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Treatment of Pesticide Residues Bi-Products in Some Iraqi Vegetables

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Abstract

Application of pesticide on vegetables will protect them from pest injury, but in another hand will hold pesticide residues inside vegetables. These residues have harmful effect against all consumers. Detection about pesticide residues has been carried out for some Iraqi vegetables (tomato, cucumber, eggplant, and zucchini) by using Gas Chromatography/Mass Spectroscopy (GC/MS). (Quick, Easy, Cheap, Effective, Rugged, and Safe) QuEChERS method has been applied for extraction pesticide residues from targeted vegetables. The GC/MS has been carried out before the treatment of residues for distinguish the vegetables that are suffering from hyper concentration in pesticide residues more than maximum residues limits (MRLs). Three kinds of solutions were used in treatment process with different concentrations: tab water, acetic acid, and citric acid. GC/MS analysis that is carried out before treatment reviled the existence of only bi-products belong to imidacloprid and oxamyl pesticides. The active ingredients of both pesticides degraded efficiently and there is no ability to trace them back. Some of the bi-products represent additives add to improve the ability of pesticide in killing pest. GC/MS had been carried out after treatment of samples with tab water, acetic acid, and citric acid to configure if the bi-products that are belong to oxamyl and imidacloprid still exist or disappeared and to evaluate the efficiency of treatment process. The GC/MS showed that treatment with tab water is the most efficient technique for mitigation pesticide residues in vegetables, whereas, treatment with acetic acid less efficient than tab water technique, whereas, treatment with citric acid is the worst technique in mitigation of pesticide residues due to appearance of more than one bi-products compounds in the results of GC/MS after treatment with citric acid.

Keywords: Mitigate, Tab water, Acetic acid, Citric acid.

معالجة المركبات الثانوية العائدة لمتبقيات المبيدات في بعض الخضروات العراقية

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الخلاصة

ان استخدام المبيدات على الخضراوات سوف يحميها من الاصابات الحشرية والفطرية، ولكن هنالك جانب اخر ضار يتعلق بتراكم متبقيات المبيدات في داخل الخضراوات. الكشف عن متبقيات المبيدات قد تم تنفيذهُ لبعض الخضروات العراقية وهي (الطماطم و الخيار و الباذنجان و والكوسا)، بواسطة استخدام جهاز كروماتوكرافيا الغاز المطياف الكتلي، و لقد تم استخلاص متبقيات المبيدات من الخضروات المستهدفة

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بأستخدام طريقة كويتشرز. اظهرت نتائج جهاز كروماتوكرافيا الغاز المطياف الكتلي قبل المعالجة تحللاً كاملاً للمركبات الفعالة للمبيدات المستخدمة في زراعة الخضروات المستهدفة وبالاخص المبيدان اوكزاميل واسمهُ التجاري فيديت او فيريت، ومبيد اميداكلوبرد واسمهُ التجاري كوميدور او كومفيدور. واظهرت نتائج جهاز كروماتوكرافيا الغاز المطياف الكتلي ايضاً وجود منتجات ثانوية عائدة لكلا المبيدين مع مبيدات اخرى غير قابلة للتحلل في العينات المدروسة. اظهرت نتائج جهاز كروماتوكرافيا الغاز المطياف الكتلي للعينات المفحوصة بعد المعالجة بالمحاليل المذكورة ان المعالجة بأستخدام مياه الصنبور هي الاكفأ بين الطرق الثلاث، بينما المعالجة بأستخدام حامض الخليك كانت اقل كفاءة، بينما المعالجة بحامض الليمون هي الاسوء من بين الطرق الثلاث.

Introduction

Pesticide residues defined as any substance or mixture of material in food for man or forage for animals resulting from the use of pesticide including any determinant derivatives, such as degradation and conversion products, metabolites, reaction products and uncleanness considered to have significant toxic effect [1]. There are two kinds of pesticide residues, bound and conjugated pesticide residues. A soil bound residue is "the un extractable and chemically un identifiable pesticide residues outstanding in fulvic acid, humic acid, and humin fraction after exhaustive sequential extraction with non polar organic and polar solvents". Conjugate pesticide residues are reflect more polar and less lipophlic than the parent pesticide molecules, and as such are therefore more basically could take out from animals and plants [2]. Agriculture in the world has altered greatly in the past one hundred years. Many farmers follow high yield by using low cost energy, plentiful water supply, efficient chemical fertilizers and pesticides [3]. Pesticide play as great value in the high productivity accomplished in agriculture through the control of plant or animal life pests. Although pesticides have advantages, some have defect, such as potential toxicity to human and other desired species. Exposure of general population to pesticide most generally occurs through consuming treated food sources [4]. Despite, good diet contain high percentage of vegetables and fruits show primary factor for reducing the risk of gastrointestinal and breast cancer disease, pesticide residues on vegetables forming possible danger to consumers and have adverse effect on human health [5]. Chemical pesticides are used extremely and regardless to manufacturing instructions. Moreover, 30% of pesticides soled in developing countries do not confront internationally quality standards [6]. Gas and liquid chromatography (GC and LC) coupled to sophisticated mass spectrometry (MS) instrument are among the most powerful analytical tools currently accessible for surveillance of pesticides in food [7].

Materials and Methods

Sample Collection

The targeted vegetables(tomato, cucumber, eggplant, and zucchini), have been collected from two sites, Al-Yusufiyah wholesaler market and Al-Rasheed wholesaler market. Table-1 shows the map of the two collection sites. The collection time were four months, (August, September, October, and November). The reason for chose those four months, are to cover the two kinds of planting for our targeted vegetables, exposed and green-house kinds of planting. Three times of collection were carried out per each month, beginning of the month, middle of the month, and the end of the month. The reason for this kind of collection are to cover all the month targeted vegetables and to take comprehensive idea about pesticide residues in targeted vegetables. The total number of samples are (48) samples were distributed in targeted months as Table-1 shows below.

Table 1-Sample Collection

Sample	Month	Date	Place of Planting	Place of Collection
Tomato	August	5/8/2016	Karbala	Al-Rasheed wholesaler
Tomato	September	5/9/2016	Erbil	Al-Rasheed wholesaler
Tomato	October	5/10/2016	Rabia'a	Al- Yusufiyah wholesaler
Tomato	November	2/11/2016	Rabia'a	Al- Yusufiyah wholesaler
Cucumber	August	5/8/2016	Sulaimaniyah	Al-Rasheed wholesaler
Cucumber	September	5/9/2016	Al-Momniyah	Al- Yusufiyah wholesaler
Cucumber	October	5/10/2016	Erbil	Al-Rasheed wholesaler
Cucumber	November	2/11/2016	Al- Harkawi	Al- Yusufiyah wholesaler
Eggplant	August	5/8/2016	Yusufiyah	Al- Yusufiyah wholesaler
Eggplant	September	5/9/2016	Al-Momniyah	Al- Yusufiyah wholesaler
Eggplant	October	5/10/2016	Yusufiyah	Al- Yusufiyah wholesaler
Eggplant	November	2/11/2016 16/11/2016	Al-Saouira Al-Saouira	Al- Yusufiyah wholesaler Al-Rasheed wholesaler
Zucchini	August	5/8/2016	Sulaimaniyah	Al-Rasheed wholesaler
Zucchini	September	9/9/2016	Erbil	Al-Rasheed wholesaler
Zucchini	October	5/10/2016	Yusufiyah	Al- Yusufiyah wholesaler
Zucchini	November	2/11/2016 16/11/2016 23/11/2016	Al-Tahialiyah Yusufiyah Yusufiyah	Al- Yusufiyah wholesaler Al- Yusufiyah wholesaler Al-Rasheed wholesaler

Sample Storage

All samples had been stored in deep-freeze in (-20 ºC). The reason of that step is to be sure that the concentration of pesticide residues, will not effect by metabolisms process of micro-organisms decomposer when we are waiting our turn for analyzing our samples by GC/MS. The other purpose is to keep the concentration of pesticide residues, the same concentration when we reach the proper time for carryout treatment of pesticide residues experiment[8].

Extraction Method

The method that carried out for extract pesticide residues from targeted fruit tissue, is QuEChERS method. The reason behind choose this technique, is coming from the abbreviation name (QuEChERS). The name represent brief for those words, quick, easy, cheap, effective, rugged, and safe. The other reason representative with that, this technique is one of the innovation technique carried out for extraction pesticide residues from vegetables and fruit. According to reference [9]. The samples should be unwashed and with the peel intact. The samples were homogenized by using blender for time more than 1 min to gain homogenized mixture. After that, fifteen gram from homogenized mixture will be putted inside polypropylene centrifuge tube. Next, 15 ml of stock solution consist of (10 ml glacial acetic acid + 1 L acetonitrile), will be added to the tube. After that, 6 g of anhydrous magnesium sulfate + 1.5 g of anhydrous sodium acetate will be add to the mixture of the tube. Then the tube should be closed properly. Then samples should be shaken by using vortex for 1 min, and centrifuge sample for 1 min at 1.6 RCF. According to [10], If your machine working with RPM unit, instead of RCF unit, we need to convert our unit. So we must apply the following equation for conversion process:

$$\mathbf{RCF=1.12 * R * (RPM/1000)^2}$$

whereas:

R: the radius of rotation centrifuge head measured in millimeters.

So the equation will be:

$$1.6=1.12 * 180 * (RPM/1000)^2$$

So RPM=89.09.

Then 2 ml of supernatant was transferred to polypropylene centrifuge tube contain 100 mg primary secondary amine + 300 mg anhydrous magnesium sulfate. Next 50 mg of graphitized carbon black was added to the tube. The tube was vortexed for 30 second and centrifuged again at 89.09 RPM for 1

min. After that, aliquot will be transferred to GC/MS vial. Now the analyte ready for GC/MS injection [9].

Determination of Pesticide Residues

The determination of pesticide residues have been carried out by using mass spectroscopy coupled with gas chromatography [9].

Result and Discussion

The results of GC/MS before treatment, shows that the collection from November months is the better one because all kinds of pesticides and pesticides bi-products have been decomposed. The reason for that return back to the kind of agriculture applied, greenhouse kind of agriculture is applied in this month. According to reference [11], five important factors affect the rate of decomposition that is happed by micro-organisms decomposer: temperature, aeration, soil pH, soil moisture, and C:N ratio. The highest average of temperature in Iraq reaches to 37.41 ºc in hottest months but there is high fluctuation in the temperatures between morning, afternoon, evening and night [12]. The optimal temperature for working micro-organisms decomposer is 30-40 ºc but the high fluctuation retard the decomposition process [11]. So this is the reason for fully decomposition for active ingredients for pesticides applied during life-cycle of targeted vegetables including the most important two pesticides that are used in planting vegetables, oxamyl and imidacloprid. But the high fluctuation in temperature do not let the decomposers done their work, that was happed in exposed kind of agriculture months, August, September, and October. but in greenhouse kind of agriculture that is happed in November, the plastic cover prevent the fluctuation of temperature due to it's ability for reverse the infrared beams that are coming from sun and return it back to soil and prevent the dispersion of them will keep the soil warm during the night and other equipments add to greenhouse that prevent the fluctuation of temperature. Best moisture soil contain for the optimal work of decomposers is 60 to 80 percent of the water-holding capacity [11]. So greenhouse kind of agriculture can set the moisture contain of soil better than exposed agriculture due to less evaporation that is happed in greenhouse. About soil aeration, soil pH and C:N ratio are the same in both kinds of agriculture because the farmer use the same field in both kinds of agriculture but the difference in plastic mulch. Aeration in both kinds of agriculture are served in optimal way and C:N ratio are kept in optimal ratio by fertilizers. Photo degradation water degradation of pesticide have great impact on increase the rate of degradation in both kinds of agriculture [13 - 14].

The GC/MS analysis conducted for samples before and after treatment with tab water, acetic acid, and citric acid, to know the efficiency of treatment processes.

GC/MS Results Before Treatments

After extraction process, we took the analyte inside vial for GC/MS analysis, the results shows only bi-products belong to oxamyl and imidacloprid pesticides but the active ingredients of both pesticides are totally dissolved. Table-2 shows full explanation of those compounds.

Table 2-GC/MS results for collected samples before treatment

Sample	Date	Compound	Formula	Retention time	Peak area	Peak height	Relationship with pesticides
Tomato	5/8/2016	2,3 butanediol	$C_4H_{10}O_2$	2.312	475729	289042	One of the components used in manufacture imidacloprid.
Tomato	5/9/2016	1-Propene, 1-(2-propenyloxy)-, (Z)-	$C_6H_{10}O$	4.098	27263	11950	Constituent belong to fungicide 1-(2-ARYL-2-R-ETHYL)1H-1,2,4-TRIAZOLES.
		3-Butenoic acid, ethyl ester	$C_6H_{10}O_2$	4.098	27263	11950	Constituents belong to insecticide 2-isopropyl-4-phenyl-3-butenoic acid benzyl esters.
		Allyl vinyl ether	C_5H_8O	4.098	27263	11950	Compound add to oxamyl pesticide.
		t-Butyl ethylideneamine	$C_6H_{13}N$	6.593	37510	17390	Compound found in both pesticides oxamyl and imidacloprid, it represent adjuvant add to pesticides for improve the transport of pesticide from soil to plant and that will increase the effectiveness of pesticides.
		Shellsol 140	C_9H_{20}	7.876	93175	50685	Compound belong to solvent of both pesticides, imidacloprid and oxamyl pesticides, it

							is forming from aromatic hydrocarbons as important compound for solvent.
		1-Hexene	C_6H_{12}	10.502	858744	130194	Very important compound used in production of Lignin emulsion, this emulsion able to control the toxicity of imidacloprid pesticide by combination with pesticide and disable it's active ingredients.
		Heksan	C_6H_{14}	12.672	29150	18573	This compound is one of the solvents used for dilute imidacloprid pesticide powder, solubility of imidacloprid in it is < 0.1 g/L at 20 ºC.
		Diheptyl phthalate	$C_{22}H_{34}O_4$	18.487	48141	26345	Compound add to imidacloprid pesticide for reduce pesticide oxidation, so this will play important role in reduce pesticide degradation, the compound play important
		Diheptyl phthalate	$C_{22}H_{34}O_4$	18.487	48141	26345	

							role in reduce amount of oxygen that are absorbed by pesticide carbon that is found in pesticide structure.
		Octamethylene glycol	$C_8H_{18}O_2$	20.691	51541	20776	Substance add to imidacloprid pesticide for reducing formation of foam when farmers dilute imidacloprid for application purposes because foam increase the insolubility of imidacloprid active ingredients and reduce the effect on pest.
		Nonyl chloroacetate	$C_{11}H_{21}ClO_2$	20.691	51541	20776	Compound used in preparing 6-(5-chloropyridin-2-yl)-2-pent-2-ynyl-4,5-dihydropyridazin-3(2H)-one. The latest compound add to imidacloprid pesticide for synergism purposes.

		Farnesol	$C_{15}H_{26}O$	28.199	57195	18850	Compound add to imidacloprid for increase the pesticide ability for killing pest.
Tomato	5/9/2016	Hexadecanoic acid	$C_{16}H_{32}O_2$	20.449	2114454	905367	Compound produced by plants when they are under stress of imidacloprid.
		Tridecanoic acid	$C_{13}H_{26}O_2$	20.449	2114454	905367	Substance add to oxamyl and imidacloprid pesticide for increase their control on pest.
		E-9-Tetradecenal	$C_{14}H_{26}O$	25.217	411509	190276	Attractive substance add to imidacloprid and oxamyl substance for conservation environment, increase the activity of pesticide by altering the pest behaviors.
		2,13-octadecadien-1-ol	$C_{18}H_{34}O$	25.217	411509	190276	Bio-pesticide add to oxamyl and imidacloprid pesticides dute to high synergism between them.
		E-11-Hexadecenal	$C_{16}H_{30}O$	25.217	411509	190276	Attractive substance add to imidacloprid and oxamyl substance for conservation environment, increase the activity of

							pesticide by altering the pest behaviors.
Tomato	2/11/2016	-	-	-	-	-	There is no compounds have relationship with pesticides or pesticides themselves.
Eggplant	5/8/2016	2,3-Butanediol	$C_4H_{10}O_2$	2.200	244549	187208	One of the components used in manufacture imidacloprid.
Eggplant	5/9/2016	Diheptyl phthalate	$C_{22}H_{34}O_4$	17.473	24686	11547	Compound add to imidacloprid pesticide for reduce pesticide oxidation, so this will play important role in reduce pesticide degradation, the compound play important role in reduce amount of oxygen that are absorbed by pesticide carbon that is found in pesticide structure.
Eggplant	5/9/2016	Diheptyl phthalate	$C_{22}H_{34}O_4$	17.473	24686	11547	
		Hexadecanoic acid	$C_{16}H_{32}O_2$	18.436	956470	254768	Compound produced by plants when they are under stress of imidacloprid.
		Oleamide	$C_{18}H_{35}NO$	22.320	697154	146643	Compound add to oxamyl pesticide for

							improve it's effect as acetyl cholinesterase enzyme inhibitor, it is consider as amide of oleic acid and classified as long chain alcohols, it play important role in block connexin molecules in acetyl cholinesterase enzyme.
		3-Heptadecanol	$C_{17}H_{36}O$	22.320	697154	146643	Compound add to imidacloprid and oxamyl pesticide as drift control agent, it represent kind of fatty alcohol.
		2,4-Dimethyl pentane	C_7H_{16}	7.084	28219	15128	Compound produced by plants for formation lignin-based matrix micro particles, the latest compound play important role in control release the active ingredients of pesticides and imidacloprid, is one of them.

Eggplant	5/10/2016	Hexadecanoic acid	$C_{16}H_{32}O_2$	15.914	2021625	875709	Compound produced by plants when they are under stress of imidacloprid.
		Tridecanoic acid	$C_{13}H_{26}O_2$	15.914	2021625	875709	Compound add to oxamyl and imidacloprid pesticides for increase the ability of pesticide on control of pest insects.
		Di isopropyl sulfite	$C_6H_{14}O_3S$	2.017	2223785	2411698	Compound add to oxamyl and imidacloprid pesticide, it play important role in formation of emulsion when we dilute pesticide for application purposes to reach more dispersion.
		Nonadecanoic acid	$C_{19}H_{38}O_2$	19.434	2021894	822358	Compound add to oxamyl and imidacloprid pesticides for formation suspension of active agricultural compounds that is important in manufacture of both pesticides.
		9-Octadecenoic acid (Z)	$C_{18}H_{34}O_2$	21.408	313707	159623	Substance add to imidacloprid and oxamyl pesticides, it play

							important role as attractant agent for pest spatially whitefly, for increase the effectiveness of pesticide on killing pests, it represent kind of fatty acid.
Eggplant	2/11/2016	-	-	-	-	-	There is no compounds have relationship with pesticides or pesticides themselves.
Zucchini	5/8/2016	2,3-Butanediol	$C_4H_{10}O_2$	2.464	54625	36359	One of the components used in manufacture imidacloprid
Zucchini	9/9/2016	Hexadecanoic acid	$C_{16}H_{32}O_2$	14.069	231864	134256	Compound produced by plants when they are under stress of imidacloprid.
		2,2 Di methyl pentane	C_7H_{16}	6.245	17611	12314	Compound produced by plants for formation lignin-based matrix micro particles, the latest compound play important role in control release the active ingredients of pesticides and imidacloprid,

							is one of them.
Zucchini	5/10/2016	Hexadecanoic acid	$C_{16}H_{32}O_2$	15.955	222273	807316	Compound produced by plants when they are under stress of imidacloprid.
		Tridecanoic acid	$C_{13}H_{26}O_2$	15.955	222273	807316	Compound add to oxamyl and imidacloprid pesticides for increase the ability of pesticide on control of pest insects.
		Z-7-Tetradecenal	$C_{14}H_{26}O$	22.475	443896	265256	Attractant substance add to oxamyl and imidacloprid pesticides for conservation environment and increase the efficiency of pesticide by altering the behaviors of pest insect.
		E-11-Hexadecenal	$C_{16}H_{30}O$	27.475	180640 1	603917	Attractant substance add to oxamyl and imidacloprid pesticides for conservation environment and increase the efficiency of pesticide by altering the behaviors of pest insect.
		Di isopropyl sulfite	$C_6H_{14}O_3S$	2.290	35791216	13202293	Compound add to oxamyl and imidacloprid pesticide, it play

							important role in formation of emulsion when we dilute pesticide for application purposes to reach more dispersion.
Zucchini Zucchini	16/11/2016 16/11/2016	- -	- -	- -	- -	- -	There is no compounds have relationship with pesticides or pesticides themselves
Cucumber Cucumber	5/8/2016 5/8/2016	2,3-Butanediol	$C_4H_{10}O_2$	3.847	6415361	2179654	One of the components used in manufacture imidacloprid
		1,3,4-thiadiazole	$C_3H_4N_2S_3$	24.375	638337	0	Kinds of fungicides
Cucumber	5/9/2016	Glycerol	$C_3H_8O_3$	9.213	72213	16918	Compound used in production of acrolein, acrolein used in the process of imidacloprid production pesticide.
		Hexadecanal	$C_{16}H_{32}O$	15.716	559743	326251	This compound represent kind of insect pheromones add to oxamyl and imidacloprid pesticides as additives play important role in as insect attractive and alter the pest behaviors, it fortified the pesticides

							performance.
		9,17-Octadecadienal	$C_{18}H_{32}O$	17.697	322515	175996	This compound represent kind of insect pheromones add to oxamyl and imidacloprid pesticides as additives play important role in as insect attractive and alter the pest behaviors, it fortified the pesticides performance.
		9,12,15-Octadecatrienal	$C_{18}H_{30}O$	17.768	1093551	544172	This compound represent kind of insect pheromones add to oxamyl and imidacloprid pesticides as additives play important role in as insect attractive and alter the pest behaviors, it fortified the pesticides performance.
Cucumber	5/10/2016	Hexadecanoic acid	$C_{16}H_{32}O_2$	19.424	700072	320558	Compound produced by plants when they are under stress of imidacloprid.
		Tridecanoic acid	$C_{13}H_{26}O_2$	19.424	700072	320558	Compound add to oxamyl and imidacloprid pesticides for increase the ability of

							pesticide on control of pest insects.
		Diisopropyl sulfite	$C_6H_{14}O_3S$	2.017	1495985	1726914	Compound add to oxamyl and imidacloprid pesticide, it play important role in formation of emulsion when we dilute pesticide for application purposes to reach more dispersion.
		9,11-Dodecadien-1-ol	$C_{12}H_{22}O$	18.675	28065	16930	Additive add to oxamyl and imidacloprid pesticides active ingredients, it make synergism with oxamyl and imidacloprid pesticides.
Cucumber	2/11/2016	-	-	-	-	-	There is no compounds have relationship with pesticides or pesticides themselves

Butanediol

According to [15], it has been discovered that determinant aqueous insecticidal composition based on combined with surfactant, inorganic carrier, antifreeze agent, insecticide of neonicotinoid, will form class of strong stable components. The additives will improve flow ability, good adherence to plant propagation material, dust-off, and excellent performance on cold or frozen seeds. Kind of neonicotinoid that is used for this purposes is imidacloprid. The aqueous insecticide comprises about 25% of at least one component of antifreeze, for example 2,3 butanediol. Due to [16], ethanol, that is one of imidacloprid solvents, when it meet 2,3 butanediol, the mixture will become toxic to rats, so the mixture has toxic properties.

1-Propene, 1-(2-propenyloxy)-, (Z)-

Due to [17], component 1-(2-ARYL-2-R-ETHYL)1H-1,2,4-TRIAZOLES. Has fungicidal properties and one of the compounds belong to that fungicide is 1-Propene, 1-(2-propenyloxy)-, (Z)- .

Butenoic acid, ethyl ester

According to [18], the compound 3-Butenoic acid, ethyl ester has pesticide properties because it is able to combatant pests.

Allyl vinyl ether

As [19] reference mentioned that Allyl vinyl ether is one of oxamyl components that are represent caprolactam and/or caprolactam derivatives.

t-Butyl ethylideneamine

According to [20], herbicide, fungicides, insecticides, miticides, acaricides, and nematocides are broadly used in agriculture. pesticides contain adjuvant like surfactants to improve the handling of active ingredients and develop the composition of pesticide. Oxamyl and imidacloprid pesticides are one of the pesticides that this compound add to them for the mentioned purpose. It support some water condition to pesticide like chelating agent.

Shellsol 140

Due to [21], shellsol 140, is one of the organic solvents that could be used for liquefying pesticides for example oxamyl from carbamate pesticides. Reference [22], mentioned that, shellsol, is one of the solvent systems consist of aromatic hydrocarbons used to make active ingredients for pesticides like imidacloprid available for plants.

1-Hexene

As reference [23] mentioned that, hexene, is one of the organic solvents that are used in emulsifier pesticides like imidacloprid. It is one of the important compounds that is used in control release of imidacloprid pesticide active ingredients for prolong activity purposes .

Heksan

According to [24], heksan, is one of the organic solvents used for dilute imidacloprid pesticide. It is also used for mitigate the rate of imidacloprid photo degradation for prolong the duration life of imidacloprid impact.

Diheptyl phthalate

Diheptyl phthalate, is compound add to imidacloprid pesticide to reduce the degradation of pesticide by oxidation. It is considered as plasticizers components that add kind of elasticity to pesticide [25].

Octamethylene glycol

According to reference [26], this compound is add for low formation of foam for enhancing the reaction between water and imidacloprid pesticide when the farmer dilute it to reach the recommended concentration for application.

Nonyl chloroacetate

Compound used in preparing 6-(5-chloropyridin-2-yl)-2-pent-2-ynyl-4,5-dihydropyridazin-3(2H)-one. The latest compound add to imidacloprid pesticide for synergism purposes. The compound allow for the reaction to be slowly acclimatized with ambient temperature for putting aside any molecular destruction [27].

Farnesol

Compound add to imidacloprid for increase the pesticide ability for killing pest. There is significant relationship between increase the concentration of the compound and the efficiency of pesticide [28].

Hexadecanoic acid

Compound has toxicity to nematodes, so it is successfully used as nematocides like oxamyl and could be add to oxamyl for synergism purposes [29]. According to reference [30], plant *Brassica juncea* L. produce this compound when it will be under stress of imidacloprid.

Tridecanoic acid

The compound add to imidacloprid and oxamyl pesticide as anion surfactant. it will help in reduce the surface tension of liquid pesticide and that will serve for more diffusion [31].

Z-7-Tetradecenal

substance produce by the plant add to pesticides like oxamyl and imidacloprid because this substance classified as pheromones, kairomones that defined as any substance that is produced by individual species for the advantages of other different recipient species or attractants [32].

2,13-octadecadien-1-ol

compound classified as pheromones or insecticidal active compounds produced by the plant naturally. It add to pesticides like imidacloprid or oxamyl as attractive material [33].

E-11-Hexadecenal

substance classified as classified as pheromones, kairomones that defined as any substance that is produced by individual species for the advantages of other different recipient species or attractants add to pesticides for fortification purposes [32].

Oleamide

This compound has great impact in inhibiting acetylcholinesterase enzyme. so it is add to oxamyl for fortified pesticide impact. The compound has ability for blocking connexin by long chain of alcohol found inside the structural formula. Connexin is class of transmembrane proteins that form assembled structures in vertebrates [34].

3-Heptadecanol

Kind of fatty alcohol, used as drift control agent that is add to pesticides like oxamyl and imidacloprid [35].

2,4-Dimethyl pentane

Organic solvent used with oxamyl and imidacloprid pesticide for producing lignin-based matrix micro-particles for the controlled release of an agricultural active ingredients includes forming an emulsion of an organic solution in an aqueous
solution [36].

Di isopropyl sulfite

This compound is used in the Process for the preparation of pesticide-comprising aqueous polymer dispersions With an average particle size of the dispersed particles of <1000 nm by radical polymerization of an oil-in-Water emulsion, In order to modify the properties of the polymers, we used Di isopropyl sulfite for that purpose. the compound is used in the process of production oxamyl and imidacloprid pesticide [37].

1,3,4-thiadiazole

Compound used in the process of production pesticide against *Rhizoctonia solani* pest [38].

Glycerol

Substance used in the process of preparing pesticide intermediate acrolein by using glycerol [39].

9,11-Dodecadien-1-ol

Compound add to imidacloprid pesticide to increase the dispersion of pesticide inside the environment applied and that will increase the activity of pesticide in killing pest [40].

GC/MS results after treatment with tab-water, acetic acid, and citric acid

Table-3 showed GC/MS results after treatment with tab-water, acetic acid, and citric acid **.** To see the efficiency of treatment method on the bi-products and some pesticides that appeared in the results of GC/MS before treatment.

Table 3- show the results of GC/MS after treatment

Sample	Date	Kind of treatment	Results
Tomato	5/8/2016	Acetic acid	All bi-products pesticides or pesticides disappear
Tomato	5/9/2016	Acetic acid	All bi-products pesticides or pesticides disappear
Tomato	5/10/2016	Acetic acid	Failure in removing 9,12-octadecadienoic acid
Tomato	2/11/2016	Acetic acid	All bi-products pesticides or pesticides disappear
Eggplant	5/8/2016	Tab-water	All bi-products pesticides or pesticides disappear
Eggplant	5/9/2016	Tab-water	All bi-products pesticides or pesticides disappear
Eggplant	5/10/2016	Tab-water	All bi-products pesticides or pesticides disappear
Eggplant	2/11/2016	Tab-water	All bi-products pesticides or pesticides disappear
zucchini	5/8/2016	Tab-water	All bi-products pesticides or pesticides disappear
zucchini	9/9/2016	Tab-water	All bi-products pesticides or pesticides disappear
zucchini	5/10/2016	Tab-water	All bi-products pesticides or pesticides disappear
zucchini	16/11/2016	Tab-water	All bi-products pesticides or pesticides disappear
Cucumber	5/8/2016	Citric acid	All bi-products pesticides or pesticides disappear
Cucumber	5/9/2016	Citric acid	All bi-products pesticides or pesticides disappear
Cucumber	5/10/2016	Citric acid	Failure in removing hexadecanoic acid and tridecanoic acid.

Samples treated with tab-water, acetic acid(vinegar) in concentration of 4-6%, and citric acid kind (330e). The results showed that tab-water is best method for removing pesticide residues and pesticides bi-products, because water is very strong polar solvent, so it has huge ability for dissolve different kind of compounds and substances. Then acetic acid, because acidic compound good in removing pesticide residues or bi-products but not all of them. Citric acid is the worst technique in removing pesticide residues or bi-products, because natural compounds weak in removing pesticide residues and bi-products [41].

Conclusion

We conclude that tab-water is the best way for removing pesticide residues and pesticides bi-products. and greenhouse kind of agriculture is better than expose agriculture in terms of pesticide residues.

References

1. Book, G. **2014**. Compendium of Chemical Terminology. *Int. Union of Pure and Appl. Chem.*
2. KAUFMAN, D. D. **1976**. Bound and conjugated pesticide residues. *ACS Publications*, 1-10.
3. Zhang, F., Yu, C., Wang, W., Fan, R., Zhang, Z., & Guo, Y. **2012**. Rapid simultaneous screening and identification of multiple pesticide residues in vegetables. *Analytica chimica acta*, 757, 39-47.
4. Marrazza, G. **2014**. Piezoelectric biosensors for organophosphate and carbamate pesticides: a review. *Biosensors*, **4**(3): 301-317.
5. Łozowicka, B., Jankowska, M., & Kaczyński, P. **2012**. Pesticide residues in Brassica vegetables and exposure assessment of consumers. *Food Control*, **25**(2): 561-575.

6. Diop, A., Diop, Y. M., Thiaré, D. D., Cazier, F., Sarr, S. O., Kasprowiak, A., ... & Delattre, F. **2016**. Monitoring survey of the use patterns and pesticide residues on vegetables in the Niayes zone, Senegal. *Chemosphere*, **144**: 1715-1721.

7. Kwon, H., Lehotay, S. J., & Geis-Asteggiante, L. **2012**. Variability of matrix effects in liquid and gas chromatography–mass spectrometry analysis of pesticide residues after QuEChERS sample preparation of different food crops. *Journal of Chromatography* A, **1270**: 235-245.

8. Sivaperumal, P., Anand, P., & Riddhi, L. **2015**. Rapid determination of pesticide residues in fruits and vegetables, using ultra-high-performance liquid chromatography/time-of-flight mass spectrometry. *Food chemistry*, **168**: 356-365.

9. Bakırcı, G. T., Acay, D. B. Y., Bakırcı, F., & Ötleş, S. **2014**. Pesticide residues in fruits and vegetables from the Aegean region, Turkey. *Food chemistry*, **160**: 379-392.

10. Gleason, K., **2012**. *How to convert Centrifuge RPM to RCF or G- force*. Lab skills, research.

11. Yue, Z. H. A. N. G. **2009**. Study on Preparing of Pesticide Intermediate Acrolein with Biological Glycerol. *Journal of Anhui Agricultural Sciences*, **4**: 018.

12. Sieverding, E., Hintz, S., Dambacher, T., Beckerath, T., & Busch, J. **2002**. *U.S. Patent Application No. 10/216,131*. Washington, DC: U.S. Patent and Trademark Office.

13. Randhawa, M. A., Akhtar, S., Asghar, A., Sohaib, M., Aadil, R. M., & Jahangir, M. A. **2016**. Assessment of different washing treatments to mitigate imidacloprid and acetamaprid residues in spinach. *Journal of the Science of Food and Agriculture*, **96**(11): 3749-3754.

14. Berg, B. **2014**. Decomposition patterns for foliar litter–a theory for influencing factors. *Soil Biology and Biochemistry*, **78**: 222-232.

15. Zakaria, S., Al-Ansari, N., & Knutsson, S. **2013**. Historical and future climatic change scenarios for temperature and rainfall for Iraq. *Journal of Civil Engineering and Architecture*, **7**(12): 1574.

16. Fenoll, J., Flores, P., Hellín, P., Martínez, C. M., & Navarro, S. **2012**. Photodegradation of eight miscellaneous pesticides in drinking water after treatment with semiconductor materials under sunlight at pilot plant scale. *Chemical engineering journal*, **204**: 54-64.

17. Fadaei, A. M., Dehghani, M. H., Mahvi, A. H., Nasseri, S., Rastkari, N., & Shayeghi, M. **2012**. Degradation of Organophosphorus Pesticides in Water during UV/H 2 O 2 Treatment: Role of Sulphate and Bicarbonate Ions. *Journal of Chemistry*, **9**(4): 2015-2022.

18. Schlatter, C., & Ramachandran, R. **2007**. *U.S. Patent Application No. 11/928,094*. Washington, DC: U.S. Patent and Trademark Office.

19. Poldrugo, F., Barker, S., Basa, M., Mallardi, F., & Snead, O. C. **1985**. Ethanol Potentiates the Toxic Effects of 1, 4Butanediol. Alcoholism: *Clinical and Experimental Research*, **9**(6): 493-497.

20. Heeres, J., Backx, L. J., & Mostmans, J. A. **1986**. *U.S. Patent No. 4,598,085*. Washington, DC: U.S. Patent and Trademark Office.

21. Meyer, W., Drabek, J., Farooq, S., Gsell, L., & Kristiansen, O. **1979**. *U.S. Patent No. 4,161,535*. Washington, DC: U.S. Patent and Trademark Office.

22. Sowa, C., & Walter, M. M. **2006**. *U.S. Patent Application No. 12/085,560*. Washington, DC: U.S. Patent and Trademark Office.

23. Modaressi, H., & Douglass, A. **2013**. *U.S. Patent No. 8,383,137*. Washington, DC: U.S. Patent and Trademark Office.

24. Taranta, C., Meier, W., Strauss, K., Kraushaar, A., & Steinbrenner, U. **2012**. *U.S. Patent No. 8,178,117*. Washington, DC: U.S. Patent and Trademark Office.

25. Westbye, P., Bergström, K., Lee, C. C., & Paul, R. **2012**. U.S. Patent Application No. 14/359,514. Washington, DC: U.S. Patent and Trademark Office.

26. Asrar, J., & Ding, Y. **2010**. *U.S. Patent No. 7,771,749*. Washington, DC: U.S. Patent and Trademark Office.

27. Kalister, K. **2011**. Fotokemijska razgradnja imidakloprida v zemlji. Doctoral dissertation, Univerza v Novi Gorici, Fakulteta za znanosti o okolju.

28. Papp, Z., Švancara, I., Guzsvány, V., Vytřas, K., & Gaál, F. **2009**. Voltammetric determination of imidacloprid insecticide in selected samples using a carbon paste electrode. *Microchimica Acta*, **166**(1-2): 169-175.

29. Baur, P., Auler, T., Deckwer, R., & Giessler, S. **2015**. *U.S. Patent No. 9,215,868*. Washington, DC: U.S. Patent and Trademark Office.

30. Kelly, M., Ross Jr, R., & Young, D. H. **2013**. *U.S. Patent No. 8,426,412*. Washington, DC: U.S. Patent and Trademark Office.
31. Tang, X., Chen, S., & Wang, L. **2011**. Isolation and Insecticidal activity of farnesol from Stellera chamaejasme. *Asian Journal of Chemistry*, **23**(3): 1233.
32. Kwok, O. C. H., Plattner, R., Weisleder, D., & Wicklow, D. T. **1992**. A nematicidal toxin from Pleurotus ostreatus NRRL 3526. *Journal of Chemical Ecology*, **18**(2): 127-136.
33. Sharma, A., Kumar, V., Singh, R., Thukral, A. K., & Bhardwaj, R. **2015**. 24-Epibrassinolide induces the synthesis of phytochemicals effected by imidacloprid pesticide stress in Brassica juncea L. *Journal of Pharmacognosy and Phytochemistry*, **4**(3).
34. Losel, P., Penners, G., & Weissmuller, J. **1998**. *U.S. Patent No. 5,707,638*. Washington, DC: U.S. Patent and Trademark Office.
35. Gewehr, M. **2013**. *U.S. Patent Application No. 14/432,503*. Washington, DC: U.S. Patent and Trademark Office.
36. Mouthon, F., & Charveriat, M. **2012**. *U.S. Patent Application No. 14/355,153*. Washington, DC: U.S. Patent and Trademark Office.
37. Goyal, R., Shanmuga, K., & Wilson, S. L. **2014**. *U.S. Patent Application No. 14/585,440*. Washington, DC: U.S. Patent and Trademark Office.
38. Asrar, J., & Ding, Y. **2010**. *U.S. Patent No. 7,771,749*. Washington, DC: U.S. Patent and Trademark Office.
39. Dyllick-Brenzinger, R., Bratz, M., Kruger, C., Oetter, G., & Gorth, F. C. **2006**. *U.S. Patent Application No. 11/908,234*. Washington, DC: U.S. Patent and Trademark Office.
40. Chen, H., Li, Z., & Han, Y. **2000**. Synthesis and Fungicidal Activity against Rhizoctonia s olani of 2-Alkyl (Alkylthio)-5-pyrazolyl-1, 3, 4-oxadiazoles (Thiadiazoles). *Journal of agricultural and food chemistry*, **48**(11): 5312-5315.
41. Inoue, N. **2014**. *U.S. Patent Application No. 14/781,119*. Washington, DC: U.S. Patent and Trademark Office.