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Pyridaben Monitoring Dissipation in Iraq Cucumber and Calculate Residues after Household Processing by Gas Chromatography

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Abstract

A gas chromatographic technique was employed as an analytical method to detect and quantify Pyridaben residues in cucumber, leaves, and soil under controlled greenhouse conditions in Iraq, using the recommended dosage, and to estimate the residual levels of Pyridaben after household processing. The samples were extracted and purified using a modified QuEChERS method, followed by analysis using gas chromatography with flame ionization detector and mass spectrometry for determination. Method validation studies yielded recovery percentages ranging from 93.9% to 98.5%. The matrix effects (ME)−12.21%, −8.82%, −5.3% for cucumber, leaves and soil respectively. The samples exhibited no signal suppression effect in all matrices, and relative standard deviation (RSD) ranged from 0.03 to 1.8%. The precision of the methods fell within the acceptable range of ≤20%. The methods demonstrated a good linearity with a determination coefficient (R^2) 0.9991 for the 0.001–50 µg mL^{-1} concentration range, pyridaben has limits of detection (LOD) of 0.001 µg mL^{-1} and quantification (LOQ) of 0.003 µg mL^{-1}. Under greenhouse conditions, pyridaben residues were found to be 3.39, 8.24 and 1.39 mg kg^{-1} for cucumber, leaves and soil, after 2hr from treatments at the suggested dose 25 ml / 20 L water. The residue levels fell below the maximum residue limit (MRL; 0.15 mg kg^{-1}) within 4 days. Pyridaben residue dissipation followed first-order rate kinetics The half-life ($t_{1/2}$) was 1.05 days, 1.03 days and 1.21 days for Pyridaben in cucumber, leaves and soil respectively. The change in pyridaben residue in cucumber samples during household processing (washing and peeling) processing was evaluated. A simple and accurate gas chromatographic method was employed after each process for determined Pyridaben using a flame ionization detector. The results indicated that washing reduced pyridaben residue by 29.41%, while 84.44% of Pyridaben residue removal by used peeling processes, showed by washing PF_S was 0.62 and peeling PF_S was 0.081.

Keywords: Pyridaben, Cucumber, Pesticide Residues, ($t_{1/2}$), Processing Factors, Gas-Chromatography

مراقبة تبدد مادة البيريدابين في الخيار العراقي وحساب متبقياته بعد معالجته منزلياً بواسطة كروماتوغرافيا الغاز

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الخلاصة

تم استخدام تقنية الغاز الكروماتوغرافي كطريقة تحليلية لكشف وتحديد كمية بقايا البيريدابين في الخيار والأوراق والتربة تحت سيطرة ظروف البيت المحمي في العراق، باستخدام الجرعة الموصى بها، وتقدير المستويات المتبقية من البيريدابين بعد المعالجة المنزلية. تم استخلاص العينات وتنقيتها بطريقة الكويشرز المعدلة وتليها تحليلها باستخدام كروماتوغرافيا الغاز مع كاشف التاين اللهبي وكاشف تحديد الكتلة. أعطت دراسات التحقق من صحة الطريقة نسب الاسترداد تتراوح من 93.9٪ الى 98.5٪ ، واظهرت جميع العينات عدم وجود تاثير لقمع الاشارة بالنسبة للخيار والاوراق والتربة على التوالي -12.21٪، -8.82٪، -5.3٪ وتتراوح قيمة الانحراف المعياري النسبي من 0.03 إلى 1.8٪ سقطت دقة الطريقة ضمن النطاق المقبول البالغ ≤ 20٪. أظهرت الطرق خطية جيدة مع معامل ارتباط 0.9991 لنطاق التركيز 0.001–50 ميكروغرام/ مل، مع تحديد الحد الادنى لقيم الكشف والحد الكمي كانا 0.001 ميكروغرام/ مل و0.003 ملغ /كجم على التوالي.تحت ظروف البيت المحمي كانت بقايا البيريدابين على الخيار والأوراق والتربة (8.24، 3.39 و1.39) ملغم/ كجم بعد ساعتين من المعالجة بالجرعة الموصى بها،انخفضت مستويات البقايا إلى أقل من الحد الأقصى المسموح خلال 4 أيام . يتبع تبدد بقايا البيريدابين المعادلة الحركية من الدرجة الأولى حيث كان عمر النصف(1.05 و1.03 و1.21) يوم للبيريدابن في الخيار وأوراق الخيار والتربة على التوالي. تم تقييم التغير في بقايا البيريدابين في عينات الخيار أثناء عملية (الغسيل والتقشير) بشكل منهجي. تم استخدام طريقة كروماتوغرافيا الغاز البسيطة والدقيقة بعد كل عملية لتحديد البيريدابين باستخدام كاشف التأين باللهب. أشارت النتائج إلى أن الغسيل قلل من بقايا البيريدابين بنسبة 29.41٪ ، بينما كان لعمليات التقشير تأثير على إزالة بقايا البيريدابين بنسبة 84.44%، مما يشير الى تم ترسيب كمية كبيرة من بقايا البيريدابين بشكل أساسي على قشر الخيار. اظهرت معامل المعالجة بالغسيل 0.62 ومعامل المعالجة بالتقشير كانت0.081

1. Introduction

Cucumber (C. sativus L.) is one of the most economically important agricultural crops, playing a significant role in both export and local consumption. To extend its cultivation period, protect it from adverse weather conditions and diseases, and increase its yield, cucumber is often grown in greenhouses, in addition to being cultivated in open fields. Cucumbers are exposed to many pests and fungal diseases that cause crop loss, and therefore appropriate pesticides must be used for that purpose [1].

The IUPAC name of Pyridaben (2-tert-butyl-5-(4-tert-butylbenzylthio)-4-chloropyridazin-3(2H)-one) Figure 1 showed the chemical structure of Pyridaben, it is a heterocyclic broad-spectrum, contact acaricide, applied to different vegetables and fruits because of low toxicity and high influence on control pests [2]. The improper use of pesticides can result in the contamination of agricultural crops and thus harms consumers [3]. Therefore, monitoring pesticide levels in cucumbers is important. The QuEChERS method, which stands for quick, easy, cheap, effective, rugged and safe, is a preparation technique is versatile, effective and simple [4], which used to extract many different pesticides from vegetables [5, 6]. This method offers several advantages than other traditional methods, given its inherent advantages of minimal use of hazardous reagents and solvents, fast sample preparation, simplicity and low cost. QuEChERS has emerged as one of the greenest and most sustainable alternatives and environmentally friendly methods in this area. For detecting and quantifying pesticide residues, it necessary to choose selective and sensitive analytical methods. In this situation, the most efficient method applies chromatographic separation with an appropriate detection system. Additionally, there are also alternative ways to estimate pesticides that are simple to use and more cost-effect [7-9].

Nevertheless, the presence of pesticide residues in cucumbers could potentially harmful for health. Various Processing applied on vegetables and fruits in home or commercially that was washing, peeling, cooking. Several studies have examined the effects of common household processing on various types of produce and found that residues were reduced as a result of various treatments [10]. Despite this, household processing methods of vegetable processing, such as frying, boiling, roasting, and blanching, result in a notable decrease in pesticide residues [11].Washing is considered the most effective primary treatment, through which pesticide residues are eliminated in acceptable proportions [12]. These effects calculated by processing factors PFs; the relation between concentration of residues after treatment and concentration of residues before treatment [13]. A processing factor greater than 1 means an increase in the residue level during processing and a processing factor lower than 1 indicates a decrease. When assessing the risk associated with the intake of pesticide residues, the processing factor (PF) are important [14]. If processing leads to an increase of the residue levels, processing factor are used to adjust maximum residue limits MRLs for products [15]. The dissipation rate is used to evaluation the residues level [16], and dissipation curves are employed to calculate the time required for residues to reach levels below the MRLs [17]. The dissipation of pesticides is influenced by various factors including , suggested dose , pesticides formulation, parameters of application, weather conditions and chemical degradation [18]. Pyridaben residues in citrus fruits, apples and bananas [19-21]. In cucumbers and strawberries under Egyptian open field conditions [22]. There is another study determine the residual concentrations of pesticides (Abamectin, Thiam Ethoxam, Pyridabin, and Spirodiclofen) used in greenhouse cucumber fields and their effects on the farmers that spray it [23]. This study does not adequately represent the degradation of Pyridaben residues and dissipation rate that is study in this work under greenhouse conditions in Baghdad, Iraq and evaluate the removal of the Pyridaben residues from cucumber by household processing including washing and peeling procedures. The QuEChERS method was utilized for extraction of samples (cucumber, leave and soil) by GC-FID and GC/MS. This research assessed Pyridaben residues in cucumber, leave and soil using an effective and fast technique using QuEChERS extraction, we validated the approach to ensure that extraction procedure was appropriate for residue analysis of pyridaben on cucumber. Precision, accuracy, linearity, range, and limits of detection and quantification were the parameters examined [24].

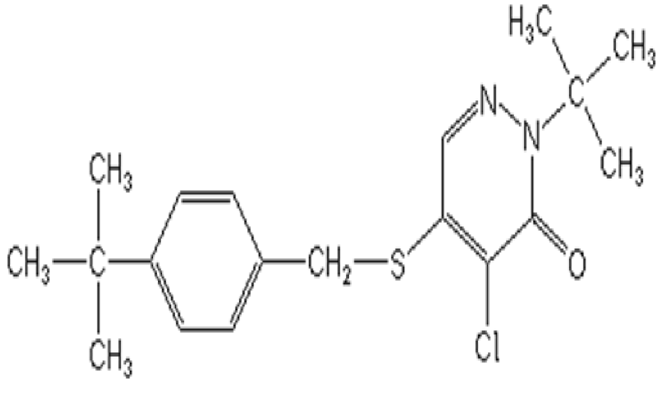


Figure 1: chemical structure of Pyridaben

2. Materials and Methods

2.1 Chemicals and apparatuses

Analytical standards of Pyridaben with purity of 98% were obtained from Bayer Crop Science (Germany). Aceton, Acetic acid glacial, n-hexane, Acetonitrile from lab scan Ltd, Ireland. Sodium acetate, Anhydrous magnesium sulfate, Sodium chloride were supplied from Sigma Aldrich. Primary secondary amine from 40 to 60 micrometers, membrane filter, 0.22 micrometers pore size purchased from Merck (Germany). Equipment used included a Vortex, Heidolph (Germany), centrifugation 4K15, from Sigma (Germany), Microcentrifuges from Hettich (Germany) and a rotary evaporator from Buchi, Switzerland.

2.2 The design of field experiment

From February to May 2022, a field experimental was conducted at the Agricultural Research Station, Abu-Ghribe, as illustrated in Figure 2(a). The experiment utilized a Randomized Complete Block design with three replicates, each measuring 60 m^2 for each one plot, was planted with cucumber seeds (CESAR F1, USA). Prior to cultivation, the soil sample was analysed in the laboratories affiliated with the same department. The analysis revealed the following results: pH 8, 0.86% of organic matter, electrical conductivity (EC) 4.27 ds.mL, texture was clay soil, 16% of sand; 39% of silt, 45% of clay, 70.0 ppm of NPK (available) with nitrogen, 592 ppm of potassium and 24.16 ppm of phosphorus. The fruit formation stage of cucumber crop in polyhouse (2 months after transplanting), Pyridaben (Promite EC 15%) spray applications were given at the recommended dose of 25 mL / 20 L water, untreated plants were kept as control was sprayed with water only. Samples were collected randomly from each plot at various intervals: 0 (2 h), 1,2, 3,4, 5, 6,7, 10,15,20,25 and 30 days after the application of Pyridaben showed in Figure 2(b). Soil samples were also collected separately from each treated plot using a tube auger at a depth of approximately 1–15 cm. All samples were transported to the laboratory enclosed in plastic receptacles and subsequently placed in a deep freezer (−20 °C) until further processing.

Figure 2: (a)The field experimental (b) samples were collected randomly

2.3 Preparation of standard solutions

The preparation of standard solutions for Pyridaben standard solution (1000 μg mL^{-1}) was prepared by weighing 0.1 g of Pyridaben in 100 mL volumetric flasks and dissolving it in 100mL acetonitrile. Working standards solutions were then prepared through serial dilution of the stock solutions, the calibration curve of standard solution was 0.001, 0.01, 0.09, 0.78, 6.25, and 50 μg mL^{-1}. For the residue analysis, GC-FID was employed, maintaining consistent instrument condition evaluating the linearity of the detector. To prepare matrix-matched standards, a control samples without spraying from (cucumber, leaves, soil) concentrated in a rotary evaporate and added appropriate concentration from working standard to make up the volume to one mL. All standard solutions were stored at −20 °C.

2.4 Sample Preparation and Processing

Cucumber samples weighing approximately two Kg were collected randomly from each treated plot. Three subsamples, were prepared, with each subsample consisting of five cucumber pieces that were chopped and blended to create unprocessed samples. For the peeled samples, from the second subsample were peeled before chopped and mixed. Third subsample, were washed by tap water, dried by absorbent paper, chopped and mixed to obtained washed samples. All of these samples after processing were kept in freezer until analysis [25].

2.5 Extraction and Cleanup

Samples were analyzed at the Pesticide Residue Department of National Center for Pesticides Control (Iraq, Baghdad). The QuEChERS acetate method was designated as the official method (2007.01) for the analysis of pesticides residues in foods samples [26]. The salting effects, such as those from ammonium or sodium acetate, combination with 1% of acetic acid solution in acetonitrile, improve the extraction efficiency of pesticides and assists to buffer the medium [27]. Cucumber and leaf samples, each weighted 15 grams, were putted in 50 mL centrifuge tubes, added 15 mL of solution containing 1% acetic acid in acetonitrile, vortexed for 1 min, after that, 6 g of magnesium sulfate $MgSO_4$ and 1.5 g of sodium acetate $C_2H_3NaO_2$ were added to the tubes and vortexed for 2 min, for 10 min at 4100 rpm. The resulting extracts were transferred to 15 mL polypropylene centrifuge tubes and subjected to dispersive solid-phase extraction (d-SPE) for purification. These tubes containing sorbent of 150 mg $MgSO_4$ and 50 mg of primary secondary amine (PSA), the tubes were vortexed for about 2 min, for 5 min centrifuged at 4000 rpm [28].

To filter the acetonitrile phase, a membrane filter was used. One mL of the extract was then taken and evaporated to dryness using a rotating evaporator. A solvent mixture of 9: 1 n-hexane and acetone were added for determinate via GC–FID.

Soil samples were analyzed according to modified [29], by weighed 10-g of dried sieved soil and transport in a 50-mL centrifuge tube then shaken for 1 min with 20 mL acetonitrile. Next, added 4 g of $MgSO_4$ and 1 g of NaCl, vortexed the solution for 1 min and centrifuged at 4100 rpm for 6 min. dispersive solid phase extraction clean-up step was carried out in 15 mL centrifuge tube that contained 1.5 g of $MgSO_4$ and 0.250 g of primary–secondary amine (PSA). The supernatant volume (approximately10 mL) was added, shaken for a few seconds, centrifuged for 6 min at 4100 rpm, filter the solution through PTFE membrane filter. Finally, the cleaned supernatant extract was evaporated to dryness at 40 °C and re-constituted with mixture of acetone: n-hexane (1:9) for analysis by use gas chromatography with flame ionisation detection (GC-FID).

2.6 Method validation

Several factors were validated in this study, including precision, accuracy, linearity, range, matrix effect , limits of detection and quantification [24]. Recovery experiments were conducted by spiking control samples with three concentrations (10, 50, and 100 mg/kg) in triplicate. The relative standard deviation (RSD) amongst the replicates was calculated. The method sensitivity was evaluated through limit of detection and quantification, which were determined from the calibration curves of standard. The LOD and LOQ were calculated statistically as:

$$LOD = 3.3\frac{\sigma}{b} \qquad \text{..........................(1)}$$

$$LOQ = 10\frac{\sigma}{b} \qquad \text{..(2)}$$

which σ is the standard deviation of y-intercepts.
b is the slope of the regression line of the calibration curves.

Matrix effect is defined as the influence of one or more undetected components in samples. The reason for this effect is the presence of matrix compounds in the final sample extracts, which may cause suppression or enhancement of the analyte signal. In GC, a commonly simple procedure, cost-effective to calculate matrix effects is the application of calibration standards [30, 31]. ME can be classified into: soft, medium, and strong, when ME values (-20% to 20%), from 20% to 50% positive , exceeding 50% positive values and below -50% negative values, respectively calculated by Eq. (1) [32].

$$ME(\%) = (\frac{slope\ of\ matrix\ matched\ calibration\ curve}{slope\ of\ solvent\ calibration\ curve} - 1) \times 100 \qquad \text{.......(3)}$$

2.7 Dissipation kinetics

The degradation kinetics of the Pyridaben in cucumber, leaves, and soil samples determined by plotting residue concentration against time. Used a first order kinetic model to estimate dissipation rate constants (k), and half-lives ($t_{1/2}$) of dissipation, by the follows:

$$\mathbf{C(t) = C_0 \times exp(- k^{diss} \times t)} \qquad \text{...................(4)}$$

Rearranging eq 1 and solving for k^{diss} yields:

$$\mathbf{k^{diss} = ln[C_0] - ln[C_t] / t} \qquad \text{..............................(5)}$$

C_t is the concentration of residual (mg/kg), in time t (d), C_0 the initial concentration (mg/kg), K the constant of dissipation rate.

$$\mathbf{t_{1/2} = (ln2) / k} \qquad \text{...(6)}$$

where $t_{1/2}$ corresponds to the time (t) at which the residual pesticide concentration C(t) equals half of the initial concentration C_0 [33].

2.8 GC-FID and GC-MS analysis

The GC instrument used the Shimadzu model 2014 (Japan) combined with flame ionisation detector was used to separation and determination of Pyridaben. To achieve the sensitivity expected, GC-FID analysis requires properly optimized GC parameters such as temperature, port of injection, temperature of detector, flow rate of column and equilibrium time. Various injector temperatures (180, 200, 230, 250, and 280 °C) and different oven temperature programs were tested, with initial temperatures set at 100, 120, and 150 °C and a temperature ramp of 20 °C/min. The column used was a capillary a Rxi 5Sil MS (5% phenyl, 95% dimethyl polysiloxane) 60m (0.25 mm × 0.25 µm) (Restek, USA), and Quantitation by peak area, approximate retention time of Pyridaben, 14.7 min (Fig 2b).

GC-MS equipped with the advanced QP2010 plus detector by Shimadzu, functioning in the electron ionization mode at 70 electronvolts (eV). The chromatographic separation of the analyte was carried out using Inertcap 1 (one hundred percent of dimethylpolysiloxane) through 30 meters of length. Helium (99.99% purity) was used as carrier gas, 30 mL min^{-1} of flow rate.

The program of temperature was firstly set at 50 °C, held to 2 min, then raised to 200 °C, the rate of 15 °C min^{-1}, by 1 min for held. Injector and ion source temperatures were 150ºC and 200ºC, respectively. The mass detector was set to electron impact (70 eV), with mode of Selective Ion Monitoring (SIM).

3 The results and discussion

3.1 Validation of Method

3.1.1 Linearity

A standard calibration curve of Pyridaben was constructed by plotting analyte concentrations against peak areas. The calibration range was linear from 0.001 to 50 µg mL^{-1}. The standard curve equation was $Y = 4729.7x - 11578$ ($R^2 = 0.9991$), where y = peak area and x = concentration (µg mL^{-1}). The linearity correlation is shown in Figure 5.

3.1.2 The Limit of Detection (LOD) and Limit of Quantification (LOQ)

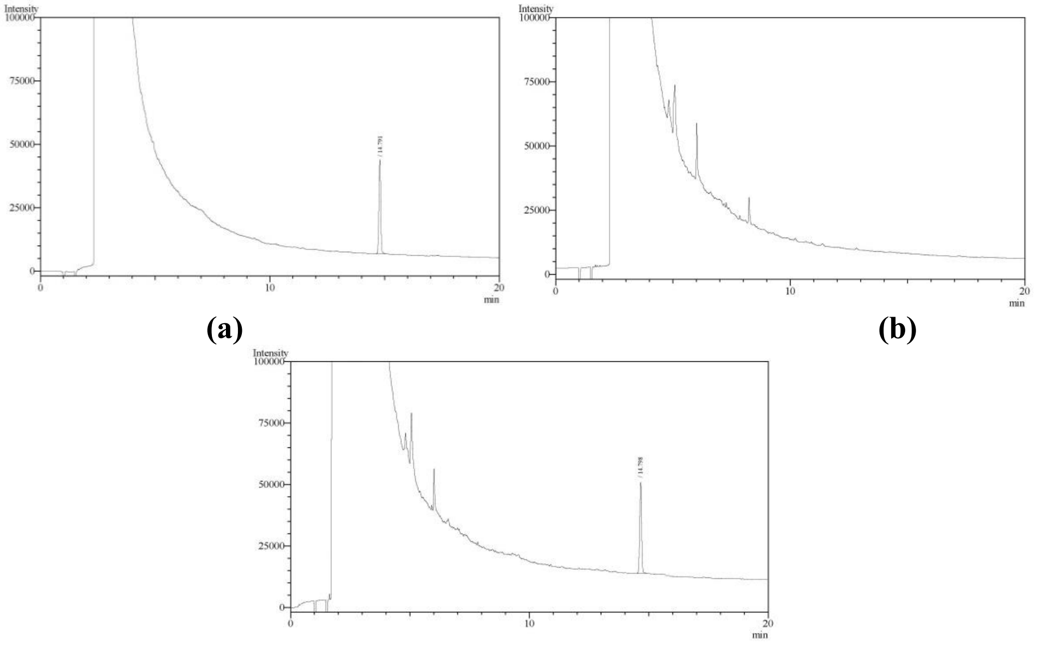
To measure the sample concentration of pyridaben, the LOD and LOQ at a signal-to-noise ratio of 3:1 and 10:1, respectively. The results indicated that LOD and LOQ values were determined equal to 0.001 µg mL^{-1} and 0.003 µg mL^{-1} respectively. The LOQ for Pyridaben was lower than MRLs recognized by diverse reviewers, confirmation that the used method is effective for the determination of Pyridaben residues in cucumber.

3.1.3 Matrix effect

The matrix-matched calibration curve was employed to mitigate the matrix effect and obtain more accurate results for each target compound in the samples. As indicated in Table 2, the analyte showed no signal suppression effect in all matrices for cucumber (ME = -12.21%), leaves (ME = -8.82%), peeled (ME=-7.8), washed (ME=-10.81) and soil (ME = -5.3%) these matrix effects could be ignored.

3.1.4 Recovery

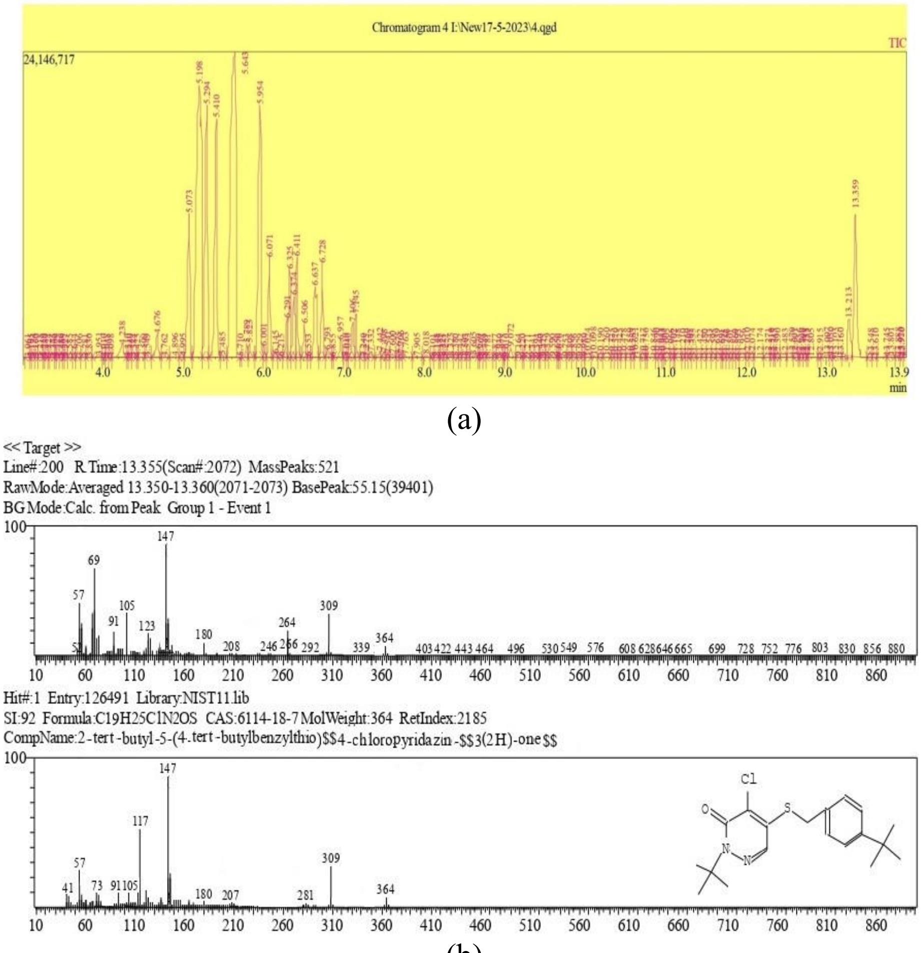
The precision and accuracy of the method were evaluated by spiking the samples by recovery experiment. The Pyridaben mean extraction recoveries (n = 5) at the spiking levels (10, 50, and 100 µg mL^{-1}) appear in Table 1. Satisfactory results were found in the 3 instances, using the QuEChERS method for cucumber. The results shows that the recoveries of leaves and soil between 93.9 and 98.5%, and relative standard deviation (RSD) ranged from 0.03 to 1.8%, that means the RSD within permissible limit of ≤ 20% [24]. The chromatograms of the Pyridaben standard, blank and spiked cucumber at 50 µg mL^{-1} showed in Figure 3. Estimation of Pyridaben was standardized by GC-MS, the mass spectrum of Pyridaben residues is given in (Fig 4b).



(a) **(b)**

(c)

Figure 3: Chromatograms of Pyridaben (a) cucumber blank (b) standard 50 µg mL^{-1} (c) cucumber spiked at 50 µg mL^{-1}



(a)

(b)

Figure 4: (a) residues of Pyridaben after one day by GC MS (b) Pyridaben mass spectrum

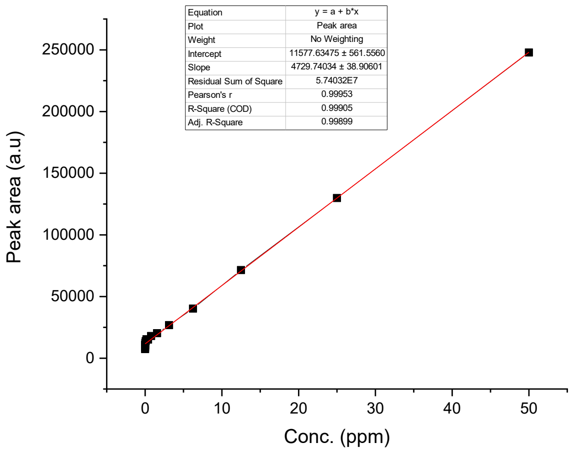


Figure 5: Calibration curve of Pyridaben ranging between 0.001 to 50 μg.mL^{-1}

Table 1: Recoveries (n = 5), RSD (%) for target compound from different matrixes at three spiked levels.

Samples	Cucumber			Leaves			Soil		
Spiked level (μg.kg^{-1})	100	50	10	100	50	10	100	50	10
Recovery	96.99	97.25	95.07	95.90	96.31	93.18	93.24	94.73	94.24
	96.56	97.50	96.11	95.77	95.88	92.43	93.45	96.01	91.85
	97.11	97.04	96.16	95.92	95.81	95.37	92.90	95.00	93.89
Average	96.88	97.26	95.78	95.87	96.00	93.66	93.20	95.25	93.33
RSD%	0.25	0.35	0.44	0.25	0.35	0.45	0.19	0.13	1.33
	0.18	0.18	0.90	0.18	0.19	0.94	0.15	0.19	0.75
	0.23	0.27	1.61	0.24	0.27	1.62	0.15	0.09	0.73
Average	0.22	0.27	0.98	0.22	0.27	1.00	0.16	0.14	0.93

Table 2: Equations of calibration, R^2, ME % = (slope M /slope solvent -1) × 100

Matrix(M)	Equation of regression	R^2	Slope ratio of (M/Solvent)	ME%
Acetonitrile	y=4678.6x+11650	0.9991	-	-
Cucumber	y=4107.3x+9892.9	0.9992	0.87	−12.2
Leaves	y=4265.5x+10747	0.9991	0.91	−8.8
Soil	y=4012.6x+9828.8	0.9992	0.85	−14.2
Peeled	y=4309.2x+11482	0.9991	0.92	−7.8
Washed	y=4172.4x+10083	0.9992	0.89	−10.8

3.1.5 Optimization of GC-FID condition

Several factors influence the choice of carrier gas including: dryness, freedom from oxygen, safety, cost and availability. Nitrogen is the preferred mobile phase used in FID giving high efficiency of heavy components of natural gas separation the 99.9995% purity (Nitrogen Generator, Claind).

Various injector temperatures (180, 200, 230, 250, and 280 °C) and oven temperature programs (initial temperatures of 100, 120, and 150 and temperature rams of 20 °C/min) were optimized. The best chromatographic conditions achieved are shown in Table 3. Table 4 presents the values of retention time t_R, capacity factor k`, and efficiency N for Pyridaben.

Table 3: The parameters condition of GC-FID

Parameter	Value
Mode of injection	**Splitless**
Temperature of injection	**280 C°**
Carrier Gas	**N_2**
Column Flow Rate	**2.5 mL/min**
First temperature of Oven	**150 C°**
Hold Time	**1min**
Rate 1	**20 C°/min**
Final temperature of Oven	**270 C°**
Hold Time	**20 min**
Total of run time	**20 min**
Volume of injection	**1 µL**

Table 4: Effect of column temperature on chromatographic parameters values

	Pyridaben		
Temp.	t_R	k`	N
80C°	18.362	6.87	33716.3
	18.688	6.652	22351.44
	18.697	7.017	34957.78
100C°	17.335	6.497	30050.22
	17.674	6.608	31237.02
	17.695	6.357	55664.53
120C°	16.334	5.897	26679.95
	16.3	5.992	47233.77
	16.055	6.038	45824.53
150C°	14.799	5.593	38935.18
	14.782	5.688	38845.78
	14.79	5.647	38887.84

3.2. Pyridaben Residual in Matrix and Dissipation Rate

The dissipation rate, and half-life time of periods of Pyridaben in samples under greenhouse conditions at recommended doses are illustrated in Table 5 and Figure 6. The average initial deposit of Pyridaben was 2.11±0.035mg/kg, measured 2 hours after application, indicating that pyridaben residues decreased over time. Within the first 24 hours post-application, the level was declined to be 1.35±0.025mg/kg. Following that period, twenty days after application the Pyridaben residues dissipated to undetectable limits.

Dissipation of Pyridaben in cucumber under greenhouse conditions was much faster compared to the cucumber leaves. Within 1 day, about 36% residue was loss from the cucumber compared to 22% in the leaves. This difference increased with time and the residue loss was 99% in the cucumber after 15 days but after 30 days the residue loss was 99% in leaves. The residues of Pyridaben in soil the 2 hours after application were 0.83 mg kg^{-1} under greenhouse conditions at recommended doses. Dissipation of Pyridaben in soil was about 21% after one day when the concentration was 0.65 mg kg^{-1} after 15 days the residue loss was 99%. First-order kinetics was utilized to describe the degradation process of pyridaben [34-36]. The experimental data for degradation kinetics of Pyridaben by plotting logarithm residue concentration against the indicated statistical of the dissipation rate (Figure 7). The results showed half-life ($t_{1/2}$) values of 1.05 day,1.03 day and 1.21 day for Pyridaben in cucumber, leaves and soil respectively.

The degradation of pesticide is influenced by various factors, including environmental conditions [37], type of application, species of plant, pesticides dosage [38], interval between applications, the relation between weight and treated surface and living state of the plant surface, and harvest time [39, 40]. These factors likely affected degradation of Pyridaben for example, the ($t_{1/2}$) of Pyridaben in open field strawberries and cucumber under Egyptian cultivation conditions were 6.4d and 1d respectively [25]. In different experimental areas, Pyridaben ($t_{1/2}$) in orange from 11.9days to 24.9days [21], the ($t_{1/2}$) was 7.3 days in apple [20], 2.8d–2.9 d [19].

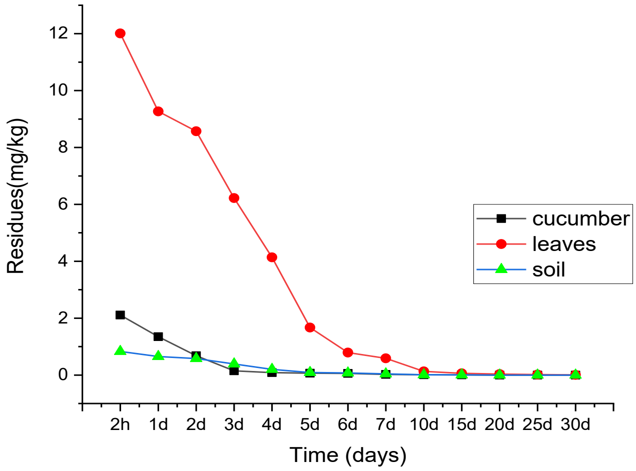
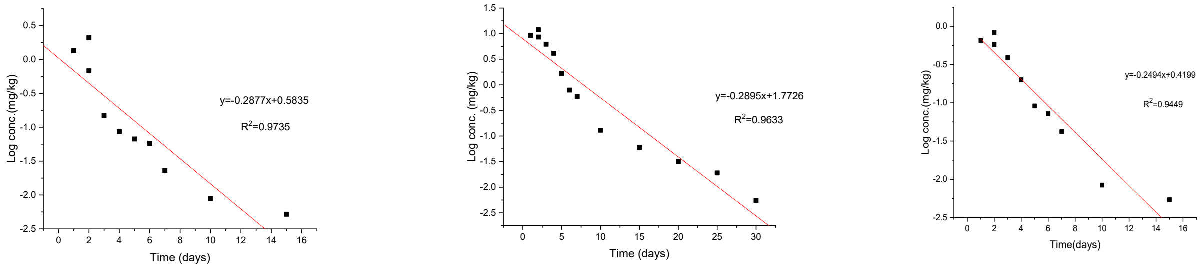


Figure 6: Dissipation of Pyridaben in cucumber, leaves and soil grown in greenhouse conditions at recommended doses

Table 5: Dissipation of Pyridaben residues (mg kg^{-1} ± SD^a) in samples

		Mean residues ± SD^a (mg kg^{-1})		Mean residues ± SD^a (mg kg^{-1})		Mean residues ± SD^a (mg kg^{-1})	
Days	**Control**	**Cucumber**	**Dissipation%**	**Leaves**	**Dissipation %**	**Soil**	**Dissipation%**
0	ND	2.11±0.035	0.00	12.01±0.125	0.00	0.83±0.060	0.00
1	ND	1.35±0.025	36.01	9.27±0.020	22.81	0.65±0.035	21.68
2	ND	0.68±0.041	67.77	8.57±0.072	28.64	0.58±0.04	30.12
3	ND	0.15±0.025	92.89	6.22±0.045	48.20	0.39±0.02	53.01
4	ND	0.086±0.004	95.92	4.14±0.035	65.52	0.2±0.036	75.90
5	ND	0.067±0.006	96.82	1.67±0.030	86.09	0.091±0.004	89.03
6	ND	0.058±0.002	97.25	0.79±0.035	93.42	0.072±0.002	91.32
7	ND	0.023±0.004	98.90	0.59±0.055	95.08	0.042±0.004	94.93
10	ND	0.0088±0.040	99.58	0.13±0.030	98.91	0.0084±0.0004	98.98
15	ND	0.0052±0.0002	99.75	0.06±0.01	99.50	0.0054±0.0004	99.34
20	ND	0	0	0.032±0.005	99.73	0	0
25	ND	0	0	0.019±0.003	99.84	0	0
30	ND	0	0	0.0055±0.0002	99.95	0	0
Dissipation equation		$y=-0.2877x+0.5835$		$y=-0.2895x+1.7726$		$y=-0.2494x+0.4199$	
R^2		0.9735		0.9633		0.9442	
K ($days^{-1}$)		0.66		0.67		0.57	
$t_{1/2}$ (days)		1.05		1.03		1.21	

a: the average of three replicate ± SD
ND: not detected



(a) (b) (c)

Figure 7: Linear plot for the first-order kinetics of Pyridaben dissipation in (a) cucumber (b) leaves (c) soil

3.3. Effects of (Washing and Peeling) processes

Washing and peeling are the initial steps in the food preparation process at home or commercially. The dissolution process is recognized an effective application for eliminating or reducing pesticide residues, especially water-soluble pesticides. The pesticide dissolution affect by other factors such as, the formulation type of pesticides, pH of the aqueous media and ionic strength, first concentration of the pesticide residue on crops, partition coefficient (Kow) of pesticides [41]. Furthermore, household processing such as washing and peeling can reduce or remove insecticide residues in fruits and vegetables [42, 43].

The effect of household washing and peeling procedures on the Pyridaben residue in cucumber after application by recommended dose under greenhouse Iraqi conditions were shown in Figure 8. Washing with tap water reduced 29.41% from the initial Pyridaben residues within 2 hours after application but proximately 84.44% of Pyridaben residues were removed from the initial residues by peeling process after 2 hours from application, removed Pyridaben residues from cucumber washing and peeling about 99.82% and 99.74% after 15days and 5days respectively. The results of this study are consistent with previous findings [44-46], which also showed that washing and peeling procedures can significantly reduce the levels of pesticide residues in greenhouse-grown cucumbers.

In Table 6 showed the processing factor of Pyridaben through washing and peeling, through the results it was shown that PFs for Pyridaben was 0.62, indicating that the process could reduce the residue of Pyridaben in cucumber, the PFs after peeling 0.081 this confirms that a large number of residues on the peel and has been removed by peeling.

Table 6: PF_s (mean ± SD^a) for different household processing

Time	Washed	Peeled
	PF_s(mean±SD^a)	**PF_s(mean±SD^a)**
0	0.80	0.29±0.030
1	0.88	0.07±0.003
2	0.73	0.01±0.0005
3	0.6	0.03±0.0007
4	0.69	0.04±0.0007
5	0.59	0.02±0.0003
6	0.34	0
7	0.34	0
10	0.68	0
15	0.57	0
20	0	0
25	0	0
30	0	0

a: average of three replicate analyses ± SD

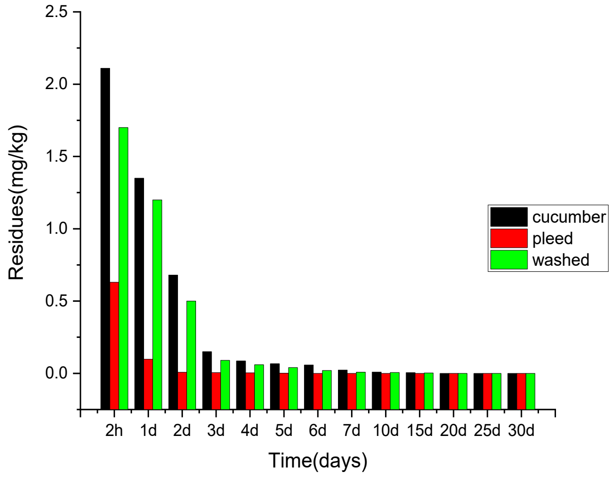


Figure 8: esidue(mg/kg) of unprocessed cucumber against residue levels in washing and peeling samples

Conclusions

The QuEChERS extraction method coupled with GC using FID and MS detectors, provided excellent results for analyzing pyridaben residues in various matrices. The range of recoveries between 93.20-97.26 % with the RSD) < 20%. The analytical technique of Pyridaben had a LOD of 0.001 µg mL^{-1} and LOQ of 0.003 mg kg^{-1}. The procedure showed good linearity with relative coefficients higher than 0.9991. The technique can be applied to analysis Pyridaben immediately in actual samples. Dissipation of Pyridaben in cucumber was much faster under greenhouse conditions compared to the cucumber leaves and soil, within 1 days 36% residue loss was observed from the cucumber compared to 22%,21% loss in the leaves and soil respectively. When time increase this difference increased and the residue loss was 99% in the cucumber and soil after 15 days but after 30 days in leaves. Pyridaben residue dissipation followed first-order rate kinetics, with the half-life ($t_{1/2}$) values of 1.05 day,1.03 day and 1.21 day for Pyridaben in cucumber, leaves and soil respectively. The PFs after washing and peeling were 0.62 and 0.081 respectively, this confirms that a large amount of Pyridaben residue is on the peel and has been removed by peeling. Therefore, we recommend the importance of washing and peeling before consuming cucumbers, as this greatly reduces the danger of pesticides to consumers.

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