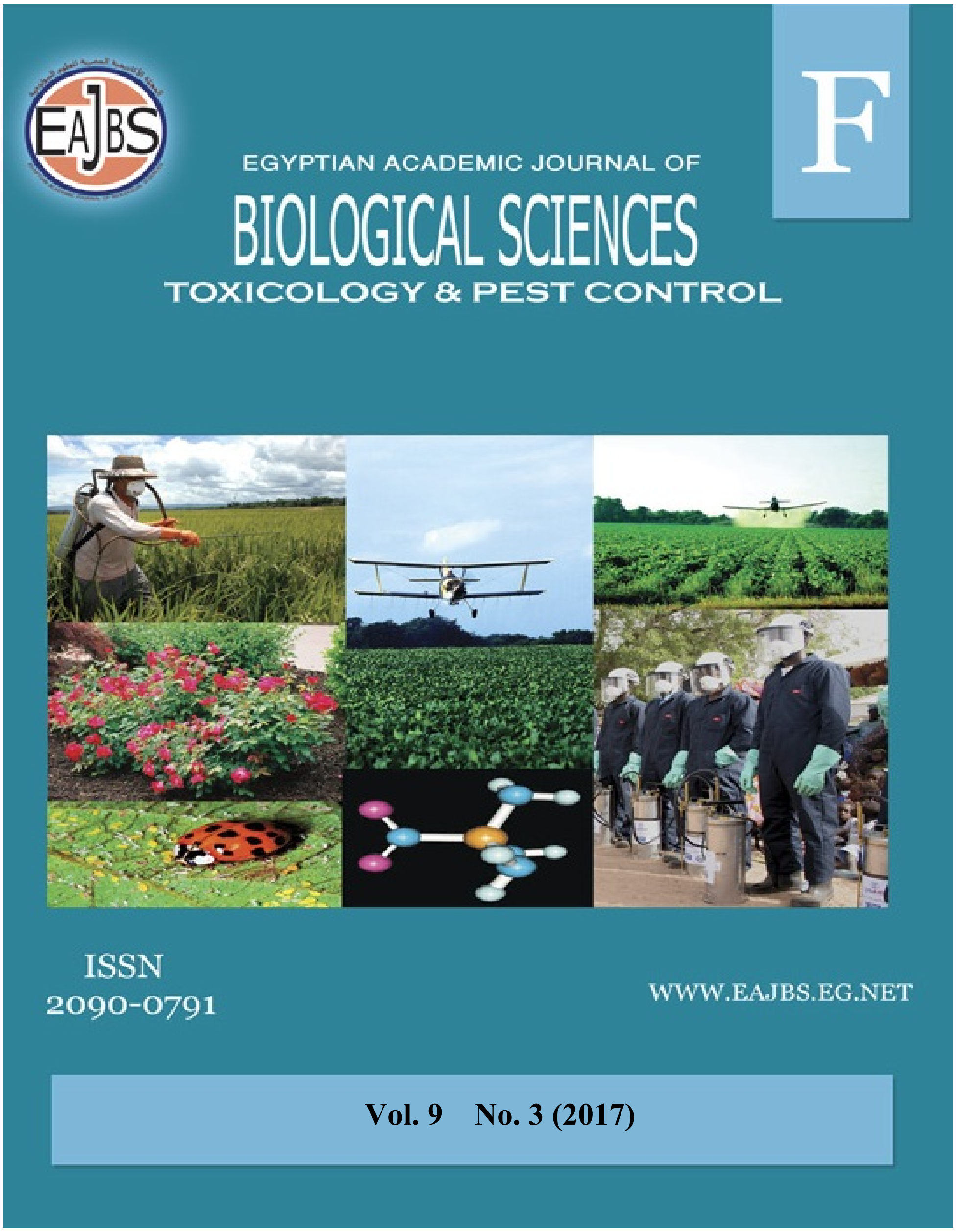

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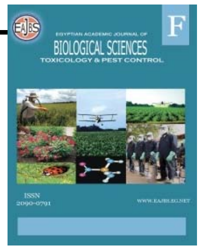

Photocatalytic Degradation of Carbamate Pesticide (methomyl) Using Synthesized TiO_2 Nanoparticles Against the Cotton Leafworm *S. littoralis*

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ABSTRACT

Photodegredation and mineralization of pesticides has becomes the key concern of scientific community. The main cause of Pesticide pollution is the excessive use of pesticides. Mainly in agriculture Estimated 1 to 2.5 million tons of active pesticide ingredients are used each year causing environmental pollution Pesticide pollution emerges as the serious environmental concern. The nanotechnology plays an important role for solving this problem using TiO_2 nanoparticles which could successfully eliminate the harmful pesticide toxicity under the sunlight radiation within a very short time. In this study three treatments of the 2nd and 4th instars of laboratory strain of *Spodoptera littoralis* larvae used and feed on three groups of cotton leaf plant the first group sprayed with solution mixture of the methomyl and TiO_2 nanoparticles the second group sprayed with methomyl alone the third group sprayed with distilled water as control. The experiment was evaluated at 0, 3, 5, 7, 9 and 12 days after the treatment. It is noticed that the insect feed on methomyl alone has large percentage of mortality than the insects treated with mixture compared by zero mortality % for the insects treated with distilled water. The mortality % varied accord to the larval instar as for methomyl alone the mortality % was 100, 100, 100, 100, 100, 80 and 100, 100, 100, 100, 100, 75 for 2nd and 4th instars respectively. And mortality % for methomyl (TiO_2) NPs mixture was 80, 70, 65, 60, 55, 50 and 100, 75, 60, 55, 50, 50 for 2nd and 4th instars respectively. The treatments had a latent effect on the biological activities of the insect as adult and pupa longevity, fecundity, hatchability morphogenic abnormality and pupal weight.

INTRODUCTION

The Egyptian cotton leafworm, *S. littoralis (Boisd.) (Noctuidae: Lepidoptera)* is an economically important pest with a wide range of host plants. This species has acquired resistance to many insecticides (Hassanein, 1999). The increased use of several groups of chemical pesticides to control this insect has led to environmental pollution causing danger to all organisms including man Intense and massive agricultural methods ultimately lead to accumulation of pesticides in high concentrations for long durations of time in soil. Also, pesticides can enter the water through spills, leaks, and back siphoning from nearby mixing, loading, storage, and equipment cleanup sites.

The conventional insecticide, methomyl was used for the lepidopterous pests control (Kassem *et al*., 1986). Methomyl, which has been classified by the World Health Organization, Environmental Protection Agency, USA, and European Commission as a very toxic and hazardous pesticide (Strathmann *et al*., 2001) is highly soluble in water (57.9 g/l, 20°C). It also has a low sorption affinity to soil and can therefore easily cause groundwater contamination in the agricultural areas (Malato *et al*., 2002). In addition, various amounts of methomyl have been detected in surface and ground waters across Europe and America, not only during actual insecticide application but also after a long period of use (Strathmann *et al*., 2001). Methomyl is widely used all over the world because of its powerful control of many different pests (Fernández *et al*., 2002). Studies on the use of various sorbets for the adsorption of methomyl have been conducted, including activated carbon (Chang *et al*., 2012), marine sediments (Yang *et al*., 2005), and hypercrosslinked polymers (Chang *et al*., 2008).Traditional and more expensive methods such as cation exchange (Hesketh *et al*., 1996) and dialysis (Devitt *et al*., 1998) have been also introduced to remove other pesticides. The use of enzymes to detoxify wastewater failed to attract much attention due to the high cost of enzyme-based systems (Kauffmann *et al*., 2000). Filtration through membranes needs another method such as oxidation reaction catalyzed by enzymes to transform the pesticide into an insoluble product; therefore this method is highly expensive (Boussahel *et al*., 2000). Photocatalytic degradation processes introduced themselves as effective strategies to remove the organic pollutants from the wastewaters. The main advantage of these processes is a complete degradation of contaminants to harmless compounds such as CO_2, water and inorganic salts. Photocatalysis proved to be an excellent new advanced oxidation technology to eliminate methomyl present in the water. Moreover, the photocatalysis process is economically acceptable. The conventional photocatalysts such as TiO_2 and ZnO could be used with low initial concentration not only with methomyl (Tamimi *et al.,* 2008 and Poulios *et al.,* 2006) but also with other organic pollutants (Yousef *et al.,* 2012 and Yousef *et al.,* 2012b). Nano crystalline TiO_2 which is prepared in an eco-friendly method and using visible light for the decomposition of organic pollutants is potential in the view of green chemistry.

The principle aim of the present study was to estimate the residual effect of methomyl mixed with nanomaterials against the *S. littoralis* larvae as evident for the detoxification of the pesticide.

MATERIALS AND METHODS

Insect rearing

The cotton leaf worm, *Spodoptera littoralis* was reared in the laboratory at room temp. ranged between 25±2 - 28 ±2 ^{0}C and 60±5 -65±5% R.H. Larvae were fed on castor bean leaves, *Ricinus communis* (L.) in a wide glass jars until pupation period and adults emergence. The newly emerged adults were mated inside glass jars supplied with a piece of cotton wetted 10% sugar solution as feeding source for the emerged moths and branches of Tafla (Nerium oleander L.) or castor bean leaves as an oviposition site according by (El- Defrawi *et al*., 1964). Egg masses were kept in plastic jars until hatching. The obtained second and fourth instar larvae were used for bioassay tests. The bioassay evaluations were performed under the same laboratory condition, at temp. 25±2−28±2 ^{o}C and 60±5 -65±5% R.H.

Nanomaterials

Synthesis of nanomaterial

Analytical grade titanium tetrachloride was adopted as the source material and sodium hydroxide as mineralizer. An aqueous solution of titanium was obtained by mixing one molar stoichiometric ratio of titanium tetraisopropoxide (TTIP) in 50 ml of distilled water. The solution 2-3 mol of NaOH with stirring at several minutes, resulting in a white colloidal sol. The final volume was adjusted to 90 ml using distilled water. Therefore, 90ml sol was transferred to a 100 ml Teflon lined auto clave vessel. The sealed vessel was heated to 240^{O}C for 12 hrs and the resultant precipitate was dried at 450^{O}C for 2 hrs to obtain TiO_2 nanoparticles (Mahshid *et al.*, 2007).

Characterization of the Samples

XRD pattern of the investigated TiO_2 sample is illustrated in Fig. (1), the sample of TiO_2 revealed anatase form with excellent crystallinity as obvious from the peak intensities. It crystallized in the well-known tetragonal symmetry with 4 molecules per unit cell. The data were compared and indexed with the ICDD card no 21-1272. The crystal size was calculated using Scherer's formula (Klug *et al.,* 1974) and was found to be 95nm. The FESEM image of the spherical TiO_2 nanoparticles is shown in Fig. (2), the TiO_2 grains appeared to be with homogenous distribution with a small degree of coalescence. The phase of TiO_2 was confirmed from FT-Raman analysis and the spectrum is shown in Fig. (3), where active peaks near 142, 305, 510 and 624 cm^{-1} are prominent for the anatase phase TiO_2 NPs because of Eg, B1g, A1g and Eg vibrational changes respectively. Neither signal characteristics of brookite nor rutile phases of TiO_2 having Raman shifts in the range of 249 to 826 cm^{-1} respectively, appear in the spectra.

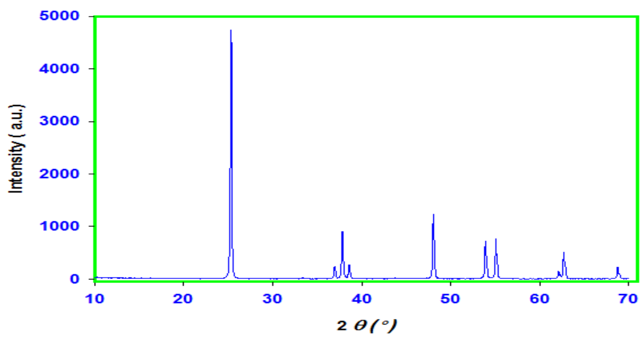

Fig. 1: XRD patterns of Spherical TiO_2 nanoparticles

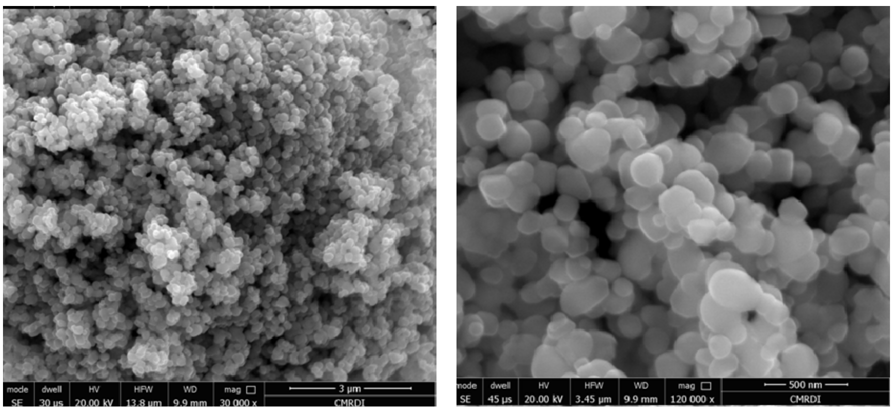

Fig. 2: FESEM images of TiO_2 nanoparticles at different magnifications.

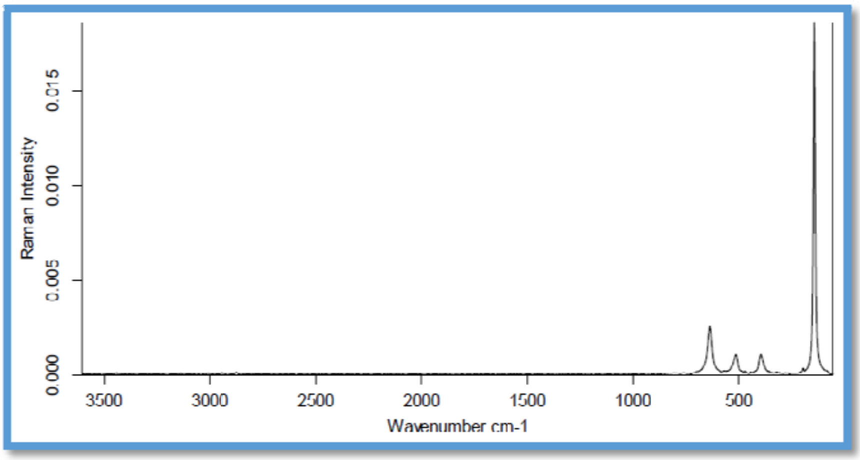

Fig. 3: FT-Raman spectra of TiO_2 nanoparticles

Methomyl

The classic pesticide methomyl obtained from insecticides testing department, plant protection institute.

Trade names: Lannate, Lanox 216, NuBait II, Nudrin, SD 14999

Chemical Name: S-Methyl-N-[(methylcarbamoyl) oxy]-thioacetimidate

Molecular formula: $C_5H_{10} N_2 O_2S$

Molecular weight: 162.20

Structure:

Semi–field tests

The present study was carried out in an isolated region within the Sids Station Farm, Beni-Suef. The planting of cotton plant was done using large pots (35x37cm) under field conditions. The mixtures of TiO_2 nanoparticles were mixed at1:1, 1gm of nano material added to 1gm of methomyl and the two dissolved in one liter of water. The solution of the mixture treatment and methomyl alone were sprayed via a simple hand atomizer on the cotton plants. three replicates of pots were used in each treatment in addition to the control ones which only sprayed with the water. The sprayed cotton leaves were random selected among the replicates at zero, 3, 5, 7, 9 and 12 days of the treatment. Three replicates of sixty larvae of both 2nd and4th instar for larval feeding on treated leaves for each treatment at the six time intervals were used for 48h.The total percent of the larval mortality after 48h of the larval feeding on the leaf residues of the treatment and control were recorded and corrected according to Abbott formula (Abbott, 1925). The different biological effects such as larval and pupal duration, pupation and adult emergence percentage, adult fecundity, eggs hatching%, adult longevity and sex ratio% were estimated at the leaf residues aged 12 day of the treatment. Also, the observed malformations were recorded and photographed.

Statistical analysis:

The data of the biology were statically calculated through Excel sheet for windows computer program to determine the F-value, P-value and L.S.D (least significant difference at 0.05 or 0.01freedom degrees).

RESULTS AND DISCUSSION

Bio-residual activities

Data presented in Table (1) demonstrated that mixing of TiO_2 nanoparticles with the methomyl, as compared with the methomyl alone decrease the toxic effect of the pesticide. Via decrease the larvae mortality. % The effect varied accord to the larval instar, and the toxic residual period The toxic effect of all treatments was the strongest at zero time causing 100% mortality, as compared to that of those fed on the leaf sprayed with distilled water(control). The second instars larvae were more susceptible for the treatments than the fourth ones. It is noticed that the mortality% decrease as period of time increase for both instars it reached to 55 and 50% for second and fourth instars respectively compared with 80 and 75% for methomyl nanoparticles mixture.

Table 1: Residual effect of methomyl mixed with TiO_2 nanoparticles against the 2nd and 4th instars of laboratory strain of *Spodoptera littoralis* larvae at 0, 3, 5, 7, 9 and 12 days after the treatment in relative to control.

Treatment	Mortality % of larvae after feeding on leaf residues 0, 3, 7, 9 and 12days											
	zero		3days		5days		7 days		9 days		12days	
	2nd instar	4th instar	2nd instar	4th instar	2nd instar	4th instar	2nd instar	4th instar	2nd instar	4th instar	2nd instar	4th instar
TiO_2 (NPs)+ Methomyl mixture	100	100	80	75	70	60	65	55	60	50	55	50
Control	0	0	0	0	0	0	0	0	0	0	0	0
Fvalue	17124	12814	192	675	147	108	507	363	155	251	411	251
Pvalue	.000006	.0000008	0.005	0.002	0.007	0.009	0.002	0.003	0.006	0.004	0.002	0.004
L. S. D at 0.05	0.8	0.3	18.4	9.2	18.4	18.4	9.2	9.2	15.4	10.1	8.7	10.1
0.01	1.4	0.5	33.7	16.8	33.7	33.7	16.8	17	28.3	18.6	16	18.6
Methomyl	100	100	100	100	100	100	100	100	100	100	80	75
Control	0	0	0	0	0	0	0	0	0	0	0	0
Fvalue	51768	11294	471	2994	996	6891	47116	74551	1282	8994	59.1	75
Pvalue	.00002	.000009	.000002	.0000003	.000001	.000002	.000002	.000001	.0000008	.0000001	0.02	0.01
L. S. D. at 0.05	1.4	0.9	0.5	0.2	0.3	0.3	0.5	0.3	0.3	0.1	33.1	27.6
0.01	2.6	1.7	0.8	0.3	0.6	0.6	0.8	0.6	0.5	0.2	60.8	50.6

The obtained results agree with those obtained by(Santhanalakshmi *et al.,* 2012) studied the catalytic degradation of the four organopesticides, Chloropyrifos, Quinolphos, Imidocloprid and Endosulphon in water by Nano crystalline TiO2. They found that the increase in the amount of the catalyst generally increases the number of active sites on the catalyst surface and the mass or concentration of the catalyst when exceeds the optimum value, the degradation rate decreases. They indicated that the four pesticides are effectively and photo catalytically degraded at lower pH itself. Also, (Zaman *et al.,* 2012) recorded that an efficient catalytic effect of petals and flowers like CuO nanostructures (NSs) on the degradation of two organic dyes, methylene blue (MB) and rhodamine B (RB). They indicated highest degradation of 95% in CuO petals and 72 % in flowers for MB at 24 h., while for RB, the degradation was 85 % and 80 % in petals and flowers, respectively for 5h. They observed that CuO petals appeared to be more active than flowers for degradation of both dyes associated to high specific surface area.Also, Barakat *et al*. (2014) reported that CdSO4-doped TiO2 nanoparticles are introduced as a powerful and reusable photocatalyst for the photocatalytic degradation of methomyl pesticide in concentrated aqueous solutions. They mentioned that the introduced nanoparticles could successfully eliminate the harmful pesticide under the sunlight radiation within a very short time (less than 1 h), with a removal capacity reaching 1,000 mg pesticide per gram of the introduced photocatalyst.They added that the increase in the initial concentration of the methomyl did not affect the photocatalytic performance; typically 300, 500, 1,000, and 2,000 mg/l solutions were completely treated within 30, 30, 40, and 60 min., respectively, using 100 mg catalyst, the photocatalytic efficiency was not affected upon multiple use of the photocatalys.Also, Khan *et al.* (2015) mentioned that Nanobased membrane filtration technology design and developed were found effective and efficient for the degradation of pesticides under UV light irradiation, as compared to photocatalytic degradation carried out using ZnO.

Latent effect:

Larval and pupal durations:

Data presented in Tables (2 and 3) demonstrate the residual effect of TiO_2 nanoparticles methomyl mixture and methomyl alone reflect the biological activities of *S. littoralis.* The feeding of 2^{nd} and 4^{th}instar larvae on leaves previous sprayed with methomyl nanoparticles mixture after 12 days of application, significant ($p<0.05$) prolonged the larval duration to average 19 and 15days compared with 16.1 and 11.3 of control for both 2^{nd} and 4^{th}instar respectively. But the results differ for methomyl treatment alone as the larval duration of 2^{nd} instar decrease to 15.9days compared with 16.1 for control while it was found 16.8days for 4^{th} instar compared with 11.3 for control.

On the other hand data presented in Tables (2 and 3) demonstrate that the feeding of 2^{nd} and 4^{th}instar larvae on leaves previous sprayed with methomyl nanoparticles mixture after 12 days of application, decrese the pupal duration to average 13.3 for 2^{nd} instar compared with 16.1 for control. And for the 4^{th} instar found 13.9days compared with 12.7days of control. But the results differ for methomyl treatment alone as the pupal duration of 2^{nd} instar non significance as 9.1days compared with 8.7 for control while it was found that pupal duration decrease for 4^{th} treatment to 8.3days compared with 12.7 for control.

The obtained results agree with those obtained by (Morillo *et al.,* 2004)who found that the duration of the larval and pupal stages and the developmental period from egg to adult of *Spodoptera frugiperda* was significantly longer in the lambdacyhalotrin-selected strain and the methomyl-selected strain compared to the control strain, from the first to the last generation. Moreover, (Ahmed 2004) mentioned that the larval period was elongated and the pupal period shorted for the new hatched larvae of pink and spiny bollworms (Laboratory strain) treated with the higher concentrations of Spinosad when compared with untreated larvae.

Pupation and Pupal weight:

Data presented in Tables (2 and 3) showed that the second instar larvae of *S. littoralis* which fed on the sprayed leaves after 12days from treatment with methomyl nanoparticles mixture treatments induced a highly significant ($p<0.01$) decrease of the pupation percentage in respect to control.

Table 2: the latent effect of TiO_2 nanoparticles methomyl mixture, on the larval and pupal durations, pupal weight, pupation and adult emergence percentage of the 2^{nd} instar larvae of the lab. strain of *S. littoralis* at 12 d. of the treatment in relative to control.

Treatments	Larval duration (days) ± SD	% Pupation		Pupal duration days	Pupal weight mg	% Moth emergence ± SD	
		Normal	Malfo.			Normal	Malfo.
Nano TiO_2 methomylmixture	19±3*	39.6±10**	0	13.3±2.5**	182±6.7**	80±10n.s	20
Methomyl alone	15.9±2.2n.s	30±8**	0	9.1±5n.s	229±41n.s	85.7±8n.s	14.3
Control	16.1±4.3	100	0	8.7±2.8	217±21	100	0
F value	6.333	103.485		9.7745	19.317	26.284	
P value	0.03601	0.01376		0.0197	0.00230	0.0360	
L.S.D. at 0.05	2.5	12.05		1.65	16.8	7.2	
L.S.D. at 0.05	3.5	22.022		2.337	24.2	42.1	

** = Highly Significant ($p<0.01$)
* Significant ($p<0.05$)
S.D. =Standard deviation
Malfo. = Malformation%
L.S.D. = Least significant difference
n. s=none Significant ($p>0.05$)

Table 3: the latent effect of TiO_2 nanoparticles methomyl mixture on the larval and pupal durations, pupal weight, pupation and adult emergence percentage of the4th instar larvae of the lab. strain of *S. littoralis* at 12 d. of the treatment in relative to control.

Treatments	**Larval periods (days) + SD**	**% Pupation + SD**		**Pupal duration days**	**Pupal weight (mg)**	**% Moth emergence + SD**	
		Normal	**Malfo.**			**Normal**	**Malfo.**
Nano TiO_2 methomyl mixture	15.3+2.5**	50+10	0	13.9+2.2n.s	168.9+29**	80.0	20.0
Methomyl alone	16.8+2.9**	30+9.2	33.3	8.3+2.8*	230+40n.s	90+10n.s	10
Control	11.3+1.3	100	0	12.7+2.5	272+29	100	0
F value	36.3798	98.972		3.959	34.7	9024.9	
P value	0.00849	0.0148		0.05	0.00367	0.0001	
L.S.D. at 0.05	1.592	12.225		2	23.5	2.4	
L.S.D. at 0.05	2.235	22.435		3.2	33.7	4.4	

** = Highly Significant (p<0.01)
S.D. =Standard deviation
L.S.D. = Least significant difference
* Significant (p<0.05)
Malfo. = Malformation%
n. s=none Significant (p>0.05

Which caused pupation % decrease to average 39 and 30 for both 2nd and 4th instar respectively as compared to 100 %pupation of control. On the other hand, the larval feeding of 2nd instar on the leaf residues aged 12 days with methomyl TiO_2 nanoparticles mixture highly significantly (p<0.01) only reduced the pupal weight of the resulting pupae to average182mg as compared to217mg of that of control. While, the feeding of the 4th instar with methomyl nanoparticles mixture highly significant (p<0.01) decreased the pupal weight to average 168.9mg as compared to 272 mg of the pupal weight produced from untreated 4thinstar larvae. The obtained results are in harmony with that obtained by (Swelam *et al.,* 2006) who reported that at different combinations of insecticides, methomyl, carbaryl, esfenvalerate and profenofos used by mixing at the level of LC_{25} with the ratios of 1: 2, 1: 1 and 2: 1 against *S. littoralis* appeared significant changes in the pupa weight compared with the control. Also, Ahmed (2004) found that the average of pupation percentages for pink and spiny bollworms gradually decreased with increasing concentrations of the tested compounds (Agerin, Diple 2x Naturalis L, Spinosad) in laboratory and field strains, respectively.

Moths emergence:

Results show that both of the 2ndinstar larvae fed on the sprayed leaves after 12days of application with the feeding of the instars with methomyl nanoparticles mixture and methomyl alone gave none significant decrease of the adult emergence averaged 80 and 85.7%, respectively, as relative to100%of that of control Tables (2 and 3). While the larval feeding of the 4th instar on methomyl nanoparticles mixture had the effect in the adult emergence inhibition to 80%, as compared to 100%of that of control.

These results are agreement to those obtained by Ahmed (2004) who found that adult emergence for pink and spiny bollworms grdually decreased with increasing concentrations of the tested compounds (Agerin, Diple 2x Naturalis L , Spinosad) in laboratory strain.

Morphogenetic abnormalities:

Data presented in Tables (2 and 3) demonstrated that the larval feeding of 2nd instars of *S. littoralis* on the leaf residues, methomyl TiO_2 nanoparticles mixture and methomyl alone didn't affect the pupae stage. But the larval treatment of the 4th instar with methomyl alone induced the highest percentage to reach 33.3%, respectively, as compared to 0% of control.

Also, the 2nd instar larvae treated with methomyl TiO_2 nanoparticles mixture gave percent reached 20% adult malformation percentages as, compared with 0% of that of control, and the malformations of *S .littoralis* pupae resulting from the larval treatment of the 2nd and 4th instars with mixtures and methomyl alone mostly as appeared as pupal moth intermediates as moth failed to emerge from the pupal skin at head and thorax (Fig. 6), or pupae with shrinkage body (Fig. 5), or moths had weakly developed wings with short body (Fig. 4), or pupal adult intermediate as moth failed to emerge (Fig. 3). As compared to normal pupae (Fig.1) and Normal adult (Fig. 2).

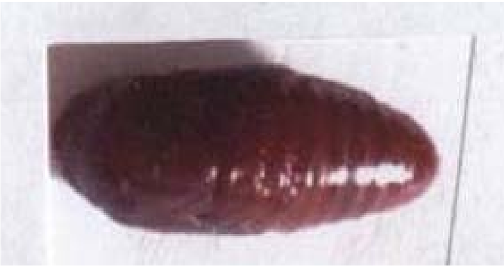

Fig. 1: Normal pupae

Fig. 2: Normal adult

Fig. 3: appeared as pupal adult intermediates as moth failed to emerge from the pupal skin at head and thorax.

Fig. 4: moths had weakly developed wings

Fig. 5: Pupae with shrinkage body

Fig. 6: larval-pupal intermediate had larval legs and pupal body

These results are in agreement with to those obtained by (Javier *et al.*, 2008) demonstrated that Align when administered orally *Lobesia botrana* gave phenotypic effects included inability to molt properly and deformities. Also, (Swelam *et al.*, 2006) reported that at different combinations of insecticides, methomyl, carbaryl, esfenvalerate and profenofos by mixing at the level of LC_{25} with the ratios of 1: 2, 1: 1 and 2: 1 used against *S. littoralis* produced some malformations in the pupae and moths stages. Also, Ahmed (2004) indicated that Spinosad gave malformed pupal and adults in both laboratory and field strains of both Pink and Spiny bollworms.

Adult fecundity and fertility

Data presented in Table (4) demonstrated that the larval feeding of *S. littoralis* on the leaf residues aged 12days sprayed with methomyl nanoparticles mixture and even the methomyl alone violent reduce the adult fecundity to reach zero eggs/female, as compared to206 eggs/female of that of control.

Therefore, the larval feeding of *S. littoralis* on the leaf residues aged12days sprayed with the tested methomyl TiO_2 nanoparticles mixture and even the methomyl alone inhibited the total number of eggs laid by adult females fed as 4th instar larvae with these treatments and also the eggs hatching to zero, as compared to that of control(100%).

Table 4: Latent effect of methomyl TiO_2 nanoparticles mixture, as compared to methomyl alone on fecundity, eggs hatching, and adult longevity and sex ratios against the 4th instar larvae of the lab. strain of *S. littoralis* at 12 d. of the treatment in relative to control.

Treatments	Fecundity eggs/ f	Eggs hatching%	Adult longevity (days)	Adult sex ratio (%)	
	Mean ± S.D.		Mean ± S.D.	Male	Female
Nano TiO_2 methomyl mixture	0	0	10.2±0.7n.s	66.7	33.3
methomyl alone	0	0	7.9±1.1*	66.7	33.3
Control	206±41	100	9.4±3.3	50	50
F value	76.5		3.368		
P value	0.0128		0.05		
L.S.D. at 0.05	65		2.1		
0.01	119.4		3.0		

** = Highly Significant (p<0.01) * Significant (p<0.05)
S.D. =Standard deviation Malfo. = Malformation%
L.S.D. = Least significant difference Lab. =Laboratory strain
n. s=none Significant (p>0.05)

These results are agreement with those obtained by (Javier *et al.*, 2008) recorded that Align When administered orally, reduced the fecundity and fertility of adults of *Lobesia botrana* treated with 1, 5, and 10 mg litre^{-1} and at the highest doses, fecundity and fertility were zero. Also, (Pineda *et al.*, 2007) demonstrated that spinosad and methoxyfenozide reduced in a dose-dependent manner the fecundity and fertility of *S. littoralis* adults when orally and residually treated. They reported that the combination of lethal and sublethal effects of methoxyfenozide and Spinosad might exhibit significant effects on the population dynamics of *S. littolaris*. Likewise, (Swelam *et al.*, 2006). Found that some of the mixtures of insecticides, methomyl, carbaryl, esfenvalerate and profenofos at the level of LC25 with the ratios of 1: 2, 1: 1 and 2: 1 against *S. littoralis* showed sterility effect. Also, (Morillo *et al.*, 2004) mentioned that the fertility of eggs of *S. frugiperda* diminished to 50.61 and 47.31% in the last generation, in the lambdacyhalotrin-selected strain and the methomyl-selected strain, respectively. They indicated that the differences in the duration of some of the insect phases represent a reproductive deterioration in compensation of the survival to the process of selection pressure with the insecticides lambdacyhalotrin and methomyl.

Adult longevity

Data presented in Table (4) showed that feeding of the fourth instar larvae on the leaf residues aged 12days sprayed with methomyl nanoparticles mixture gave none significant decrease of the adult longevity, as respect of that control. These results contracted with those obtained by (Javier *et al.,* 2008) who recorded that Align when administered orally, the longevity of *Lobesia botrana* adults was not affected. While (Morillo *et al.,* 2004) found that the longevity of males and females of *Spodoptera frugiperda* only showed differences in some generations in the strains exposed to insecticides.

Adult sex ratio:

Data in Table (4) indicated that the 4th instar larvae of *S. littoralis* fed on the leaf residues aged 12days sprayed with, methomyl nanoparticles mixture and methomyl alone gave adult males increase to 66.7%, and decreased the adult females to 33.3% as compared to50:50% adult females: males ratios, respectively, of that of control.

CONCLUSION

The results of the present work demonstrated that by adding the TiO_2 nanoparticles to methomyl pesticide decrease its toxicity effect and decrease the toxic residual period as TiO_2 cause photodegredation to the methomyl pesticide. By using the 2nd and 4th instars larvae of *S. littoralis* as toxic residual indicator. thus in agriculture process we can use these nanoparticles by mixing it with pesticides by this way we can reduce pollution effects resulted from using these pesticides.

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ARABIC SUMMERY

التحلل الضوئى لمبيدات الكاربميت (ميثوميل) باستخدام جزيئات ثانى اكسيد التيتانيوم النانوية ضد حشره دوده ورق القطن

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لقد اصبح التحلل الضوئى وتكسير المبيدات العضوية هو الشغل الشاغل الذى يشغل المجتمع العلمى واصبح السبب الرئيسى للتلوث بالمبيدات هو الاستخدام المفرط لتلك المبيدات كما تقدر الكمية المستخدمة من المبيدات من ١الى ٢.٥ مليون طن سنويا والتى بدورها تسبب تلوثا بيئيا خطيرا. ولذلك تلعب تكنولوجيا النانو دورا هاما لحل هذه المشكلة باستخدام جزيئات ثانى اكسيد التيتانيوم النانوية والتى لها دور كبير فى ازالة الاثر السام الخطير للمبيدات تحت تاثير ضؤ الشمس وفى فتره زمنيه قصيره . فى هذه الدراسة يتم استخدام ثلاث معاملات على العمر الثانى والرابع من دودة ورق القطن وذلك بالتغذية على هذه المعاملات باستخدام ورق نبات الخروع بعد غمسة فى كل معاملة على حده ثم اطعام يرقات العمر الثانى والرابع لحشرة دودة ورق القطن والثلاث معاملات هم خليط من مبيد الميثوميل مع جزيئات ثانى اكسيد التيتانيوم النانوى والمعاملة الثانية مبيد الميثوميل منفرد والمعامله الثالثة ماء مقطر وقد تم تقييم التجربة خلال فترات زمنيه متفاوته ٣، ٥، ٧، ٩، ١٢ يوم وقد لوحظ انه باستخدام الخليط من مبيد ميثوميل مع جزيئات ثانى اكسيد التيتانيوم النانوية خفض فى نسب الموت ليرقات العمر الثانى والرابع لحشرة دودة ورق القطن مقارنة بمبيد الميثوميل منفرد .اما المعاملة الثالثة باستخدام الماء المقطر لايوجد نسب موت وهذا مؤشر قوى على انه بعد خلط مبيد الميثوميل بجزيئات ثانى اكسيد التيتانيوم النانوية تم تحلل ضوئى للمبيد وتقليل معدل سمية المبيد ولذلك يمكن اضافة جزيئات ثانى اكسيد التيتانيوم النانوية لمبيد الميثوميل للتقليل من تاثيره السمى المتبقى.