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Dissipation kinetics of cyantraniliprole residues in melon grown in field trials using QuEChERS and HPLC-UV

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Abstract

Cyantraniliprole is one of the novel anthranilic diamide insecticides designed to target the insect ryanodine receptor and has been used widely in many vegetables and fruits, especially melon. A highly selective and sensitive determination method is required to ensure that only permitted levels of cyantraniliprole are consumed. In this work, the combination of quick, easy, cheap, effective, rugged, and safe (QuEChERS) with high-performance liquid chromatography-ultraviolet (HPLC-UV) is proposed for the determination of cyantraniliprole in melon. Insecticide was spiked into melon samples before analysis, extracted by using QuEChERS, and determined by HPLC-UV. The important parameters that affect the QuEChERS efficiency were investigated. NaCl was the best partitioning salt with the highest recovery (129.8%-140.9%, relative standard deciation (RSD) 4.5%) while Florisil (60-100 mesh) was the sorbent, which provided chromatograms with less interference. The mean recoveries were within 129.2%-111.7% (RSD 7.1%). Under the optimized conditions, the proposed extraction method provided higher sensitivity compared with the traditional solvent extraction method. The limit of detection and the limit of quantification for cyantraniliprole were determined to be 0.14 and 0.46 mg/kg, respectively. Moreover, the matrix effect was evaluated, and the matrix-matched calibration method was applied. The cyantraniliprole residues on melon grown in the experimental field were mainly found in leaves, and no residues were detected in fruit on the harvest day. The half-life of cyantraniliprole on melon leaves was determined as 4.4 days. This study could guide the anticipated use of cyantraniliprole for melon.

Keywords: Anthranilic diamides, Cyantraniliprole, HPLC-UV, Melon, QuEChERS, Dissipation kinetics

1. Introduction

Melon (*Cucumis melo*) belongs to *the Cucurbitaceae* family and has attracted increasing attention in recent years. It contains many essential nutrients, such as vitamin C, vitamin B, antioxidants, fiber, and other minerals, and has thus become an economic crop in many countries, including Thailand. However, the yield and quality of melon can be affected by many insect pests. Therefore, various insecticides have been developed to control pests. One of the most novel insecticides in melon production is cyantraniliprole. The use of cyantraniliprole has increased due to its precise mechanism, ability to activate insect ryanodine receptors [1], low dosage, and high efficiency on many pests, including *Bactrocera dorsalis* [2], *Leucinodes orbonalis* [3], *Bemisia tabaci* [4], and *Agrotis ipsilon* [5]. The maximum residue limit (MRL) of cyantraniliprole in *Cucurbitaceae* is 0.3 mg/kg [6]. Thus, reliable, sensitive methods of extracting and determining cyantraniliprole in fruits are still required.

Dissipation kinetic study of the pesticide is gaining interest nowadays. It indicates the current risk and impacts assessment of the produce. Three terms which are rate constant (k_{diss}), half-lives ($t_{1/2}$), and the residual pesticide concentration of a harvested plant (C_t) are used as the dissipation representations [7]. The half-lives of diamide insecticides were in the range from 2 to 17 days for broflanilide [8], flubendiamide [9], fluopicolide [9], tetraniliprole [10], and chlorantraniliprole [11-13]. However, the persistence of the insecticides also depends on environmental influences during the growth stage, including light sources, temperatures, moisture regimes, and

carbon dioxide levels [14]. For example, the half-lives of chlorantraniliprole were 16-17 days for apple [11] and 2.21 days for okra [13]. Moreover, the distribution of residual insecticide is different. Tharayil et al. [15] found that the green fruits of the tomato had the highest cyantraniliprole residues and decreased toward red ripening stages. To the best of our knowledge, no prior study on the dissipation kinetics of cyantraniliprole residues in melon is available.

The outstanding quick, easy, cheap, effective, rugged, and safe (QuEChERS) method has proven to be an effective method for extracting many insecticides, including organophosphates [16,17], carbamates [16], and organochlorines [16,18]. The partition and cleanup steps are the major keys of efficient QuEchERS. Yang et al. [17] studied the selection of sorbent and salt in their analysis of organophosphorus and pyrethroid pesticides in vegetables. Each salt type promoted phase separation differently for each pesticide. Moreover, the modification of sorbent plays an important role in removing interferences [19]. Ferreira et al. [20] showed that a suitable modification allowed a large amount of different pesticides to be extracted from different food classes and matrices.

In addition to the simple sorbents used in the traditional QuEChERs, some studies reported the new types of sorbents for complicated-matrix samples, including carbon nanotubes [21-23], zirconia-based sorbent [24-26], and microporous UiO-66 [27]. Owing to unique physical characteristics, including thermal, electronic, and chemical properties, multiwalled carbon nanotubes (MWCNTs) can be used as an adsorbent in extracting pesticides. Han et al. [23] used MWCNTs to remove the interferences of pigments in leek, leaf lettuce, and garland chrysanthemum. While zirconium dioxide is used to eliminate the lipophilic-based matrix, UiO-66 is suitable for removing small organic contaminants based on the uniform pores. In this study, the effect of salts and sorbents was studied for the determination of cyantraniliprole in melon. The efficiency of modified QuEChERS was determined by HPLC-UV. A field study was performed to demonstrate the decline pattern of cyantraniliprole in melon.

2. Materials and methods

2.1 Materials

Standards of cyantraniliprole (purity, 92.59%) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The stock solution was prepared in acetonitrile and stored at -20°C. HPLC-graded acetonitrile and HPLC-graded water were purchased from RCI Labscan (Bangkok, Thailand). Sodium chloride (NaCl), anhydrous magnesium sulfate ($MgSO_4$), sodium sulfate (Na_2SO_4), and ammonium acetate (CH_3COONH_4) are analytical grade and purchased from Kemaus (New South Wale, Australia). Various sorbents purchased from Merck (Darmstadt, Germany) included Florisil (particle size: 100-200 mesh) and silica gel, while Florisil (particle size: 60-100 mesh) was purchased from J.T. Baker (New Jersey, USA). To filter the extracted samples, 0.22 μm nylon syringe filters from Finetech (Berlin, Germany) were used.

2.2 Sample preparation and extraction method

2.2.1 Traditional solvent extraction method

A total of 10 g of water samples (double deionized water) were weighted in 50 mL polypropylene centrifuge tubes, and 10 mL of acetonitrile was added. Cyantraniliprole at 2.5 mg/kg was added to the sample, vortexed for a minute, and stored at room temperature for 30 min. The mixture was then shaken in a water bath shaker at 110 rpm for 30 min. After filtration by a vacuum pump, the sample was washed with 20 mL acetonitrile. The filtrate was collected and diluted to 50 mL with acetonitrile. This solution was purified on an in-house packed column. The weighted sorbent was packed into a 15 cm glass dropper. After the column was washed several times until the sorbent was set completely, 2 mL acetonitrile was used for conditioning. The sample was loaded and then eluted with 1 mL of acetonitrile. Before HPLC-UV analysis was performed, the collected fraction was filtered with a 0.22 μm syringe filter.

2.2.2 QuEChERS.

A total of 10 g of homogenized samples (water or melons) were weighed in 50 mL polypropylene centrifuge tubes. Then, 2.5 mg/kg of cyantraniliprole was spiked into the sample and vortexed for a minute. The tube was capped and stored at room temperature for 30 min. The extraction process was started by adding 10 mL acetonitrile and then vortexed for 3 min. Partitioning salts (NaCl or $MgSO_4$ or Na_2SO_4) were added. The tubes were shaken vigorously for a minute and centrifuged for 10 min at 3600 rpm. The supernatant was transferred into the tubes containing sorbent (Florisil 60-100 mesh or Florisil 100-200 mesh or silica gel) and $MgSO_4$. The samples were

vortexed for a minute and centrifuged for 5 min at 3600 rpm. The supernatant was filtered with a 0.22 μm syringe filter before injection to HPLC-UV.

2.3 Instrumentation

The separation of cyantraniliprole was performed on HPLC 1260, Agilent. The Poroshell C18 column (4.6 × 100 mm, particle size 2.7 μm) was used at a fixed temperature (30°C). The mobile phase consisted of acetonitrile (Solvent A) and 2 mM ammonium acetate aqueous solution (Solvent B). The flow rate was set at a constant value of 0.5 mL/min with a total run of 5 min. The injection volume was 10 μL. Detection of cyantraniliprole was monitored at 280 nm.

2.4 Matrix effect evaluation

The matrix effect of different matrices was studied because various compositions in melons, such as sugar, pigments, and fatty acids, might interfere with the HPLC signals. Three sets of standard solutions (0, 0.6, 1.3, 3.2, 6.4, 12.7, 31.8, 65.1, 508.0 mg/kg) were prepared and analyzed. Solution set A was cyantraniliprole standards in pure acetonitrile. The other two sets were prepared by using the extracted control sample solution as a solvent. Solution set B was water-extracted cyantraniliprole standards, and solution set C was prepared in the melon-extracted ones. The matrix effect was calculated according to the following Equation 1:

$$\text{Matrix effect} = \left(\frac{\text{Slope}_x}{\text{Slope}} - 1\right) \times 100 \quad (1)$$

where slope is the slope of the calibration curves prepared with acetonitrile standards (set A), and Slope_x is the slope of the calibration curves prepared with matrix-matched standards (set B or C).

2.5 Method validation

The proposed extraction method was evaluated by performing a validation procedure that includes the linear range, the limit of detection (LOD), the limit of quantification (LOQ), accuracy, and precision. Four sets of calibration curves were plotted between the concentration of cyantraniliprole standard and the standard peak area. The LOD and LOQ were defined as a concentration that produced a S/N ratio of 3 and 10, respectively. For recovery assays, three replicates of spiked samples (water and melon) at two different levels (0.5 and 10 mg/kg) were studied. The samples were extracted using the optimized method followed by HPLC-UV determination. The precision was expressed as RSD.

2.6 Plant experimental model

K99 melons were grown under greenhouse conditions in Phetchaburi, Thailand. Melons have been cultivated in this area for more than 10 years. Field trials were conducted between February 2, 2021, and April 4, 2021. The growth stages in melon consist of melon seeds (day 1-7), vegetative growth (day 8-21), flowering (day 22-35), fruit set (day 36-63), and harvesting (day 64-75). The experimental area has four plots. Plot numbers 1 and 2 were untreated control, while plot numbers 3 and 4 were treated with cyantraniliprole. Plot numbers 2 and 3 were designed to be the buffer zone. Cyantraniliprole suspension concentrates (10% active ingredient) from Sotus International Co., Ltd. (Nonthaburi, Thailand) were applied at the dose (30 mL/20 L) prescribed by the manufacturer on days 7 and 14 after planting. The area of the experimental plot was 0.4 m × 20 m. Each plot was separated by 0.8 m. Samples were randomly collected from plots 1 and 4 (10 samples from each plot) on days 7, 14, 21, 28, 35, 42, 63, and 75. The samples were chopped and blended. The homogenized samples were then weighed in a 50-mL conical tube and stored at -20°C until the day of analysis.

2.7 Dissipation kinetics

The dissipation kinetics of cyantraniliprole in melons grown under greenhouse conditions were assessed using the first-order kinetic equation, as shown in Equation 2.

$$C_t = C_0 e^{-kt} \quad (2)$$

where C_0 and C_t represent the initial concentration and the concentration at time t (mg/kg), respectively. The half-life ($t_{1/2}$), where the concentration of cyantraniliprole falls to half its initial value, was calculated according to Equation 3.

$$t_{1/2} = \frac{\ln 2}{k} \quad (3)$$

3. Results and discussion

3.1 Optimization of traditional solvent-solvent extraction method

The sorbent was useful in removing matrices after the solvent extraction methods. Thus, the type and number of sorbents were studied. First, three types of sorbents, namely, Florisil (60-100 mesh), Florisil (100-200 mesh), and silica gel, were tested to clean up the sample. The amount of sorbent was fixed at 500 mg. Florisil (60-100 mesh) exhibited higher extraction efficiencies for cyantraniliprole and was therefore selected for further experiments. This activated magnesium silicate interacts and adsorbs the interferences, such as lipids and carbohydrates. Shalaby et.al. suggested the interaction between cyantraniliprole and the anionic silicon moiety of florisil via dipole-dipole or hydrogen bonding [28]. Second, the amount of Florisil (60-100 mesh) was compared to evaluate the effects on the purification recoveries. The results showed that 1000 mg provided better recovery than 500 mg. The flow rate might be the crucial influence, given the gravitational purification. The flow rate of the 1000-sorbent column was 1.50 mL/min, whereas the flow rate of the 500-sorbent column was 0.83 mL/min. The slower flow rate may promote interaction between the sorbent and matrix, leading to a higher degree of purification.

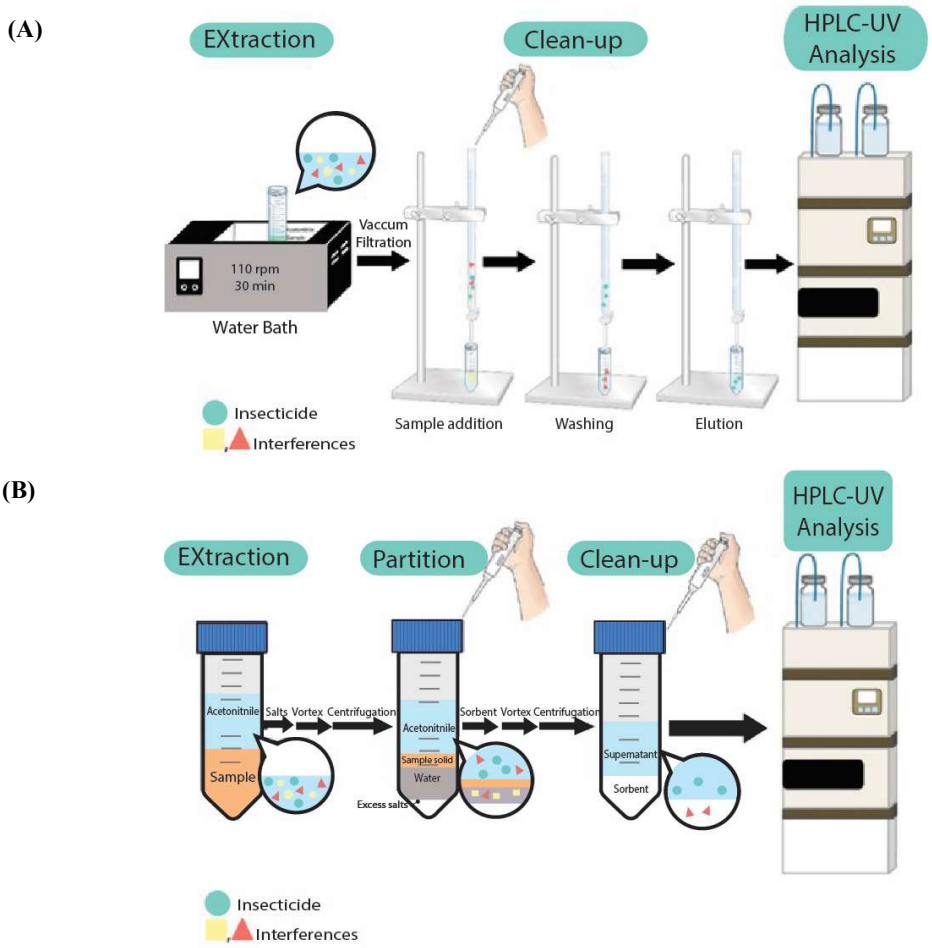

Figure 1 Schematic of (A) the traditional solvent extraction method (B) the developed QuEChERS with HPLC-UV method.

3.2 Optimization of QuEChERS parameters

QuEChERS has three main steps: extraction, partition, and cleanup (Figure 1). Adding salts plays a vital role in the partition step via the salting-out mechanism. The effect of salts was investigated by employing several types of salts (NaCl, $MgSO_4$, and Na_2SO_4) at different ratios. As shown in Figure 2A, the highest percent recovery was observed when the mixture of NaCl and $MgSO_4$ (0.7 g :1.3 g) was used for the water sample, while NaCl was the best salt for melon. The presence of $MgSO_4$ reduces the amount of water in the extract. The amount of salt also affects the extraction efficiency. A higher concentration of salt gave a higher percent recovery. However, using a too- high concentration of $MgSO_4$ reduced the peak area of target analytes. Interactions between the target insecticide and Mg^{2+} possibly occurred, which may have hindered the extraction procedure. Therefore, the combination of NaCl and $MgSO_4$ at 0.7 g :1.3 g was selected for the water sample, and 4 g of NaCl was used for further experiments with melon.

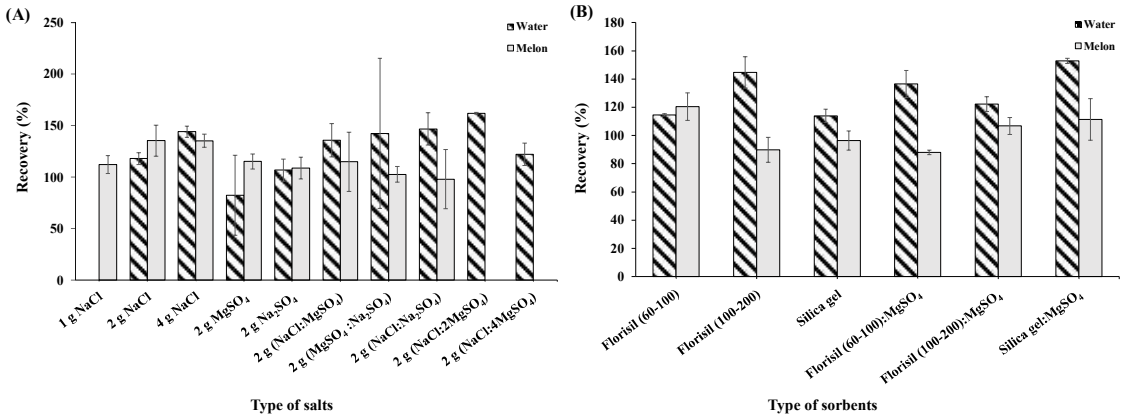

Figure 2 Effects of type and amount of partition salts on the recoveries of the cyantraniliprole (A) Effects of type and number of sorbents on the recoveries of the cyantraniliprole (B).

The cleanup step often promotes extraction performance, especially with high-pigment samples such as melon. Thus, different sorbents were evaluated. The experiments were conducted with 50 mg of sorbent in the absence and presence of 50 mg of $MgSO_4$. Florisil (60-100 mesh) was chosen for all samples according to Figure 2B. A total of 50 mg of $MgSO_4$ was added to the water sample to remove the water residues in the extract.

3.3 Analytical characteristics of the methods

To compare the efficiency of the extraction methods, water spiked with cyantraniliprole at 2.5 mg/kg was extracted. Additional cleanup with Florisil was performed in both methods, but partition salts are not involved in traditional solvent extraction. Figure 3 shows that the peak areas of standard cyantraniliprole extracted by QuEChERS and pure standard cyantraniliprole are similar, thereby indicating that no significant loss of the analyte occurred during this extraction process. In contrast, the traditional solvent extraction method gave only a small peak area. Interferences and baseline noise were also produced. Therefore, QuEChERS was performed for further experiments. The mobile phase optimization was performed using mixtures of water and acetonitrile (data not shown). The highest resolution was attained when using the gradient program. Nevertheless, gradient elution provided longer separation times. Moreover, the sensitivity of the acetonitrile-water phase was lower than that of the ammonium acetate- acetonitrile one. To achieve the optimal sensitivity and minimize the running time ammonium acetate-acetonitrile was adopted as the mobile phase. The injection volume was also studied between 5 µL and 50 µL, and 10 µL was selected because it provided the highest sensitivity and no overlapping of the peaks with the elution program selected.

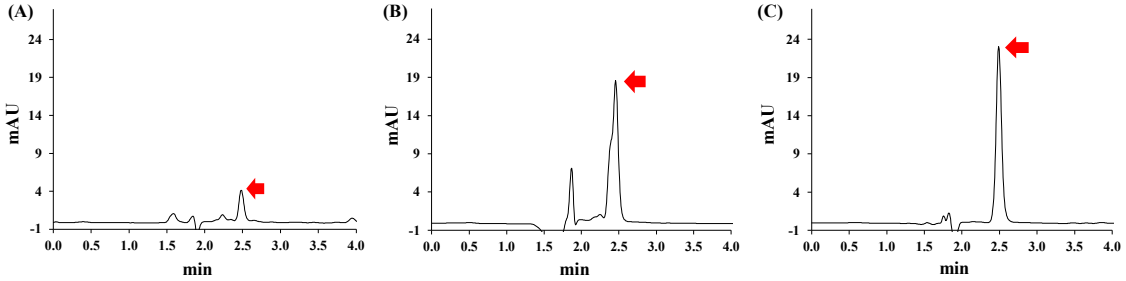

Figure 3 Chromatogram of the cyantraniliprole obtained with traditional solvent extraction method (A), QuEChERS method (B), and standard 2.5 mg/kg (C) (red arrows indicate peak of cyantraniliprole).

The matrix effect varies for each analyte and matrix. In this experiment, matrix effects were calculated according to the method described in method validation. A value between -0.53% and -1.82% (Table 1) indicates that the standard curve prepared in the acetonitrile solution and the extracted (water or melon) are almost identical. In conclusion, no substantial matrix effect was achieved by using QuEChERS extraction and HPLC-UV to determine this insecticide.

The cyantraniliprole standard peak was detected at 2.438 min, and no other peaks were interfering at the same time. The calibration range was linear from 0.6 to 508.0 mg/kg, with mean coefficients of determination (R^2) higher than 0.9999, as shown in Table 1. For melon, LOD and LOQ were estimated to be 0.14 and 0.46 mg/kg, respectively. The recoveries of cyantraniliprole in spiked samples under the optimum conditions are shown in Table 2. The values were calculated using a calibration curve obtained from a standard solution (set A). Recoveries and RSDs were in the acceptable ranges, thereby suggesting the good accuracy and reproducibility of this method.

Table 1 Analytical performance of the QuEChERS extraction and HPLC-UV.

Matrix	Calibration range	Standard calibration curve			Matrix effect
		Slope	Intercept	R^2	
Acetonitrile	0.6 - 508.0	24.68	37.64	0.9999	-
Water	0.6 - 508.0	24.55	20.10	1.0000	-0.53
Melon	0.6 - 508.0	24.23	42.14	1.0000	-1.82

Table 2 Accuracy and precision of the optimized method for cyantraniliprole determination (n=3).

Sample	Spiked level (mg/kg)	Average recoveries (%)	RSD (%)
Water	0.5	117.4	2.5
	10.0	117.8	2.5
Melon	0.5	71.3	9.5
	10.0	125.5	3.9

3.4 Residues in fruit and leaves

The samples were collected on days 35, 42, and 75 after planting and days 7, 14, 21, 28, 35, and 75 after planting for fruit and leaves. The results showed that cyantraniliprole residue was mainly found on leaves than on fruit. On the harvest day (day 75), no detectable residues were found on fruit, while 0.001±0.0002 mg/kg of cyantraniliprole was found on leaves. Residue concentrations on leaves decreased progressively over planting time.

Young fruit (day 35) was the only fruit sample that expressed remaining cyantraniliprole at 0.0886±0.0052 mg/kg. However, this concentration was far lower than the MRL for cyantraniliprole.

3.5 Dissipation of cyantraniliprole in K99 melons

Cyantraniliprole residues on leaves were employed to express the dissipation pattern. Figure 4 shows the exponential model that best fits the experimental data ($Ct = 0.1005e^{-0.1564t}$, $R^2=0.8568$). A rapid decrease in cyantraniliprole concentrations was observed during the first 14 days after the application followed by a slow decline during the next weeks. The decay half-life was calculated to be 4.4 days, which is in the same range as the one reported by Shalaby et al. (2.65 days) [28]. The time discrepancy might be due to the plant species and the growth condition. This reason is supported by Shim et al.'s work on the half-lives of flubendiamide on melon cultivated in greenhouse conditions; the half-lives were 5.8 and 6.5 days [9].

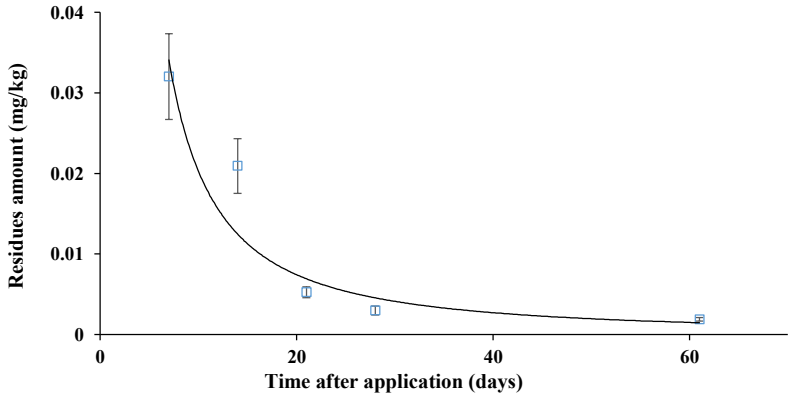

Figure 4 Dissipation pattern of cyantraniliprole in melon at the recommended dosage.

4. Conclusion

The developed method, which is simple, inexpensive, quick, and effective, was successfully applied in the determination of cyantraniliprole in melon. It is composed of an optimized QuEChERS method for sample pretreatment and HPLC-UV analysis of cyantraniliprole. Compared with the traditional solvent extraction, the optimized QuECHERs can produce the desired sensitivity considerably faster. This work represents that the selection of suitable salts and sorbents is a crucial parameter in QuEChERS for each sample type. The optimized QuEChERS was successfully applied to field-grown melon treated with cyantraniliprole. Cyantraniliprole residues were mainly detected in leaves. The exponential model was the best fit with the degradation of cyantraniliprole, and the half-life was determined to be 4.4 days. These results indicate that melon could be consumed safely.

5. Acknowledgments

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