DEGRADATION KINETICS OF CARBOFURAN INSECTICIDE IN TOMATO FRUITS

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The degradation rate and kinetic parameters of carbofuran insecticide in tomato fruits were calculated. The degradation of carbofuran was found to follow first-order reaction kinetics. The rate constants for carbofuran were 0.082 day^{-1} and 0.073 day^{-1} for the recommended application rate (10 kg $feddan^{-1}$) and for the application rate used by farmers (13.5 kg $feddan^{-1}$) respectively. The half-life time ($t_{1/2}$) values for the recommended application rate and for the application rate used by farmers were 8.45 days and 9.50 days, respectively. The safe application time of carbofuran insecticide for the recommended application rate and for the application rate used by farmers were after 28 days and after 35 days , respectively. Spectrophotometry was employed to determine the carbofuran residues in tomato fruits, with a limit of detection (LOD) of 0.039 ppm and percent recovery in the range from 92.87 to 95.54%

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INTRODUCTION

Carbofuran belongs to the carbamate class of pesticides, which is often applied directly to the soil. Kinetic parameters as well as the degradation of carbofuran are widely affected by different factors, such as temperature, soil type, soil and water pH, microorganisms present in the environment and matrix under study. Hence, it is appropriate to investigate these parameters under specific environmental conditions. Moreover, these parameters reflect the degradation behaviour of carbofuran in a specific environment. Several studies have reported the degradation of carbofuran in different matrices and environments.

3-Ketocarbofuran is the major metabolite of carbofuran in soil, while the higher conversion rate occurs in the muck soil.[1] Yang et al. have employed response surface methodology to investigate the photodegradation kinetics of carbofuran in TiO_2 and determined nine degradation intermediates.[2] Rouchaud et al. have reported that carbofuran is converted to 3-ketocarbofuran, carbofuran phenol, and 3-ketocarbofuran phenol.[3] Gong et al. have investigated the use of chlorpyrifos and carbofuran, which are applied together to control pests, and reported that a higher degradation rate is observed in non-inoculated soils.[4] Wang et al. have measured the degradation rates of carbofuran by employing the embedding-adsorption method and reported that the use of immobilized fungal laccase can attain an 86 % degradation rate for carbofuran in soil.[5] Gong et al. have utilized the engineered biosafe strain *Pseudomonas putida* KT2440 and reported the degradation of carbofuran within 30 h; moreover, the complete removal of carbofuran is observed within 15 days.[6] Kaur and Balomajumder have investigated the degradation of carbamate mixtures using *Ascochyta* sp. CBS 237.37 and reported a rate constant of 0.03412 day^{-1} and a $t_{1/2}$ of 26 days.[7] Bachman and Patterson have investigated the photodecomposition of carbofuran in different samples of dissolved organic matter and reported that degradation follows the first-order reaction kinetics.[8] Ying-Chih et al. have employed the ultrasound/Fenton process to examine the effects of H_2O_2 and Fe^{2+} on the degradation of carbofuran and reported a >99 % degradation rate of carbofuran.[9] Tomasevic et al. have performed a comparative examination of pure carbofuran and Furadan 35-ST (commercial product) to assess the effects of inert ingredients present in Furadan 35-ST. They reported that the degradation rate of pure carbofuran is greater than that of Furadan 35-ST.[10]

Different analytical techniques have been employed to determine carbofuran residues and carbofuran degradation processes.[11-16] Zhnag et al. have employed time-resolved fluorescent immunochromatographic method for the detection of carbofuran residues in agricultural products and reported a limit of detection (LOD) in the range of 0.04–0.76 μg cm^{-1}.[17] Ogawa et al. have developed a solid phase extraction technique with LC analysis using a UV detector for the determination of carbofuran and 3-hydroxycarbofuran in coconut water and reported an LOD in the range of 0.008 to 0.01 ppm (μg g^{-1}).[18] Appaiah et al. have developed a spectrophotometric method to determine carbofuran residues in rice, wheat, jowar, and pigeon pea and reported the maximum absorbance at 475 nm.[19] Yong-jia et al. have employed a fluorospectrophotometric technique to determine carbofuran residues in vegetables and reported a detection limit of 0.025 mg kg^{-1} and linear dynamics in the range of 0.09–1.2 mg L^{-1}.[20]

In this study, the degradation rate of carbofuran in tomato under environmental conditions was investigated. Kinetic parameters such as the degradation rate, order of the reaction, percentage degradation (%), half-lifetime ($t_{1/2}$), and rate constant were determined.

Experimental

Chemicals and Reagents

All analytical-grade chemicals and reagents were used. Carbofuran (99.0 % purity) was obtained from Riedel-de-Haen Company. The standard solution was prepared by

dissolving carbofuran in methanol. The granular form of Furadan 10, containing 10 % of carbofuran, was produced by FMC corporation agricultural production group.

Field experiment and sample collection

The study was conducted in Khartoum North, near the Nile River, with clay soil; its cultivation area was 18 Sarabs (ridge) with a length of 15 m and a width of 1m, and its total area was 270 m^2. Every Sarab contained 30 plants of tomato. 90 m^2 of this area was treated with Furadan 10 at a rate of 10 kg $feddan^{-1}$ (10 kg 4200 m^{-2}), which was sown beside the roots of the plants. Another area of 90 m^2 was treated with Furadan 10 approximately at a rate of 13.5 kg $feddan^{-1}$ (as farmers used to sow Furadan 10).The remaining 90 m^2 was kept for control samples and recovery tests. Each area of 90 m^2 was divided into four plots, and eight fruits were randomly picked from each plot. Collection and transportation were conducted to avoid analyte loss and sample contamination. The fruits were chopped into small homogenous pieces with a stainless-steel knife.

Extraction of carbofuran

100 g of an immature tomato or 200 g of a mature tomato was taken and homogenized using a mechanical shaker for 30 min in 150 mL dichloromethane. Next, the liquid was decanted, and the cake was filtered, followed by the addition of 100 g of anhydrous sodium sulphate powder and subsequent filtration. The extract volume was evaporated to ~4 mL.

Sample clean-up

Sample clean-up was performed using the method reported by Leppert et al. with some modifications,[21] and further purification was performed using a coagulation solution, containing 0.5 g of ammonium chloride in 400 mL double-distilled water and 1mL of 85 % phosphoric acid.

Qualitative analysis

The extracts were subjected to thin layer chromatography (TLC) to confirm the presence of carbofuran according to the method reported by Mondoza and shield, Bevalkar et al.[22-23]

Quantification and kinetic analysis

Sample extracts were spectrophotometrically analyzed according to the procedure reported by Appaih et al.[19] The standard calibration curve, LOD, and percent recovery were determined. The environmental conditions were measured and recorded (soil pH, water pH, and pH of tomato fruits, temperature, and rainfall).

The kinetic parameters for carbofuran degradation, such as degradation rate, percentage (%) degradation, rate constant, order of the reaction, and $t_{1/2}$, were calculated by the following equations.

$$ln(a - x) = -k \times t + \ln a \quad (1)$$

$$ln(\text{residue ppm}) = -k \times t + \ln a \quad (2)$$

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

$$t_{1/2} = ln\, 2/k \quad (4)$$

RESULTS AND DISCUSSION

All concentrations obtained here were expressed as $x \pm s$, (x and s represent the mean values and standard deviation, respectively). Microsoft Excel was used for statistical analysis. LOD and percentage (%) recovery of spiked carbofuran were 0.039 ppm and 92.87 % to 95.54 %, respectively (Table 1). Correlation coefficient (R^2) for the standard calibration curve was 0.999, indicative of a good linear relationship (Table 2 and Figure 1). To confirm the presence of carbofuran residues in tomato samples, TLC was employed, and the retention factor (R_f) of carbofuran was 0.38. The pH values of soil and water samples are 7.3 and 7.4, respectively, while the pH of tomato fruits ranges between 4.5 and 4.9. During this study, the temperature in the winter season in Sudan was recorded for 45 days, with an average maximum temperature of 32 °C and an average minimum temperature of 21 °C.

Table 1. Recovery(%) of carbofuran in tomato.

Carbofuran spiked, µg	Absorbance	Carbofuran detected, µg	Recovery, %
15	0.051	13.93	92.87
100	0.346	95.54	95.54
250	0.868	237.16	94.86

Table 2. Standard calibration curve of carbofuran.

Concentartion, ppm	Absorbance	SD of 6 blank readings
0.6	0.05	
1	0.091	
2	0.183	
4	0.366	0.001169
8	0.744	
12	1.095	
16	1.46	
20	1.82	

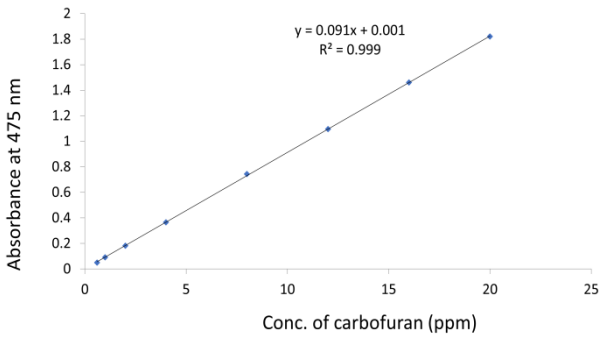

Figure 1. Standard calibration curve of carbofuran.

Table 3. Carbofuran residues in tomato (application rate 10 kg fedd^{-1}).

Day after application	Carbofuran residues, ppm	ln[Residue ppm]	Degradation %
5	0.31	-	-
8	0.42	-0.8675	0
14	0.22	-1.5141	47.62
21	0.13	-2.0202	69.05
28	0.079	-2.5383	81.19
35	0.048	-3.0366	88.57
45	0	-	100

Table 4. Carbofuran residues in tomato (application rate 10.3 kg fedd^{-1}).

Day after application	Carbofuran residues, ppm	ln[Residue ppm]	Degradation %
5	0.36	-	-
8	0.49	-0.7133	0
14	0.31	-1.1712	36.7
21	0.19	-1.6607	61.22
28	0.12	-2.1203	75.51
35	0.065	-2.7334	86.73
45	0	-	100

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

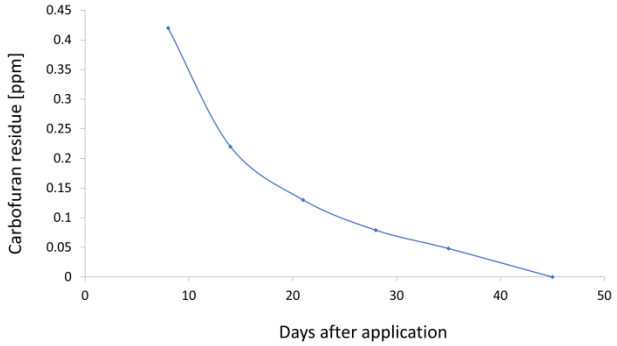

Figure 2. Degradation rate of carbofuran in tomato (application rate 10 kg feddan^{-1}).

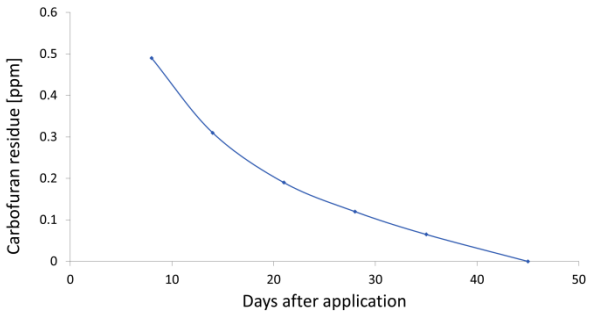

Figure 3. Degradation rate of carbofuran in tomato (application rate 13.0 kg feddan^{-1}).

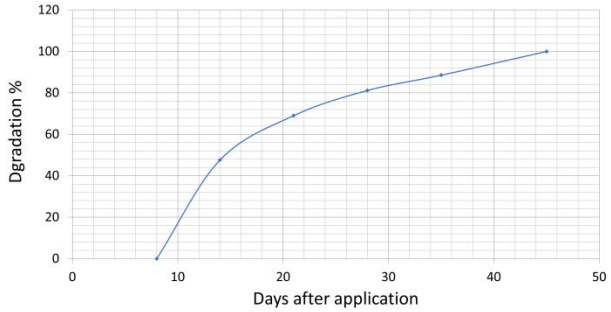

Figure 4. Degradation % of carbofuran in tomato (application rate 10 kg feddan^{-1}).

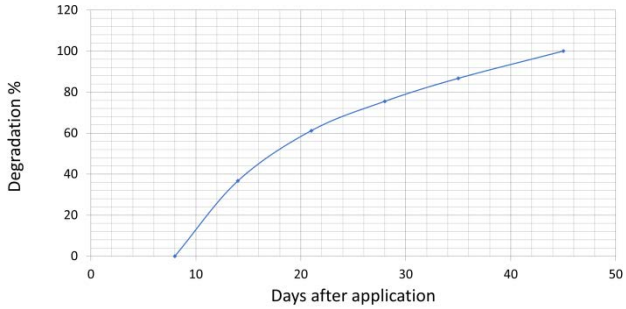

Figure 5. Degradation % of carbofuran in tomato (application rate 13.0 kg feddan^{-1}).

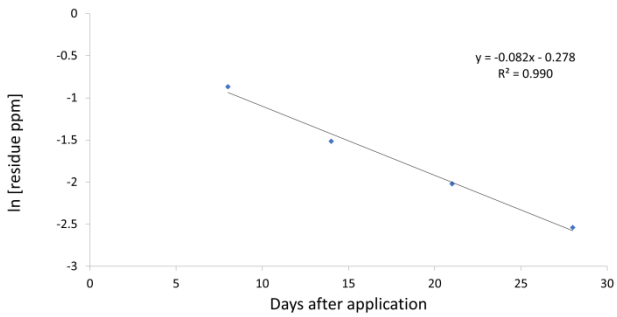

Figure 6. First order plot of residual carbofuran in tomato (application rate 10 kg feddan^{-1})

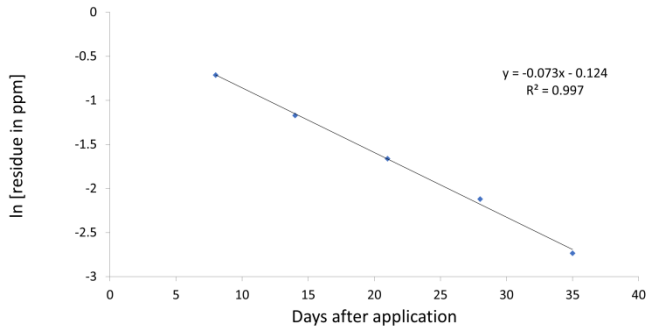

Figure.7. First order plot of residual carbofuran in tomato (application rate 13.0 kg feddan^{-1}).

Residues of carbofuran in tomato at an application rate of 10 kg feddan^{-1} (recommended rate) after 5, 8, 14, and 21 days were greater than the maximum residue limit (0.1 ppm) (Table 3), but after 28 days, the residue was less than 0.1 ppm, and the residue was not detected after 45 days, hence it is safe after 28 days.[24,25] Moreover, residues of carbofuran in tomato at an application rate of 13.5 kg feddan^{-1} after 5, 8, 14, 21, and 28days (Table 4) were greater than 0.1 ppm, and after 35 days, the residue was less than 0.1 ppm. The results indicate that it is safe after 35 days of application. Moreover, a higher application rate led to the increase in not only the residue concentration but also the degradation time. As Furadan 10 was sown in the soil beside the plant roots, carbofuran probably penetrated via the roots and stem until

it reached the fruits of the tomato plant; hence, this need a time before the beginning of the degradation of carbofuran in tomato fruits. As a result, residues detected in tomato fruits after 5 days are excluded from the first-order plot, degradation rate plot, and percentage (%) degradation plot (Figures 2–7). The degradation of carbofuran was more rapid in alkaline media than in acidic media (Table 5),[1] hence, owing to the acidic media in the matrix under study (pH 4.5–4.9 of tomato fruits), degradation took a long time. Figures 2 and 3 show the degradation rate, and Figures 4 and 5 show the percentage (%) degradation. In the first 7 days, rapid degradation was observed, and complete degradation was observed after 45 days after the application of Furadan 10 (Figures 2–4), according to the LOD of the method (0.039 ppm).

Table 5. Half-lives of carbofuran insecticide in water.

Water type	Temp., ^{0}C	pH	$t_{1/2}$, h
paddy	27±2	7.0	240
paddy	27±2	8.7	13.9
paddy	27±2	10.0	1.3
deionized	27±2	7.0	864
deionized	27±2	8.7	19.4
deionized	27±2	10.0	1.2

Table 6. Rate constant of carbofuran degradation of tomato from the curves of figures 6 and 7.

Rate of application	Slope from the curve	Rate constant, day^{-1}	R^2
10 kg fedd^{-1}	-0.082	0.082	0.990
13.0 kg fedd^{-1}	-0.073	0.073	0.997

The first-order reaction obeys Eqn. (1). By applying this equation and equation 2 and by plotting ln (a–x) against t, Figures 6 and 7 are obtained. The curves are straight lines with R^2 values of 0.99 and 0.997 for the recommended rate (10 kg feddan^{-1}) and for the application rate used by farmers (13.5 kg feddan^{-1}), respectively. The results indicate that the degradation of carbofuran follows the first-order reaction kinetics, and this result is in agreement with that reported by Ying-Shih et al.[9] In addition, similar rate constants were obtained (using eqn. 3) for both application rates (Table 6). Half-life time ($t_{1/2}$) was calculated for the recommended application rate and the application rate used by farmers by using eqn. (4), which were 8.45 day^{-1} and 9.50 day^{-1}, respectively. The obtained results were in slight agreement with those obtained at pH 7 in paddy water, but were different from other results in the same study (Table 5).

CONCLUSION

Degradation of carbofuran followed first-order reaction kinetics. Similar rate constants were calculated for the recommended application rate (10 kg feddan^{-1}) and the application rate used by farmers (13.5 kg feddan^{-1}). The corresponding half-life ($t_{1/2}$) values were 8.45 and 9.50 days. The safety time of carbofuran insecticide for the recommended rate (10 kg feddan^{-1}) and for the application rate used by farmers (13.5 kg feddan^{-1}were after 28 days and after 35 days, respectively. Farmers should be advised to apply the recommended application rate of Furadan 10.

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