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# EVALUATION AND RECENT TECHNICAL DECONTAMINATION OF DIFFERENT PESTICIDE RESIDUES ON DATE PALM FRUITS

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Food safety problems caused by pesticide residues especially in date palm fruits have become one of the most important issues that threaten human health regarding that some farmers are not looking to the optimal use of these pesticides. In the present study, Evaluation of initial residues of different pesticides (Chlorpyrifos, Fipronil, Methomyl, and Carbendazim) varied from (0.34-3.11 mg/kg) above MRLs reflecting improper use. In order to deal that, recent technologies where utilized to reduce residues. Barhee cv date palm samples were subjected to two recent decontamination methods (Ozone and $^{60}CO$ γ-Radiation). The remaining residues were analyzed by GC-MS/MS and LC-MS/MS using validated QuEChERS methodology. The results showed that removal of pesticides (89.6%-97.3%) using 1.0 KGy $^{60}CO$, γ-Radiation was effectively reduced chlorpyrifos residues to lower than MRLs while ozone method at 60 min reduced carbendazim residues (89.7%-96.8%) below its MRLs. Both technologies were able to decrease the residues for other pesticides and decrease the risk.

***Keywords:*** Pesticide residues, Ozone, Gamma-radiation, GC-MS/MS, LC-MS/MS, Date palm fruits

## INTRODUCTION

Pesticides are a group of synthetic chemical compounds that are used in farms to control pests and diseases to improve agricultural production. The use of pesticides, however, is emerging, particularly in developing countries representing a risk on health and environment. In recent years, the scientific community has shown great concern about the possible adverse effects of these pesticides (Saravi and Shokrzadeh, 2011). These residues cause detrimental effects on human health such as neurotoxicity, carcinogenesis, abnormal reproduction and cell development especially in countries where pesticide contamination is widespread (Mostafalou *et al*., 2017). In Egypt and various Arab countries, there is a frightening and incorrect way in the use of dangerous and internationally banned chemical pesticides in most agricultural crops including date palm fruits (Gad Alla *et al*., 2015).

Date palms (*Phoenix dactylifera* L. family *Arecaceae*) are plants of enormous nutritional, medicinal and economic values, they are one of the oldest known fruit crops in the world (Al-Shahib and Marshall, 2003). Date palm fruits are a staple food in the diet of many countries which consumed in large quantities fresh, dried, or in various processed forms. In Egypt, Date palm fruits are one of the most important crops because of their religious, nutritional and economic significance (Biglari *et al*., 2008). The Barhee date variety is one of the famous soft varieties cultivated in Egypt. Although Barhee cv. is extremely sweet, research suggests

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that it contains invert sugar, which makes it safe to eat for diabetics. Barhee fruits are small, round and have a soft, somewhat chewy texture (Bekheet and El-Sharabasy, 2015). In Egypt, there are many pests and insects attack date palm trees causing damage to date palm plants and reduce annual crop production from dates fruits. Among insects diagnosed attacking palm trees there are Red Palm Weevil (RPW) (Zaid *et al*., 2002). Rhynchophorus ferrugineus, Oryctes elegans Prell (Scarabaeidae: Coleoptera) and Parlatoria blanched. In addition, there are some fungal diseases that have been diagnosed in palm tree such as Black Scorch disease caused by Thielaviopsis paradoxa and Deploying Rot disease caused by Diplodia phoenix (Bekheet and El-Sharabasy, 2015; and El-Shafie *et al*., 2017).

The Diagnosed insects and fungal diseases in date palm should be controlled and treatments using several chemical pest control protocols recommended by the Ministry of Agriculture and Land Reclamation of Egypt, 2018 (APC-Egypt, 2018). The best insecticides used for the diagnosed insects and pests are Chlorpyrifos representing organophosphates pesticides, Fipronil representing a phenylpyrazole group and Methomyl representing carbamates family while Carbendazim broad-spectrum benzimidazole fungicide used for control of the fungal diseases in a date palm tree (Garcia *et al*., 2012). Since pesticides are potentially harmful to the environment and consequently to a human being through the consumption of pesticide-contaminated food, governments and international organizations established Maximum Residue Levels (MRLs) for each pesticide based on the assumption of applying good agricultural practices when use of these pesticides in order to avoid the health hazards caused by pesticide residues (Jallow *et al*., 2017) When these compounds are applied according to good agricultural practices, MRLs are not exceeded, but their incorrect application may leave harmful residues, which involve possible health risks for human especially when these commodities are freshly consumed leading to the accumulation of those residues in the human body and causing kidney failure, liver failure, cancer and damage of the immune system in old age. Therefore, exceeding MRLs are strong indicators of contravention of good agricultural practices which include non-compliance with the pre-harvest period recommended for each pesticide and may also non-compliance with the recommended concentrations (Nougadére *et al*., 2012; and Grewal *et al*., 2017).

Therefore, pesticide residues should be monitored and evaluated in foods and modern technologies should be invented helping in its removal or even its reduction, especially when pesticide residues are detected after harvest with high levels in a trial to assure that the MRLs of these pesticides are not exceeded (EL-Saeid and AL-Dosari, 2010; and Wang *et al*., 2011).

Several technics and methods can be employed for the removal of various classes of pesticides from contaminated food. Advanced Oxidation Process (AOP), including ozone, hydrogen peroxide, ultra-violet, and gamma-irradiation are promising technologies depends on generating OH radicals for removing organic pollutants from date fruits (Mahapatra *et al*., 2005).

Radiation process is one of the most powerful AOPs, where radiation with a beam of accelerated electrons or gamma radiation is employed for decomposition of various organic pollutants compared to other processes. This technique has the advantage that no chemicals have to be added to the treated product. Limited studies have focused on the effect of gamma-radiation for the removal of pesticide residues (Basfar *et al*., 2012).

Ozone ($O_3$) is natural gas at ambient and refrigerated temperatures. It is generated by the passage of air or oxygen gas through a high voltage electrical discharge or by ultraviolet light irradiation. Ozone has been used for deodorization, sterilization, virus inactivation, bleaching, organic matter decomposition, mycotoxin degradation, and others. It is generally recognized as safe for food contact applications and it changes to oxygen by autolysis. Recently, ozone water dips have been commercialized for the removal of pesticides and microbes from food surfaces (Balawejder *et al*., 2013; and Wang *et al*., 2018).

The aim of the present study was to determine and evaluate the residual levels of different pesticides on date palm fruit before the pre-harvest period and studying the effect of advanced technologies as radiation and ozone technology on its removal.

## MATERIALS AND METHODS

### Pesticides and Chemicals

Fipronil (Regent 20% SC), Chlorpyrifos (Tafaban 48% EC), Methomyl (Neomyl 90%) and Carbendazim (Kemazed 50% WP) were purchased from local suppliers in Egypt. Pesticides reference materials include (Fipronil, Chlorpyrifos, Methomyl, and Carbendazim) (purity > 98%) were

purchased as individual standards from Dr Ehrenstorfer GmbH (Augsburg, Germany), Acetonitrile pesticides grade from Sigma Aldrich, QuEChERS Kit, and SPE tube contain PSA and $MgSO_4^{-2}$ from (Agilent, USA). Methanol and ammonium formate were purchased from Fluka (Sigma Aldrich Corp., St Louis, MO, USA). A Milli Q integral system was used to produce ultra pure water.

## Field Diagnosis and Applied Pesticides

Diagnosis of many insects and fungal diseases infects the date palm trees (Barhee cv). Insects as Red Palm Weevil: Rhynchophorus ferrugineus, and Parlatoria blancherdi. Fungal disease as Deplodia Rot Disease caused by Diplodia Phoenicia. The infected date palm trees were treated by recommended pesticides once a week for 3 weeks using foliar application by a knapsack sprayer and trunk injection for treatment of Red Palm Weevil with the recommended rates of each pesticide according to the Approved Recommendations for the Control of Agricultural Pests, 2018 from Ministry of Agriculture and Land Reclamation – Egypt (APC-Egypt, 2018). Control trees were sprayed with an equal volume of water. Each treatment had three replicates.

- Fipronil (3 ml/l of Regent 20% SC) = 600 mg/l
- Chlorpyrifos (3 ml/l of Tafaban 48% EC) = 1440 mg/l
- Methomyl (2 g/l of Neomyl 90%) = 1800 mg/l
- Carbendazim (3 g/l of Kemazed 50% WP) = 1500 mg/l

## Date Samples Collection and Preparation

Approximately 2 kg of date palm fruits were randomly collected from each tree before the pre-harvest interval for each pesticide. The samples were placed in sterile polyethene bags and kept in an ice chest for transportation to the laboratory. In the laboratory, the subsampling and sample preparations were performed according to the European Commission guidelines (2002) and the samples were frozen until analysis. Triplicate samples from each palm tree treated with every pesticide (Commission Directive, 2002).

## Sample Extraction and Clean Up

The extraction and clean-up method used was based on QuEChERS (quick easy cheap effective rugged and safe) sample preparation method for pesticides according to European method EN 15662:2018. The re-hydrated date fruit samples (10 g sample) were weighed in 50 mL PTFE centrifuge tubes and then 10 mL of acetonitrile (containing 1% glacial acetic acid) was added. The samples were vigorously shaken in tubes for 2 min using a vortex, add Agilent Bond Elut QuEChERS extraction kit (p/n 5982-7650) which contain (4 g $MgSO_4$; 1 g NaCl; 1 g Na Citrate, 0.5 g disodium citrate sesquihydrate) then vigorously shaken for 1 min then adjust pH. In the range of (5.0-5.5). The tubes were centrifuged at 3000 rpm for 5 min at a temp. below 5 °C (using the Thermo Scientific™ Sorvall™ ST 16 Centrifuge), cleaned up using an Agilent Bond Elut QuEChERS dispersive kit (p/n 5982-5121) 6 ml from extract were added to 15 ml SPE tube contain (25 mg PSA, 25 mg $C_{18}$EC and 150 mg $MgSO_4$) vortex for 1min, centrifuged for 5 min then the upper layers were filtered through a 0.25 µm PTFE syringe filter (Whatman, USA) into 1.8 mL vials for direct chromatographic analysis. ISTD (Triphenyl Phosphate) as internal standard was added to the sample before extraction to control the entire analytical process (EURL, 2017; and BS EN 15662, 2018).

## Gas Chromatography-Mass Spectrometry (GC-MS/MS) Analysis

A GC/MS/MS Multiple Reaction Monitoring (MRM) method has been developed on the Agilent 7890A/7000D GC triple quadrupole mass spectrometer system (GC/QQQ). Autosampler Agilent 7693A injector and sample tray, Inlet Multimode, Carrier gas Helium, Inlet pressure 27.420 psi (constant pressure mode) during run 2.0 psi (during backflush). Oven temperature program 70 °C (1 min), 50 °C/min to 150 °C (0 min), 6 °C/min to 200 °C (0 min), 16 °C/min to 280 °C (5 min). Cold splitless mode, inlet parameters; temperature program 60 °C (0.01 min), 700 °C/min to 280 °C (hold). Inlet liner Helix double taper deactivated (P/N 5188-5398) Injection volume 5 µL Purge flow to split vent 30 mL/min at 1.25 min. Transfer line temperature 280 °C Source temperature 230 °C Quadrupole temperature 180 °C, Threshold 100, sampling rate A/D = 4 Gain factor 1. Backflushing conditions timing 5 min duration, during post-run oven temperature 280 °C. For each compound, two Multi-Reaction Monitoring (MRM) transitions were monitored. The pesticides detected are Chlorpyrifos and Fipronil. Analyses were run in triplicate with GC-MS/MS.

## Liquid Chromatography-Tandem Mass Spectrometry (LC-MS/MS) Analysis

LC-MS/MS analysis was performed using liquid chromatography (Agilent 1200, Santa Clara, CA, USA) coupled with a triple quadrupole mass detector (Agilent 6460), and an Agilent ZORBAX C-18 analytical column of 50 mm x 2.1 mm internal diameter and 1.8 µm particle size. The sheath gas temperature was kept at 40 °C, and the

sheath gas flow was 12 L $min^{-1}$. Deionized water containing 0.1% formic acid (mobile phase A), and acetonitrile and deionized water (95:5, v/v) containing 0.1% formic acid (mobile phase B) were used for the gradient program, which started with 10% B for 3 min, and was linearly increased to 90% B over 15 min. The column was then reconditioned for 20 min back to 10% B. The column temperature was kept at 35 °C, and the injection volume was 10 µL with a constant flow rate of 0.6 mL $min^{-1}$. For each compound, two Selective Reaction Monitoring (SRM) were monitored. The pesticides detected are Methomyl and Carbendazim, Analyses were run in triplicate with LC-MS/MS.

## Radiation Treatment

Date samples Barhee cv. after determining the initial pesticides level were packed into sterilized low-density polyethene (LDPE) plastic bags before being sealed with a sealer. The packets were individually labelled. Cobalt-60, Gamma Cell, Canada Co. Ltd. gamma-irradiator (located at the National Centre for Radiation Research and Technology (NCRRT), Nasr City, Cairo, Egypt) was used as the source of gamma radiation with two different radiation doses (0.5 and 1.0 KGy) with contact time 23 min 34 sec. The non-irradiated sample from Al-Barhee date fruit was kept as a control sample. After the radiation treatment, both the irradiated and the non-irradiated samples were analyzed for the presence of pesticides. All radiation treatments were performed in triplicate.

## Ozonation Treatment

Dates samples Barhee cv. after determining the initial pesticides level. Date samples (1.0 kg) were immersed in 5.0 L of distilled water maintained at 25 ºC in an ozone chamber (60 cm diameter and 120 cm height). Ozone was continuously bubbled at gas concentrations of 2-3 mg $L^{-1}$, through a spiral disperser located at the bottom of the treatment chamber with a continuous flow of 2.0 L $min^{-1}$ and under magnetic stirring for 30 and 60 min using ozone generated ProMinent®OZONFILT OZVa. 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). All ozone treatments were performed in triplicates.

## Standard and Quality Control

The individual pesticide stock standard solutions (100 mg/L) and intermediate standard solutions (10 mg/L) were prepared in acetonitrile. All prepared solutions were stored at –18 °C. The multi levels working calibration standard prepared invidually according to MRLs to each pesticide. Chlorpyrifos (0.005-0.5 mg/kg), Fipronil (0.01- 1.0 mg/kg), Methomyl (0.01-1.0 mg/kg) and Carbendazime (0.05-2.0 mg/kg) with add ISTD (Triphenyl Phosphate) for each level. Good linearity and reproducibility of calibration curves were achieved for each pesticide ($r^2 > 0.99665$), ($r^2 > 0.99842$), ($r^2 > 0.99751$), ($r^2 > 0.99927$) respectively for each pesticide (EURL, 2017).

Quality control and quality assurance were incorporated into the analysis. The accuracy and precision were validated in accordance with the European Commission (EC) guidelines SANTE (2017) guideline (EURL, 2017).

The performance of the QuEChERS method was evaluated by performing recovery studies the recovery rate and precision of the method (expressed as Relative Standard Deviation (RSD, %). The method accuracy is expressed by the pesticide recovery from spiked blank date fruit samples. The recovery of each pesticide for three spiked levels, 0.1, 0.05 and 0.01 mg/kg, was investigated with three replicates for each level. The recovery values for each pesticide were in the range from (71-118%). The LOQ for Chlorpyrifos 7.3 µg/kg, Fipronil 5.2 µg/kg, Methomyl 10.7 µg/kg and Carbendazim 51.6 µg/kg with recovery (83-118%). The RSD values between the replicates of each level were < (11.5-12.4), (14.1-15.9) and (17.2-18.9%) for 0.1, 0.05 and 0.01 mg/kg, respectively for each pesticide (EURL, 2017).

## Statistical Analysis

All obtained results are expressed as a mean of the determination result of tested pesticide residue for triplicate Date palm fruit samples of each treatment + standard error. The statistical comparison between the effect of treatments and decontamination methods on tested pesticide residues were performed using a one-way analysis of variance (ANOVA) followed by Duncan, S-test using SPSS version 22 computer program (Steel *et al.*, 1996).

## RESULTS AND DISCUSSION

The initial levels of pesticide residues in date palm fruit samples after 24-hours of treated the infected tree before the pre-harvest interval are detected to evaluate the level of pesticides residue in date Palme is within MRL limit or not. The initial concentration detected for pesticide residues in (Table 1) reflect one of the wrong behavior of some farmers as they don't follow the instructions by the optimum use of agricultural pesticides in terms of non-compliance with the

**Table 1: Initial Pesticide Residues Level Detected in Date Palm Samples**

| Detected Pesticides | Initial Level of Pesticide Residues (mg/kg) | MRLs (mg/kg) (European Commission) |
|---|---|---|
| Chlorpyrifos * | 0.34±0.02[b] | 0.01 |
| Fipronil* | 1.73±0.05 | 0.005 |
| Methomyl** | 2.04±0.10 | 0.01 |
| Carbendazim** | 3.11±0.12 | 0.1 |

**Note:** [b] Average concentration ± Standard Deviations for triplicate experiments.* GC/MS-M; **LC-MS/MS.

pre-harvest interval which leads to an increase in the level of pesticide residues in food above the permissible limits (MRLs) (EU-MRL, 2008). Also, MRLs can from wrong behaviour for not following the recommended concentration for each pesticide during treatments.

From Table 1 the level of pesticides residue detected in date fruit represent a health risk to the consumer that may cause a lot of chronic diseases and threaten human life so should decrease that level using advance decontamination technique in order to decrease the risk especially if large quantities of the crops are harvested and contaminated with these hazard and dangerous pesticides.

In this study ozone and radiation, techniques are utilized to remove and decrease the level of different pesticide residues in Post-harvest crops of date palm (Figure 4).

In the present study, the experiments were carried out to investigate the effect of radiation from $^{60}$Co γ-ray and Ozone technology with contact time 30 min and 60 min to decontaminate the residue of detected pesticides in Date palm fruits that normally eaten raw and large quantities enter in different food industries. The optimal safe radiation dose level useful for the reduction of pesticide residues selected from the WHO recommended doses of radiation for fruits and vegetables at 0.5-1.0 KGy (FAO/WHO, 2007).

## Decontamination Chlorpyrifos Pesticide Residues

The results of chlorpyrifos Pesticides residue (0.0089±0.003 mg/kg) in Barhee dates variety after decontamination with 1.0 KGy $^{60}$Co γ-ray (Table 2 and Figure 3a) reach to lower MRLs listed in (Table 1) the removal with $^{60}$Co γ-ray achieved (97.6%) in comparing to Ozone technology at contact time 60 min with ozone gas in Deionized water (89.7%) (Figure 1). In present study the efficiency of $^{60}$Co Gamma-radiation to remove Organophosphorus pesticide (Chlorpyrifos) at Level 0.5 KGy and 1.0 KGy (56.1%-97.3%) is in agreement with (Chowdhury *et al*., 2014) for reduction of Chlorpyrifos (35%-91%), Diazinon (48%-90%) and Phosphamidon (45%-95%) applied on different vegetables commodity in Malaysia while ozone method in contact time 60 min at 25 °C is more effective to remove chlorpyrifos residue in date palm (89.7%) is in agreements with study achieved by (Khaled *et al*., 2017)

**Table 2: Removal % and Concentration of Different Pesticide Residues on Date Palm Fruits Using Ozone and Radiation Technologies**

| Pesticides Types | Ozone Treatments (mg/Kg) & Removal % | | Radiation Treatments (mg/Kg) & Removal % | |
|---|---|---|---|---|
| | Oz30 min | Oz60 min | 0.5 KGy | 1.0 KGy |
| Chlorpyrifos | 0.198±0.02[b] | 0.035±0.01[b] | 0.149±0.04[b] | 0.0089±0.003[b] |
| | **(41.7%)** | **(89.7%)** | **(56.1%)** | **(97.3%)** |
| Fipronil | 1.12±0.06 | 0.361±0.03 | 0.620±0.03 | 0.149±0.03 |
| | **(35.2%)** | **(79.1%)** | **(64.2%)** | **(91.9%)** |
| Methomyl | 1.36±0.15 | 0.320±0.02 | 1.050±0.12 | 0.105±0.05 |
| | **(33.4%)** | **(84.3%)** | **(48.6%)** | **(94.8%)** |
| Carbendazim | 1.22±0.06 | 0.097±0.05 | 1.478±0.13 | 0.322±0.07 |
| | **(60.7%)** | **(96.8%)** | **(52.4%)** | **(89.6%)** |

**Note:** [b] Average concentration ± Standard Deviations for triplicate experiments.

using Ozone water at 25 °C (83%) removal in pepper and other vegetables in the study.

## Decontamination Fipronil Pesticide Residues

Fipronil is a broad-spectrum insecticide that belongs to the phenylpyrazole family classed as a WHO Class II moderately hazardous pesticide. The initial residue level detected in date palm samples (Table 1) is in agreement with (Abbassy *et al*., 2017). This level by Estimated dietary Exposure Dose (EED) and Risk Quotient (RQ), causes a health risk. Radiation at 1.0KGy technology and Ozone at contact time 60 min can decrease the risk of that pesticide (Table 2 and Figure 1).

**Figure 1: Removal % for Pesticide Residues Using Radiation and Ozone in Date Palm Fruits**

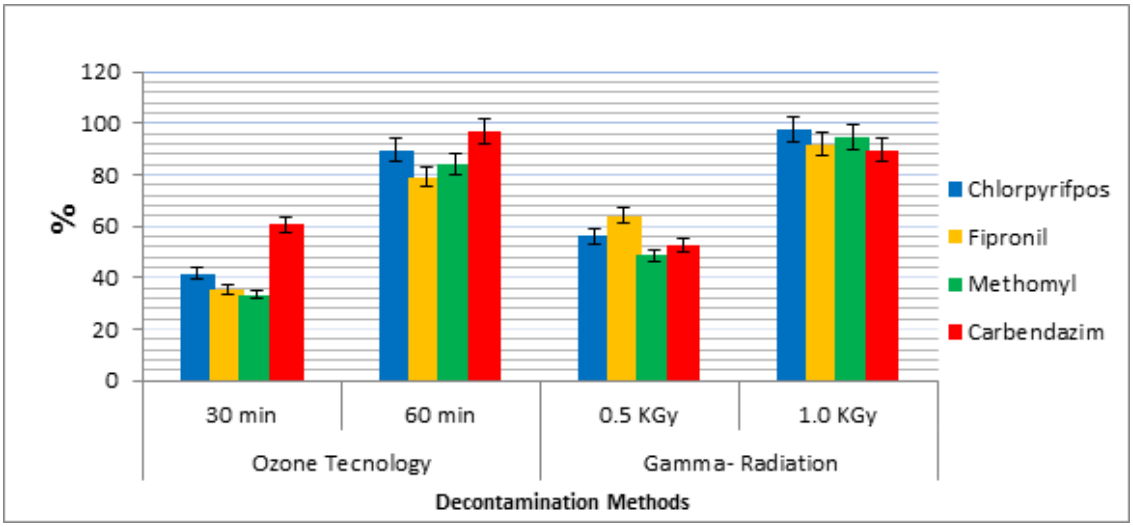



**Figure 2: The Efficiency of Decontamination Techniques for Reduction of Pesticides Residues in Date Palm Fruits in Comparison with the Initial Level**

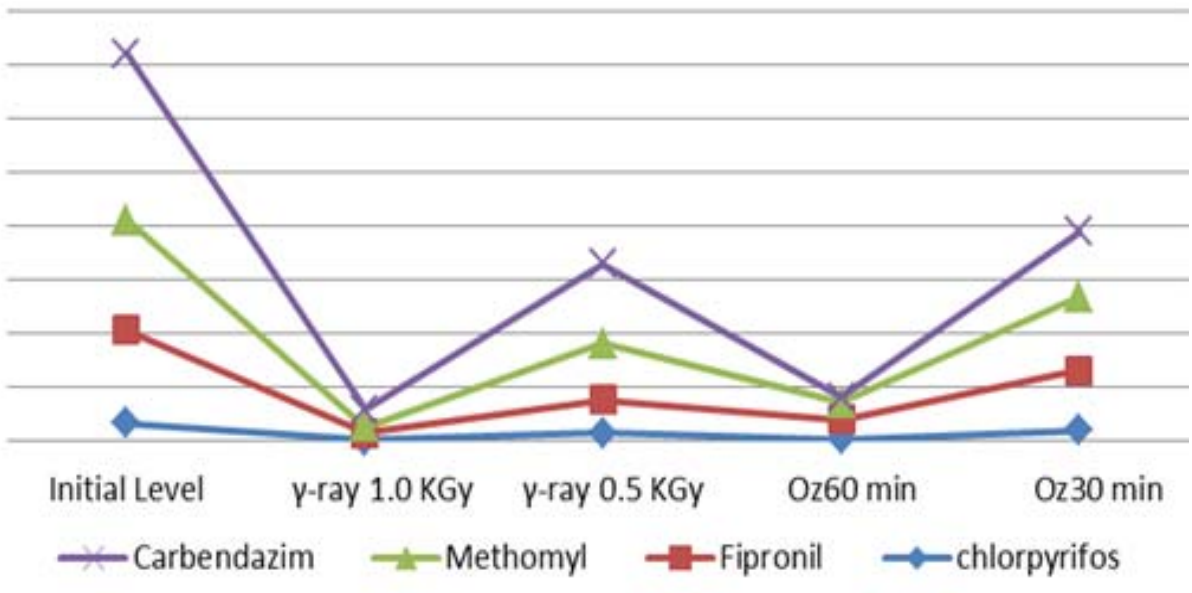


**Figure 3a: GC-MS/MS Peaks of Initial Level and Removal Chlorpyrifos Residues from Dates Samples by $^{60}$Co γ-Ray at 1 KGy**

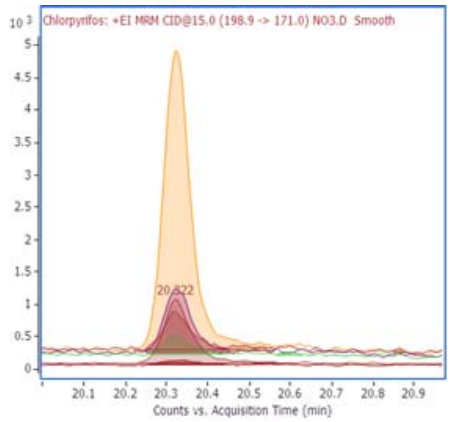
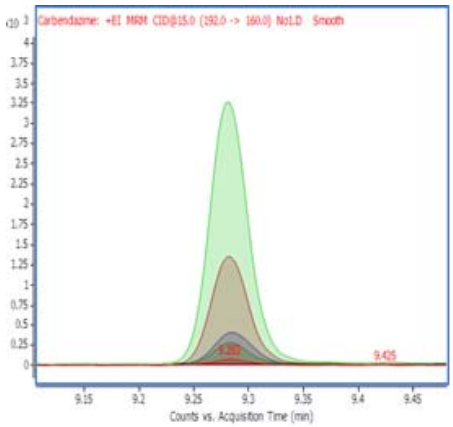



**Figure 3b: LC-MS/MS Peaks of Initial Level and Removal Carbendazim Residues from Dates Samples by Ozone at 60 min Contact Time**



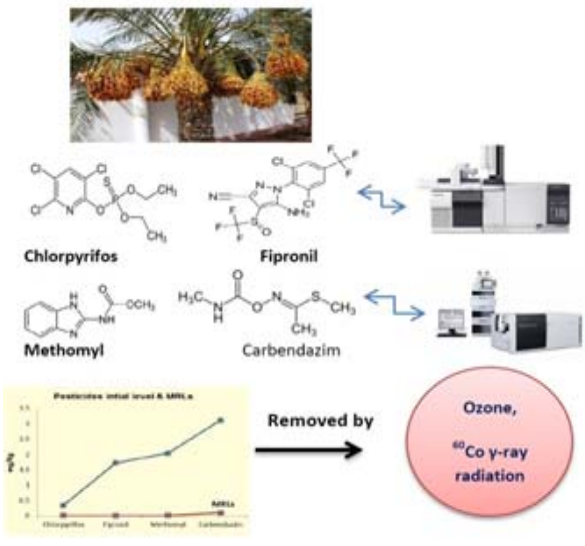

## Decontamination Methomyl Pesticide Residues

Methomyl classified by the World Health Organization (WHO) as highly hazardous (class IB) belongs to Carbamates family pesticides. Removal of Methomyl residue from date palm fruits using ozone achieves reduction (33.4%- 84.3%) (Table 2) and these results are in agreement with (Al-Dabbas *et al*., 2014). The reduction % for Methomyl after 30 min of ozonation reach 92.13% in tomatoes juice spiked with 10 ppm. The ability of ozonation in reduction related to the ability of ozone to generate hydroxyl radicals in aqueous solution, which are highly effective to decompose Methomyl, so as the time of exposure increased hydroxyl radicals continued to be generated throughout the treatment, and more residues degraded. From (Figure 2) observe the decontamination of Methomyl using gamma rays achieve reduction 94.8% which decrease the residue risk from (2.04 to 0.105 mg/kg) (Figure 2). In agreement with (Abdel Aal *et al*., 2001), where Lannate (Methomyl) has aliphatic compounds are very sensitive to ionizing radiations which cause radiation degradation but in disagreement with (Al-Antary *et al*., 2014) when using UV-radiation in tomatoes juice achieved treatment 19.59% that may be due to photodegradation needs to long exposure time to cause hemolytic cleavage of C-N bond to form radical pairs.

## Decontamination Carbendazim Pesticide Residues

Carbendazim belongs to benzimidazole fungicide family used for protection and treatments of crops, fruits and vegetables against fungal diseases. The initial level of carbendazim residue is higher than MRLs in date fruit after the post-harvest (Table 1) which involves possible health risk and environmental pollution. The efficiency of ozone decontamination at contact time 60 min for removal residue of carbendazim in date fruits are better than $^{60}$Co γ-ray radiation method at 1.0 KGy as shown in (Figures 1 and 2). Level of the residue using ozone reaches to lower MRLs and becomes safe for human (Table 2 and Figure 3b). The removal percentage using ozone in the present study is in

**Figure 4: Decontaminations Different Pesticides Residues Using Recent Techniques**



agreement with (Liu *et al*., 2014; and Xia *et al*., 2015) while the % decontamination of carbendazim using $^{60}$Co γ-ray in is agreement with (Bojanowska-Czajka *et al*., 2011).

## CONCLUSION

The present study shows the importance of detecting and evaluation of the residue levels of pesticides in Date palm fruits before being marketed. The results revealed that the residue level of certain insecticides and fungicides were higher than the Maximum Residue Levels (MRLs) and here is claimed that urgent need to educate farmers about the dangers posed by residues of these pesticides, when not used it according to instructions which may lead to serious health risk for humans. The work has been extended to study the modern technical methods to get rid of those harmful residues of pesticides using ozone and radiation, which proved high efficiency in the relative decontamination of pesticide residues in the date palm crops. Through this study, other studies can be done on different pesticides and many types of vegetables and fruit Which assess high levels of pesticide residues, especially if they are in large harvest quantities and therefore attempt to protect the consumer from the dangers of these compounds.

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