last application and harvest of citrus fruits, most residue levels of AMZ were less than the temporary MRL for oranges of 0.5 mg/kg, even at the relatively high rates of use (FAO/WHO 1985), while MRL for amitraz in pears is 0.05 mg/kg in the EU (European Commission EC 2008). The maximum residue limit (MRL) definition is “the sum of amitraz plus all its metabolites containing the 2,4-aniline moiety (Kamel et al. 2007; Codex 2008; European Commission EC 2008) and the analysis of all metabolites containing this structure is advisable. It was found that the metabolite 2,4-dimethylaniline (DMA) is the mutagenic, oncogenic and genotoxic stable end-point of amitraz degradation (Ulukaya et al. 2001). AMZ has been shown to produce side effects and toxicity in several animal species by targeting α 2-adrenergic receptors, produces effects similar to that produced by a pure α 2-adrenergic agonist drugs such as clonidine (Costa et al. 1988; Jorens et al. 1997), inhibits monoamine oxidase (MAO) enzyme (Moser and Macphail 1988), increases blood glucose and decreases insulin secretion (Gupta RC 2007). Therefore, AMZ was restricted as a pesticide in 1985 but re-evaluation of the evidence has led to the classification of it as an unrestricted or a general use pesticide (Gupta RC 2007).

Food safety is an area of growing worldwide concern on account of its direct bearing on human health. The presence of harmful pesticide residues in food has caused a great concern among the consumers and the removal of residues present in vegetables and fruit can be achieved many chemical procedures. These technologies utilize powerful oxidizing intermediates (mainly OH radicals) to oxidize organic pollutants, leading not only to their destruction, but also, given sufficient conditions, to their complete mineralization. The OH radicals can be generated, for example, by the application of O_3/H_2O_2 , ultraviolet radiation/ozone, ultraviolet radiation/hydrogen

peroxide, ozone/electron beam (Legrini et al. 1993). Several of them are currently employed for the elimination of pesticides, as the combinations O_3/H_2O_2 (Meijers et al. 1995), O_3/UV (Kuo 1999), photo-Fenton system (Walling 1975; Doong and Chang 1998; Gallard and De Laat 2001; Wang and Lemley 2002), UV (Benitez et al. 2002), UV/H_2O_2 (Wu and Linden 2008), biotreatment (Liu et al. 2004), titanium dioxide catalytic treatment (Kouloumbos et al. 2003), powdered activated carbon filtration and reverse osmosis (Heijman and Hopman 1999), O_3 (Masten and Davies 1994), microwave irradiation (Zhang et al. 2007a, b) and electrochemical oxidation processes (Brillas et al. 2000). Hence, the use of such simple and non-toxic washing treatments to reduce such residues in fruit samples can facilitate the commercialization and reduce the impact over the consumer health (Krol et al. 2000; Osman et al. 2012). The solutions for washing fruits must be of low toxicity and easily biodegradable in order to allow their use at home and at processing-food industries.

O_3 is a triatomic form of oxygen and is referred to as activated oxygen, allotropic oxygen or pure air and considered as a powerful oxidant. It has a pungent, characteristic odor described as similar to “fresh air after a thunderstorm” (Coke 1993). It is an unstable gas and the half-life of ozone in distilled water at 20 °C is about 20–30 min and degrades in pure water rather quickly to oxygen, and even more rapidly in impure solution (Hill and Rice 1982), while it has a long half-life in the gaseous state (Rice 1986). Thus, it does not accumulate substantially without continual ozone generator (Peleg 1976). These attributes make O_3 an attractive candidate for controlling insects and fungi in stored products and prolong the storage life of fruits by controlling decay fungi (Karaca et al. 2012) as well as approved for use as a disinfectant or sanitizer in foods and food processing in the United States (USDA 1997; Beuchat 1998; Anonymous 2001; Palou et al. 2002; Guzel-Seydim et al. 2004; Lafi and Al-Qodah 2006; Karaca et al. 2012) and to increase shelf-life of the products (Beuchat 1998; Guzel-Seydim et al. 2004). Antioxidant compounds play a significant role in the detoxification process that results from the formation of different reactive oxygen species (ROS), such as H_2O_2 , superoxide radicals (O_2^-), and hydroxyl radicals ($OH^\bullet$) inside the plant cell (Moldaem 1966). When O_3 enters plant tissue, it may induce oxidative stress in fresh fruit resulting in various physiological responses, including synthesis of antioxidants, polyamines, ethylene, phenolic compounds, and other secondary metabolites (Fomey 2003) and the quality of fruits is affected.

Date palms (*Phoenix dactylifera* L.) are a staple food in the diet of many countries and are considered as the major fruit of the Near East and North Africa where they are consumed in large quantities fresh, dried, or in various processed forms since they are rich in carbohydrate (mainly glucose, fructose and a small amount of sucrose), protein and minerals (Considine 1982; Al-Showiman and Fayadh 1990). Date

fruits serve as a good source of sugar (70–80 %), natural antioxidants such as phenolic compounds (Al-Farsi et al. 2007) which contribute significantly to total antioxidant activity and have many beneficial effects for human health (Besbes et al. 2009), tannins and ascorbic acid (Kulkarni et al. 2010). In the Kingdom of Saudi Arabia (KSA), dates are one of the most important crops because of their religious and nutritional significance. KSA is considered one of the largest date producer in the world, with production amounting to 970,488 tones per year and the number of date palm trees is over 18 million (Anonymous 2004). As a result of its high economic value as well as the large number of pests that infest dates during growth, significant quantities of pesticides are often necessary for the protection of this crop. DCF and AMZ are registered by the Ministry of Agriculture to control mites, which infest dates and causes severe damage and applied at a rate of 200 ml/100 L (Al-Rehiyani and Osman 2003, 2005). This leads to the presence of residues on (or in) the fruits at harvest and there is increasing concern by consumers about these residues in date fruits and their carryover in its products. Unfortunately, no data are available on DCF or AMZ removal from date fruits and the search for means to improve the production of dates in KSA is always the target of consumers, scientists, politicians and businessmen, who seek new techniques to enhance the quality and safety of this product. Therefore, the present study was carried out to evaluate the effectiveness of ozone (O_3) as a new technology for different contact times as simple wash treatments for removal of DCF and AMZ residues from different varieties of date fruits namely Khalas, Sakay, Nabout Seif and Nabtet Aly, the most preferred date varieties grown in Al-Qassim region, KSA. In relation to the importance of antioxidant compounds in date fruits, the objectives of this research were also to study the effect of these wash treatments on fruit quality parameters such antioxidant capacity (AC), total phenolic contents (TP) and total sugars in dates.

Materials and methods

Chemicals Technical grade standards of dicofol, DCF, (98 %) (4-chloro- α -(4-chlorophenyl)- α -(trichloromethyl) benzenemethanol) and amitraz, AMZ, (98.5 %) (*N*'-(2,4-dimethylphenyl)-*N*-[[[(2,4-dimethylphenyl) imino] methyl]-*N*-methylmethanimidamide) were obtained from Environmental Protection Agency (EPA, USA) and Chem Service (West Chester, PA, USA), respectively. Certified HPLC-grade of acetone, methanol, acetonitrile and toluene were purchased from BDH Company, while the Water spe-20G Column Processor designed vacuum manifold capable of processing up to 20 solid phase extraction (SPE) columns and SPE columns (Waters speTM, C18, 500 mg per column) were purchased from Waters, USA. Ultra-pure deionized water of

15 M Ω cm resistivity was obtained from a water purification system (PURELAB Option-R, ELGA, UK) and used throughout this study. Glucose, Gallic acid and 1,1-diphenyl-2-picryl [hydrazil (DPPH) were obtained from Sigma Co, while, Trolox and Folin-Ciocalteus reagent (2 N) were obtained from Aldrich and Merck, respectively. All other chemicals used in this study were of the highest grade available.

Date fruits treatment Different varieties of date fruits (*Phoenix dactylifera* L.) namely Khalas, Sakay, Nabout Seif and Nabtet Aly were obtained from organic farming without the use of pesticides located in Al-Qassim region, KSA. They were harvested in September 2011 at tamer stages and untreated post-harvesting. Tamer samples (fully ripe date fruits, about 25 weeks after pollination) were collected randomly with no preference to size, color, appearance or firmness and then divided into equal size (1 kg each). DCF or AMZ was dissolved in acetone and then mixed with 4 l of distilled water (DW) to give a concentration of 2 mg/l. Fresh and unblemished pesticide-free fruits were immersed into pesticide solution for 2 min with gentle rotation by hand. Date samples with pesticide on the surface were then air-dried at static air for about 24 h at 25 ± 1 °C.

Ozone generation Ozone gas (100 ppm at air flow rate of 2.5 L/min with ozone output of 300 mg/h) was produced by a laboratory corona discharge ozone generator (Xetin Ozone Air & Water purifier, Model XT 301, Xetin Co. Ltd, Taiwan). The ozone generator was warmed up for 15 min before the experiment was conducted. The concentrations of dissolved ozone were measured using a portable ozone detector (DO3, Echo Sensors Inc., USA) in the range between 0 and 10 ppm with the accuracy of 0.01.

Removal of Residual Pesticide from Date Fruits Removal of DCF and AMZ from date fruits was studied by immersing in either DW having pH of 7.0 or 2 mg/L of ozone dissolved in DW (OZW) in polypropylene reactor provided with a heater to keep a temperature at 25 ± 0.1 °C and under magnetic stirring for 15, 30, 45 and 60 min. The pH was adjusted to 7 by using orthophosphoric acid and sodium hydroxide. Triplicate random date samples spiked with the tested pesticides were divided into the following treatment groups: control (no wash); rinsing in DW and ODW for 15, 30, 45 and 60 min. The duration of dissolved ozone levels was controlled via adjusting the duration of bubbling. Excessive gaseous ozone was trapped in 2 % potassium iodide solution.

Sample preparation and solid-phase extraction Fruits were chopped and a subsample (10 g) was weighed into 50 ml glass tube and extracted with 20 ml acetonitrile using a homogenizer (Euroturax, IKA Labortechnik Staufen, Germany) at full speed for 5 min. After addition of 10 g sodium chloride, the

sample was shaken for 15 min in ultrasonic bath (LA-Bultrasonic- Line Instruments, Inc, USA) at 40 °C and speed 250 rpm. The extract was centrifuged at 3,000 rpm for 5 min and the supernatant was transferred to a clean graduated cylinder. Solid-phase extraction was carried out using SPE columns preconditioned by passing 5 ml of acetonitrile:toluene (3:1 V/V). The sorbent of SPE was never allowed to dry during the conditioning and sample loading steps. The pesticides were eluted with 2x5 ml aliquots of acetonitrile: toluene (3:1 V/V). The eluates were collected in 12 ml tubes under gravity flow only. After all the elution solvent had passed through the extraction column, the residual solvent was forcibly removed from the column. The eluate was evaporated with a rotar to 2 ml, purged almost to dryness with nitrogen, reconstituted with acetonitrile to 1 ml and then analyzed by gas chromatography-mass spectroscopy (GC-MS).

Recovery studies We confirmed that date fruits used in the recovery test were DCF and AMZ free. For recovery studies, subsamples of known blanks (10 g) were spiked prior to extraction by addition of 2 ml of DCF and AMZ standard solutions in acetone to give 0.01, 0.02, 0.20 or 0.50 mg/kg. They were then prepared according to the proposed procedure as described previously and then absolute recovery and precision (expressed as relative standard deviation) were measured by analyzing three samples. The recovery values were 95–106 and 93–98 % with precision values of less than 10 % for DCF and AMZ, respectively. Limits of detection (LOD) and quantitation (LOQ) were calculated from the signal-to-noise ratios obtained by analyzing unspiked samples (n=10); LOD and LOQ were taken to be the concentrations of pesticide resulting in a signal-to-noise ratio of 3 and 10, respectively. The LOD values were 0.90 and 0.4 ng/g, while and LOQ values were 3 and 1.3 ng/g for DCF and AMZ, respectively.

Gas chromatography–mass spectrometry (GC-MS) Gas chromatography (Model GC 450, Varian Inc., The Netherlands) with a mass spectrometry (MS 220.41) detector equipped with split/splitless injector with electronic pressure control was employed. A Fused silica CP-Sil 8 CB-LB/MS capillary column (30 m ×0.25 mm i.d) was used in combination with the following oven temperature programme: initial temperature 50 °C, 5 °C/min ramp to 160 °C held for 10 min (first step) and from 160 to 250 °C (20 min) at 15 °C (final step). The injector temperature was 280 °C and mass range from 50–650 amu. The carrier gas (helium, 99.999 %) flow rate was set to a constant head pressure of 200 kPa at a flow rate of 1.0 ml/min with split ratio of 1: 20 min. The mass spectrometer was operated in electron ionization mode with a transfer line temperature of 280 °C, manifold temperature 40 °C, ion trap temperature 200 °C, ion source 240 °C and selected ion monitoring (SIM) mode. The ion energy for electron impact (EI) was kept at 70 eV. MS Workstation version 6.9.1. was used for

data acquisition. For positive identification, both retention time (Rt) and the presence of five fragment ions (z/m ions: 139, 141, 251, 253 and 75 for DCF and 162, 121, 132, 147 and 293 for AMZ) were considered. Figures 1 and 2 represent the GC-MS profiles for DCF and AMZ, respectively.

Extraction of sugars and phenolics Fruit sample was weighed (1 g) into 50 ml Teflon centrifuge tube and extracted with 25 ml 80 % ethanol using the homogenizer at full speed for 2 min. The extract was centrifuged at 4,000 rpm for 10 min and the supernatant was used to measure total sugars (TS), total phenolics (TP) and antioxidant capacity (AC).

Total sugars Ethanol extracts were used to determine TS according to the phenol-sulfuric colorimetric method of Dubois et al. (1956) using glucose (Sigma) as standard, the results were expressed as g/100 g of fresh weight.

Total phenolics Total phenolics content (TP) was determined according the method of Singleton and Rossi (1965) using the Folin-Ciocalteu reagent. In brief, 0.1 ml of extract was added to 7.9 ml of distilled water, 0.5 ml of Folin-Ciocalteu reagent, 1.5 ml of sodium carbonate solution (200 g/l) and then mixed vigorously. The mixture was allowed to stand for 1 h at the room temperature and then the absorbency was measured at a wavelength of 765 nm. Gallic acid was used as a standard and the results were expressed as mg gallic acid equivalents (GAE)/100 g sample.

Antioxidant capacity Antioxidant capacity (AC) or free radical scavenging activity was determined according to Brand-Williams et al. (1995) using 1,1-diphenyl-2-picryl-hydrazil (DPPH) reagent. In brief, 1.5 ml of freshly prepared methanolic DPPH solution (0.02 mg/ml) was added to 0.75 ml of 80 % ethanol extract and then stirred. The decolourizing process was recorded after 5 min of reaction at a wavelength of 517 nm and compared with a blank control using the Spectrophotometer . The DPPH radical scavenging activity of the extracts was measured using the Trolox standard curve. Results were expressed as μ mol Trolox equivalent (TE) antioxidant capacity/100 g sample.

Statistical analysis Data were calculated as mean $\pm$ SD analyzed using ANOVA. A probability of 0.05 or less was considered significant. The statistical package of the Costat Program (1986) was used for all chemometric calculations.

Results and discussion

Removing of dicofol and amitraz by wash treatments In the present study, the effects of DW and OZW wash treatments for

Fig. 1 GC-MS chromatogram corresponding to date fruits immersed in 2 mg/kg dicofol and immersed in O₃

different dipping times on either DCF and AMZ residues in different varieties of date fruits were investigated. The initial levels of DCF and AMZ were differed within the date varieties, where these levels were 131.96, 23.73, 23.25 and 29.92 $\mu\text{g/g}$ (Table 1), while they were 61.85, 72.30, 65.86 and 75.03 $\mu\text{g/g}$ (Table 2) in Khalas, Sakay, Nabout Seif and Nabtet Aly, respectively. The levels of natural waxing and properties of fruits impact the quantity of pesticide retained by fruits (Wu et al. 2007), where non-polar pesticides are tenaciously held in the waxy layer of peel of fruits and vegetables (Kaushik et al. 2009). Also, it was found that, the amount of either DCF and AMZ residues were significantly decreased exponentially as the contact time increased in the fruits treated with different wash treatments. There were significant variations between all the OZW treatments and control with respect to their abilities to remove the residues within the contact times. Also, the data showed that the dipping in DW only was less effective than OZW to remove either DCF and AMZ from all the tested varieties and either DW or OZW were less effective to remove DCF residues from Sakay than other varieties.. The percentages of DCF removal by DW ranged

from 7–78, 9–54, 34–56 and 14–73 %, while in case of OZW they were 87–95, 45–79, 67–99 and 84–100 % in Khalas, Sakay, Nabout Seif and Nabtet Aly, respectively, when the contact time was 15–60 min (Table 1).

Data in Table (2) result showed that when date fruits contaminated with 2 mg/l of AMZ and then washed with DW, the percentages of removal were 4–25, 52–80, 62–86 and 45–77 %, while in case of OZW the percentages of removal were 75–95, 61–95, 57–96 and 77–96 %) in Khalas, Sakay, Nabout Seif and Nabtet Aly, respectively, within 15–60 min as contact times.

The present results are in parallel with many investigations (Wu et al. 2007; Karaca et al. 2012) where tap water and ozonated water treatments significantly ($p < 0.05$) reduced pesticide residual levels on vegetable, compared with the no wash treatment. Also, the washing with water or soaking in solutions of salt and some chemicals e.g. chlorine, chlorine oxide, H₂O₂, ozone, acetic acid, hydroxyl peracetic acid, iprodione and detergents are reported to be highly effective in reducing the level of pesticides (Meijers et al. 1995; Doong

Fig. 2 GC-MS chromatogram corresponding to date fruits immersed in 2 mg/kg amitraz and immersed in O₃

and Chang 1998; Wang and Lemley 2002; Wu and Linden 2008; Bajwa and Sandhu 2011; Osman et al. 2012). Azinphos-methyl, captan and formetanate hydrochloride in solution and on fresh and processed apples decreased by 50–100 % with ozone treatment (Ong et al. 1996), mancozeb residues decreased by 56–97 % with ozone treatment at 1 and 3 ppm of ozone (Hwang et al. 2001). The quantity of pesticide being retained by vegetable highly depends on the levels of ozone and temperature (Wu et al. 2007). Also, washing cabbage with acetic acid solutions (at 100 g/l for 20 min) caused 79.8 %, 65.8 %, 74.0 % and 75.0 % loss of chlorpyrifos, *p*, *p*-DDT, cypermethrin, chlorothalonil, while washing with tap water (for 20 min) caused 17.6 %, 17.1 %, 19.1 % and 15.2 % loss (Zhang et al. 2007a, b). On the other hand, washing nectarines treated with chlorpyrifos, fenarimol, iprodione, malathion, methidathion, myclobutanil, parathion and pirimicarb with aqueous citric acid, H₂O₂, KMnO₄, sodium hypochlorite, sodium metabisulfite, and urea solutions produced results without significant differences with those obtained with the tap water (Pugliese et al. 2004). From the results obtained in this research work and assuming the criterion that a treatment is efficient in degrading pesticides if a

removal percentage of above 70 % is obtained (Ormad et al. 2008), OZW at 2 mg/l removed more than 70 % especially when the dipping time ranged from 30–60 min. The present study revealed that removing of either of dicofol or amitraz from date fruits depends on the contact times. Also, the amount of pesticide removed by washings is related to its water solubility and octanol–water partition coefficient (Pugliese et al. 2004).

One of the health concerns of using oxidants to degrade pesticide is the formation of toxic intermediates. The present study investigated the efficacy of OZW to remove DCF and AMZ from date fruits. O₃ was assayed for washings has a powerful oxidant having electrochemical oxidation potential of 2.0 V, and thus, can modify the chemical structure of the selected pesticides creating derived by-products. If these by-products are more toxic than the parent pesticide, such washing treatments should not be utilized to reduce pesticide residue levels in fruits. The possible formation of toxic by-products of either DCF or AMZ was investigated by gas chromatography–mass spectrometry (GC-MS) in SCAN mode by monitoring *m/z* ions: 109, 197, 242, 270 and 298 for 4,4'-dichlorobenzophenone, 162 for N-(2,4-

Table 1 Levels ($\mu\text{g/g}$) and removal percentages (in parenthesis) of dicofol from different varieties of date fruit after distilled water and ozone wash treatment

Date varieties	Distilled water						Ozone					
	Contact time (min)											
	15	30	45	60	15	30	45	60	15	30	45	60
Khalas	131.96 $\pm$ 6.30aA	122.50 $\pm$ 10.50aA	72.86 $\pm$ 0.44aB (45)	32.22 $\pm$ 1.49aC (76)	29.27 $\pm$ 0.80aC (78)	16.81 $\pm$ 0.33aB (87)	15.29 $\pm$ 0.96aB (88)	8.22 $\pm$ 1.49aC (94)	7.22 $\pm$ 0.48aC (95)			
Sakay	23.73 $\pm$ 0.92bA	21.71 $\pm$ 1.07bA (9)	13.29 $\pm$ 1.50bB (44)	12.73 $\pm$ 0.13bB (46)	11.03 $\pm$ 0.53bB (54)	6.96 $\pm$ 0.39bC (71)	5.73 $\pm$ 0.13bB (75)	5.05 $\pm$ 0.25aC (79)				
Naboot Seif	23.25 $\pm$ 0.27bA	15.35 $\pm$ 0.75cB (34)	11.98 $\pm$ 0.10bC (48)	11.66 $\pm$ 0.08bC (50)	10.12 $\pm$ 0.01bC (56)	7.60 $\pm$ 1.04aB (67)	4.19 $\pm$ 0.37bC (82)	1.06 $\pm$ 0.08bC (94)	0.27 $\pm$ 0.01bD (99)			
Nabiet Aly	29.92 $\pm$ 1.47bA	25.74 $\pm$ 0.43 dB (14)	17.14 $\pm$ 0.01dC (43)	8.23 $\pm$ 0.16cD (72)	8.33 $\pm$ 0.24cD (73)	4.67 $\pm$ 0.16bB (84)	2.59 $\pm$ 0.13bBC (91)	1.23 $\pm$ 0.16cD (94)	0.07 $\pm$ 0.00bD (100)			

Each value is the mean $\pm$ S.D of three replicates

Means having different small letters in column or capital letters in row are significantly different ($P<0.05$)

Table 2 Levels ($\mu\text{g/g}$) and removal percentages (in parenthesis) of Amitraz from different varieties of date fruit after distilled water and ozone wash treatment

Date varieties	Distilled water						Ozone					
	Contact time (min)											
	15	30	45	60	15	30	45	60	15	30	45	60
Khalas	61.85 $\pm$ 1.70aA	59.17 $\pm$ 1.53aA (4)	55.73 $\pm$ 2.16aA (10)	50.61 $\pm$ 1.71aB (18)	46.60 $\pm$ 0.57aB (25)	15.35 $\pm$ 1.53aB (75)	11.16 $\pm$ 0.19aC (82)	6.40 $\pm$ 0.61aCD (89)	3.22 $\pm$ 0.22aD (95)			
Sakay	72.30 $\pm$ 0.82bA	34.37 $\pm$ 0.88bB (52)	24.54 $\pm$ 0.66bC (66)	16.93 $\pm$ 0.77bD (77)	14.55 $\pm$ 0.33bE (80)	28.17 $\pm$ 0.88bB (61)	21.81 $\pm$ 0.32bC (70)	4.48 $\pm$ 0.34aD (94)	3.56 $\pm$ 0.42aD (95)			
Naboot Seif	65.86 $\pm$ 0.45aA	24.72 $\pm$ 0.74cB (62)	19.91 $\pm$ 0.65cC (70)	16.43 $\pm$ 0.99bC (75)	9.17 $\pm$ 0.75bD (86)	28.48 $\pm$ 0.74bB (57)	5.87 $\pm$ 0.17cC (91)	3.33 $\pm$ 0.52aC (95)	2.62 $\pm$ 0.61aC (96)			
Nabiet Aly	75.03 $\pm$ 2.44bA	41.48 $\pm$ 1.10 dB (45)	27.26 $\pm$ 0.45bC (64)	21.12 $\pm$ 0.56bD (72)	17.23 $\pm$ 0.91cD (77)	37.06 $\pm$ 1.10cB (77)	11.06 $\pm$ 0.25 dB (85)	3.36 $\pm$ 0.48aC (96)	2.81 $\pm$ 0.30aC (96)			

Each value is the mean $\pm$ S.D of three replicates

Means having different small letters in column or capital letters in row are significantly different ($P<0.05$)

Table 3 Kinetic parameters for the dicofol dissipation in different varieties of date fruits in presence of distilled water and ozone treatments

Date varieties	Distilled water					Ozone				
	α (min ⁻¹)	$t_{1/2\alpha}$ (min)	β (min ⁻¹)	$t_{1/2\beta}$ (min)	Regression coefficient (R ²)	α (min ⁻¹)	$t_{1/2\alpha}$ (min)	β (min ⁻¹)	$t_{1/2\beta}$ (min)	Regression coefficient (R ²)
Khalas	0.020	34.70	-	-	0.980	0.086	8.10	0.010	69.30	0.958
Sakay	0.015	46.20	0.011	63	0.916	0.039	17.80	0.009	77.00	0.996
Nabout Seif	0.022	31.50	0.009	77	0.974	0.040	17.30	0.020	34.70	0.998
Nabtet Aly	0.020	34.70	-	-	0.972	0.086	8.10	0.023	30.10	0.999

α and β are the disappearance rate constants for the first and second and phases, while $t_{1/2\alpha}$ and $t_{1/2\beta}$ are the half-life times for the first and second and phases

Each value is the mean of three replicates

dimethylphenyl)-N-methyl formamidine, 149 for 2,4-dimethylformanilide and 121 for 2,4-dimethylamin. Only single peak at a retention time of 3.88 and 3.55 min corresponding to DCF and AMZ, respectively, was observed in the GC-MS chromatogram and there is no intermediate or dead-end product detected using the analytical method described in the present study (Figs. 1 and 2). It is well known that DCF was found to be more easily degradable than DDT and other organochlorine insecticides (Van Dijk and Van De Voorde 1976) due to the susceptibility of trichloromethyl group to cleavage to form 4,4'- dichlorobenzophenone (Walsh and Hites 1979) which is degraded by oxidation processes with elimination levels of 80 and 85 % by O₃ and O₃/H₂O₂, respectively (Ormad et al. 1997). The lack of DCF metabolites may support its complete degradation especially when Nabout Seif and Nabtet Aly were dipped in OZW for 60 min. In case of AMZ, the degradation products are N-(2,4-dimethylphenyl)-N-methyl formamidine and 2,4-dimethylformanilide (FAO/WHO 1982). The differences in degradation might result from the differences of the structures. The present results are in accordance with many investigators who found that no toxic by-products such as chlorpyrifos-oxon were detected in date fruits (Osman et al. 2012), chlorpyrifos-oxon, malaoxon, methidaoxon and methyl para-oxon in the extracts of the washed samples for the washing-

time and low concentrations of sodium hypochlorite, KMnO₄ and H₂O₂ (Pugliese et al. 2004) and ethylenethiourea residue at 1 ppm of spiked mancozeb after both 3 and 30 min of ozone treatment (Hwang et al. 2001). On the other hand, at high concentrations of sodium hypochlorite, KMnO₄ and H₂O₂, axons from the organophosphorus pesticides were identified (Pugliese et al. 2004). O₃ selectively reacts with compounds containing heteroatoms such as S, N, O, and Cl via two different pathways, namely direct molecular and indirect radical chain-type reactions (Gottschalk et al. 2000). The reactivity of compounds with ozone varies largely due to their diverse structural features (Karaca et al. 2012). Thus, pesticides, which usually have some heteroatoms on the molecules, are often expected to be destroyed by ozonation (Reynolds et al. 1989). However, as has been found by many researchers, the reactivity of pesticides with O₃ varies largely due to their diverse structural features (Reynolds et al. 1989), the pH, concentration of O₃ decomposition initiators, promoters and scavengers in the reacting medium may affect (Glaze et al. 1987). So it is recommended to use O₃ as non-toxic washing treatment to reduce such residues in date fruits.

It can be observed that removing of DCF and AMZ by washing process with water in this study were higher than other studies (Abou-Arab 1999; Cengiz et al. 2006) where 9-

Table 4 Kinetic parameters for the amitraz dissipation in different varieties of date fruits in presence of distilled water and ozone treatments

Date varieties	Distilled water					Ozone				
	α (min ⁻¹)	$t_{1/2\alpha}$ (min)	β (min ⁻¹)	$t_{1/2\beta}$ (min)	Regression coefficient (R ²)	α (min ⁻¹)	$t_{1/2\alpha}$ (min)	β (min ⁻¹)	$t_{1/2\beta}$ (min)	Regression coefficient (R ²)
Khalas	0.005	138.6	-	-	0.965	0.040	17.3	0.019	36.5	0.850
Sakay	0.050	14.0	0.017	40.80	0.999	0.031	22.4	0.024	28.9	0.983
Nabout Seif	0.057	12.20	0.016	43.30	0.951	0.042	16.5	0.014	49.5	0.981
Nabtet Aly	0.031	22.40	0.013	53.30	0.999	0.077	9.0	0.029	23.9	0.999

α and β are the disappearance rate constants for the first and second and phases, while $t_{1/2\alpha}$ and $t_{1/2\beta}$ are the half-life times for the first and second and phases

Each value is the mean of three replicates

23 % of the initial pesticide levels were reduced by washing fruits by tap water. It was found that rinsing fruits and vegetables with tap water for 15–30 s produced significant reductions in residue levels of malathion, iprodione and other pesticides but not of chlorpyrifos (Krol et al. 2000), while washing rice grains with water removed approximately 60 % of the chlorpyrifos residues (Lee et al. 1991).

Kinetic studies A biphasic model was assumed in order to carry out the statistical study of the loss of either DCF or AMZ in (equation 1) in case OZW and DW treatments, except in case of Khalas variety treated with either DCF or AMZ and Nabtet Aly treated with DCF and then treated with DW a mon-phasic model was assumed (equation 2).

$$C_t = A_0 e^{-\alpha t} + B_0 e^{-\beta t} \quad (1)$$

$$C_t = A_0 e^{-\alpha t} \quad (2)$$

where C_t is the recovered amount of pesticide at t min, while α and β are the disappearance rate constants for the first and

second and phases, respectively. The half-life ($t_{1/2}$) of the exponential decay was calculated according to the equation (3).

$$t_{1/2} = (2.303 \log 2) / \text{rate constant} \quad (3)$$

The data fitting results in most of different wash treatment using second order kinetic showed that the coefficients of determination (R^2) ranged from 0.916–0.980 and 0.958–0.999 for DCF (Tables 3), while they were 0.951–0.999 and 0.850–0.999 for AMZ (Table 4) when the date fruits washed with DW and OZW, respectively. The overall reaction of ozone with organic compounds is generally of second-order, with first-order to each reactant (Hoigné and Bader 1983; Yao and Haag 1991; Chelme-Ayala et al. 2001). The biphasic model is characterized by a rapid phase (first phase), and a much slower phase (second phase). This is clearly reflected in the half-live values ($t_{1/2}$), where $t_{1/2\alpha}$ values of DCF were 34.7, 46.2, 31.5 and 34.7 min in DW wash treatment and 8.1, 17.8, 17.3 and 8.1 min in OZW wash treatment of Khalas, Sakay, Nabout Seif and Nabtet Aly, respectively

Table 5 Effect of distilled water and ozone treatments on antioxidant capacity of four date varieties treated with either dicofol or amitraz

Variety	ExposureTime (min)	Dicofol Water	Ozone	Amitraz Water	Ozone
Khalas	0	72.60	72.60	78.20	78.20
	15	74.70	72.80	76.8	76.8
	30	74.80	73.6	79.5	78.8
	45	70.40	76.8	71.2	79.0
	60	73.20	76.8	75.2	81.5
	Mean	72.34±1.82	74.52±2.11	76.18±3.21	78.86±1.71
Sakei		LSD _{5%}	0.66	1.20	
	0	71.50	71.50	75.50	75.50
	15	70.80	70.40	73.60	76.40
	30	68.80	74.80	73.40	71.20
	45	69.60	70.00	74.20	76.00
	60	66.00	75.20	75.30	70.40
Nabou Seif		Mean	69.34±2.14	72.60±2.38	74.40±0.96
		LSD _{5%}	1.11	0.77	
	0	104.50	104.50	110.00	110.00
	15	100.40	100.00	105.80	107.20
	30	104.80	102.40	100.20	108.80
	45	100.00	102.00	104.80	105.20
Nabt Ali	60	104.00	100.20	102.00	106.80
		Mean	103.80±1.44	101.82±1.84	104.56±3.77
		LSD _{5%}	0.78	1.59	
	0	106.80	106.80	108.80	
	15	106.40	101.20	105.20	102.80
	30	100.80	96.80	101.60	104.00
Nabt Aly	45	97.60	93.20	104.80	105.30
	60	90.40	85.20	105.80	107.50
		Mean	100.40±6.80	96.64±8.17	105.24±2.57
		LSD _{5%}	3.44	1.29	

Each value is the mean of three replicates

Data are expressed as μmol Trolox equivalent (TE) antioxidant capacity/100 g fresh weight of date

(Table 3). In case of Amitraz, the $t_{1/2}$ (values were 138.6, 14, 12.2 and 22.4 min in DW wash treatment and 17.3, 22.4, 16.5 and 9 min in the OZD wash treatment of Khalas, Sakay, Nabout Seif and Nabtet Aly, respectively (Table 4). On the other hand, the $t_{1/2}$ (values of DCF ranged from 63–77 and 30.1–77 min, while for amitraz they ranged from 40.8–53.5 and 23.9–49.5 min when date fruits washed with DW and OZW, respectively. The present findings are in accordance with those of many investigators who reported that the kinetics of pesticide degradation is commonly biphasic with a very rapid degradation rate at the beginning followed by a very slow prolonged dissipation (Chelme-Ayala et al. 2001; Osman et al. 2009). The relative importance of the phases depends on the availability of the pollutants, hydrophobicity, and affinity for organic matter. Also, the present investigation showed that the reaction rate constants for the first and second phases between ozone and either DCF or AMZ were relatively low and is similar to alachlor (Yao and Haag 1991).

Effect of wash treatments on date fruits quality parameters

The effect of wash treatments on quality

parameters of date fruits is of interest since the wash treatment may be performed by dates' processors and consumers. Quality of fruits and vegetables is greatly affected by post-harvest treatments and storage (Ismail et al. 2008) by affecting the nutritional and sensory quality of the product (Laurila and Ahvenainen 2002).

Antioxidant capacity (AC) and total phenolic content (TP) Because date fruits are rich in antioxidant compounds, therefore, its consumption is considered to be one of the main factors of healthy lifestyle (Laurila and Ahvenainen 2002; Alothman et al. 2010). Unfortunately, few studies dealt with the effect of wash treatments on fruits quality parameters (Tzortzakis et al. 2007) especially date fruits (Osman et al. 2012). Thus, research is needed to investigate the effect of current wash treatments on AC, TP and TS, and ultimately devise ideal conditions of wash treatments suitable for the date fruits.

Variations in the levels of AC (Table 5) and TP (Table 6) contents were observed between the tested varieties, however fruits of Nabout Seif variety tended to have the highest values of either

Table 6 Effect of distilled water and ozone treatments on total phenolics of four date varieties as treated either dicofol or amitraz

Variety	Exposure Time (min)	Dicofol Water	Ozone	Amitraz Water	Ozone
Khalas	0	2.30	2.30	2.70	2.70
	15	2.25	2.06	2.30	2.59
	30	2.02	2.04	2.29	2.22
	45	1.71	1.89	2.43	2.09
	60	1.96	1.98	2.08	2.18
	Mean	2.05±0.24	2.05±0.15	2.36±0.23	2.36±0.27
Sakei	LSD _{5%}	0.11	0.18		
	0	2.66	2.66	2.68	2.69
	15	2.57	2.38	2.88	2.49
	30	2.32	2.15	2.38	2.78
	45	2.25	2.16	2.55	2.41
	60	2.21	2.22	2.21	2.29
Nabout Seif	Mean	2.04±0.20	2.31±0.21	2.46±0.18	2.53±0.20
	LSD _{5%}	0.19	0.10		
	0	2.80	2.80	2.82	2.82
	15	2.68	2.73	2.67	2.56
	30	2.30	2.38	2.57	2.55
	45	2.22	2.29	2.76	2.52
Nabtat Ali	60	2.49	2.32	2.49	2.51
	Mean	2.50±0.25	2.50±0.24	2.66±0.13	2.59±0.13
	LSD _{5%}	0.09	0.07		
	0	2.22	2.22	2.28	2.28
	15	1.74	1.86	2.23	2.27
	30	2.08	1.93	1.86	1.89
Nabtet Aly	45	1.84	1.59	2.11	2.00
	60	1.61	1.74	2.03	1.86
	Mean	1.90±0.25	1.87±0.24	2.01±0.18	2.06±0.20
	LSD _{5%}	0.13	0.16		

Each value is the mean of three replicates

Data are expressed as mg gallic acid equivalents (GAE)/100 g fresh weight of date

Table 7 Effect of distilled water and ozone treatments on total sugars of four date varieties treated with either dicofol or amitraz

Variety	Exposure Time (min)	Dicofol Water	Ozone	Amitraz Water	Ozone
Khalas	0	73.20	73.20	73.55	73.55
	15	71.60	70.40	66.10	66.70
	30	70.70	69.70	66.40	68.30
	45	70.90	75.60	70.40	68.60
	60	69.50	71.70	69.50	69.50
	Mean	71.18±1.36	71.12±1.37	69.10±3.08	69.33±2.57
	LSD _{5%}	1.12	1.16		
Sakei	0	65.10	65.27	63.11	64.12
	15	62.50	63.30	60.90	63.30
	30	62.60	64.90	62.60	62.20
	45	67.80	69.50	60.70	62.30
	60	67.30	63.60	65.90	63.60
	Mean	65.06±2.24	65.27±2.22	63.64±1.88	63.30±0.63
	LSD _{5%}	1.09	1.33		
Nabout Seif	0	76.60	75.20	75.50	75.80
	15	78.00	75.60	77.20	78.10
	30	70.60	71.80	73.70	72.80
	45	76.80	74.40	73.10	73.40
	60	73.70	74.60	73.70	73.70
	Mean	75.14±2.67	74.32±1.33	74.64±1.55	74.76±1.95
	LSD _{5%}	1.89	1.44		
Nabtati Ali	0	72.20	72.20	72.80	72.80
	15	70.00	72.10	73.10	75.30
	30	70.60	71.60	73.30	75.50
	45	71.80	73.20	75.10	74.30
	60	72.70	72.20	72.50	74.80
	Mean	71.47±1.13	72.26±0.58	73.17±0.79	74.54±1.08
	LSD _{5%}	0.77	0.99		

Each value is the mean of three replicates

Data are expressed as g/100 fresh weight of date

AC or TP. Variations in both parameters between date varieties were previously reported (Al-Farsi et al. 2007). Also the present study revealed that levels of AC and TP of date fruits showed variations throughout the dipping times. However, levels of these beneficial constituents tended to decrease by extending the dipping time due to the increase in the ability of fruits to absorb water (data not shown). OZW treatments did not produce a permanent trend as compared with DW treatments, throughout the dipping time for all tested date varieties, where DW tended to produce slight increases in mean values of AC and TP relative to OZW, but these increases did not reach the level of significance for all tested varieties. The present study is in parallel to that found in tomatoes where O₃-enriched atmosphere (concentration up to 1 µmol mol⁻¹) did not attain statistical significance change in AC and TP (Tzortzakakis et al. 2007).

It is established that the AC of dates was due mainly to the presence of water-soluble compounds with potent free radical-scavenging effects, including the phenolic compounds (mainly cinnamic acids) and flavonoids (flavones, flavonols and

flavanones) (Wang et al. 1996; Connor et al. 2002; Vayalil 2002; Guo et al. 2003; Mansouri et al. 2005; Biglari et al. 2008). Significant correlation between AC and TP in date palm fruits has been established by many investigators (Allaith 2008; Biglari et al. 2008) confirming that these compounds play important role in antioxidant activities (Kosanić et al. 2011).

Total sugars content (TS) TS content of the four date fruit varieties as affected by soaking in distilled water or ozonated water for 15–60 min are shown in Table 7. To exclude the efficiency of date fruit to absorb water by extending the dipping time, TS contents were calculated depending on dry fruits. Data showed that fruits of all date varieties contained high amounts of sugars as expected, since sugars are considered the main date palm constituent (Al-Farsi et al. 2007). Levels of TS of date fruits appeared slight variations throughout the dipping time; however, OZW treatments fail to attain any significant changes in sugar contents when compared with DW treatments for all tested varieties. This result indicated that using O₃ for pesticide removal did not produce any

undesirable effect on the main nutritional compound of date fruits. The present investigations are in parallel with Selma et al. (2008) who illustrated that there was no evidence of damage in melons treated with hot water, O₃ or their combination and they maintained initial texture and aroma. However, due to its strong oxidizing activity, O₃ may also cause physiological injury to fresh-cut produce (Selma et al. 2008). Therefore, the possible negative impact of O₃ treatment on fruits sensory quality warrants further study (Selma et al. 2008). For the postharvest of fresh fruit, O₃ can be used as a relatively brief pre-storage or storage treatment in air or water, or as a continuous or intermittent component of the atmosphere throughout storage transportation (Palou et al. 2002).

Conclusion

Food is the basic necessity of life and its contamination with pesticides is associated with severe effects on the human health. Hence it is pertinent to explore strategies that address this situation of food safety especially for the developing countries where pesticide contamination is widespread due to indiscriminate usage. Due to the large amount of dates consumed by Saudi residents (100 g daily of dates daily per person), which is the highest in the world, a higher risk of exposure to pesticides may, especially in children and other vulnerable individuals may occur. Therefore, the search for safe pesticides with negligible residual deposits has always been preferred. In KSA, the industry of date fruits is constantly growing due to consumers demand and new techniques for maintaining quality and removing undesired pesticide residues are demanded in all the steps of the production and distribution chain. Also, washing with water and solutions for domestic use are necessary to decrease the intake of pesticide residues. It is therefore of significance to evaluate simple and effective strategies to enhance food safety from harmful pesticides. In the present study, DCF and AMZ were significantly removed more from all the tested date fruit varieties by water and/or O₃ at all the tested time intervals compared with unwashed-fruits (treated with acaricide only) and O₃ treatment is more potent than water to remove these pesticides. By the end of the experiment more than 95 % of the initial levels of the tested acaricides were removed in O₃-washed fruits and less than 86 % in water-washed fruits. Although, water wash treatment significantly reduced the tested pesticide residue levels on date fruits compared with no wash treatment, but still less effective than O₃ treatment. The removing pattern could be attributed to the low water solubility and high octanol-water partition coefficient of the tested acaricides. Due to its high oxidability, high reaction rate and absence of any secondary pollution, ozonolysis technique should be used in pesticide-treated date fruits to remove

residues adhering on dates surface without significant changes in antioxidant capacity, and phenolic and sugar contents. Also, because O₃ decomposes rapidly to molecular oxygen without leaving a residue, this makes it as an attractive candidate for controlling pesticides and as a postharvest treatment of crops.

The present study validated that ozone as wash treatment is safe and promising process for the removal of acaricides from date fruits surface. The results found in the present study must not be extrapolated to other pesticides, crops or conditions.

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