



Research Paper

Degradation of malathion in aqueous solutions using advanced oxidation processes and chemical oxidation

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Induced degradation of Malathion in aqueous solutions with advanced oxidation processes (AOPs), using ultraviolet irradiation (UV), ozonation and chemical oxidation using (sodium hypochlorite, calcium hypochlorite, monochloride-isocyanuric acid (MCICA), dichloroiso-cyanuric acid (DCICA), trichloroisocyanuric acid (TCICA)) was studied. Malathion and its degradation products were extracted using solid phase extraction (SPE) method, identified using GC-MS. Results showed that the degradation of malathion in aqueous solutions followed the first order reaction, and its half life was 2.37, 4.53, 6.64 and 8.84h under ozonation, UV, 1.5%TCICA and 1.5% DCICA, respectively when malathion solutions treated for 12 h. The concentrations of chemical oxidative substances, active chlorine content and time of treatments had a significant effect on degradation rate of Malathion,

which increased with increasing of each. The most enhancement of Malathion degradation was observed in treatment with ozonation, UV, TCICA and DCICA where the dissipations % of the parent compounds were 96, 68.43, 47 and 40.14%, respectively. The intermediates products of Malathion degradation using chemical method were identified as O, O-dimethyl hydrogen phosphorothioate (DMHP) and diethyl succinate. UV leads to formation of dimethyl phosphate (DMP), diethyl succinate and malaoxon. Ozonation leads to formation of phosphorothioic acid, O, O, S-trimethyl ester (PSA), 2-mercapto-succinic acid diethyl ester (MSA) and malaoxon.

Key words: Pesticide, malathion, degradation, UV-irradiation, ozonation

INTRODUCTION

Organophosphorus insecticides are a group of chemical compounds which worldwide used in agricultural to prevent bad effects of insects and other pests to increase the yields of the crops. Malathion in Egypt has a significant importance due to its wide distribution, persistence and extensive use. Malathion led to contamination of soil, surface, air, and groundwater. Wide range of harmful effects of organophosphates affect on humans. The immediate effect of an acute exposure is the accumulation of acetylcholine at the receptors, giving rise to the characteristic symptomatology of the acute

organophosphorus poisoning, which in turn has resulted in undesirable side effects such as acute toxicity and chronic toxicity i.e. teratogenicity, carcinogenicity and mutagenicity (Juraske et al., 2007). Their residues are presented in different environmental compartment: soil, air, Food and water (Ioannidou et al., 2010; Hussein et al., 2015).

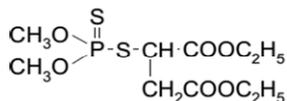
The contamination of surface and ground water by pesticides is an important issue so as the scientists are dealing with over the years to prevent accumulation or contamination (Hussein et al., 2002). Since the presence

of pesticides in water can cause serious problems in both the environment and human being, their removal from water is often required. Water treatment methods include precipitation, coagulation/flotation, sedimentation, filtration, membrane process, electrochemical techniques, ion exchange, biological process, adsorption onto activated carbon and chemical process were used for removing pesticides from water (Miltner et al., 1985; Pirbazari et al., 1984; El-Geundi et al., 2005). Each method has its own merits and limitations in applications.

Among chemical treatments, physicochemical and biological treatments are generally referred to as advanced oxidation processes (AOPs), which include UV irradiation, photo-catalysis (hydrogen peroxide and ozone), chemical oxidation (Briceño et al., 2012) and biodegradation (Hussein et al., 2002, Hussein et al., 1999; Singh et al., 2004; Burrows et al., 2002). Chemical degradation process is one of the most powerful methods to change the structure molecule of insecticide and change it to nontoxic compounds with a beam of accelerated electrons or chemical catalysis was employed for decomposition of various pollutants. Many publications were devoted to the degradation of organic compounds by oxidation compounds and ionizing radiation (Cooper et al., 1989; Basfar et al., 2007; Mohamed et al., 2009). The aim of this study is to degrade organophosphorus insecticide malathion by using chemical oxidation using (NaOCl, Ca(OCl)₂, MCICA, DCICA, TCICA), UV and ozone in simulated wastewater to select method which can remove malathion with maximum percent in the minimum time.

MATERIALS AND METHODS

Malathion insecticide used in this experiment was active ingredient materials 1000 ppm was supplied from Standard Co. USA and Malathion 57% EC formulation was supplied from Central Laboratory of Residue Analysis of Pesticides (Egypt). Chemicals used for chemical degradation were NaOCl, Ca(OCl)₂, (MCICA), (DCICA) and (TCICA) in which supplied from ISIPAC company (Egypt) with 90%, 70%, 98%, 99%, 98% purity respectively. All chemical reagents used were analytical grade. Dichloromethane (CH₂Cl₂), methanol (CH₃OH) and ethyl acetate (CH₃COOC₂H₅) of HPLC quality were purchased from Sigma-Aldrich, Malathion (Diethyl (dimethoxy thio phosphryl thio) succinate).



Chemical Formula: C₁₀H₁₉O₆PS₂

Physical properties of Malathion are as follows: Density, 1.23 g/cm³, Melting point 2.9°C, Boiling point 157°C, Molar mass, 330.35 g/mol, LD₅₀, 290 mg/kg.

Stock solutions

Individual stock solutions at 14 µg/ml (ppm) of the malathion were prepared in 10 mL dark volumetric flasks with dichloromethane (DCM) and stored at -20°C and from it working standard sets were prepared using the serial dilution method malathion (Barr et al., 2006). These standards were used to calculate calibration curve, limits of detection (LOD), limits of quantification (LOQ) and the recovery %. The retention time (RT) and the area of standards were calculated, and their concentrations were automatically calculated according to the standard. Peak area against concentration was plotted to draw calibration curve using Excel program.

Extraction of malathion from water

Malathion from water was extracted using Environmental Protection Agency (EPA) method (525.2) using Thermo Scientific Dionex Auto Trace 280 Solid-Phase Extraction (SPE) instrument. The recovery % was 84.3-96.5% with relative standard deviations 6.19-11.8%. The recoveries obtained are within the EPA recommendations (from 65 to 115%). LOD were calculated as follows:

LOD = 3.3 * Sd / b and LOQ = 10* Sd / b (Shrivastava, 2011) Where Sd= standard deviation of calibration curve, b= slope of calibration curve.

Mass spectrometer configuration

Detection and calibration curve of Malathion and its degradation products were done using an Agilent 5975T LTM GC/MSD gas chromatograph equipped with a mass spectrometer. The GC column was a fused silica capillary column HP-5MS, 5% phenyl methylpolysiloxane, with the dimensions of 20 m × 0.18 mm i.d. and a 0.18 µm film thickness (Agilent Technologies). A purified helium carrier gas was used at a constant flow. The MS was operated in electron impact (EI) ionization mode at an EM voltage of 1811.8 volts (injection volume 1.0 µl in split less mode) with 2 minutes solvent delay. The total ion current (TIC) chromatograms were recorded between 50-800 m/z, at a rate of 37 scans per second. EI mass spectrum database searches were carried out in a mass spectral library National Institute of Standard Technology (NIST) search program version 1.5, Gaithersburg, MD, USA. To measure the molecular weight by the GC device access to the mass spectrometer, the Mass spectrum of a sample of a certain material compared with the standard

mass spectrum and then definition of unknown components (Singh et al., 2004). The temperature program used was as follows: Initial temperature, 80°C held for 1 min, then at the rate of 10°C /min to 180°C, rate 30°C/min to 25°C held for 2 min, 15°C /min to 320°C and then maintaining this temperature for 10 min. The temperature of the injection port was 220°C and a 1 µl volume was injected. The temperatures of ionization source were kept at 210°C. For identification, the major ions (m/z) and retention times both were considered.

Degradation of malathion using chemical method

Oxidation of Malathion was achieved by preparing a stock solution of 26 liters 14 ppm commercial Malathion EC in deionized water for preparation of simulated wastewater. Then 250 ml of stock solution were transferred to thirty dark 250 ml bottle numbered from 1 to 30. NaOCl, Ca(OCl)₂, (MCICA), (DCICA) and (TCICA) were added to malathion EC with six different concentrations varies from 0.3% to 1.8% in three replicates and left at room temperature in dark room, and stir well for about 50 min to let the reaction takes place. After 24 h three samples 250 ml volume of each treatment were extracted using SPE technique using different solvents, ethyl acetate, methylene chloride and methanol. These solvents were used for extraction and then analyzed on GC/MS. LT₅₀ and removal percent of pesticide were calculated from peak area of pesticide.

Degradation of Malathion using Ultraviolet Irradiation (UV)

The used UV Photolytic reactor was dark cylindrical shape having dimensions of 27 cm length, 2.5 cm diameter and made up of stainless steel. The photo reactor filled with 250 ml of 14 ppm Malathion EC solution. The source of UV light is a 10 W high-pressure mercury lamp (mean wavelength 254 nm). Irradiation interval ranged from 2 to 12 h, then extracted using SPE and finally analyzed on GCMS.

Degradation of Malathion using Ozone (O₃)

Ozonation experiments were carried out using ozone generator model 1KNT-24 (ENALY Co. China). The bubbling gaseous ozone was of 5 mg/l concentration and constant flow rate of 80 ml/min into a 500 ml round dark bottom flask connected with gas dark scrubber with a disperser at the column bottom. The volume of 250 ml Malathion (initial concentration: 14 ppm) was ozonated for different time periods (from 2 to 12 h). The excess gaseous ozone was trapped in 2% potassium iodide (KI)

solution.

Kinetic Studies

The degradation rate of malathion was calculated mathematically according to (Timme et al., 1980), in which degradation behavior of insecticide residues was described mathematically obeying pseudo-first order reaction, degradation rate (K) could be calculated using common logarithms as in the following equation:

$$\text{Log } R = \text{log } R_0 - 0.434Kt$$

Where R₀: residue level at the initial time (zero time),
R: residue level at interval (days) after application.
Kt: degradation rate constant at the successive intervals in days,
K: mean of Kt.

Malathion half-life value (RL₅₀) was calculated mathematically according to (Moye et al., 1987) from the following equation:-

$$RL_{50} = \frac{\text{Ln}2}{K}$$

Detection of chlorine content

Detection of chlorine content of each treatment was done using Egyptian standard test method (ES: 1462/2008) as follows: Available chlorine content = (3.545 x N x V) / W
Where N is the normality of sodium thiosulfate, V is the final volume taken from burette and W is the weight of treatment.

Statistical analysis

Data analysis was performed using Costat software. Insecticide data removal was analyzed in different chemical agent samples via one-way ANOVA and LSD (least significant difference) test at $p < 0.05$ levels. Several trials had been done to reach to optimum detection of insecticide and its degradation products on gas chromatograph instrument. Figure 1 shows good sensitivity and repeatability obtained with detection limits of 0.099- 0.14 ppm. LOD and LOQ were 0.39 ppm, 1.20 ppm respectively. Correlation coefficient was 0.9993.

RESULTS AND DISCUSSION

Degradation of malathion using chemical method

Oxidation Products of malathion at using chemical oxidants (NaOCl, Ca(OCl)₂, MCICA, DCICA, TCICA) is

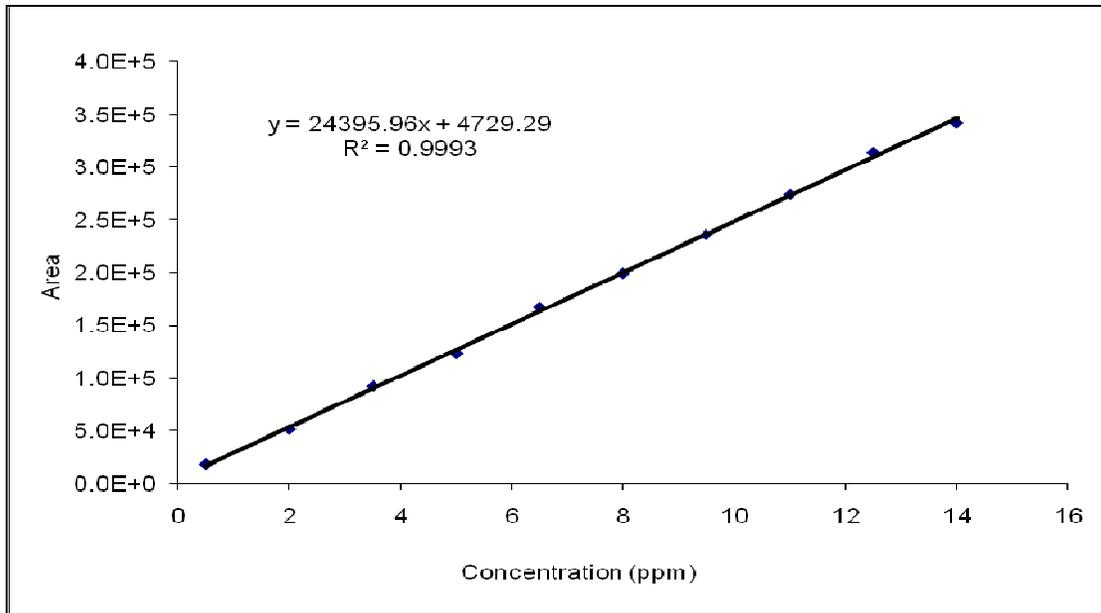


Figure 1. Calibration Curve of Malathion.

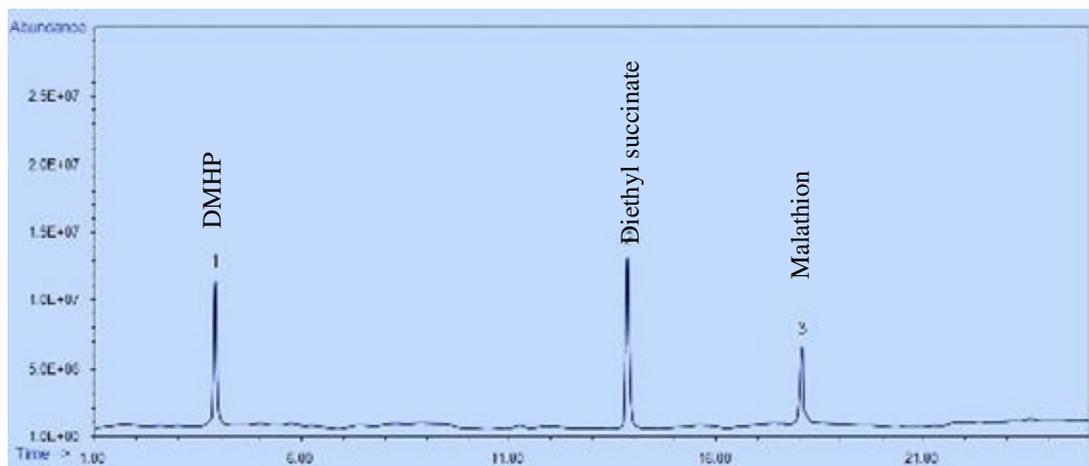


Figure 2. Total ion chromatogram (TIC) of Malathion degradation products using chemical method.

shown in (Figure 2) in which peak1 was O,O-Dimethyl hydrogen phosphorothioate (DMHP), peak2 was diethyl succinate, peak3 was malathion comparing with National Institute of Standards and Technology (NIST) library. In Figure 3 data reveal those main fragment ions of peak1 at m/z 143, 126, 124, 111, 110, 79, 32, 18 and 15 comparing with NIST library giving reasonable matching quality of about 97.5% for DMHP.

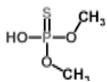


Figure 4 shows main fragment ions of peak2 at m/z 174,

129, 101, 73, 55, 29 and 15 comparing with NIST library giving the quality of about 98.4% for diethyl succinate. The main fragment ions of peak3 at m/z 330, 285, 173, 127, 93 and 29 comparing to NIST library gave good matching quality about 98.3% for Malathion (Figure 5). The degradation products of Malathion resulted from the oxidation pathway of Malathion using chemical method is shown in (Table 1). Presence of peak 1 compound agreed with Lawless et al. 1975, reported that Malathion in acidic medium yields O,O-dimethyl hydrogen phosphorothioate (DMHP). Sukeo et al. 1976, agreed with my results. Figure 6 shows the relation between oxidant percent and removal percent of Malathion. The

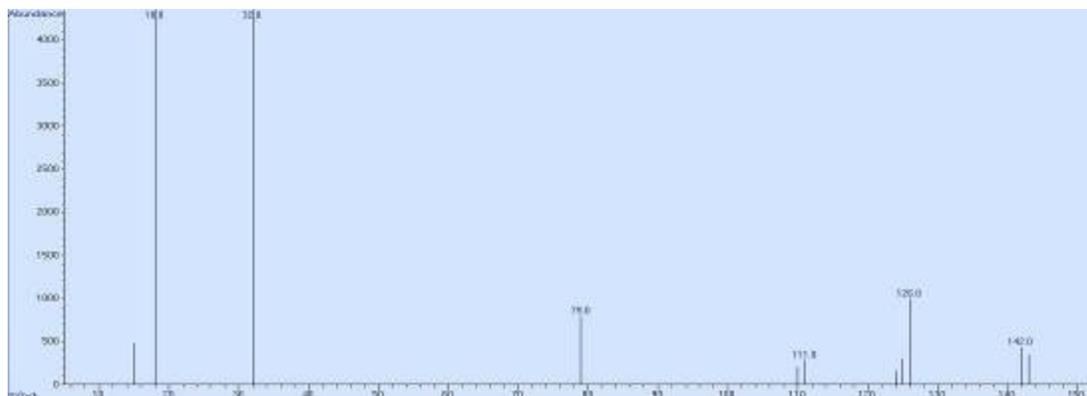


Figure 3. Main fragments of peak1.

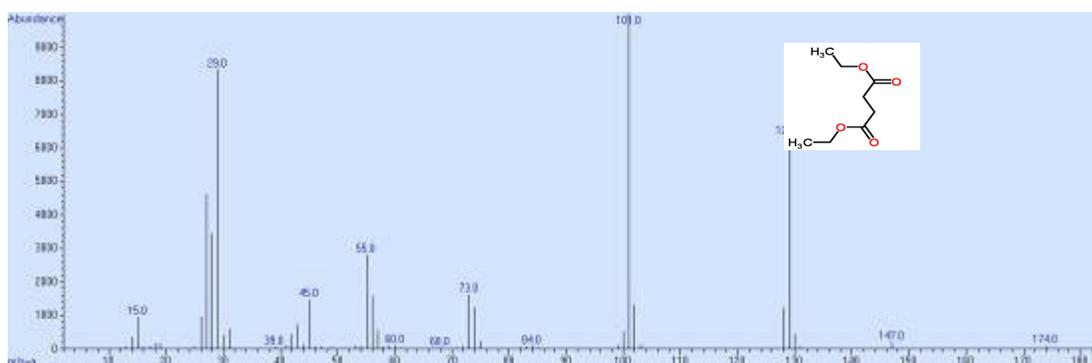


Figure 4. Main fragments of peak2.

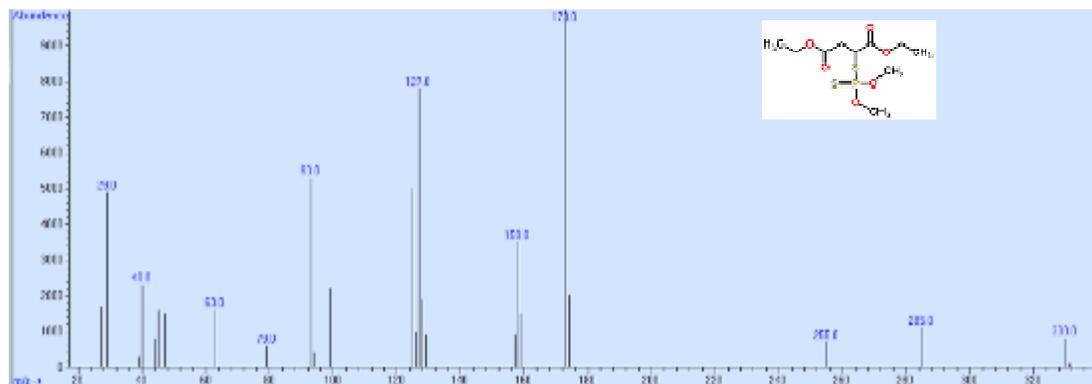


Figure 5. Main fragments of peak3.

optimum oxidation of Malathion achieved after treatment with 1.5% TCICA reaching 50.24% removal, While 1.8% TCICA gave better oxidation 50.49% than that of 1.5% but treatment with 1.8% cause a precipitation of TCICA due to saturation of the solution. Therefore, it is better to use 1.5% to avoid the precipitation of the oxidant on one hand, and on the other hand to reduce the cost of the process. When NaOCl, was used at concentrations

ranging from 0.3-1.8%, it led to degradation of 2.01-18.05%. On the other hand, when $\text{Ca}(\text{OCI})_2$ was used at 0.3-1.8%, led to degradation of 4.61-22.99%. Using MCICA at 0.3-1.8%, the degradation was 8.40-27.75%. The same concentration of DCICA degraded Malathion from 13.28-46.02%. The highest loss of Malathion was achieved from 18.18-50.49% when TCICA was used with same concentration mentioned before. From these

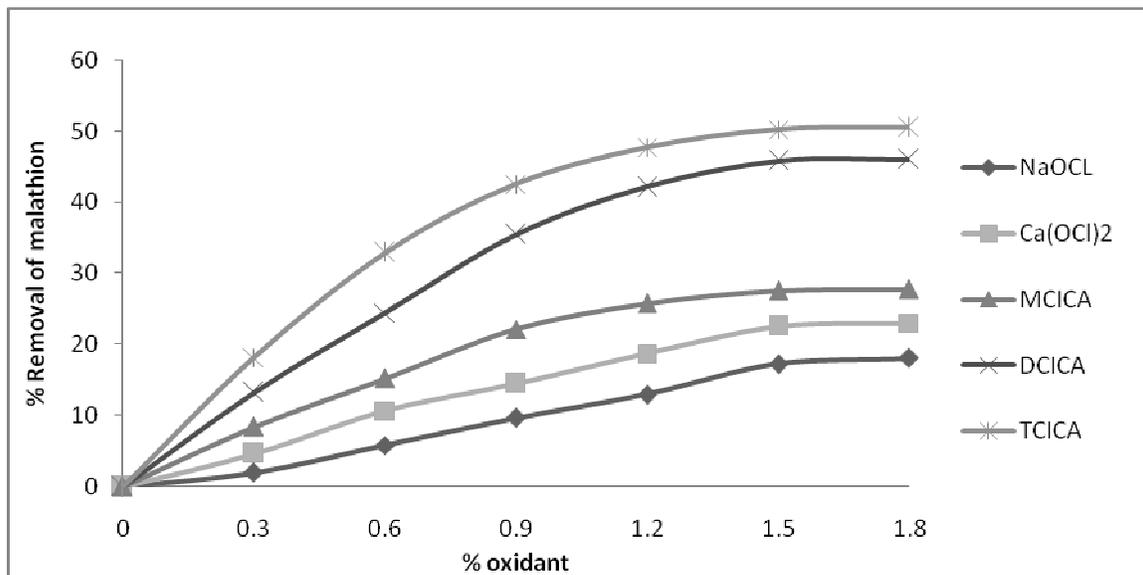


Figure 6. Oxidation trend of Malathion using different oxidants after 24h.

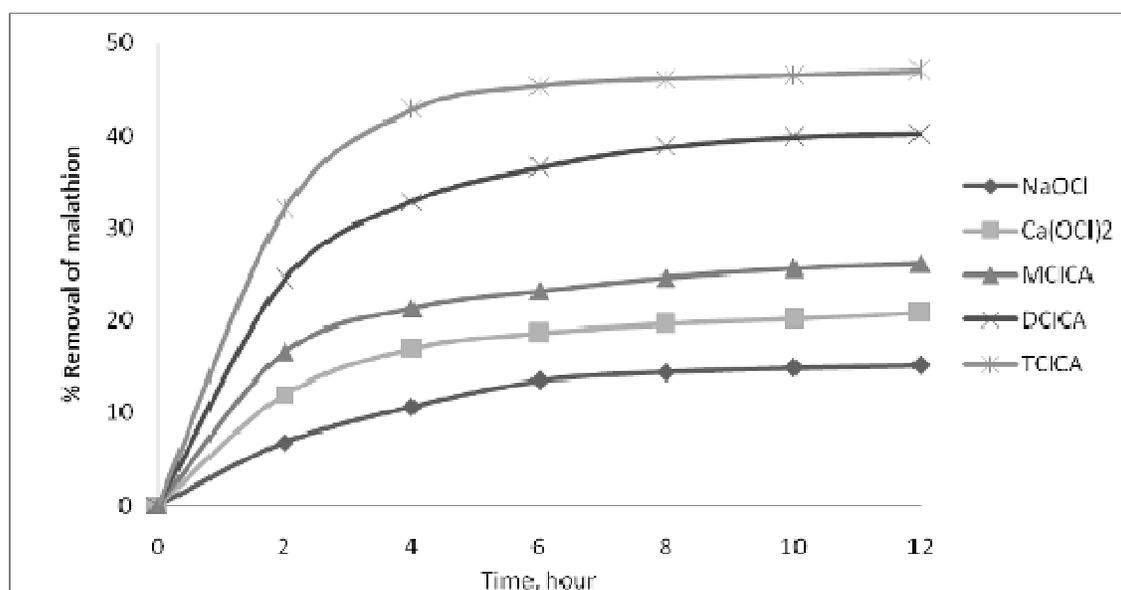


Figure 7. Kinetic trend of Malathion using different oxidants after 12h.

results it is clear that when the oxidant percent increase leads to increase degradation of Malathion, due to increase of the chlorine content.

Figure 7 shows the degradation trend of Malathion using different oxidants for 12h. Half life time of Malathion using DCICA was 8.84 hours while when using TCICA, it was 6.64h as shown in (Table 4). Figure 8 shows that when chlorine content increases, the degradation percent of Malathion increased. Using TCICA (25.28% chlorine) the degradation was 50.49%, while when NaOCl (6.92% chlorine) was used the loss was 18.05%. TCICA has

found applications in chlorination, oxidizing agent and as a mild homogeneous catalyst in organic chemistry and also disinfectant (Paseta et al., 2016). Figure 9 shows chemical formula of (TCICA) and its reactions in water producing first cyanuric acid ($C_3H_3N_3O_3$) and hypochlorous acid (HClO) and then Cl_2 upon oxidation of HClO.

Effect of ultraviolet irradiation on malathion

Exposure of Malathion to different time interval from 2 to

Table 1. Oxidation products using chemical method.

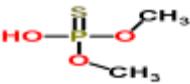
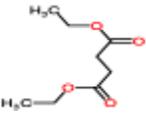
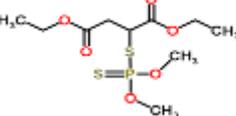
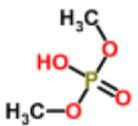
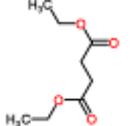
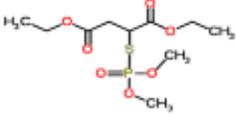
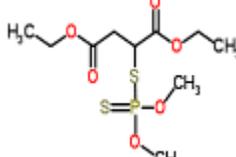
Peak no.	Chemical name	Structure	RT(min)	Mwt	Molecular formula
1	DMHP		3.9	142.11	C ₂ H ₇ O ₃ PS
2	Diethyl succinate		13.9	174.09	C ₈ H ₁₄ O ₄
3	Malathion		18.1	330.36	C ₁₀ H ₁₉ O ₆ PS ₂

Table 2. Chemical structure of Malathion oxidation using UV.

Peak no.	Chemical name	Structure	RT(Min)	M.Wt	Molecular formula
1	DMP		6.9	126	C ₂ H ₇ O ₄ P
2	Diethyl succinate		13.9	174	C ₈ H ₁₄ O ₄
3	Malaoxon		17.4	314	C ₁₀ H ₁₉ O ₇ PS
4	Malathion		18.1	330	C ₁₀ H ₁₉ O ₆ PS ₂

12 h using high-pressure mercury lamp (254 nm) led to degradation of the insecticide. Malathion EC (14 ppm) was oxidized to DMP, diethyl succinate and malaoxon. Percent removal of Malathion reaches 68.43% at exposure of 12 hours as shown in (Figure 16). Half life time of Malathion using ultraviolet irradiation was 4.53 h as shown in (Table 4). The total ion chromatogram of oxidation products of Malathion using UV in which peak1 was dimethyl phosphate, peak2 was diethyl succinate, peak3 was Malaoxon, and peak4 was Malathion as shown in (Figure 10). Based upon the identification of degradation products of Malathion, the oxidation pathway of Malathion using Ultraviolet irradiation were presented in (Table 2). These oxidation products agreed with those reported by Aires et al. 1992 and Newhart, 2006. Also Kralj et al. 2007, reported that photodegradation of

Malathion using UV results in formation of diethyl succinate and malaoxon.

Effect of ozonation on malathion

Exposure of Malathion to different time interval from 2 to 12 h using ozone leads to degradation of insecticide. Malathion EC (14 ppm) was oxidized to phosphorothioic acid, O,O,S-trimethyl ester (PTA), 2-mercapto-succinic acid diethyl ester (MSA) and malaoxon. Percent dissipation of insecticide varies from 0 % to 96.0% at exposure of 12 h as shown in (Figure 16). Half life time of Malathion using ozonation process was 2.4 (Table 4). Figure 13 illustrates the total ion chromatogram of oxidation products of Malathion using ozone in which

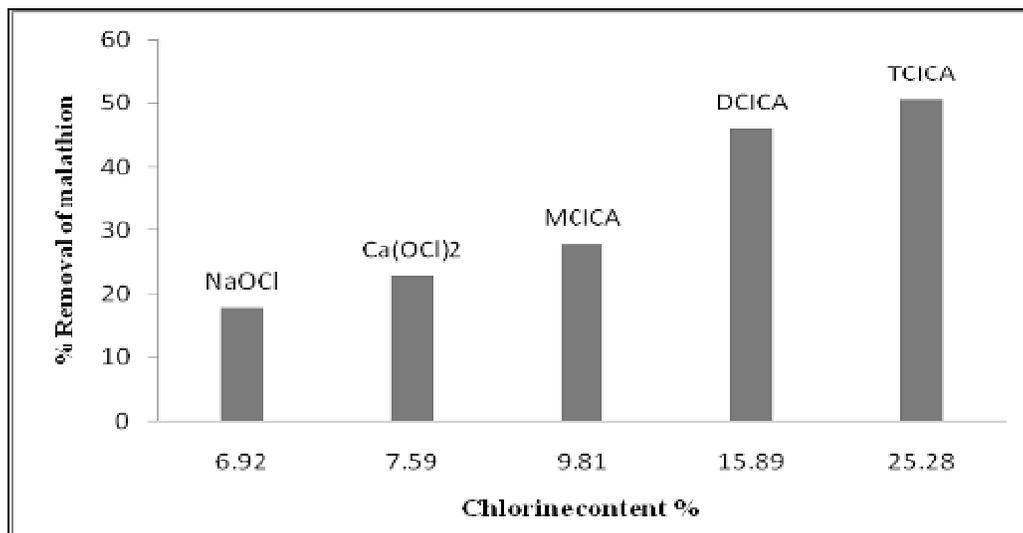
Table 3. Chemical structure of Malathion oxidation using ozone.

Peak no.	Chemical name	Structure	RT(min)	M.Wt	Molecular formula
1	Phosphorothioic acid, O,O,S-trimethyl ester (PTA)		14.8	156	C ₃ H ₉ O ₃ PS
2	2-mercapto-succinic acid diethylester (MSA)		15.6	206	C ₈ H ₁₄ O ₄ S
3	Malaoxon		17.4	314.29	C ₁₀ H ₁₉ O ₇ PS
4	Malathion		18.1	330	C ₁₀ H ₁₉ O ₆ PS ₂

Table 4. Malathion removal % after treatment with UV, O₃ and 1.5% chemicals.

Time(hr)	Malathion degradation%					UV	O ₃
	NaOCl	Ca(OCl) ₂	MCICA	DCICA	TCICA		
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	6.79	11.97	16.59	24.43	32.00	39.21	44.60
4	10.64	17.00	21.29	32.86	42.79	52.07	68.70
6	13.50	18.61	23.21	36.50	45.36	59.00	84.50
8	14.36	19.64	24.64	38.79	46.14	64.21	90.60
10	14.86	20.14	25.64	39.86	46.57	67.00	94.60
12	15.14	20.86	26.07	40.14	47.00	68.43	96.00
K	0.02	0.04	0.05	0.08	0.10	0.15	0.29
LT ₅₀	>12	>12	>12	8.84	6.64	4.53	2.37

LT₅₀: Half-life value, K: Degradation rate constant.

**Figure 8.** Bar chart showing the degradation percent of Malathion.

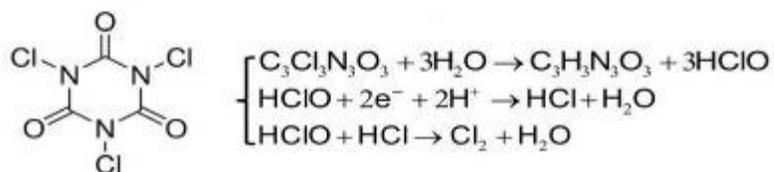


Figure 9. Reaction of (TCICA) in water.

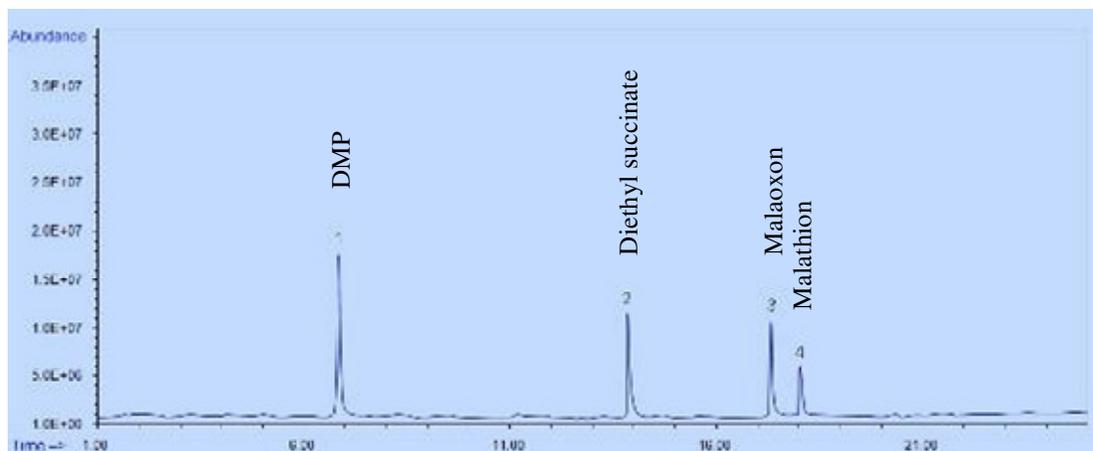


Figure 10: TIC of degradation products of Malathion using UV.

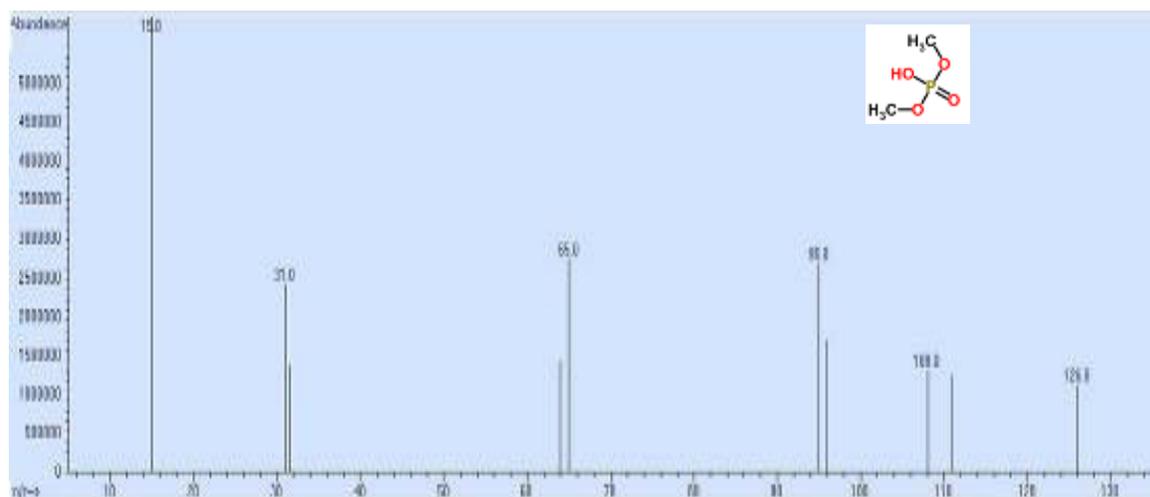


Figure 11. The main fragment ions of peak1 at m/z 126, 111, 108, 95, 64, 31 and 15 in accordance with NIST library giving good matching quality of about 98.2% for Dimethyl phosphate (DMP).

peak 1 was PTA, peak2 MSA, peak3 malaoxon, peak4 Malathion. Based upon the identification of degradation products of Malathion, the oxidation pathway of Malathion using ozone are presented in (Table 3). These oxidation

products coincide with that reported by (Reynolds et al., 1989). Masten et al. 2001, reported that Malathion concentrations were decreased after ozonation and its by-products were malaoxon, phosphoric acid and

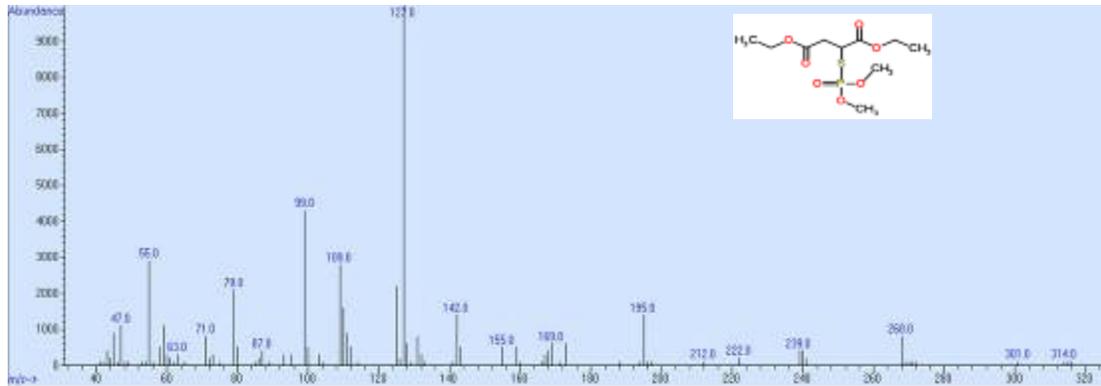


Figure 12. The main fragment ions of peak3 at m/z 314, 195, 142, 127, 99, 79, 55 and 47 according to NIST library, good matching quality of about 97.3% for malaoxon.

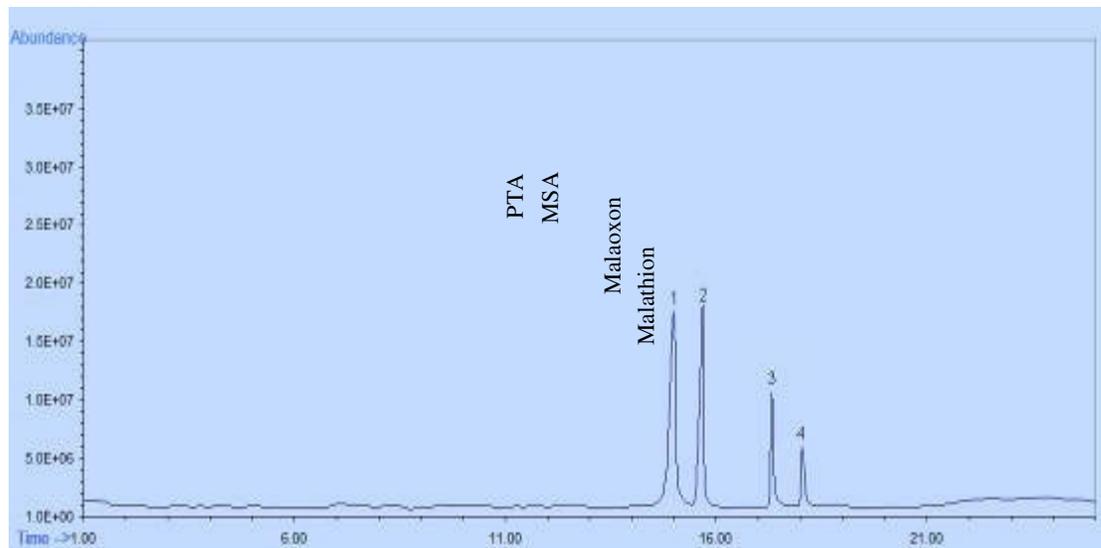


Figure 13. TIC of degradation products of Malathion using ozone.

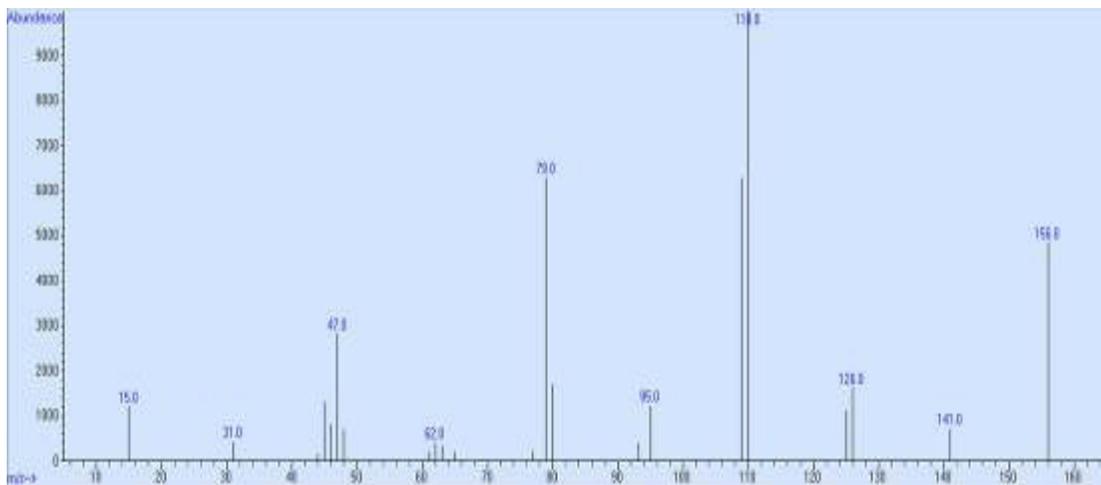


Figure 14. The main fragment ions of peak1 at m/z 156,126,110, 79, 47 and 15 according to NIST library, good matching quality of about 97.3% for Phosphorothioic acid, O, O, S-trimethyl ester (PTA).

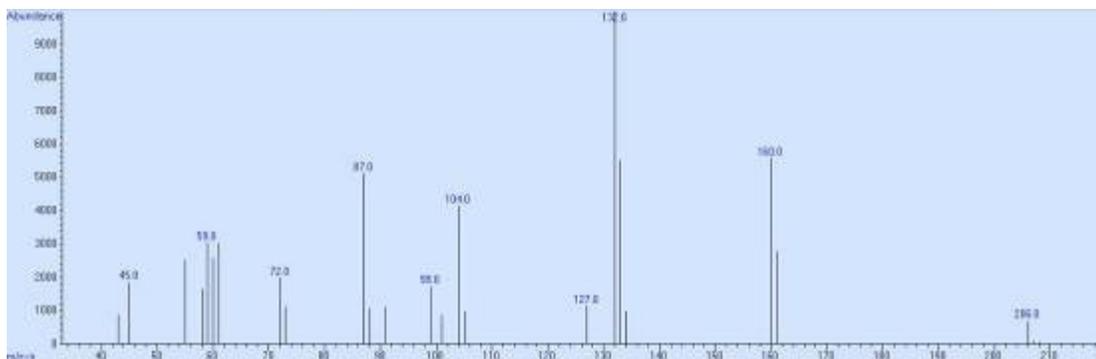


Figure 15. The main fragment ions of peak2 at m/z 206, 160, 132, 104, 87, 72 and 45 according to NIST library, good matching quality of about 97.3% for 2-mercapto-succinic acid diethylester (MSA).

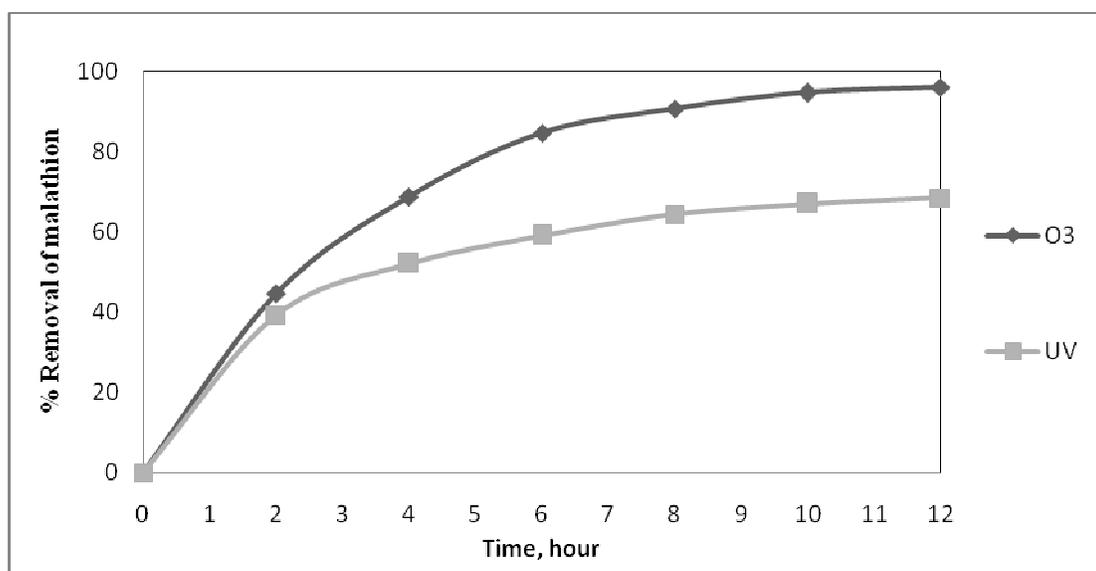


Figure 16. Removal % of Malathion (EC) versus time using UV and O₃

succinic acid derivatives. From data shown in (Table 4), the highest degradation for Malathion by ozone was 96 % while at using chemical method (TCICA) was 47%.

Conclusions

Analysis of Malathion showed the validity of the optimized method used, which allowed the determination of Malathion. The method of detection of pesticide and degradation products was simple, rapid and accurate which have a high level of linearity over a wide range of analyte concentrations with correlation coefficient of 0.9993. The proposed method is efficient, rapid, and low cost and can be scaled up for the destruction of

organophosphorus matter in simulated wastewater samples. Advanced oxidation processes were tested for the breakdown of organophosphorus pesticides from the simulated wastewater using chemical method, ozonation, and ultraviolet irradiation. The degradation of Malathion using chemical oxidation process was affected by active chlorine content of the oxidant and the amount of oxidant. Problems appear at using sodium and calcium hypochlorite in solubility and preservation of chlorine content due to their instability. The removal percent was 15.14, 20.86, 26.07, 40.14, 47.0% for 1.5% (NaOCl, Ca (OCl)₂, MCICA, DCICA and TCICA) respectively using chemical method after 12hrs. While percent removal was 68.43% when the pesticide exposed to UV irradiation and 96.0% in ozonation process for 12 h. From the foregoing results it should be emphasized that in order to achieve

conceivable breakdown of the organophosphorus insecticide, Malathion residues, and chlorination process should be followed. However UV and ozonation gave the best results in the dissipation of Malathion reaching 68.43 and 96.0% respectively but, more toxic product malaoxon was produced. Moreover, their uses are practically more sophisticated and more expensive over the chlorination processes. No toxic products appeared after chlorination of Malathion. The use of chlorination process seems to be practically easier from one hand, and on the other hand in expensive. TCICA is recommended to be used as it was more effective among the other chlorinating material giving 47.0% breakdown of Malathion after 12 h exposure.

Authors' declaration

We declare that this study is an original research by our research team and we agree to publish it in the journal.

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