Efficacy of Zinc Oxide Nanoparticle Adding to Two Neonicotinoids Pesticides against *Spodoptera litura* (Lepidoptera: Noctuidae) and *Aphis gossypii* Glover

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**ABSTRACT**

In recent years, pesticide residues have become a danger to the food chain, the environment, and human health. Some nano metal oxides had been applied with pesticides to solve these problems and enhanced their insecticidal Activity. This new technology for the complete mineralization of pesticides is necessary to convert them to non-toxic forms. In this study, we investigated the synergistic effect of ZnO nanoparticles (NPs) with some neonicotinoid pesticides (Thioxam 25%WG and Actara 25% WP) against 4th instar larvae of *Spodoptera litura* (Lepidoptera: Noctuidae) and cotton aphid, *Aphis gossypii* Glover (Homoptera: Aphididea). These cotton pests were allowed to feed on castor leaves after impregnated with pesticides at recommended rate with the composite of ZnO (NPs). Observations showed an increase in mortality (48.57 %, 93.51 % increased mortality). The addition of the ZnO nanoparticles to insecticides increased the insecticidal activities and a reduction (%) against tested cotton pests. The synthesized nano metal oxide was characterized by different techniques as FTIR spectroscopy, TEM and UV spectroscopy used for a determination band gap of the prepared ZnO NPs. This present study suggests that nanoparticles metal oxide as (ZnO) applying as eco-friendly nanomaterial in the field of pest control.

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**INTRODUCTION**

In all the world, the crops were raided by various insects' groups, causing sharp damage to plants (Wardle, *et al.*, 2004). Different groups of synthetic insecticides were much used to control these pests (Damalas and Koutroubas, 2016; Jameel, *et al.*, 2019). Pesticides are mostly used in agricultural production in controlling pests, fungi, and weeds. Therefore, there are extensively pesticide residues in soils, ground waters, and drinking waters (Nasrabadi, *et al.*, 2011; Gilliom, *et al.*, 1999).

Manganese, ferric, zinc, aluminum, magnesium, cerium, and titanium nanometal oxides are extremely effective adsorbents for a wide range of pesticides. Also, they have a high adsorption capacity, low cost, high surface area, and short diffusion distance (Armaghan and Amini, 2012; Moradi Dehaghi, *et al.*, 2014; Tavakkoli, Yazdanbakhsh, 2013; Cheng, 2013; Bardajee, and Hooshyar, 2013). In the last years, many nanometal particles are applied for progressing the insecticidal activity each alone or with the combined form against the different insects (Johnston, *et al.*, 2009; Malaiakozhundan, *et al.*, 2017; Ishwarya, *et al.*, 2018). Instead of traditional insecticides (e.g., neonicotinoids) were
introduced into the market because they have more resistant than most conventional insecticides on insect pests (such as aphids) became and subsequently replacing the organophosphates and methyl-carbamates (Tomizawa et al., 2007). Abd-Ella et al., (2015) determined the efficiency of acetamiprid, thiamethoxam, imidacloprid, dinotefuran, and malathion on cotton aphid. The results indicated that thiamethoxam, imidacloprid, acetamiprid and dinotefuran proved to be the most effective insecticides in reducing cotton aphid population up to 21 days after treatment. Mohd, et al., 2020 studied the insecticidal activity and persistence effect of adding ZnO NPs to thiamethoxam and thiamethoxam alone on Spodoptera litura and measured their effectiveness on in the environment. Nano metal oxides can be added to pesticides to reduce their dose (Perez and Rubiales, 2009) and increase their efficacy in pest control (Liu et al., 2008; Werdin Gonza´lez et al., 2014; Patil et al., 2016). Nano metal oxide materials as aluminum oxide (ANP), zinc oxide (ZNP), titanium oxide (TNP), and silver NPs have shown insecticidal efficacy.

This study aimed to investigate the effect of adding ZnO nanoparticles (NPs) to Thioxam 25%WG and Actara 25% WP against 4th instar larvae of S. litura (Lepidoptera: Noctuidae) and cotton aphid, A. gossypii Glover (Homoptera: Aphididea).

MATERIALS AND METHODS

Chemicals:
- The tested neonicotinoids pesticides are Thioxam 25%WG and Actara 25% WP.
- The tested metal oxide is zinc oxide (ZnO) from Sigma Aldrich.

Synthesis of Nano Metal Oxide (ZnO NPs):
Zinc oxide nanoparticles were synthesized by Shoeb et al. method. The nanometal was added to the tested pesticides (neonicotinoids) water solutions by (1:5 ratio) under continuous magnetic stirring for 1h at (25°C) room temperature. Then, the mixture was heated to 50°C for 1h (Shoeb, et al., 2013). The white formed precipitate was washed two times with distilled water then it dried at 50°C in the oven for 2 hour (Mohd, et al., 2020).

Characterization of Nano Metal Oxide (ZnO NPs):
Nicolet 550 FTIR spectrometer with 128 scans and resolution 4 cm⁻¹ in the mid IR (400-4000 cm⁻¹) region. The measured sample is prepared with KBr (1-100mg), and pressed into a thin wafer and then the spectrum was recorded. TEM images were determined by a (JEOL-JEM-2100) electron microscope by dipping onto a copper grip coated with holey carbon foil and dried at an ambient temperature. UV spectroscopy used for determination band gap of the prepared ZnO NPs from the energy fixed values of the orbitals involved in electronic transitions by the appearance of new bands at definite λmax (nm) by using Perkin-Elmer S52 Spectrophotometer.

Field Experimental Design:
The cotton seeds (Egyptian cultivar Giza 90) were planted in Experimental Farm (Mansoura, Egypt), on July 27, 2020. The field area was divided into three plots, 3 ×3.5 meters. A sampling of aphid, A. gossypii and S.litura were reared weekly on April, 15, 2020 till the pest’s disappearance. The S. litura larvae were rearing around the agricultural fields. They were set in a jar of 15 × 20 cm size, in the laboratory conditions of 28 ± 2°C temperature, 65–70% humidity and a photoperiod (10 h dark: 14 h light) in an incubator.

Mode of Application of Nano Metal Zno With Different Concentrations in Each Thiamethoxam Pesticides:
Each tested pesticide was dissolved in distilled water to form four concentrations, Thioxam 25%WG (20, 40, 60, and 90 mg/L) against S. litura (4th instar larvae) and Actara 25% WP (5, 10, 30, and 50 mg/L) against cotton aphid, A. gossypii. Each pesticide alone
was considered as the control. The cotton leaves were sprayed with different concentrations of diluted pesticide and pesticide with ZnO NPs. The replicate concentrations were four and the control.

**RESULTS AND DISCUSSION**

Characterization of Nano Metal Oxide (ZnO NPs):

In Figure (1), the FTIR spectrum of Nano metal ZnO shows a strong absorptions peak at 508.4 cm\(^{-1}\) expressed oxygen gaps in ZnO. The band at 3459.4 cm\(^{-1}\) may show the vibration of the (H-OH) bones groups. The broadband at 1638.1 cm\(^{-1}\) represents the expansion vibration of the carbonyl peak. The stretching band at 2945.1,2854.9 cm\(^{-1}\) expressed the (N, C, S) vibration. In Figure (2), TEM image analyzed the traced of the insecticides on Nano metal ZnO surface. There are two separated phases on the scale of 100 nm. The dark phase belongs to Nano metal ZnO. In Figure (3), the quaternization of Nano metal ZnO was confirmed by the appearance of new bands at definite \(\lambda_{\text{max}}\) at 338 nm by using Perkin-Elmer S52 Spectrophotometer.

**Fig. 1.** FTIR spectrum pattern of Nano metal ZnO.

**Fig. 2.** TEM images of Nano metal ZnO on the scale of 100 nm.
Effect of Adding Zno Nps/Thioxam 25%WG and Zno Nps/Actara 25% WP on Mortality Percentage and Mean Residual Effect:

1. Effect on Mortality Percentage:
Mortality percentage increases after treating Thioxam 25%WG and Actara 25% WP formulations with ZnO NPs (Table 1) in comparison with pesticides alone. Thioxam 25%WG (in the highest concentration) with ZnO NPs, we observed 28.3% increase in the mortality percentage than the groups treated with Thioxam 25%WG alone against S. litura (4th instar larvae). Also, the highest Actara 25% WP concentration with ZnO NPs enhanced mortality 39.8% than Actara 25% WP alone against cotton aphid, A. gossypii Glover (Homoptera: Aphididea). These manifest differences in the mortality percentage showed the effect of adding the ZnO NPs to the two pesticides formulations. The obtained results in table (1) show that Thioxam 25%WG concentration with ZnO NPs showed the LC50's of 58.16 mg/L. While Actara 25% WP with ZnO NPs showed the LC50's of 14.95 mg/L. The insecticidal activity increases with adding ZnO NPs to pesticides solutions spray solutions. Nanometal oxides as zinc oxide were highly attractive toward showing modern methods for formulating the pesticides (active ingredients) in nanoscale sizes and easily delivering them, these are known as the implementation of nanotechnology in crop protection (Smith et al., 2008; Yasur and Usha Rani, 2013; Benelli et al., 2017).

Table 1: The effect of adding ZnO NPs to Thioxam 25%WG and Actara 25% WP on mortality percentage and insecticidal activity.

| Cotton Pests | Treatment                  | LC50 (mg/L) | Mortality % |
|--------------|----------------------------|-------------|-------------|
| S. litura    | Thioxam 25%WG              | 90.04       | 49.72       |
|              | Thioxam 25%WG/ ZnO NPs     | 58.16       | 78          |
| A. gossypii  | Actara 25% WP               | 28.46       | 50          |
|              | Actara 25% WP/ ZnO NPs     | 14.95       | 89.78       |

Effect on the Mean Residual Percentage:
Data presented in table (2) showed that; ZnO NPs improved the insecticidal action of Thioxam 25%WG and Actara 25% WP formulations at the complete recommended rate. Using Thioxam 25%WG in the complete recommended rate of an application gave 48.57% initial larval mortality while the addition of ZnO NPs to Thioxam 25%WG gave a higher larval mortality 66.49%. Also, using Actara 25% WP at the complete recommended rate of an application gave 84.70% initial mortality while the addition of ZnO NPs to Actara 25% WP gave a higher mortality 93.51%. Generally, it was noticed that ZnO NPs increased the percentage of mortality at the recommended rate.
Table 2: The effect of adding ZnO NPs to Thioxam 25%WG and Actara 25% WP on the mean residual effect.

| Cotton Pests | Treatments                  | Tested concentration (mg/L) | 1 DAY       | 7 DAY       | 15 DAY      | 21 DAY      | % of the mean residual effect |
|--------------|-----------------------------|-----------------------------|-------------|-------------|-------------|-------------|-----------------------------|
| S. litura    | Thioxam 25%WG               | 180                         | 84.31       | 56.13       | 38.73       | 15.10       | 48.57                      |
|              | Thioxam 25%WG/ ZnO NPs      | 87.80                       | 79.05       | 63.14       | 35.99       |             | 66.49                      |
| A. gossypii  | Actara 25% WP                | 50                          | 96.54       | 99.50       | 91.12       | 51.66       | 84.70                      |
|              | Actara 25% WP/ZnO NPs       | 100                         | 100         | 94.95       | 79.08       |             | 93.51                      |

CONCLUSION:

The findings of this new study proposed that adding of ZnO nanoparticles to Thioxam 25%WG, and Actara 25% WP was used to control the population of S. litura (4th instar larvae), and the cotton aphid, A. gossypii Glover. The adding of the ZnO nanoparticles composite to insecticide solutions played important roles in the insecticidal activity, and the reduction (%) of S. litura and cotton aphid and A. gossypii Glover.

REFERENCES

Armaghan, M., Amini, M. 2012. Adsorption of diazinon and fenitrothion on nanocrystalline alumina from non-polar solvent. *Journal of Colloid Science,* 74: 427-433.

Bardajee, G., Hooshyar, Z. 2013. Degradation of 2-Chlorophenol from Wastewater Using γ-Fe₂O₃ Nanoparticles. *International Journal of Nanoscience and Nanotechnology,* 9: 3-6.

Benelli G, Pavela R, Maggi F, Petrelli R, Nicoletti M. 2017. Commentary: making green pesticides greener? the potential of plant products for nanosynthesis and pest control. *Journal of Cluster Science,* 28(1):3–10.

Cheng, Y. 2013. Effective organochlorine pesticides removal from aqueous systems by magnetic nanospheres coated with polystyrene. *Journal of Wuhan University of Technology, Materials science edition,* 29: 168-173.

Damalas, C., Koutroubas, S. 2016, Farmers’ Exposure to Pesticides: Toxicity Types and Ways of Prevention. *Journal of Toxics,* 4(1), 1.

Gaber, A. S., Abd-Ella1, A. A., Abou-Elhagag, G. H., Abdel-Rahman, Y. A. 2015. Field efficiency and selectivity effects of selected insecticides on cotton aphid, Aphis gossypii Glover (Homoptera: Aphididea) and its predators. *Journal of Phytopathology and Pest Management,* 2(1): 22-35.

Gilliom, R. J., Barbash, J. E., Kolpin, D. W., Larson, S. J.1999. Peer reviewed: testing water quality for pesticide pollution. *Journal of Environmental Science and Technology,* 33: 164A-169A.

Ishwarya, R., Vaseeharan, B., Subbaiah, S., Nazar, A. K., Govindarajan, M., Alharbi, N. S., Kadaikunnel, S., Khaled, J. M., Alanbr, M. N. 2018. Sargassum wightii-synthesized ZnO nanoparticles from antibacterial and insecticidal activity to immunostimulatory effects on the green tiger shrimp Penaeus semisulcatus. *Journal of Photochemistry and Photobiology,* B (183): 318–330.

Jameel, M., Alam, M. F., Younus, H., Jamal, K., Siddique, H. R. 2019. Hazardous subcellular effects of Fipronil directly influence the organismal parameters of Spodoptera litura. *Journal of Ecotoxicology and Environmental Safety,* 172:216–224.

Johnston, H. J., Hutchison, G. R., Christensen, F. M., Peters, S., Hankin, S., Stone, V. 2009. Identification of the mechanisms that drive the toxicity of TiO (2) particulates: the
contribution of physicochemical characteristics. *Journal of Particle and Fibre Toxicology*, 6: 33.

Liu, Y., Tong, Z., Prud’homme, R.K. 2008. Stabilized polymeric nanoparticles for controlled and efficient release of bifenthrin. *Journal of Pest Management Science*, 64:808–812.

Malaikozhundan, B., Vaseeharan, B., Vijayakumar, S., Thangaraj, M. P. 2017. Bacillus thuringiensis coated zinc oxide nanoparticle and its biopesticidal effects on the pulse beetle, Callosobruchus maculatus. *Journal of Photochemistry and Photobiology*, B (174): 306–314.

Mohd, J., Mohd, S., Mohd, T. K., Rizwan, U., Mohammad M., Mohd K. F., Sayed M. A. 2020. Enhanced Insecticidal Activity of Thiamethoxam by Zinc Oxide Nano particles: A Novel Nanotechnology Approach for Pest Control. *Journal of American Chemical Society*, 5: 1607–1615.

Moradi Dehaghi, S., Rahmanifar, B., Moradi, A. M., Azar, P. A., 2014. Removal of permethrin pesticide from water by chitosan–zinc oxide nanoparticles composite as an adsorbent. *Journal of Saudi Chemical Society*, 18: 348–355.

Nasrabadi, T., Bidhendi, G. N., Karbassi, A., Grathwohl, P., Mehrdadi, N. 2011. Impact of major organophosphate pesticides used in agriculture to surface water and sediment quality (Southern Caspian Sea basin, Haraz River. *Journal of Environmental & Earth Science*, 63: 873-883.

Patil CD., Borase HP., Suryawanshi RK., Patil SV. 2016. Trypsin inactivation by latex fabricated gold nanoparticles: a new strategy towards insect control. *Journal of Enzyme and Microbial Technology*, 92:18–25.

Perez de L. A, Rubiales, D. 2009. Nanotechnology for parasitic plant control. *Journal of Pest Management Science*, 65:540–545.

Shoeb, M.; Singh, B. R.; Khan, J. A.; Khan, W.; Singh, B. N.; Singh, H. B.; Naqvi, A. H. 2013. ROS-dependent anticanidal activity of zinc oxide nanoparticles synthesized by using egg albumen as a biotemplate. *Journal of Advances in Natural Sciences: Nanoscience and Nanotechnology*, 4: 035015.

Smith K, Evans DA, El−Hiti GA. 2008. Role of modern chemistry in sustainable arable crop protection. *Journal of Philosophical Transactions of the Royal Society*, B (363):623–637

Tavakkoli, H., Yazdanbakhsh, M. 2013. Fabrication of two perovskite-type oxide nanoparticles as the new adsorbents in efficient removal of a pesticide from aqueous solutions: Kinetic, thermodynamic, and adsorption studies. *Journal of Microporous and Mesoporous Materials*, 176: 86-94.

Tomizawa, M, Maltby, D, Medzhiradszky, KF, Zhang, N, Durkin, KA, Presly, J, Talley, TT, Taylor, P, Burlingame, AL, Casida, JE. 2007. Defining nicotinic agonist binding surfaces through photo affinity labeling. *Journal of Biochemistry*, 46: 8798-8806.

Wardle, D. A., Bardgett, R. D., Klironomos, J. N., Setala, H., vander Putten, W. H., Wall, D. H. 2004. Ecological linkages between aboveground and belowground biota. *Journal of science*, 304: 1629–1633.

Werdin Gonza´lez JO., Gutie´rrez MM., Ferrero AA., Ferna´ndez Band B. 2014 Essential oils nanoformulations for stored-product pest control-characterization and biological properties. *Journal of Chemosphere*,100:130–138.

Yasur J., Usha Rani P. 2013. Environmental effects of nano silver: impact on castor seed germination, seedling growth and plant physiology. *Journal of Environmental Science and Pollution Research*, 20:8636–8648.
ARABIC SUMMARY

فاعلية إضافة جزيئات أكسيد الزنك النانوية على اثنين من المبيدات (نيونيكوتينويد) ضد دوده ورق القطن

من القطن

نيره سمير المصري

معهد بحوث وقاية النباتات - مركز البحث الزراعي - مصر

في السنوات الأخيرة، أصبحت بقايا المبيدات تشكل خطراً على السلسلة الغذائية، البيئة، وصحة الإنسان. تم استخدام بعض أكاسيد النانو المعدنية مع مبيدات الآفات لحل هذه المشاكل وتعزيز نشاط المبيدات الحشرية. هذه التكنولوجيا الجديدة للتمعدن الكامل لمبيدات الآفات ضرورية لتحويلها إلى أشكال غير سامة. في هذه الدراسة، درسنا التأثير التآزر لجسيمات النانو لأكسيد الزنك مع بعض مبيدات عائلة النيونيكوتينويد مثل كيمكس 25% وآكتر 25% لمكافحة يرقات دوده ورق القطن (الطور الرابع) وحشرة من القطن. تم السماح لأفات القطن هذه بالتعقيبة على أوراق الخروع بعد تشريها بالمبيدات الحشرية بالمعدل الموصى به ومع أضافته مركب أكسيد الزنك في حجم النانو. أظهرت النتائج زيادة في معدل الوفيات (57.97% تزيد المستفيدين). أدت إضافة الجسيمات النانوية لأكسيد الزنك إلى المبيدات الحشرية إلى زيادة النشاط المبيدات الحشرية وتدفق نسبة أفات القطن المختارة. وتتم التعرف على شكل أكسيد الفلز النانو المركب بطرق متعددة مثل التحليل الطيفي (FTIR) والميكرسكوب الإلكتروني (TEM) و الأشعة فوق البنفسجية(UV) لتحديد شكل و نطاق الجسيمات النانوية لأكسيد الزنك المحضر. تشير هذه الدراسة الحالية إلى أن أكاسيد معدن الزنك يستخدم كمواد نانوية صديقة للبيئة في مجال مكافحة الآفات.