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# Efficacy of Methomyl after Application Against Cotton Leaf Worm in Soybean and Removal Kinetics of its Residue 

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#### Abstract

Soybean crop (Glycine max L.) is a very important economic crop belongs to leguminosae, through-out considered one of the high potentially protein source that attacked by Cotton leaf worm, Spodoptera littoralis (Boisd), the major pest thorugh-out the growing season. Therefore, this study aimed to evaluate the insecticidal activity of methomyl against the cotton leaf worm (Spodoptera littoralis) on soybean genotype, Giza 21. Furthermore, to investigate the persistence of this tested insecticide after application under some of the environmental factors (direct sunlight, ultraviolet rays and temperature). Moreover, to evaluate the effect of some commercial processes on the safe removal of methomyl residues from soybean seeds. The results showed that methomyl was effective against cotton leaf worm. The exposure of methomyl to the direct sunlight, ultraviolet rays and different temperature degrees significantly reduced levels of the tested insecticide. Cooking procedure showed higher effect than dry heating at ( $90-95^{\circ} \mathrm{C}$ ) on removal of tested insecticide from soybean seeds. The results showed that the food processing is an important way for minimizing methomyl in the final products lower than the maximum residue limits.


Key words: Methomyl, removal, residues, soybean

## INTRODUCTION

In Egypt, soybean considered very important crop and cultivated in more than 90000 hectare. Soybean used in wide range of foodstuffs derived for soybean. Moreover, there are an increasing consumption of soybean products as a result of the interesting properties associated with the use of soybeans which promoted the appear of a wide range of foodstuffs derived from this soybean: soybean flour, textured soybean, soybean milks, soybean infant formulas, etc. (Garcia et al., 1997). Soybean oil is a concentrated, hydrophobic liquid containing volatile aromatic compounds extracted from soybean (Glycine max). Soybean oil is popularly used in food processing and cooking. Soybean oil accounts for over $75 \%$ of the total vegetable oil in human foods (Nguyen et al., 2010).

Soybean crop attacked by many insects such as spider mites, aphids, cotton leaf worm and many other pests (Bastawisy et al., 2008). The pests infest all parts of the soybean plant at all growth stages and can lead to yield losses from $20-50 \%$ thus lead the farmers into the use of pesticides to protect their crops. Among the different control measures such as cultural, mechanical, biological and chemical methods, the farmers prefer the use of chemicals to control pests because
it gives quick results. Besides the usefulness of pesticides in protecting the crop, it has some drawbacks, not only to environment but also to consumers in case of residues in the edible parts (Nguyen et al., 2010).

Food processing techniques implies the set of methods and techniques used to transform raw ingredients into food or to transform food into other forms for consumption by humans or animals either in the home or by the food processing industry. These food processing techniques aid in pesticide dissipation and reduced its residues (Kaushik et al., 2009).

Thus major focus on the fate and persistence of this type of insecticides after application and the effect of environmental factors such as temperature and light are needed. Furthermore, the effect of commercial industrial processes on the safe removal of its residues or minimizing it lower than the maximum residue limit in crop products are in demand to protect human health.

Therefore, the present study was carried out to evaluate the bio-residual efficacy of methomyl insecticide against cotton leaf worm, Spodoptera littoralis (Boisd.); to determine the residues of methomyl insecticide on and in whole soybean plant leaves, pods and seeds under normal field conditions and to justify the effect of different environmental factors (light and temperature) on the persistence of methomyl after application and finally to investigate the role of industrial processes on the safe removal of methomyl in and on soybean products.

## MATERIALS AND METHODS

Insecticidal activity of methomyl against cotton leaf worm, S. littoralis on soybean: Soybean (Glycine max) "Giza-21" was planted at the farm of Zarzora Research Station, Etay El-Baroud, at Beheira Governorate, Egypt. A complete randomized design was used, two treatments including the control were prepared and each treatment was divided into three replicates. The area of each treatment was about $3 / 100$ hectare. A knapsack sprayer was used for applying the insecticide at the recommended field rate. Leaves were collected randomly from each treated and untreated plots at zero time (one hour after treatment), 14 h (as the initial deposit), $1,3,5,10$ and 15 days after treatment in August. The 4th instars leaf worm larvae of the field strain which were obtained from the farm of Zarzora Research Station were exposed to the collected soybean leaves. Fifty larvae's were used for each treatment and divided into 5 replicates (10 larvae in each glass jar). The 7 mortality counts were recorded in 24 h , after feeding of the larvae on the treated soybean leaves. The mortality percentage was corrected according to Abbott (1925).

Residues of methomyl in soybean leaves, pods and seeds: Samples were collected randomly from treated and untreated plots at zero time (one hour after treatment) as the initial deposits for all parts (leaves, pods and seeds), then $1,3,5,10,20$ and 49 days after treatment (harvest day). Three replicates of plant samples 500 g each were collected. All undesired parts involved in samples were discarded and then seeds were removed out from pods. The samples (leaves) were cut into small pieces, each sub sample was taken at rate of 10 g , transferred to laboratory and kept under deep freezing until analysis of methomyl residues and calculation of residual half-life value ( $\mathrm{RL}_{50}$ ) mathematically according to Moye et al. (1987) as shown in Eq. 1 and 2:

$$
\begin{align*}
\mathrm{RL}_{50}\left(\mathrm{t}_{1 / 2}\right) & =\ln 2 / \mathrm{K}^{\prime}=0.6932 / \mathrm{K}  \tag{1}\\
\mathrm{~K} & =1 / \mathrm{t}_{\mathrm{x}}^{*} \ln \mathrm{a} / \mathrm{b}_{\mathrm{x}} \tag{2}
\end{align*}
$$

where, K refer to rate of decomposition, $\mathrm{t}_{\mathrm{x}}$ is the time in days, a is the initial residue of the compound and $b_{x}$ is the residue of the compound at x time.

## Residues analysis

Extraction and clean up: Ten grams of soybean leaves, pod and seeds were macerated with 25 g activated anhydrous sodium sulfate till complete mixing achieved, then 200 mL chloroform were added and blended for two minutes on high speed using warring blender. The macerate was filtered through a glass wool using amount of activated anhydrous sodium sulfate ( 30 g ) and finally washed with 25 mL of chloroform. The filtrate was evaporated to dryness with a rotary evaporator at $35-40^{\circ} \mathrm{C}$.

The clean up for methomyl was achieved according to the method of Mills et al. (1972). A 20 mm (i.d.) glass column was prepared by adding successively, a plug of glass wool, 5 g of activated florisil (60-100 mesh) and compact thoroughly. The column was pre-washed using 40 mL n-hexane and drained to the level of the solvent down to the top of florisil. Residue extract was transferred to the florisil column, already saturated with hexane. The column was eluted with 100 mL of the eluant ( $50 \%$ methylene chloride $+48.5 \%$ hexane $+1.5 \%$ acetonitrile) at a rate of $5 \mathrm{~mL} \mathrm{~min}{ }^{-1}$. The collected elute was concentrated in rotary evaporator and dissolved in 2 mL of ethyl acetate for residue analysis by High Performance Liquid Chromatograph (HPLC).

Determination procedure: High Performance Liquid Chromatograph (HPLC), LDC analytical equipped with Diode Array Detector (DAD). Column $\mathrm{C}_{18}$ nuclosil ( $250 \mathrm{~mm} \times 4.6 \mathrm{~mm} \times 5 \mu \mathrm{~m}$ ), system was isocratically reversed phase with mobile phase of methanol; water at the ratio of $80: 20 \mathrm{v} / \mathrm{v}$, with flow rate of $0.8 \mathrm{~mL} \mathrm{~min}^{-1}$, detector was adjusted at 254 nm for methomyl. Retention time at these conditions was 4.12 min .

Oil removal from pods and seeds extracts: Dried extracts were dissolved in 15 mL , light petroleum ether (b.p., $40-60^{\circ} \mathrm{C}$ ) and transferred quantitatively to a 125 mL separating funnel. After that extracts were partitioned using $3 \times 30 \mathrm{~mL}$ acetonitrile completely saturated with light petroleum ether and then fractions were combined together and evaporated under vacuum till dryness.

Recovery evaluation: The efficacy of the analytical steps used was evaluated through recovery by fortifying untreated samples of leaves, pods and seeds with known amounts of methomyl at level $10 \mathrm{mg} \mathrm{kg}^{-1}$. Then extraction, cleaning up and determination procedures that mentioned before were performed. Average percentages of recoveries for the tested insecticide were showed in Table 1.

Effect of direct sunlight, UV-rays and temperature on the persistence of the tested insecticide: The effect of different environmental factors (direct sunlight, UV-rays and two temperature degrees) on the degradation rate of methomyl (active ingredient) was investigated.

Table 1: Percentage recovery rates of methomyl on soybean leaves, pods and seeds at level of $10 \mathrm{mg} \mathrm{L}^{-1}$

|  | Recovery rate (\%) |  |  |
| :---: | :---: | :---: | :---: |
| Insecticide used | Leaves | Pods | Seeds |
| Methomyl | $83.83 \pm 0.14$ | $88.01 \pm 0.17$ | $88.31 \pm 0.21$ |

Stock solution of tested insecticide contains $500 \mu \mathrm{~mL} \mathrm{~mL}^{-1}$ of the active ingredient (dissolved in ethyl acetate) had prepared. One milliliter aliquots of prepared stock solution were spread uniformly as possible on uncovered Petri dishes surface ( 5 cm i.d.) and were left to dry at room temperature.

Effect of direct sunlight exposure: A group of dried Petri dishes prepared as mentioned above was exposed to the direct sunlight, then dishes were withdrawn after $0,1,3,6,12,24,48$ and 96 h of exposure. Residues remained in Petri dishes were quantitatively transferred to volumetric flasks using suitable solvents and then were determined by GLC as mentioned previously.

Effect of UV-ray exposure: A second group of dried Petri dishes prepared as mentioned above was exposed to short UV rays at 254 nm at a distance 12 cm for $0,1,3,6,12,24$ and 48 h of exposure in a dark isolated box. Residues remained in Petri dishes were quantitatively transferred to volumetric flasks using suitable solvents and then were determined by GLC as mentioned previously.

Effect of exposure to different temperature degrees: A third group of Petri dishes prepared as mentioned before was exposed to two temperature degrees ( 35 and $45^{\circ} \mathrm{C}$ ) for $0,1,3,6,12,24$, 48,96 and 144 h in a dark electric oven provided with temperature regulating system. Residues remained in Petri dishes were quantitatively transferred to volumetric flasks using suitable solvents and then were determined with GLC as mentioned previously.

Elimination of methomyl residues: Stock solution of used insecticide that contains $297 \mathrm{gg} \mathrm{m}^{-1}$ of methomyl $(90 \% \mathrm{SP}) 0.33 \mathrm{~g}$ dissolved in 1000 mL tap water. A sample $(10 \mathrm{~g})$ seeds was soaked in 7 mL ( 0.5 mL stock solution +6.5 mL tap water) in 100 mL glass beaker and stirred slowly for three hours to ensure good mixing and even distribution of the insecticides according to the method decribed by Zayed et al. (2007). After that the seeds were allowed to dry at room temperature.

Effect of direct sunlight exposure: The spiked seeds were spread on uncovered Petri dishes surface ( 15 cm i.d.) and were exposed to the direct sunlight. Then dishes were withdrawn after $0,1,3$ and 6 h of exposure to sunlight followed by analysis as mentioned before.

## Effect of industrial commercial processes on the safe removal of methomyl residues in

 soybean productsEffect of dry heating at $\left(90^{\circ} \mathrm{C}\right)$ : The spiked seeds were ground with a mixer for 2 min ; the mixture was heated at $90-95^{\circ} \mathrm{C}$ for 10 min with careful stirring and cooled in a refrigerator. The cooled samples were analyzed as mentioned before.

Effect of cooking procedure: The spiked seeds ( 10 g ) were soaked in 50 mL of tap water and were heated at $90-95^{\circ} \mathrm{C}$ for 10 min with careful stirring. After that seeds were ground in a warring blender with 50 mL hot water followed by filtration through gauze. The filtrate (soybean milk) was heated at the same temperature for 10 min and the soybean milk was subjected to analysis after cooling.

Analytical procedure for soybean milk: Each sample was extracted by partitioning twice with 100 mL of ethyl acetate using separating funnel 125 mL . The layer of ethyl acetate was evaporated
under vacuum till dryness with a rotary evaporator $\left(35-40^{\circ} \mathrm{C}\right)$ according to Miyahara and Saito (1994). Removal of oil and the clean up for tested insecticide were done according to the method mentioned previously. The recovery for methomyl in soybean milk was $77.43 \%$. Data were statistically analyzed according to the method described by Steel and Torrie (1980).

## RESULTS AND DISCUSSION

Insecticide activity of methomyl against the cotton leaf worm S. littoralis on soybean leaves: Data in Table 2 clearly showed that the initial residue of methomyl was effective against the 4th instars larvae of cotton leaf worm with mortality percentage of ( $88 \%$ ) after application of tested insecticide. Methomyl residual toxicity decreased gradually with increasing the time after treatment. The prolongation of time to 1 day revealed less mortality, i.e., $42 \%$, followed by 14,8 and $2 \%$ after 3, 5 and 10 days of application. The $\mathrm{LT}_{50}$ value for residual toxicity of methomyl was 14.4 h ( 0.6 days) as shown in Table 2. The initial methomyl residues were effective against cotton leaf worm insect and decreased gradually with increasing the time after treatment. This is may be due to the further exposure of methomyl residues to environmental conditions that highly decreased its amounts and bio-residual effectiveness. The results obtained were agreed with those obtained by Bayoumy et al. (2003), who showed that methomyl was the most effective insecticide towards cotton leaf worm larvae. Also, the results in this study was in agreement with those obtained by Ahmed and Hassanein (2005) and Abdel-Rahim and Azab (2008), who concluded that methomyl gave average initial mortality $100 \%$ for both the 2nd and 4th instars larvae of cotton leaf worm. The level of residues in and on leaves affected by many factors i.e., applied dosage, properties of insecticide, meteorological and biological factors depending on the kind and properties of the plant surface.

Determination of methomyl residues in soybean leaves, pods and seeds: Residues and loss rates of methomyl on and in soybean leaves, pods and seeds of the tested genotype Giza-21 were illustrated in Table 3. Data in Table 3 clearly showed that the values of methomyl residues on and in leaves, pods and seeds decreased with the time. Also, there were significantly differences in methomyl residues among intervals after application; continuous loss was significant for methomyl to 20 days.

The initial deposit of methomyl which remained on leave one day after treatment was 35.79 ppm . Then methomyl residues gradually decreased to $14.37,8.59,4.22,1.09$ and 0.06 ppm , respectively indicating a loss rate of $59.85,76.88,96.95,99.84$ and $100 \%$, respectively after 1,3 ,

Table 2: Insecticidal activity of methomyl against the larvae of cotton leaf worm Spodoptera littoralis on soybean leaves

| Time of application (days) | Mean |
| :--- | :---: |
| Initial | $88.00 \pm 0.8^{\mathrm{a}}$ |
| 1 | $42.00 \pm 0.4^{\mathrm{e}}$ |
| 3 | $14.00 \pm 0.12^{\mathrm{e}}$ |
| 5 | $08.00 \pm 0.31^{\text {ef }}$ |
| 10 | $02.00 \pm 0.1^{\text {ef }}$ |
| 15 | $00.00^{f}$ |
| $M$ ean | $25.66 \pm 0.12^{\mathrm{b}}$ |
| $\mathrm{LT}_{50}$ (days) | 14.4 |

*L.S. $\mathrm{D}_{0.05}$ between intervals $=6.49$, *Values are Mean $\pm$ Standard deviation $(\mathrm{n}=3$ ), *Mean followed by a common letter are not signific antly different at the $5 \%$ level
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Table 3: Residues and loss rates of methomyl on and in soybean leaves, pods and seeds

| Time of application (days) | Residues in leaves |  | Residues in pods |  | Residues in seeds |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Residue ( $\mu \mathrm{g} \mathrm{g}^{-1}$ ) Mean $\pm$ SD | Loss (\%) | Mean ( $\mu \mathrm{g} \mathrm{g}{ }^{-1}$ ) | Loss (\%) | Mean ( $\mu \mathrm{g} \mathrm{g}{ }^{-1}$ ) | Loss (\%) |
| Initial | $35.79 \pm 2.59^{\text {b }}$ | 00.00 | $10.34 \pm 0.5^{\text {b }}$ | 00.00 | $0.25 \pm 0.04^{e}$ | -- |
| 1 | $14.37 \pm 1.6^{e}$ | 59.85 | -- | -- |  | -- |
| 3 | $8.59 \pm 0.57^{\text {E }}$ | 76.00 | -- | -- |  | -- |
| 5 | $4.22 \pm 0.52^{\text {h }}$ | 88.21 | $6.11 \pm 0.9^{\text {d }}$ | 40.91 | $2.29 \pm 0.03^{\text {a }}$ | -- |
| 10 | $1.09 \pm 0.04^{\text {ij }}$ | 96.95 | $2.27 \pm 1.13^{\text {e }}$ | 78.05 | $1.96 \pm 0.15^{\text {b }}$ | -- |
| 20 | $0.06 \pm 0.12^{\text {j }}$ | 99.84 | $0.39 \pm 0.39^{\text {f }}$ | 96.23 | $0.27 \pm 0.13^{e}$ | -- |
| 49 ( Harvest day) | N.D. | $\approx 100.00$ | N.D. | 100.00 | N.D. ${ }^{\text {g }}$ | -- |
| Mean | $9.16^{\text {b }}$ |  | $3.82{ }^{\text {a }}$ |  | $0.94{ }^{\text {a b }}$ | -- |
| K | 0.496 |  | 0.146 |  | -- |  |
| $\mathrm{RL}_{50}$ (days) | 1.39 |  | 4.76 |  | -- |  |

*N.D. $=$ Detected, *LOD $=0.01 \mathrm{mg} \mathrm{L}^{-1}$, *Values are Mean $\pm$ Standard deviation ( $\mathrm{n}=3$ ), *Mean followed by a common letter are not signific antly different at the $5 \%$ level

5, 10 and 20 days of treatment. Methomyl residue at harvest day was below the detection limit ( $0.01 \mathrm{mg} \mathrm{L} \mathrm{L}^{-1}$ ) and the $\mathrm{RL}_{50}$ value was 1.39 days from application with degradation rate of 0.49 .

The initial deposit which remained on pods after treatment was 10.34 ppm . Methomyl residues gradually decreased to 6.11, 2.27 and $0.39 \mathrm{mg} \mathrm{L}^{-1}$ indicated loss rates of 40.91, 78.05 and $96.23 \%$, respectively after $5,10,20$ days of treatment. Methomyl residue at harvest day were below the detection limit ( $0.01 \mathrm{mg} \mathrm{L}^{-1}$ ) and the $\mathrm{RL}_{50}$ value was 4.76 days from application with degradation rate of 0.15 . The results showed that the initial deposit which remained on seeds was 0.25 ppm . Methomyl residue in seeds was gradually increased at 5, 10 and 20 days after treatment, respectively.

Residues and loss rates of methomyl on and in soybean leaves, pods and seeds of the tested genotype Giza-21 were decreased with the time. Since, the level of residues in and on leaves and seeds were affected by many factors i.e., applied dosage, properties of insecticide, meteorological and biological factors depending on the kind as well as properties of the plant surface. The obtained data were in agreement with those reported by Gambacorta et al. (2005).

Soybean seeds were free from any detectable residues of methomyl at the mentioned detection limit; the Maximum Residue Limit (MRL) of methomyl residues on soybean crop is 0.2 ppm . The estimated Pre-Harvest Interval (PHI) for methomyl residues on soybean crop was 22 days from application. These findings indicated that soybean plants treated with diazinon during growing and ripening stages should stay in the field about 22 days before harvesting to be consumed and marketed safely for human and animal consumption. Since, the rates of soybean seeds contamination with methomyl will be below the estimated MRL's. The obtained data were in agreement with those reported by Ahmed and Ismail (1995), Gil et al. (1996) and Nasr et al. (2008).

Effect of direct sunlight and UV radiation on the persistence of methomyl: Data in Table 4 showed that there was a significant influence of direct sunlight and UV radiation on the dissipation rate of methomyl. Also, there were significant differences in insecticide residues among intervals after exposure either to sunlight or UV radiation. Results revealed that residue of tested insecticide were decreased after one hour of exposure to direct sunlight and UV radiation by 43.47 and $10.5 \%$, respectively. Continuous degradation was positively correlated with the exposure period
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Table 4: Influence of direct sunlight and UV radiation on dissipation rate of methomyl residues

| Time (h) | Sunlight |  | UV radiation |  |
| :---: | :---: | :---: | :---: | :---: |
|  | Mean $\mu \mathrm{g}$ found | Loss (\%) | Mean $\mu \mathrm{g}$ found | Loss (\%) |
| Initial | $500.00^{\text {a }}$ | 0.00 | $500.00^{\text {a }}$ | 0.00 |
| 1 | $282.64 \pm 2.62^{\text {b }}$ | 43.47 | $447.5 \pm 1.01^{\text {a }}$ | 10.50 |
| 3 | $164.58 \pm 1.08{ }^{\text {d }}$ | 67.19 | $320.00 \pm 1.3^{\text {e }}$ | 36.00 |
| 6 | $90.5 \pm 1.0{ }^{5}$ | 81.90 | $259.33 \pm 3.14^{\text {i }}$ | 48.13 |
| 12 | $45.83 \pm 1.33{ }^{\text {i }}$ | 90.83 | $188.19 \pm 1.78{ }^{\text {e }}$ | 62.36 |
| 24 | $42.17 \pm 2.00^{\text {i }}$ | 91.57 | $50.10 \pm 0.46^{p}$ | 89.98 |
| 48 | $11.11 \pm 2.61^{\mathrm{k}}$ | 97.78 | $30.21 \pm 1.39^{\text {a }}$ | 93.96 |
| 96 | $5.72 \pm 0.71^{1}$ | 98.86 | $11.11 \pm 1.79^{\text {s }}$ | 97.78 |
| 144 | $00.00^{\text {m }}$ | 100.00 | $00.00^{\text {t }}$ | 100.00 |
| Mean | $127.14^{\text {a }}$ |  | $200.31^{\text {c }}$ |  |
| K | 3.18983 |  | 2.20978 |  |
| $\mathrm{T}_{112}(\mathrm{~h})$ | 5.22 |  | 7.53 |  |

*LOD $=0.01 \mathrm{mg} \mathrm{L}^{-1}$, *Values are Mean $\pm$ Standard deviation ( $\mathrm{n}=3$ ), *Mean followed by a common letter are not significantly different at the $5 \%$ level
that the long exposure period gave a high loss rate for the tested insecticide. Loss rate values for methomyl residues were $67.19,81.9,90.83,91.57,97.78$ and $98.86 \%$ for methomyl residues at 3 , $6,12,24,48$ and 96 h . While loss rate values for methomyl residues after exposure to UV radiation were $36,48.13,62.36,89.98,93.96,97.78$ and $100 \%$ at $1,3,6,12,2448,96$ and 144 h of exposure to UV-rays, respectively.

The data showed that there was a significant influence of direct sunlight and UV radiation on the dissipation rate of methomyl. The significant influence of sunlight or UV radiation on methomyl has been reported by Zhang et al. (2010). The data showed that there was a significant influence of direct sunlight and UV radiation on the dissipation rate of methomyl. The significant influence of sunlight or UV radiation on methomyl has been reported by Zhang et al. (2010). Photodegradation by sunlight is one of the promising method for pesticides degradation after their release to the environment. Factors that influence pesticides photodegradation are the intensity of light and properties of pesticide (Fishel, 1997). Nasr et al. (2008) estimated the photodecomposition rate by exposing methomyl a.i. to the direct sunlight and short UV-rays. The obtained results indicated that direct sunlight were more effective than UV-rays in accelerating the degradation rate of methomyl. This is may be due to the thermal evaporation and light intensity consideration (Abd El-Baki et al., 1999).

Effect of different temperature degrees on methomyl persistence: The results in Table 5 revealed that the loss percentage values of methomyl residues were 2.68 and $18.35 \%$ one hour after exposure at 35 and $45^{\circ} \mathrm{C}$, respectively. The degradation rate values were $4.82,10.6,16.67,24$, $36.64,50.32$ and $67.59 \%$ after $3,6,12,24,48,96$ and 144 h of exposure to temperature at $35^{\circ} \mathrm{C}$ degree, respectively. The degradation rate values were $25.55,27.17,33.05,55.39,73.58,91.84$ and $97.4 \%$ at the same mention periods at $45^{\circ} \mathrm{C}$ degree, respectively. The results showed that the calculated $\mathrm{RL}_{50}$ values of methomyl were 48.65 and 11.04 h , indicating degradation rates of 0.34 and 1.51 at 35 and $45^{\circ} \mathrm{C}$ degrees, respectively.

The results showed that the temperature play role in methomyl dissipation and the rate increase with increasing temperature and prolongation of exposure. The obtained data agreed with
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Table 5: Influence of temperature degrees ( 35 and $45^{\circ} \mathrm{C}$ ) on the dissipation rate of methomyl residues

| Time (h) | Loss (\%) |  |
| :---: | :---: | :---: |
|  | $35^{\circ} \mathrm{C}$ | $45^{\circ} \mathrm{C}$ |
| Initial | 00.00 | 00.00 |
| 1 | $2.68 \pm 0.20$ | $18.35 \pm 0.19$ |
| 3 | $4.82 \pm 0.30$ | $25.55 \pm 0.23$ |
| 6 | $10.60 \pm 0.10$ | $27.17 \pm 0.31$ |
| 12 | $16.67 \pm 0.22$ | $33.05 \pm 0.34$ |
| 24 | $24.00 \pm 0.31$ | $55.39 \pm 0.54$ |
| 48 | $36.64 \pm 0.35$ | $73.58 \pm 1.1$ |
| 96 | $50.32 \pm 0.51$ | $91.84 \pm 0.98$ |
| 144 | $67.59 \pm 0.63$ | $97.4 \pm 1.3$ |
| K | 0.341 | 1.51 |
| $\mathrm{T}_{112}(\mathrm{~h})$ | 48.65 | 11.04 |

*Values are Mean $\pm$ Standard deviation ( $n=3$ ), *Mean followed by a common letter are not significantly different at the $5 \%$ level

Table 6: Influence of direct sunlight on elimination methomyl on and in soybean seeds

| Time of application (days) | Residues in leaves |  |
| :---: | :---: | :---: |
|  | Residue ( $\mu \mathrm{g} \mathrm{g}{ }^{-1}$ ) Mean $\pm$ SD | Removal (\%) |
| Initial | $14.08 \pm 0.92^{\text {a }}$ | 00.00 |
| 1 | $11.08 \pm 1.58{ }^{\text {b }}$ | 21.31 |
| 3 | $8.90 \pm 1.20^{\circ}$ | 36.77 |
| 6 | $5.51 \pm 0.49^{\text {de }}$ | 60.87 |
| Mean | $9.89{ }^{\text {a }}$ |  |
| K | 0.654 |  |
| $\underline{\mathrm{RL}_{50} \text { (days) }}$ | 1.06 |  |

$* \mathrm{LOD}=0.01 \mathrm{mg} \mathrm{L}^{-1}$, *L.S. $\mathrm{D}_{0.05}$ between intervals $=0.84$., *Values are Mean $\pm$ Standard deviation $(\mathrm{n}=3)$ *Mean followed by a common letter are not significantly different at the $5 \%$ level
the findings of Nasr et al. (2008) who mentioned that methomyl showed a high degradation when exposed to high temperature degrees $\left(55^{\circ} \mathrm{C}\right)$, therefore, it is recommended to use methomyl in areas with dominated temperature not exceed $35^{\circ} \mathrm{C}$. The results revealed that the loss rate values of methomyl increased significantly by increasing the degrees of temperature. There were significant differences in methomyl loss rate among intervals after application under both selected temperatures. Abd El-Baki et al. (1999) and Nasr et al. (2008) found that the increasing of temperature degrees and prolongation of exposure, increase the percentage of insecticides. Another study indicated that the temperature play role in insecticides degradation and the rate increase with increasing temperature and prolongation of exposure.

## Elimination of methomyl residues using commercial processing on soybean seeds

Effect of direct sunlight exposure: Data in Table 6 clearly showed that the significant influence of direct sunlight on the dissipation rate of methomyl formulation on and in soybean seeds. Also, there were significantly differences among intervals after exposure, continuous loss was significant by intervals. The tested insecticide was decreased after one hour of exposure to direct sunlight by $21.31 \%$. Continuous degradation was positively correlated with the exposure period, since the long exposure period gave a high loss rate for the tested insecticide. The percentage removal values for methomyl residues were 36.77 and $60.87 \%$ at 3 and 6 h after exposure, respectively.

Table 7: Influence of commercial processes on removal of methomyl on and in soybean seeds

| Commercial processes | Mean residue $\left(\mu \mathrm{g} \mathrm{g}{ }^{-1}\right)$ | Removal (\%) |
| :--- | :--- | ---: |
| Before treatment | $13.06 \pm 1.94^{\mathrm{a}}$ | 00.00 |
| Dry heating | $4.68 \pm 0.72^{\mathrm{c}}$ | 64.18 |
| Cooking procedure | $00.00^{\mathrm{d}}$ | 100.00 |
| Mean | $5.91^{\mathrm{c}}$ |  |
| *LOD $=0.01 \mathrm{mg} \mathrm{L}^{-1}$ for methomyl, *Values are Mean $\pm$ Standard deviation $(\mathrm{n}=3)$, *Mean followed by a common letter are not significantly |  |  |
| different at the $5 \%$ level |  |  |

Effect of commercial processes of soybean on the removal of methomyl: Data in Table 7 that the residues of methomyl in soybean seeds were significantly decreased by application of the two tested commercial processes. Whereas, cooking procedure was higher than dry heating at ( $90-95^{\circ} \mathrm{C}$ ) on removal of the tested insecticide from soybean seeds. The percentage removal value of methomyl residue from soybean seeds by dry heating were $64.18 \%$. While the percentage removal value of methomyl residue from soybean seeds by cooking at $\left(90-95^{\circ} \mathrm{C}\right)$ for 20 min was $100 \%$.

The residues of methomyl in soybean seeds were significantly decreased by application of the two tested commercial processes. Thus, all stages of the processing play a significant role in removing the tested insecticide from soybean seeds. The results of this study agree with those obtained by Miyahara and Saito (1993), Miyahara and Saito (1994), Youssef et al. (1995), Zayed et al. (1998), Abdel-Megeed et al. (2000) and Zayed et al. (2003).

## CONCLUSION

From all the previous data, it could be concluded that the residue levels of methomyl on the tested soybean genotype Giza-21 were in the safe limits for human consumption, when applied with the recommended rates. The exposure to the main environmental factors, direct sunlight and short UV-rays affected the degradation rates of tested insecticides, also the high temperature degrees. Also, it could be said that the stages of the food processing of soybean play a significant role in removing the insecticide.

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