Assessment of the Kinetic reaction and residue Determination of four insecticides using High Liquid Performance Chromatography Technique on Tomato Fruits

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Abstract

The imidacloprid, avaunt, karate, and coragen residues in the fruits were investigated. The results show that imidacloprid residues started to decrease over the time to reach 313.5, 180.93, and 131.15 into 0 mg L respectively after 14 days of the application. While karate residues slowly decreased into 62.88 mg L^{-1} after 14 days of the application. The kinetic assessment, the dissipation of imidacloprid, avaunt, and coragen residues underwent the first order model with the degradation rate 0.322, 0.395, and 0.322 a day. Subsequently, the half-life scored 2.14, 1.75, 6.72, and 2.14 days for the same order above respectively. Whilst Karate undergoes the second order model, giving 0.009 a day degradation rate. This resulted in a slow breakdown with the half-life being 770.16 days based on the current result. Overall, these results suggest that the use of those insecticides are safe and not be tended as harmful due to their fast degradation, except karate needs extra time to reach at low level.

Keywords: Avaunt, Coragen, Imidacloprid, Karate, Kinetic evaluation.

Introduction

Plants belonging to the Solanaceae family, tomato (*Lycopersicon esculentum*) Mill. One of the most produced crops, tomatoes will yield 186.8 million tonnes worldwide in 2020 [1]. It is one of the most popular fruit vegetables, especially rich in vitamins, minerals [2]. Tomatoes are infected with many of diseases and insects, one of the most significant pests on tomatoes is the tomato pinworm (*Tuta absoluta)* (Meyrick) (Lepidoptera: Gelechiidae) crop loss. Pesticides are essential to control *T. absoluta* that may cause the loss 80% of tomato production[3] . Some pesticides have tolerance to biological or chemical degradation and have a tendency to bioaccumulate in plant leaves, fruits and animal tissues [4] . The pest has a brief life cycle of around 28 to 29 days and may produce 10 to 12 generations annually. *T. absoluta* has been subjected to a variety of controls[5]. Since other approaches alone have failed to stop the harm of this insect , chemical treatment has been applied, and spraying chemical insecticides is considered a preferred method for managing pests and keeping better production of tomatoes [6]. Insecticides can kill natural predators and have a

negative impact on the environment and human health, even though they are successful in reducing the population of *T. absoluta* [7]. Additionally, reports suggest that the tomato leafminer is becoming less susceptible to some synthetic pesticides, leading to failed treatments[8] ,[9]. Insecticide overuse raises production costs and has negative effects on the environment and human health another issue is pesticide residue, especially for tomato exports, Pesticide residual studies have been an important topic worldwide due to human health concerns, to combat the numerous pests that might at tack tomatoes, several pesticides are utilise d, and however these pesticides have long-lasting effects on the crop. [10]. There are several publications regarding the examination of pesticide residues in various types of vegetables and their derivatives in the literature [11].Additionally, few research on the thiamethoxam residue analyses in tomato fruits were published [12]. Studies on the dissipation and residual behaviours of imidacloprid, chlorantraniliprole, lambda cyhalothrin, and indoxacarb in tomato fruits, however, were few. Using high performance liquid chromatography, the dissipation of four pesticides in tomato fruit was studied, as well as their residual levels and preharvest windows in tomatoes cultivated in the field.

Materials and Methods

The field experiment was conducted at the Basra government located in the south of Iraq. The field is approximately 500 m2, which is cultivated with the common tomato variety called Yassamin. This variety was obtained from Syngenta Company. The Yassamin variety was planted in the plastic tunnels. The distance between the tunnels was 1.5m, and the length was 10 m. Each tunnel was planted with 20 tomato plants, and the distance between each plant was 40 cm. Moreover, each tunnel contained three replicates plus the control treatment. These plants were treated by the insecticides (Table 1) when the plants have become in the fruited level.

Determination of Insecticide residues

The field experiment was applied in the season of 2022 (April) in Basra governorate. Different insecticides including, Coragen 20% SC (Chlorantraniliprole), Avaunt 15% EC (Indoxacarb), Karate (with zeon technology) 10% CS (Lambda-Cyhalothrin) and Modesta 35% SC (Imidacloprid) was sprayed on the tomato plants. The insecticide rates were 0.85 ml / L, 1.53 ml / L, 2.84 ml. / l and 1.32 mL / L for the pesticides respectively. Each treatment was replicated three times plus the control. Tomato fruits were collected after one, three, seven and 14 days after treatment and placed inside polyethylene bags that had written the date and name of the sample [12].

The extraction of Imidacloprid and Indoxacarb

The QuEChERS method was used to extract the samples of Modesta 35% SC (Imidacloprid) and Avaunt 15% EC (Indoxacarb) [13] and [14]. A 250 mL polypropylene centrifuge tube with 20 g of the fruit samples within were used for the extraction. The addition of 30 mL of distilled water. The sample was then given 10 mL of acetonitrile and vigorous shaking using vortex shaker was applied for 1 min. Then, the following salts were added: 0.5 g

disodium citrate hydrogen citrate sesquihydrate, 1 g sodium chloride, 1 g sodium citrate trihydrate, and 4 g anhydrous magnesium sulphate. The mixture was then centrifuged at 4000 rpm for 10 minutes to separate the phases. A single-use 15 mL centrifuge tube containing 8 mL of extract was filled with it and placed in the freezer for an hour. A single-use aliquot of the extract, measuring 6–15 mL, was placed into a centrifuge tube after the extract gradually disintegrated. This tube contains 900 mg of MgSO4 and 150 mg of primary and secondary amine. To get rid of interferences and lessen device contamination, it was employed for flushing. After completing an additional centrifugation cycle, the extracts were transferred to a storage vial with a screw cap and kept in the freezer before being analysed.

The extraction of Chlorantraniliprole

15 g of homogenised fruit samples were taken in order to extract the Coragen 20% SC (chlorantraniliprole). They were weighed and placed in a 50 mL centrifuge tube. The screw cap was closed, 15 mL of ethyl acetate was added, and the tube was shaken rapidly at 4000 rpm for 1 min. Then, 15 g of anhydrous sodium sulphate was added, and the mixture was extracted for 10 minutes by vigorously shaking with the hands, up and down, and at 4 °C. The supernatant was divided into four equal portions and placed in a fresh, clean 15 mL centrifuge tube.

The dispersed solid phase was used to clean the extracts, along with 20 mg of graphite carbon black (GCB) and 100 mg of primary and secondary amines (PSA). After that, centrifugation was carried out as described. The supernatant was then removed, and 2 ml of it was evaporated to dryness [15] .

The extraction of Lambda cyhalothrin

Karate 10%CS (Lambda cyhalothrin) residues were extracted using a volumetric 100 mL flask after 20 g of the fruit samples were precisely weighed. The mobile phase, 50 mL, was applied. A cap was used to secure the flask, and it spent 10 minutes in an ultrasonic bath. When the volume reached the desired level during the mobile phase, it was capped and thoroughly mixed. The sample was put into a 2 mL sample vial after being filtered with a 0.45 m filter [16] .

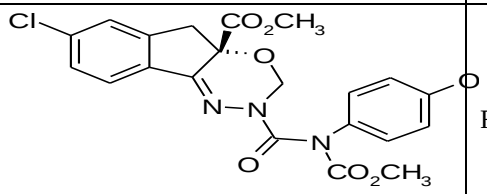
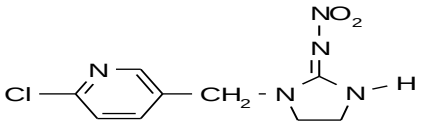
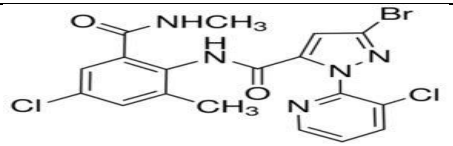
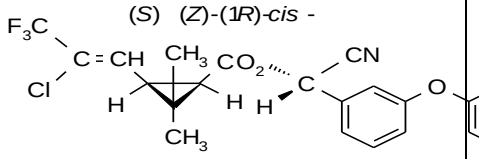
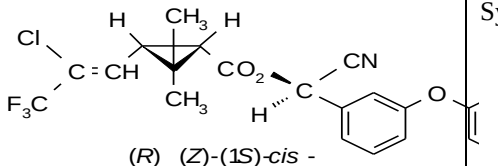
Analysis conditions

The samples were examined using the HPLC instrument in order to assess and find pesticide residues in tomato fruits. It is referred to as the German SYKAMN HPLC model. Equal flows of a 40/60 (volume/volume) water mixture with a pH of 7.0 made up the mobile phase. A UV detector with a 250 nm wavelength, a C18-ODS type separation column, and a flow rate of 1.0 mL/min of acetonitrile were used. The standard curve was used to measure the pesticide residues. While the identification of the insecticide was done by comparing the retention times (RTs) of the sample peaks with the RTs of the standards that were injected[16].

Statistical Analysis

The insecticide kineticity assessment was carried out by utilising the first-order and second-order, DT50, and degradation rate outlined in [17]. The SPSS Software was used to analyse all these data.

Table 1. List of the insecticides used in the study

active ingredient name	Chemical group	Common name	Chemical name	Chemical structure	Company
Indoxacarb	oxadiazine	Avaunt	methyl (*S*)-7-chloro-2,5-dihydro-2-[[(methoxycarbonyl)[4-(trifluoromethoxy)phenyl]amino]carbonyl]-indeno[1,2-*e*][1,3,4]oxadiazine-4a(3*H*)-carboxylate.		FMC
Imidacloprid	neonicotinoid	Modesta	1-[(6-chloro-3-pyridinyl)methyl]-N-nitro-2-imidazolidinimine.		AgroScience LTD
Chlorantraniliprole	Anthranilic diamide	Coragen	3-Bromo-N-[4-chloro-2-methyl-6-(methylcarbamoyl)phenyl]-1-(3-chloro-2- pyridine-2-yl)-1H-pyrazole-5-carboxamide.		FMC
Lambda-Cyhalothrin	Pyrethroid	Karate	[1□(*S**),3□(*Z*)]-(±)-cyano(3-phenoxyphenyl)methyl 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate.	(*S*) (*Z*)-(1*R*)-*cis* -  (*R*) (*Z*)-(1*S*)-*cis* - 	Syngenta

Results and Discussion

The graphs in Fig (1) shows that there have been four different dissipation patterns of Imidacloprid, Avaunt, Karate, and Coragen insecticide residues on tomato fruits. It is noted that Imidacloprid, Avaunt, and Coragen residues reduced from 313.5, 180.93, and 131.15 into 0 mg/ L respectively after 14 days of treatment. This fast degradation due to non-biological factor effects. For example, temperature, wind, sunlight play a crucial role in speedy residue dissipation.

This result is quite compatible in several studies, in particular the residues decline. But unlike some other studies. For example, a study by[18] reported that Imidacloprid residues gradually decrease with time and completely during 28 days. But the recent study investigated that Imidacloprid dissipated within 14 days. This is because the Basra weather is quite hot and the temperature average was recorded 40^{o}C in April.

Also the study showed that Imidacloprid residues on cucumbers decreased 100% after one hour and 35-73% after one day[19] during 10 days. While in our study, the Imidacloprid residues were significantly decreased during 7 days. The difference in the duration of the disappearance of the pesticide between the previous study and our study is due to the fact that the previous study was conducted in Baghdad, which differs in its temperature from the city of Basra, in which our study was conducted. Furthermore, the length of sunlight was scored 14.48 hours during the experiment. Therefore, the insecticide residues have disappeared at the end of the sample collection course.

In terms of Indoxacarb, Naik's study [20] also showed that the dissipation period of Indoxacarb reached 15 days of treatment on green bean pods. Hence, the half-life ranged between 1.13 to 1.23 days**.** Moreover, the study was performed by using a photonic sensor to monitor chlorantraniliprole residues in tomatoes. The residual fell to 0.5 g kg^{-1}, which is less than the tolerance criterion of 1.4 mg kg^{-1}. [21].

On the contrary, the study of [22]revealed that chlorantraniliprole residues were dissipated by 96% within 53 days. But our study demonstrated that chlorantraniliprole dissipated within 14 days. This might be due to the temperature, and most significant is the water properties. For example alkalinity or acidity can have a direct impact on the stability of insecticides used in the spraying tank or when it reaches the soil. All these factors assist in the chlorantraniliprole degradation effectively under Basra circumstance.

In contrast, Karate residues declined from 239.27 into 62.88 mg/ L after 14 days. The reason is that karate is It can be applied directly in the soil. Its active ingredient releases gradually depend on the soil humidity. It usually takes a long time to degrade compared to the other insecticide formulations. As the study of[23] demonstrated that dissipation of lambda-cyhalothrin residues were subjected to the first order rate kinetic and the DT50 scored 3.12 days . The study also demonstrated that the level of lambda cyhalothrin was below the 0.05 mg Kg-1 maximum residue limit after 14 days.

On the other hand, lambda-cyhalothrin residues disappeared from the zucchini fruits with a half-life of 4 days. Also, the study

recommended that the harvest must be after 5 days of the application [24].

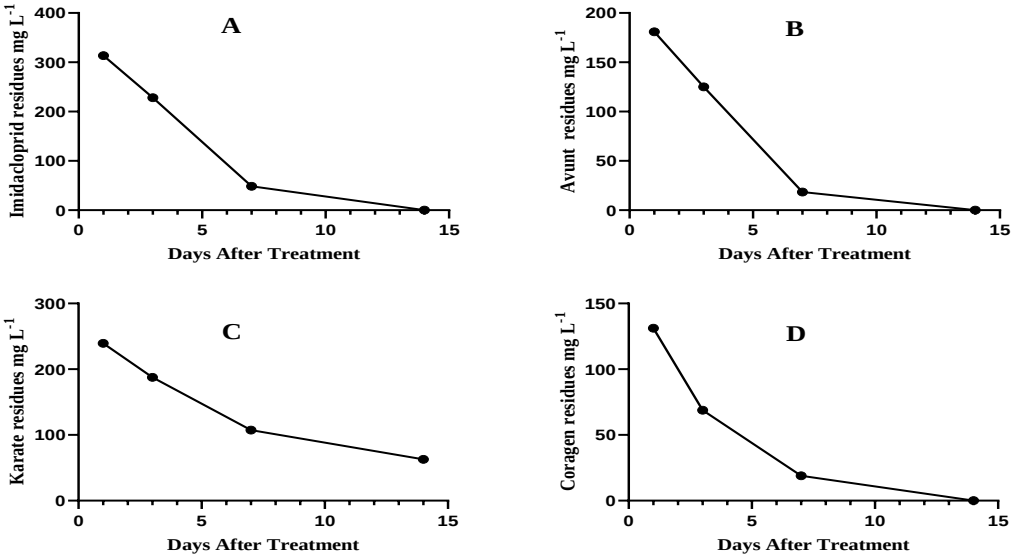


Fig 1. Dissipation Curve of A: Imidacloprid, B: Avunt, C: Karate, and D: Coragen on Tomato fruits.

All insecticides were kinetic reactions evaluated by using the first and second order model. By comparing the coefficient of relationship R^2, the results revealed that Imidacloprid, Avaunt, and Coragen (Fig 2) were subjected to the first-order reaction model (FOM). Whilst the Karate undergoes the second-order reaction model (SOM) (Fig 3).

Similarly, Table (2) confirmed the kinetic data of all studied insecticides. It illustrated that the degradation rate of all insecticide was higher based on the FOM than the SOM. It was scored 0.322, 0.395, 0.103, and 0.322 mg L^{-1} in a day for Imidacloprid, Avaunt, Karate, and Coragen. It is also noted that the karate was the lowest degradation compared to the rest of insecticide.

Consequently, the time requires to degrade 50% of initial concentration (day) has recorded 2.14, 1.75, and 2.14 a day for Imidacloprid, Avaunt, and Coragen respectively. Otherwise, Karate has registered 6.72 day according to the first order model.

However, the second order model was performed to investigate which model can be most effect on the insecticide residues dissipation. The outcomes pointed out that the only Karate undergoes the second order reaction model, providing R^2 0.997 compared to the R^2 of the first order reaction model which was 0.978.

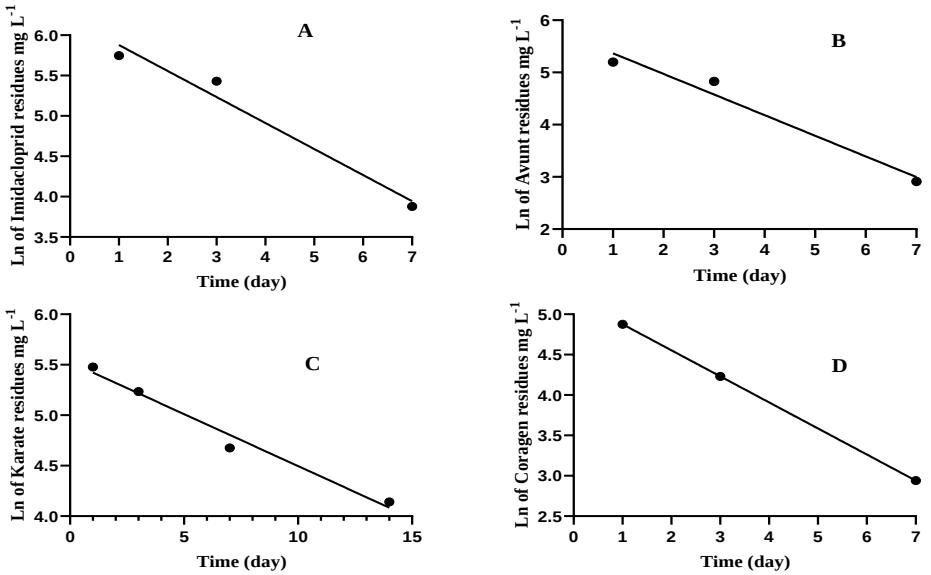


Fig 2. Four insecticide residues reaction assessment on tomato fruits according to the PFO: A: Imidacloprid, B: Avant, C: Karate, D: Coragen.

In this context, many studies have been conducted on pesticides belonging to different chemical groups. For example, Carbendazim fungicide subjected to the pseudo-first order reaction [25] glyphosate herbicide undergoes also to the pseudo-first order reaction [17]. Additionally [26] observed that the chlorantraniliprole is subjected to the second order reaction (PSO), whereas indoxacarb, imidacloprid, and lambda-cyhalothrin are exposed to the pseudo-first order reaction (PFO).

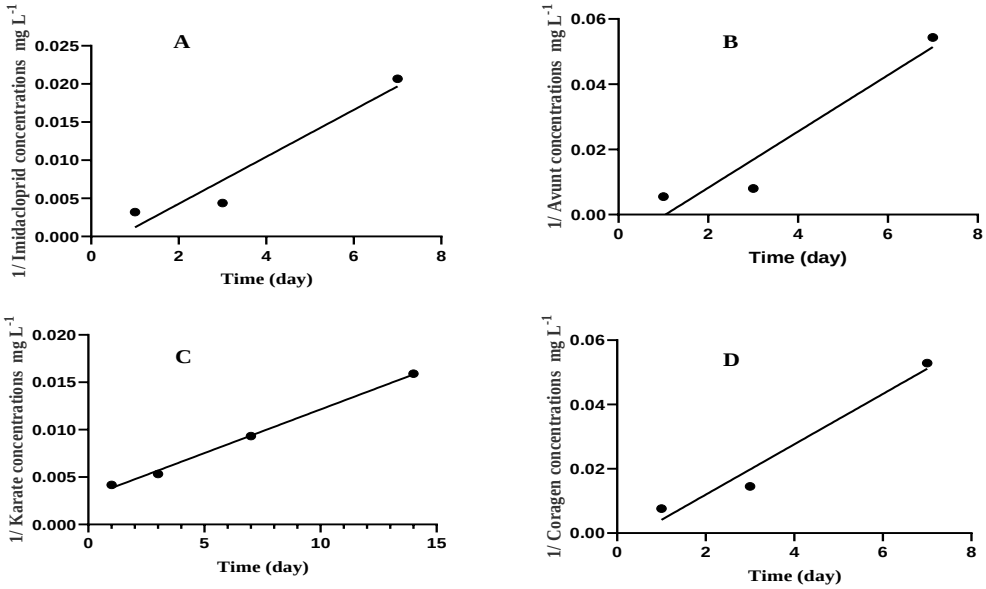


Fig 3. Four insecticide residues reaction assessment on tomato fruits according to the PSO: A: Imidacloprid, B: Avant, C: Karate, D: Coragen.

Table 2. The dissipation rate of Imidacloprid, Avunt, Karate, and Coragen residues in Tomato fruits.

Insecticides	The dissipation rate mg kg^{-1}/day based on				Time requires to degrade 50% of initial concentration (day) based on	
	PFO	R^2	PSO	R^2	PFO	PSO
Imidacloprid	0.322	0.97	0.0031	0.92	2.14	223.59
Avaunt	0.395	0.96	0.0086	0.91	1.75	80.59
Karate	0.103	0.97	0.0009	0.99	6.72	770.16
Coragen	0.322	1	0.0078	0.96	2.14	88.86

Conclusion

In this investigation, the aim was to determine the imidacloprid, Avaunt, karate, and coragen residues in tomato fruits using the high liquid performance chromatography. The second aim of this study was to assess their insecticides kineticity in the soil. This study provides that the studied insecticide residues decreased over the time. And their residues reached under maximum residue limit. Except for karate, its dissipation has occurred slowly due to its formulation as a capsule. The kineticity evaluation revealed that all insecticide residue dissipation underwent the first order reaction model except Karate undergoes the second order reaction model. While the time required for the breakdown of 50% of the initial concentration amounted to a few days in the case between the second order reaction and the first order reaction exemplary.

Conflict of interest

The authors declare no conflict of interest.

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