

Kinetics Study of Carbaryl Degradation in Squash and Cucumber Fruits

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ABSTRACT: *In this study, residual levels of carbaryl insecticides were determined in squash (summer squash, ronde de nice) and cucumber (C. sativus) fruits using spectrophotometry. The degradation rate, degradation percentage, half-life and activation energy of carbaryl degradation were calculated. The degradation reaction of the carbaryl was found to follow first-order reaction kinetics. The half-lifetimes ($t_{1/2}$) ranged between 2.18 and 2.32 days, and the activation energies (E_a) of carbaryl degradation for squash and cucumber samples were 10.34 kcal/mole and 8.95 kcal/mole respectively. The degradation of carbaryl residue was greatly affected by small increases in temperature. Based on the maximum residue limit (MRL), the safety time was found to be five days after carbaryl application. The limit of detection (LOD) of the method used for carbaryl measurement in fruits in this study was 0.023 ppm, and the average recovery percentage of carbaryl was 95.98%.*

Keywords: carbaryl, kinetic, degradation, squash, cucumber

1. INTRODUCTION

Carbaryl, a broad-spectrum insecticide belonging to the carbamate family, is widely used in Sudan to control insects and pests of cotton, vegetables and fruits. Residues, kinetic analysis and the carbaryl degradation rate in the environment are important indicators for ensuring a clean environment and safe food for both human beings and animals. The degradation rate of carbaryl varies widely among different environments and plants.¹

Derbalah et al. studied the degradation rate of carbaryl based on the photoformation of reactive oxygen species, reporting that the rate constants for hydroxide (OH) and oxygen (O₂) reactions with carbaryl were $(4.68 \pm 0.52) \times 10^9$ and $(2.98 \pm 0.10) \times 10^5 \text{ M}^{-1}\text{s}^{-1}$.² Khaghani et al. cleaned up carbaryl using kinetic models, reporting that the adsorption process followed the pseudo-second-order model.³ Celebi et al. found that the degradation of carbaryl with hydroxyl radicals was pseudo first-order under.⁴ Elsabay et al. studied different kinetic parameters of carbaryl degradation, finding it to be pH-dependent.⁵ Meanwhile, Ye et al. studied the kinetics of carbaryl degradation by anodic fenton, showing that the degradation involved a pseudo first-order reaction.⁶ A study of carbaryl photodegradation and biodegradation rates conducted by Derbalah et al. revealed higher degradation in river water (0.330 and 0.029 day⁻¹, respectively) than in sea water (0.23 and 0.001 day⁻¹, respectively).⁷ Ihsan studied labelled carbaryl in leaves of tomato, eggplant and okra, reporting that carbaryl application resulted in fast degradation during the first two hours, followed by slower rates in the following days.⁸ A literature review of carbaryl residues under various field conditions discussed its effects as a reversible inhibitor of cholinesterase and its use in the control of more than 150 major pests.⁹ The presence of carbaryl in marine environments was studied by Karinen et al., who concluded that carbaryl is likely to persist for 2–6 weeks in bottom mud.¹⁰ Caro et al. investigated the persistence and run-off of carbaryl in soil. One hundred and thirty five days after the application of 4 kg of carbaryl, 95% of the carbaryl was found to be degraded, although only 5.77 g was lost during the season through run-off water and sediments.¹¹ Dorough studied the residual nature of conjugated and bound metabolites within animals and plants.¹² Similarly, Marshall and Dorough studied in vivo administration of these metabolites in rats and found that the bound residues were readily absorbed and biodegraded.¹³ Starner et al. measured the degradation rate of carbaryl at different temperatures, reporting that carbaryl degraded more rapidly at higher temperatures. Specifically, the half-lifetimes ($t_{1/2}$) at 10°C was 16–22 days, while at 25°C $t_{1/2}$ it decreased to 1–2 days. The authors calculated the activation energy of carbaryl in river water as 29 kcal/mol.¹⁴ Szeto et al. studied carbaryl in water and reported that the $t_{1/2}$ was 20 days at 9°C.¹⁵ According to Lartiges and Garrigues, the $t_{1/2}$ of carbaryl in river water at 6°C was 45 days, decreasing to less than two days in the same water at 22°C. They reported an activation energy value of 15 kcal/mole.¹⁶ In seawater, Armbrust and Crosby reported a $t_{1/2}$ of one day at 24°C.¹⁷ Moreover, Hamada et al. studied the degradation of carbaryl by different types of bacterial isolated from soil, finding that bacteria of genus *Bacillus* exhibited the highest biodegradation rate.¹⁸ Lowery carried out a comparative study of carbaryl degradation in different aquatic environments, using fluorescence to measure carbaryl residues. He reported that the degradation rate in the dark was $4.39 \times 10^{-4} \mu\text{g/L}$ per minute,

while the rate under a lamp was 5.53×10^{-4} $\mu\text{g/L}$ per minute.¹ Using pseudo first-order reaction, Hawker reported carbaryl $t_{1/2}$ ranges from 10 min to 1.5 h at different pH levels.¹⁹

Different analytical techniques have been used to measure the degradation of carbaryl in different samples and environments.^{2,3,20–26} Analysis of carbaryl in vegetables requires several steps, including sampling, extraction, clean-up, confirmation and quantification of the residues.^{1,4,27–31}

The aim of the present study was to investigate the carbaryl degradation rate, degradation (%), rate constant, $t_{1/2}$ and activation energy of carbaryl in squash and cucumber fruits in environmental conditions.

2. EXPERIMENTAL

2.1 Material

All chemicals and reagents used in this study were of analytical grade. Standard carbaryl (99.9%) was obtained from the Agricultural Research Corporation (ARC) – Sudan. Sevin® 85 is a wettable microfine powder containing 85% carbaryl. It is mixed with water and applied as a broad-spectrum insecticidal spray.

2.2 Sampling Techniques

The cultivated area of each vegetable under study was approximately 450 m², containing 30 sarabs (ridge) 15 m in length and 1 m in width. Each sarab contained 30 plants.

An area of 150 m² was sprayed with carbaryl (Sevin® 85) at the rate of 1 kg/acre (1 kg/fedd; recommended rate). Another 150 m² was sprayed with Sevin® 85 at an approximate rate of 1.45 kg/fedd (as was the farmers' custom). The remaining 150 m² were left for control samples and recovery tests.

Fruit samples were randomly picked, collected and transported in a suitable way to avoid contamination. The samples were chopped into small homogenous pieces with a stainless steel knife.

2.3 Extraction of Carbaryl

Fruit samples were extracted directly after collection and chopping following the procedure of Benson and Finocchiaro, with some modification.³²

2.4 Clean Up by Column Chromatography

The extract was cleaned up (purified) by column chromatography on florisil (synthetic magnesium silicate) using a modified version of the method described by Lawrence and Leduc.²⁹ Further clean-ups was performed using a coagulation solution that was prepared by adding 0.5 g of ammonium chloride to 400 mL distilled water containing 1 mL of phosphoric acid (85%).

2.5 Confirmation Analysis

The presence of pure carbaryl in the extracts was examined by thin-layer chromatography (TLC) using silica gel GF₂₅₄ and saturated hexane/acetone (4:1 v/v) as a developing system.

2.6 Quantification and Kinetic Analysis

The recovery (%), limit of detection (LOD), standard calibration curve and residual carbaryl concentration at different intervals was determined using the spectrophotometric method.²⁶ The temperature and rainfall during the study were recorded. The average maximum temperatures of the two days before taking the samples were calculated, and the carbaryl residues were determined to calculate the rate constant at different temperatures. The degradation rate constant, $t_{1/2}$ and activation energy of the reaction were calculated using the following equations:

$$\text{Log } [a - x] = (-k / 2.303) t + \text{log } a \quad (1)$$

$$\text{Log } [\text{residue ppm}] = (-k / 2.303) t + \text{log } a \quad (2)$$

$$k = -2.303 \times \text{slope} \quad (3)$$

$$t_{1/2} = (2.303 \times \text{log } 2) / k \quad (4)$$

$$k = A e^{-E_a / RT} \quad (5)$$

$$\ln k = \ln A - E_a / RT \quad (6)$$

$$E_a = -R \times \text{slope} \quad (7)$$

where k = rate constant, A = frequency factor, E_a = activation energy, R = gas constant and T = temperature

3. RESULTS AND DISCUSSION

The concentrations were expressed as $x \pm s$, where s represents the standard deviation and x is the mean value. Microsoft Excel and Origin software were used to assess the significance of the differences between the different variables in this study. The standard calibration reading and curve are shown in Table 1 and Figure 1. The LOD was found to be 0.023 ppm, and the recovery (%) was almost the same for squash (95.82%) and cucumber (96.14%) fruits (Table 2 and Table 3). TLC was used to confirm the persistence of residues in the plant. The R_f values of carbaryl and 1-naphthol (the main hydrolysis product of carbaryl) were found to be 0.36 and 0.55, respectively. Table 4 shows the environmental conditions during the experiment.

Table 1: Standard calibration curve of carbaryl study

Concentration (ppm)	Absorbance
0.4	0.026
1.0	0.065
2.0	0.140
4.0	0.259
8.0	0.482
12.0	0.774
16.0	1.059
20.0	1.345

Note: Standard deviation of six blanks absorbance (s) = 5.16×10^{-4} ;
Slope of the curve = 0.066

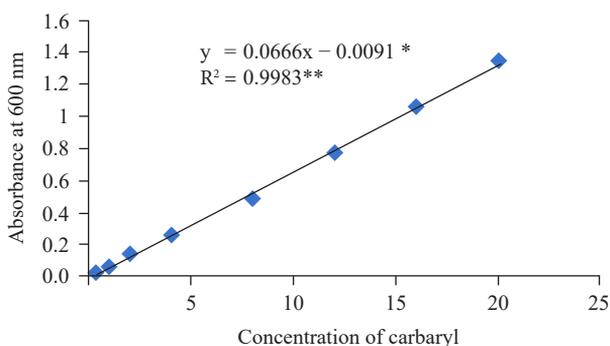


Figure 1: Standard calibration curve of carbaryl.

Notes: *linear equation and the slope was calculated according to Microsoft Excel 10 program; ** R^2 was calculated according to Microsoft Excel 10 program

Table 2: Recovery (%) of carbaryl in squash

Carbaryl spiked in squash (μg)	Absorbance	Carbaryl detected (μg)	Recovery (%)
10	0.0243	9.35	93.35
100	0.2520	96.92	96.92
300	0.7580	291.54	97.18

Note: Each value is a mean of three replications; The mean of recovery is 95.82%.

Table 3: Recovery (%) of carbaryl in cucumber

Carbaryl spiked in cucumber (μg)	Absorbance	Carbaryl detected (μg)	Recovery (%)
10	0.0246	9.46	94.46
100	0.2520	96.92	96.92
300	0.7570	291.15	97.05

Note: Each value is a mean of three replications; The mean of recovery is 96.14%.

Table 4: Environmental condition prevailing during the experimental study of the carbaryl insecticide

Date after application	Maximum temperature ($^{\circ}\text{C}$)	Average of maximum temperature before taking the sample ($^{\circ}\text{C}$)	Rainfall
*0	45		–
**1	43	44	–
2	41		–
**3	41	41	–
4	40		–
5	38	39	–
6	37		–
**7	41	39	–
8	40		–
9	37	38	–
**10	37		–

Note: *Spraying day of the carbaryl insecticide; **Day of taking the sample.

Table 5 to Table 8 and Figure 2 to Figure 5 show the degradation rates of carbaryl in squash and cucumber. The highest degradation rate observed on the first and second days after carbaryl application and the degradation (%) are presented in Table 5 to Table 8 and Figure 6 to Figure 9. Most carbaryl (95%) was degraded after 10 days of application on both squash and cucumber. These results are consistent with those reported by Ihsan for leaves of tomato, eggplant and okra, but they disagree with those reported by Caro et al., who found that that 95% of carbaryl degraded after 135 days.⁸ This difference may be due to the different environmental conditions in the studies.¹¹ Based on the

degradation rate, degradation (%) (Table 5 to Table 8) and maximum residue limit (MRL = 3 ppm), the safety period was found to be five days following the application of carbaryl (Sevin® 85).^{33–35}

Table 5: Carbaryl residues in squash *(application rate 1 kg/fedd)

Day after application	Carbaryl residues (ppm)	Log (Residue ppm)	Degradation (%)
0	6.46	0.810233	0
1	4.19	0.622214	35.14
3	2.14	0.330414	66.87
5	1.19	0.075547	81.58
7	0.59	-0.229150	90.87
10	0.28	-0.552840	95.67

Note: *1 feddan = 4,200 m²; Each value is a mean of three replications after recovery correction.

Table 6: Carbaryl residues in squash (application rate 1.45 kg/fedd)

Day after application	Carbaryl residues (ppm)	Log (Residue ppm)	Degradation (%)
0	11.07	1.044148	0
1	7.32	0.864511	33.87
3	3.93	0.594393	64.50
5	2.24	0.350248	79.77
7	1.20	0.079181	89.16
10	0.54	-0.267610	95.12

Note: Each value is a mean of three replications after recovery correction.

Table 7: Carbaryl residues in cucumber (application rate 1 kg/fedd)

Day after application	Carbaryl residues (ppm)	Log (Residue ppm)	Degradation (%)
0	5.94	0.774517	0
1	3.90	0.591065	34.34
3	1.95	0.290035	67.17
5	1.10	0.041393	81.48
7	0.57	-0.244130	90.40
10	0.24	-0.619790	95.96

Note: Each value is a mean of three replications after recovery correction.

Table 8: Carbaryl residues in cucumber (application rate 1.45 kg/fedd)

Day after application	Carbaryl residues (ppm)	Log (Residue ppm)	Degradation (%)
0	9.22	0.964731	0
1	6.10	0.785330	33.84
3	3.21	0.506505	65.18
5	1.84	0.264818	80.04
7	0.90	-0.045760	90.24
10	0.41	-0.387220	95.55

Note: Each value is a mean of three replications after recovery correction.

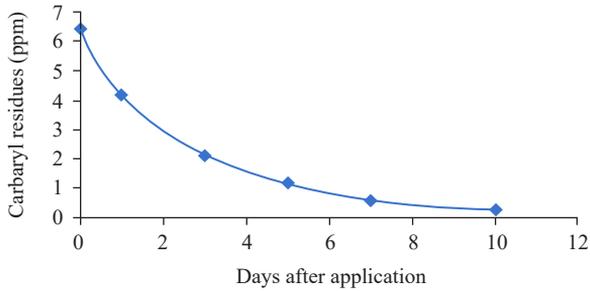


Figure 2: Degradation rate of carbaryl in squash (application rate 1 kg/fedd).

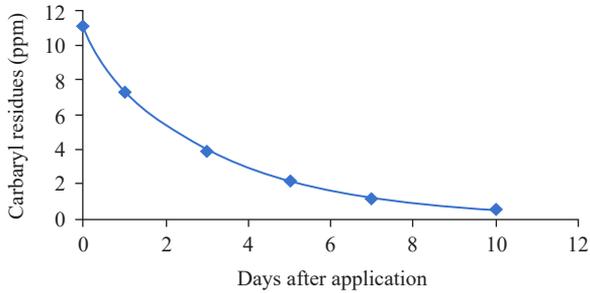


Figure 3: Degradation rate of carbaryl in squash (application rate 1.45 kg/fedd).

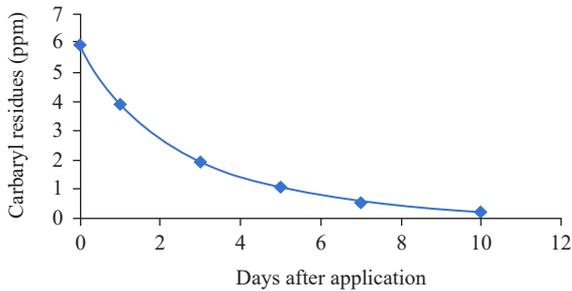


Figure 4: Degradation rate of carbaryl in cucumber (application rate 1 kg/fedd).

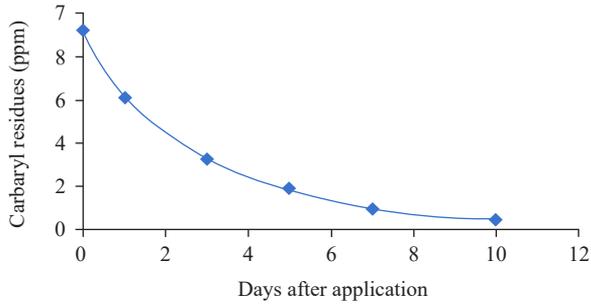


Figure 5: Degradation rate of carbaryl in cucumber (application rate 1.45 kg/fedd).

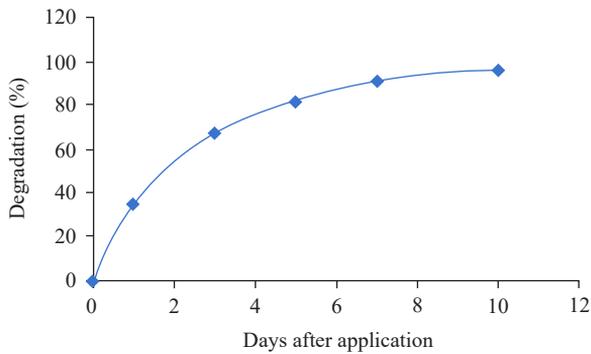


Figure 6: Degradation (%) of carbaryl in squash (application rate 1 kg/fedd).

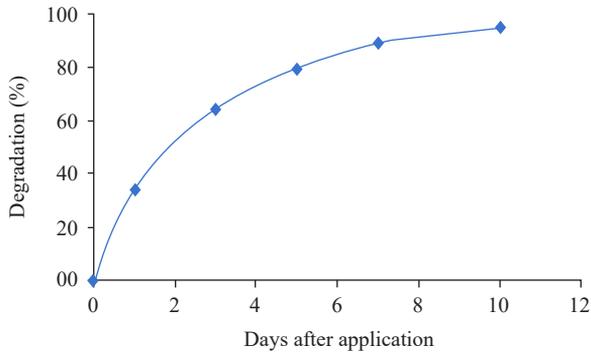


Figure 7: Degradation (%) of carbaryl in squash (application rate 1.45 kg/fedd).

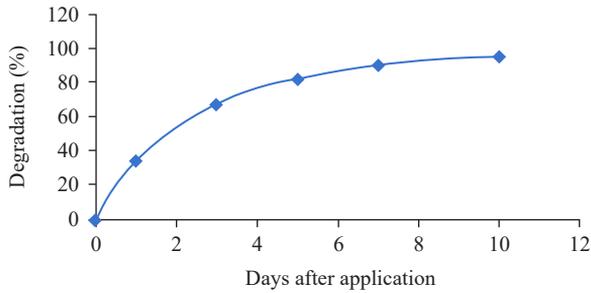


Figure 8: Degradation (%) of carbaryl in cucumber (application rate 1 kg/fedd).

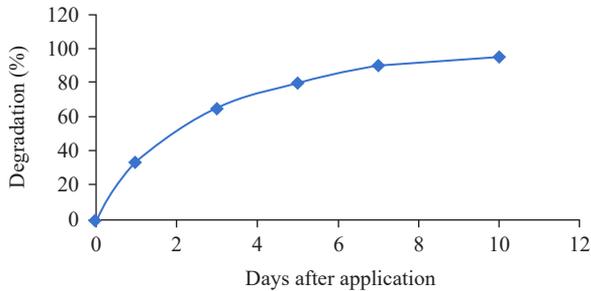


Figure 9: Degradation (%) of carbaryl in cucumber (application rate 1.45 kg/fedd).

A first-order plot of residual carbaryl (using Equation 1 and Equation 2) in squash and cucumber showed that the degradation of carbaryl obeys first-order reaction kinetics (Figure 10 to Figure 13). The correlation coefficient (R^2) of the curve was 0.997, which indicated a good linear relationship. To confirm the first-order degradation of carbaryl, the rate constants of carbaryl degradation in squash were calculated (Table 9) using Equation 3. They were found to be 0.3132 day^{-1} and 0.2994 day^{-1} for application rates of 1 kg/fedd and 1.45 kg/fedd, respectively, while the rate constants of the degradation reaction of carbaryl in cucumber were found to be 0.3178 day^{-1} and 0.3086 day^{-1} for application rates of 1 kg/fedd and 1.45 kg/fedd, respectively. These results indicated that the degradation rates are similar in squash and cucumber in the same environment, and both follow a first-order kinetic reaction. These results agree with results recorded in the literature.^{2,3,6}

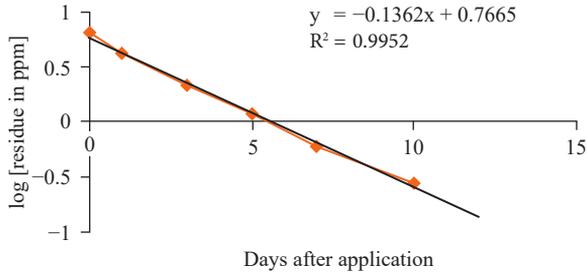


Figure 10: First-order plot of residual carbaryl in squash (application rate 1 kg/fedd).

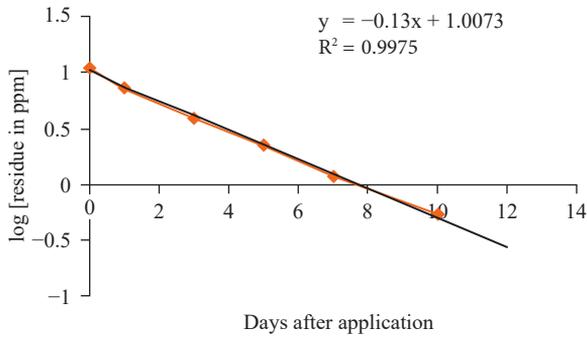


Figure 11: First-order curve of residual carbaryl in squash (application rate 1.45 kg/fedd).

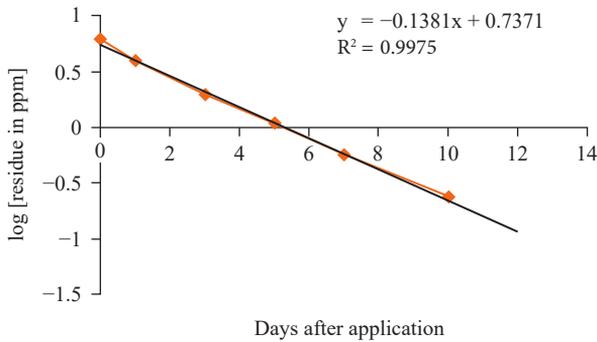


Figure 12: First-order curve of residual carbaryl in cucumber (application rate 1 kg/fedd).

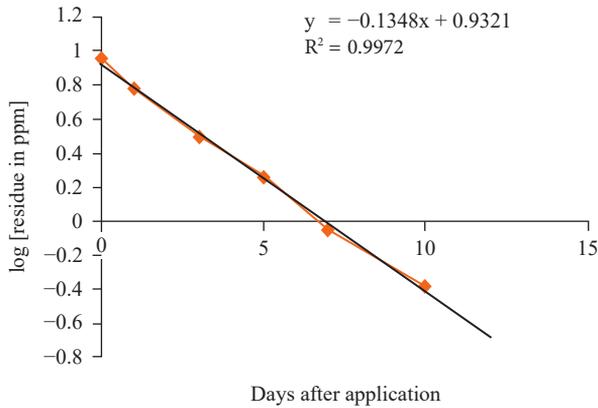


Figure 13: First-order curve of residual carbaryl degradation in cucumber (application rate 1.45 kg/fedd).

Table 9: Rate constant of carbaryl degradation of squash and cucumber from the curves of Figures 10, 11, 12 and 13

Sample	Rate of application	Slope from the curve	*Rate constant day ⁻¹	R ² from the curve
Squash	1 kg/fedd	-0.136	0.3132	0.997
Squash	1.45 kg/fedd	-0.130	0.2994	0.997
Cucumber	1 kg/fedd	-0.138	0.3178	0.997
Cucumber	1.45 kg/fedd	-0.134	0.3086	0.997

Note: *Rate constant = - slope \times 2.303

The half-life times of carbaryl in squash (using Equation 4) were 2.21 day and 2.32 day, respectively, while they were 2.18 day and 2.24 day in cucumber for the different application rates, respectively. In addition, the calculated $t_{1/2}$ of the application rates used by farmers were slightly greater than the $t_{1/2}$ of the recommended application rate. These results are aligned with the values obtained by Starnier et al. at 25°C, but they are far from the values they reported at 9°C.¹⁴ Moreover, the $t_{1/2}$ values obtained in this study are consistent with the results reported by Lartiges and Garrigues at 22°C in river water samples, but they are far from the results reported by Szeto et al. at 9°C in water samples.^{15,16}

The activation energy values (calculated using Equations 5 to 7), shown in Table 10 and Table 11 and Figure 14 and Figure 15, were found to be 10.34 kcal/mole and 8.95 kcal/mole, respectively. These values are less than those (15 kcal/mole) reported by Lartiges and Garrigues for carbaryl degradation in river water.¹⁶ Additionally, the values in this study are lower than the calculated activation

energy value (29 kcal/mole) reported by Starner et al.¹⁴ The activation energy values obtained in this study indicate that carbaryl degradation is highly sensitive to temperature changes.

Table 10: Rate constant (k) of carbaryl degradation in squash (application rate 1 kg/fedd) at different temperatures

$1/T(10^{-3} \text{ K}^{-1})^*$	t (day)	**Rate constant (k) day ⁻¹	ln k
0.003155	1	0.4330	-0.8370
0.003185	3	0.3683	-0.9987
0.003205	5	0.3384	-1.0835
0.003215	10	0.3139	-1.1586

Note: *Average of the maximum temperature; **Day of taking the sample; ***k = $(2.303/t) \times \log(a/a-x)$

Table 11: Rate constant (k) of carbaryl degradation in cucumber (application rate 1 kg/fedd) at different temperatures

$1/T (\text{K}^{-1})^*$	**t (day)	***Rate constant (k) day ⁻¹	ln k
0.003155	1	0.4208	-0.8656
0.003185	3	0.3714	-0.9906
0.003205	5	0.3373	-1.0867
0.003215	10	0.3209	-1.1365

Note: *Average of the maximum temperature; **Day of taking the sample; ***k = $(2.303/t) \times \log(a/a-x)$

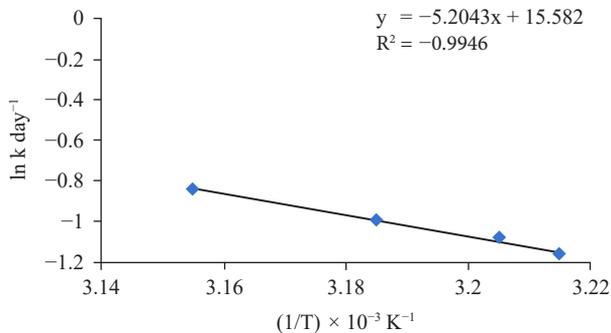


Figure 14: Plot of $\ln k$ (day⁻¹) versus $(1/T) \text{ K}^{-1}$ (squash vegetable).

Note: $E_a = -\text{slope} \times 10^3 \times 1.987 = 10.34 \text{ kcal/mole}$

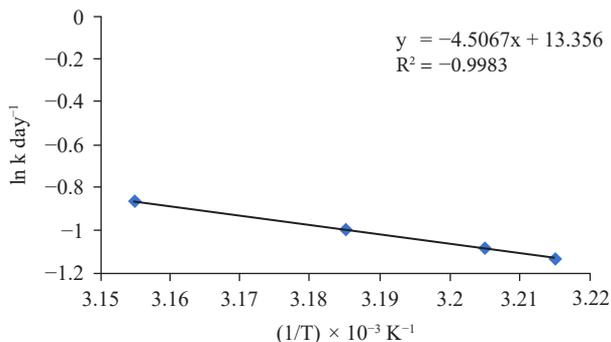


Figure 15: Plot of $\ln k$ (day⁻¹) versus $(1/T) K^{-1}$ (cucumber vegetable).

Note: $E_a = -\text{slope} \times 10^3 \times 1.987 = 8621.6 \text{ cal/mole} = 8.95 \text{ kcal/mole}$

4. CONCLUSION

The carbaryl degradation rates in squash and cucumber fruits were approximately similar in the same environmental conditions. The degradation rate, degradation (%) and $t_{1/2}$ of carbaryl were found to be significantly affected by temperatures changes and environmental conditions. In this study, safe residual carbaryl were found five days after application. Strong restrictions are necessary to ensure that farmers follow the recommended rate of application when using carbaryl-based insecticides.

5. ACKNOWLEDGEMENTS

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