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Innovative Enhancement of Zinc Oxide Nanoparticles (ZnO-NPs) Toxicity for Effective Weevils Control

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ABSTRACT
The research elucidates the innovative toxicity enhancement of ZnO NPs using a low-level laser of 405 nm wavelength (Ths-1220, China) for cowpea weevil control. Two batches of ZnO NPs were subjected to 15 and 30 minutes of laser irradiation. Irradiations were carried out in borosilicate glass test tubes using a 500 mW power laser beam spot of 4.0 mm. The 100 grams of non-infested cowpea samples were weighed in six replicates (R1, R2, R3, R4, R5, and R6) and a control. 90 active weevils (Callosbruchus maculatus) were obtained from an infested source of cowpea. The first batch of 15 minutes irradiated ZnO NPs was applied to the healthy beans in R1-R3, and the second batch of 30 minutes to R4-R6, likewise, the control. Replicates in the first batch registered weight losses between 0.70% and 1.20%, whereas the second batch showed minimal losses between 0.02% and 0.05%. By contrast, the control group experienced higher weight loss, between 1.10% and 2.80%. Statistical analysis via ANOVA did not reveal significant variations between groups and the Levene test indicated significant heterogeneity of variances (Sig. = 0.007). The application effect demonstrated a mortality rate of 99% compared to 70% in the 15-minute and 30-minute irradiated sample treatment groups, respectively, and 40% in the control group within 3 days. It is plausible that the 15-minute exposure delivered a concentration of nanoparticles sufficient to induce acute toxicity, facilitating maximal interaction without oversaturation. Therefore, exhibiting ZnO NPs with promising insecticidal properties against weevils, resulting in optimal maximal mortality.

Keywords:
Cowpea (Beans),
Weevils,
Low-Level Laser,
Zinc Oxide Nanoparticles,
Irradiation,
Mortality rate.

INTRODUCTION

Cowpea (*Vigna unguilata* (L) Walp) is one of the most popular grain legumes in Africa as well as in some regions of America and Asia. The main subspecies is *Vigna unguiculata* (L) Walp. subsp.unguiculata (L) Walp. Cowpea is often called "black-eye pea" due to its black- or black- brown-ringed hilum; it can also be"hungry-season crop" because it is the first crop to be harvested before the cereal crops (Gomez, 2004). Its fresh or dried seeds, pods, and leaves are commonly used as human foodSince they are highly valuable as a source of plant protein, occasionally utilized to feed livestock, but the hay and silage can be an important fodder. Moreover, they have great flexibility in use: farmers can choose to harvest them for grains or livestock, depending on economic or climatic constraints (Gomez, 2004). Dual-purpose varieties have been developed in order to provide both grain and fodder while suiting the different cropping systems encountered in Africa. Cowpea by-products, such as cowpea seed waste and cowpea hulls (which result from hulling of the seeds for food), have been used to replace conventional feedstuffs in some developing countries (Ikechukwu, 2000).

Cowpea grows in the savannah vegetation at temperatures ranging from 25ºC – 35ºC and in areas where annual rainfall ranges from 750 mm to 110 mm (Madambo et al., 2006) and is tolerant of shading, which can be combined with tall cereal plants such as sorghum and maize (FAO, 2013). It also grows on a wide range of soils provided they are well-drained (Madamba et al., 2006). One of the major problems facing the agricultural sector is the control of pests and insects, which cause serious damage to the bean crop, leading to substantial losses. The bean weevil c*allosbruchus maculatus*) *is* a common pest that infests cowpea and most leguminous crops in Nigeria and most other countries. Most traditional pest control techniques the use of synthetic or petroleum-based pesticides, which have raised great concerns and caused adverse effects on human health and the ecological environment. Thus, it is necessary to explore alternative approaches such as bio-based, renewable, and sustainable materials approache to manage pest infestation of cowpea effectively.

In this regard, Zinc Oxide nanoparticles (ZnO NPs) have in recent times attracted meaningful attention due to their potential applications in various fields, including pest management. The word "nano" emerged from the Greek word "dwarf". Nanoparticles refer to materials having nanoscale external dimensions or internal structures and have a nanoscale size upper limit of about 100nm (Bhattachayya et al., 2010; Anandhi et al., 2020). ZnO NPs are known for their biocompatibility, photocatalytic properties, and antimicrobial activity. These properties make them attractive for pest control applications. However, to solve the problem posed by the bean weevil, it is important to enhance the toxicity of ZnO NPs using laser irradiation (Qi et al 2017). Laser radiation technology is a well-established technique that has been widely used for various purposes such as preservation, sterilization, and pest control. It involves the use of a relatively low-energy laser beams to induce changes in the biological properties of organisms. Laser radiation can be applied to ZnO NPs through a controlled and regulated process to enhance their potency. The enhanced toxicity of ZnO NPs can change the size, surface charge, and reactive oxygen species (ROS). These modifications, to a large extent, influence the toxicity of ZnO NPs, making them more potent against bean weevil (Yin et al., 2010, Biswas et al., 2022).

Gutiérrez-Ramírez et al. (2021) researchedzinc oxide nanoparticles (NPs), whichgenerated an alternative pest control. According to the work, which was to evaluate the insecticidal effect of zinc oxide nanoparticles (ZnO NPs), titanium dioxide nanoparticles (TiO_2 NPs), and their combination on *Bactericera cockerelli* (Hemiptera: Triozidae) second-stage nymphs under laboratory and greenhouse conditions in tomato. This experimental research was carried out with the bioassay method of leaf immersion under a completely randomized design, and in the greenhouse by direct plant spraying under a randomized block design; in both designs, a control without NPs was added. Mortality was recorded every 24 hours for 4 days. Both NPs in the laboratory and greenhouse showed toxicity to *B. cockerelli* nymphs. Their laboratory results demonstrated that nanoparticles significantly resulted in increased mortality of 88, 99, and 100 % 96 hours after ZnO NPs, TiO_2 NPs, and their combination treatments, at 1000, 100, and 250 ppm, respectively. Their direct spraying of plants in the greenhouse demonstrated low mortality with 27, 32, and 23% after 96 h of ZnO NPs, TiO_2 NPs, and their combinations, at 3000, 500, and 250 ppm, respectively. These results on *B. cockerelli* control seem promising. Nanoparticles as insecticides are a novel strategy; however, further investigation is required in field tests to obtain suitable efficacy for use in a pest management system (Gutiérrez-Ramírezal et al. 2021).

Another research was carried out by Pittarate et al. (2021) on the Fall armyworm, which has devastating effects on several crops around the world, especially maize, which is commonly grown and of high importance globally. According to their study, ZnO NPs in have been demonstrated to be efficacious against several insect pests, of which some are in the same genus as SPODOPTERA FRUGIPERDA. Their study aimed to find out the insecticidal effects of ZnO nanoparticles on SPODOPTERA FRUGIPERDA under laboratory conditions. They observed body deformations, reduced fecundity, reduced oviposition, and mortality when insects were fed on food treated with several concentrations of ZnO nanoparticles, yet the ones fed on the control were normal in all aspects. Therefore, they recommended ZnO nanoparticles for further studies to use them as an alternative control agent against fall armyworms under field conditions (Pittarate et al., 2021; Ruiz-Aguilar, et. al.,2025).

Moreover, Eskinet al. (2022), discovered that ZnO NPs have the ability to absorb UV radiation and possess catalytic, antibacterial, and semiconducting properties, making them increasingly being used in consumer goods. Because nanoparticles are used so often, accurate methods for determining any associated toxicity are crucial. The greater wax moth, *Galleria mellonella* (L.) (Lepidoptera: Pyralidae) is a suitable experimental model organism because to immune defense of the larvae is very strong. Also, larvae are a good model for carrying out toxicity studies. In this study, to determine the effects of ZnO NPs on the biology (larval development time, the weight of the last stage larvae, the pupal development time, the pupal weight, the eclosion rate, the maturation period, the adult weights, the adult longevity, and the percentage of adults) of *G. mellonella*, zinc oxide NPs were added to the larvae diet (honeycomb) at different doses (100, 500, 1000, 3000, and 5000 ppm). Their experimental results demonstrated that pupal weights decreased significantly at 1000, 3000, and 5000 ppm doses of ZnO nanoparticles

compared with the control. The weight of adults improved at 100 ppm ZnO nanoparticles, and the *G. mellonella* showed longevity in the 5000 ppm ZnO nanoparticles exposed group, which was longer than the control group. Lastly, there was an average male longevity extended in 500, 1000, 3000, and 5000 ppm groups of ZnO nanoparticles, comparable to the group of control group (Eskinet al., 2022).

Observing the efficacy of the ZnO NPs controlling these pests, there still exists a challenge to most farmers due to pests' ability to breed faster and their resistance tendency to synthetic pesticides, as well as other factors. However, synthetic pesticides have been a threat to the farmlands, the environment, and human ecosystem; hence, there arises a need to explore deeper alternative research using ZnO nanoparticles. The experimental research is expected to unravel the underlying mechanisms such as nanoparticle dispersion, dosage optimization, and potential plant-nanoparticle interactions - to better harness ZnO NPs in agricultural applications. Therefore, this study will elucidate the proposed multi-disciplinary approach by studying ZnO NPs modification on weevils' bioassay to explore how best it will be explored in addressing the international challenges of postharvest losses due to weevils and general insecticidal attacks, meanwhile improving food security and resource control.

MATERIALS AND METHODS

Samples Collection, and Equipment Description

The following materials were used for the research work: Zinc Oxide Nanoparticles Nanografi, Turkey), cowpea (Vigna unguilata), a 405 nm diode laser device (Ths-1220, China), laboratory test tubes, bean weevil (Callosbruchus maculatus), cylindrical transparent plastic containers, spatula, precision weighing balance, a black piece of cloth, retort stand, masking tape, safety goggles, white piece of cloth. The experimental research was carried out at the Postgraduate laboratory, Biological Science Department, Benue State University, Makurdi, Nigeria, under laboratory conditions.

25g of Zinc Oxide (ZnO) Nano powder (Purity: > 99.5%, 1,400.00, Cat. No.: NG04SO3802G25). The diode laser device used in this work has a low level of continuous mode of 405 nm laser beam, with a beam spot of 4.0 mm. It has a power of 500 mW at a distance (d) of 10cm.

Zinc Oxide Nanoparticles (ZnO NPs) Irradiation

ZnO NPs samples of size 30 – 50 nm with a percentage purity of 99.9% were used. 1g of ZnO NPs was weighed on a precision weighing balance and stored in a plastic waterproof bag and sealed in twenty (20) bags of 1g of ZnO NPs were obtained as shown in Figure 1.

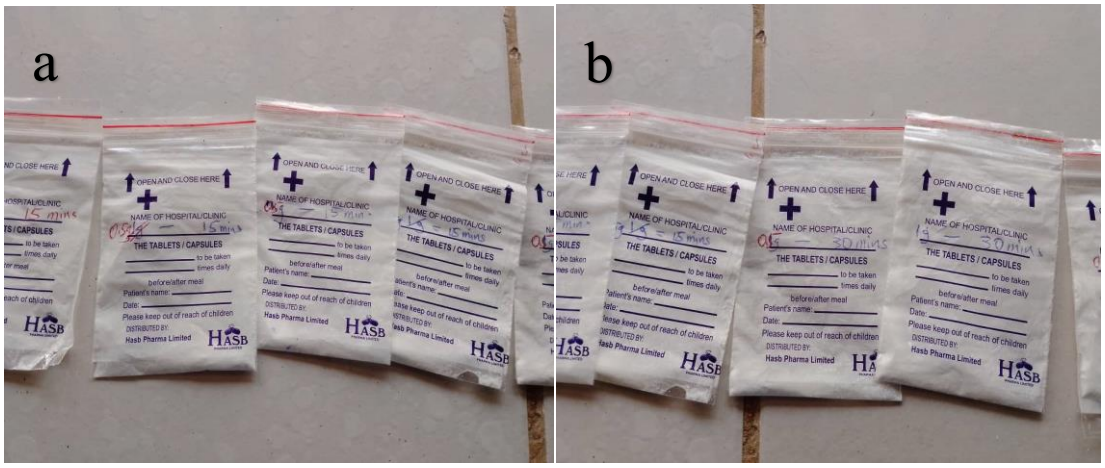


Figure 1: Irradiated samples in plastic bags at (a) 15 minutes and (b) 30 minutes

The 1g samples of ZnO NPs were divided into three groups: first group was irradiated for 15 minutes, the second group was irradiated for 30 minutes, and the third group was considered as Control (un-irradiated). A Glass laboratory test tube, retort stand, and a low-level laser (LLL) of continuous mode of 405 nm wavelength were used. The first two groups were each irradiated with a laser beam spot of 4.0 mm. The irradiation process was carried out at a power output of 500 mW at a distance (h) of 10 cm from the sample, as highlighted in Figure 2.

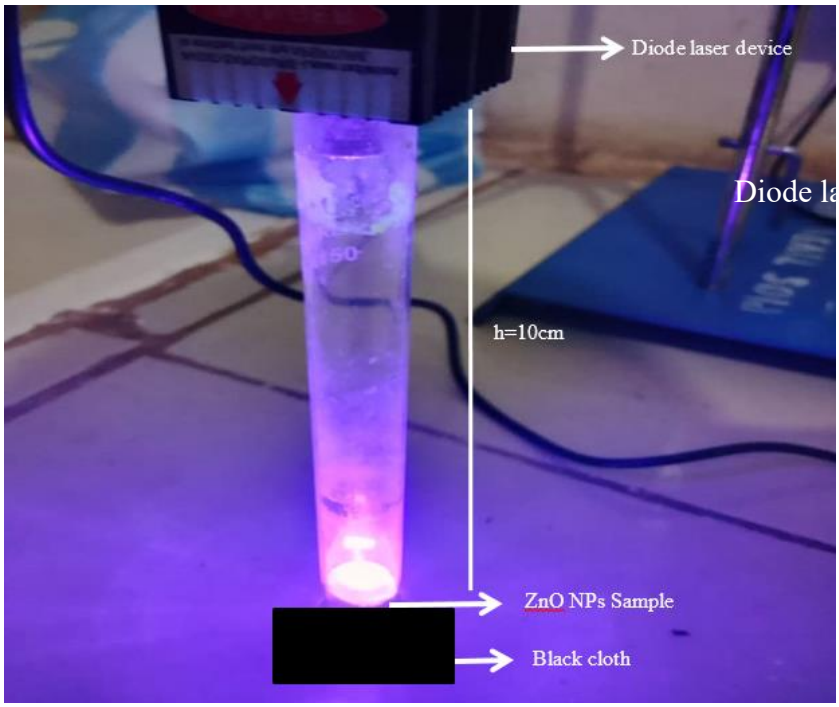


Figure 2: Shows samples irradiation above a black cloth to prevent laser light reflection

Zinc Oxide Nanoparticle Characterization

The Zinc oxide nano particles characterization was carried out before and after laser irradiation to observe structural and physicochemical modification. The Field Emission Scanning Electron Microscope (FESEM) & Energy Dispersive X-ray (EDX) Spectroscopy were carried out on the samples. The X-Ray Diffraction (XRD) and uv-vis spectrophotometer were also used to observe the samples' laser light absorption.

Cowpea (white shade) Harvesting and Preparation for Treatment

The cowpea was harvested within the State and not treated with any conventional pesticides to the experiment. The 100g of non-infested (without weevils) cowpea(bean) samples were also weighed using the precision weighing balance and placed in transparent cylindrical plastic containers in six replicates, R (R1, R2, R3, R4, R5, R6) and a control as shown in Figure 3 below:



Figure 3: Inoculated Samples of Cowpea treated with ZnO NPs

Weevil Collection and application of ZnO NPs on the harvested Cowpea

The bean weevils (Callosbruchus maculatus) were obtained from an infested source of cowpea. A total of 90 healthy and active ones were harvested for the research work.

The application of the irradiated and non-irradiated samples of Zinc Oxide Nanoparticles (ZnO Nps) on the non-infested cowpea was done at the Research Laboratory and was monitored for the period of twenty-one (21) days. Each day, was used to observe the mortality rate of the weevils was observed hourly, and the mortality of the weevils was monitored for three days. The masses of the samples(replicates) of the cowpeas were weighed after every seven days to note any change in mass. The batch of 15-minute irradiated ZnO Nps was applied on the healthy beans in three different replicates (R1, R2and R3). The next batch of 30 minutes was also applied to the healthy beans in three replicates (R4, R5, and R6). The non-irradiated ZnO Nps were applied on the healthy beans as a Control and observed alongside the others from day one (1). The application of the ZnO Nps was done inside cylindrical transparent containers and covered with white cotton muslin clothes that were not air-proof and tightened with rubber bands as shown in Figure 4.



Figure 4: Innoculated Compea Samples treated with 15 mins, 30 mins irradiated ZnO Nps and the Control

The above cleaned and treated cowpea seed packaged in transparent plastic containers were stored at room temperature (27 °C). The experimental insecticidal weevils were bred from a sample obtained from infested stored grain supplied by a local farmer. The thirty (30) weevils were transferred into the plastic containers containing 100g of cowpea grain, thereafter covered with a white muslin cotton cloth and kept in a room at 25 ± 5°C and allowed to stand for 21 days. In the first experiment, 100 g of cowpea was inoculated with the 15-minute ZnO Nps in three replicates and was transferred into a litre jar and infested with 30 adult *C. maculatus*. The jar was covered with a piece of muslin cloth and firmly secured with a rubber band. Another three replicates were established and inoculated with the 30-minute ZnO Nps and transferred into a jar and infested with 30 adult C. maculatus. The jar was covered with a muslin cloth and firmly secured with a rubber band. The setup was monitored for 21 days. The percentage weight loss of each setup(cowpea) was determined after every seven (7) days.

Data on percentage weight loss were computed according to the following Equation 1:

$$SWL = \frac{ISW - FSW}{ISW} \times 100\% \quad (1)$$

where SWL is the percentage seed weight loss, ISW is the initial seed weight, and FSW is the final seed weight.

The mortality rate of the weevil was monitored hourly for three days (72 hours).

RESULTS AND DISCUSSION

To obtain the research results, proper observation was carried out on the prepared uninfected obtained white-coloured cowpea seeds (weighing 100g) used for the following research data.

Effect of Irradiated Zinc Oxide Nanoparticles on Weight Loss in Cowpea and the mortality of weevils

The research elucidated the mortality rate following treatment of 100 g of cowpea inoculated with the 15 and 30 minutes irradiated ZnO NPs using low-level laser and

treatmenttreatment using the controlled ZnO NPs, all in three replicates, transferred into a litre jar and infested with 30 adult *C. maculatus*.

Effect of ZnO Nps on weevils

The mortality rate of the weevil was monitored hourly for three days (72 hours) as shown below in Table 1. Samples of weevils were exposed to ZnO NPs under three conditions: a 15-minute treatment, a 30-minute treatment, and a control condition with no nanoparticle exposure. Over the three-day observation period, these groups' mortality rates varied noticeably. In particular, the 15-minute treatment group experienced the highest mortality, with 29 out of 30 weevils dying by the third day, compared to 23 in the 30-minute group and 22 in the control group. This suggests that there might be an optimal concentration or exposure duration for ZnO NP effectiveness. One possibility is that shorter exposures prevent nanoparticle agglomeration, thereby ensuring better dispersion and bioavailability, while prolonged exposure could reduce their efficiency through aggregation or allow for adaptive responses in the weevils.

The higher mortality rate of weevils was observed in the group exposed to 15 minutes irradiated ZnO NPs, in contrast to the 30 minutes of exposure and the Control group, which may initially appear counterintuitive. However, this result could be attributed to an optimal dosage effect. It is plausible that the 15-minute exposure delivered a concentration of nanoparticles sufficient to induce acute toxicity, facilitating maximal interaction without oversaturation. Conversely, prolonged exposure may have resulted in nanoparticle agglomeration, leading to a reduction in their effective surface area and, consequently, diminished efficacy. The larger aggregates formed during extended exposure periods may exhibit reduced bioavailability, thereby decreasing their capacity to penetrate the weevils' cuticle or access their respiratory system.

Table 1: The effect of Zinc Oxide nanoparticles on weevils

ZnO NPs	No of sample insects (Active)	Mortality rate per day			Total
		Day 1	Day 2	Day 3	
15min	30	10	8	11	29
30min	30	5	9	9	23
Control	30	1	4	7	12

Effect of ZnO NPs on the mass of cowpea

The effect of ZnO NPs on the weight of cowpeas was observed over a three-week period as presented in Table 2. The cowpea samples were divided into groups corresponding to 15-minute and 30-minute ZnO NP treatments, alongside a control group. All samples started at 100 grams, and subsequent measurements showed minor variations in weight loss percentages across the groups. The replicates in the 15-minute treatment group registered weight losses of approximately 0.70% to 1.20%, whereas the 30-minute group displayed minimal losses ranging from 0.02% to 0.05%. By contrast, the control group experienced higher weight loss, ranging from about 1.10% to 2.80%. Despite these observable differences, statistical analysis via ANOVA did not reveal significant variations between groups (ANOVA Sig. = 0.227), and the Levene test indicated significant heterogeneity of variances (Sig. = 0.007). Additional robust tests like Welch's and the Games-Howell post hoc comparisons also found no significant pairwise differences. This suggests that while there may be a trend toward reduced weight loss in the ZnO NP treated groups—particularly the 30-minute treatment—the effect on cowpea mass is not statistically significant under the conditions of this experiment.

In terms of the cowpea weight retention, the samples treated with ZnO NPs, particularly those in the 30-minute group, experienced less weight loss over three weeks than the control group. This suggests that ZnO NPs may offer a preservative effect. The nanoparticles can inhibit the growth of spoilage organisms such as those observed with weevils, which are major contributors to post-harvest losses in legumes. This insecticidal action could have slowed down the processes responsible for the degradation of cowpea, thereby preserving mass over time. Additionally, ZnO NPs may serve as a physical barrier, reducing moisture loss and limiting oxidation by forming a protective coating on the seed surface.

Overall, the results indicate that ZnO nanoparticles exhibit promising insecticidal properties against weevils, with an optimal application window potentially around 15 minutes for maximal mortality. For cowpea, however, the nanoparticles seem to offer limited preservation benefits, as the reduction in weight loss does not reach statistical significance. These findings warrant further research to understand the underlying mechanisms—such as nanoparticle dispersion, dosage optimization, and potential plant-nanoparticle interactions—to better harness ZnO NPs in agricultural applications.

Table 2: Percentage Weight Loss for Zinc Oxide Treated Cowpea

ZnO Np Group	Replicates	Weights(gram) per week				Percentage weight loss (%)
		1	7	14	21	
15mins	R1	100	100	100	99.30	0.70
	R2	100	100	99.91	98.98	1.02
	R3	100	100	99.23	98.80	1.20
30mins	R4	100	100	98.97	97.01	0.03
	R5	100	100	99.98	98.25	0.02
	R6	100	100	98.95	96.50	0.05
Control	R7	100	100	99.60	97.20	2.80
	R8	100	100	99.50	98.90	1.10
	R9	100	100	99.91	97.99	2.01

Table 3: Test of Homogeneity of Variances for weight

Test of Homogeneity of Variances for weight			
Levene Statistic	**df1**	**df2**	**Sig.**
5.701	2	33	.007

Table 4: ANOVA Test for Weights Variation of Cowpea

ANOVA FOR WEIGHT					
	Sum of Squares	**df**	**Mean Square**	**F**	**Sig.**
Between Groups	2.270	2	1.135	1.552	0.227
Within Groups	24.135	33	0.731		
Total	26.405	35			

Table 5: Welch's Robust Test for Equality of Means

Robust Tests of Equality of Means				
	Statistic[a]	**df1**	**df2**	**Sig.**
Welch	.973	2	20.050	.395

a. Asymptotically F distributed.

Zinc Oxide Nanoparticle Characterization

Structural and optical properties of the NPs were evaluated to examine the physicochemical modifications of the zinc oxide before and after laser radiation. The examinations made clearer the modifications of the various durations of 15 and 30 minutes laser exposures, and compared with the controlled (non-irradiated) conditions.

UV-Visible Spectroscopy was carried out using a spectrophotometer (Shimadzu UV-1800, Japan) to analyse the absorption spectra of the ZnO NPs across wavelengths ranging from 200 to 800 nm. The elemental composition, morphology, and size of the nanoparticles were examined using an ultra-high resolution scanning electron microscope (SEM) (Hitachi, Japan) operated at 5 kV, coupled with an energy-dispersive X-ray spectroscopy (EDX) (Oxford Instruments X-Max, UK), and the crystalline quality of the NPs was viewed using X-ray diffraction (XRD) (Bruker A8 Advance, Germany) with a Cukα anode (λCukα = 1.54 Å).

UV-Vis Spectrophotometer

The UV-Vis (UV-1800 Spectrophotometer, Shimadzu, Japan) spectrophotometer was used. The graph illustrates the absorbance spectra of ZnO nanoparticles (ZnO NPs) before and after laser irradiation. The non-irradiated sample shows a broad absorption band with a peak close to 378 nm, corresponding to the energy band gap of ZnO, which excites electrons from the valence to the conduction band. After 15 minutes of irradiation (G15), an increase in absorbance across the entire wavelength range is observed, showing the formation of defects or impurities within the ZnO NPs, which act as additional sites for light absorption. An increase in absorbance is evident after 30 minutes of irradiation (G30), suggesting cumulative defect formation. The steady rise in absorption intensity, with G30 exhibiting the highest absorbance, reflects enhanced optical activity due to laser exposure (Atta et al., 2024). In addition, a slight red shift in the absorption peak from 374 nm (non-irradiated) to 378 nm (G30) suggests modifications in electronic structure caused by laser treatment (Abdelghani et al., 2022). The introduction of defects within the crystal lattice produces localized states in the band-gap, aiding light absorption at energies lower than the original band-gap. WiderWider absorption bands in irradiated ZnO Nps samples reflect increased lattice disorder, while cumulative defects explain both the red shift and enhanced absorption in the

visible region. Surface defects and oxygen vacancies at wavelengths of 399.86 nm and 422.18 nm, along with increased surface roughness and modified crystallinity, contribute to these changes (Farooq et al., 2014).

Laser irradiation also changes the surface structure and crystallite size, affecting the electron de-excitation pathways and improving light absorption across the visible spectrum (Abdelghani et al., 2022). Changes in the surface-to-volume ratio, grain boundaries, and root mean square roughness of the nanoparticles change their reflectance and refractive index, more and more improving their optical properties (Adelghani et al., 2022), (Asif et al., 2022). The structural and electronic changes caused by laser irradiation directly contribute to the observed improvements in light absorption, as shown by the modified optical spectra and electronic characteristics of irradiated ZnO NPs.

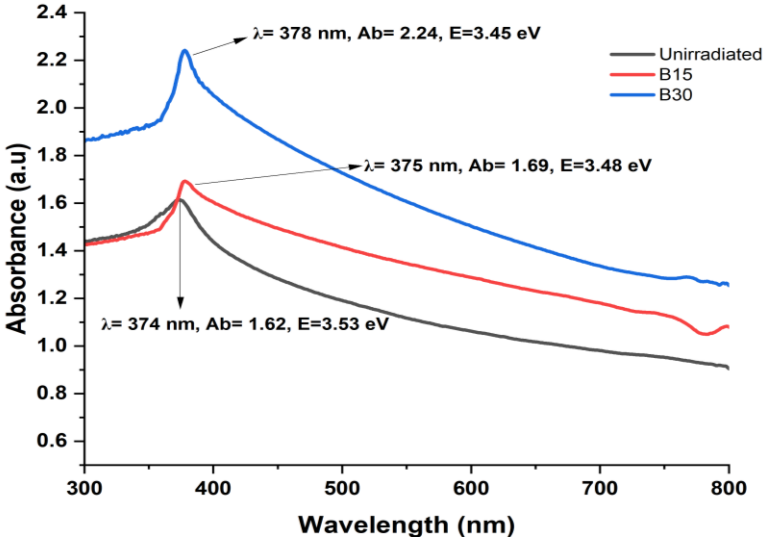


Figure 5: ZnO Nanoparticles Absorbance spectra before and after laser irradiation

Field Emission Scanning Electron Microscope (FESEM) & Energy Dispersive X-ray (EDX) Spectroscopy

The FESEM model (FEI Nova NanoSEM 450) was used to examine the structural and morphological properties of the ZnO NPs, while EDX spectra show the atomic and weight percentage composition of Zn and O elements. The mean particle size distribution of the samples was calculated using ImageJ software. Figure 6 shows the result of the FESEM and EDX of unirradiated and irradiated ZnO NPs. Unirradiated ZnO NPs showed a relatively uniform distribution with some agglomeration, with the O: Zn ratio of 0.81, typical of ZnO synthesized through conventional methods (Asif et al, 2022~~0~~). The morphology indicates a nanoscale structure with minimal surface modifications, as expected in samples not subjected to external sources like laser irradiation. Figure 7 shows the particle size distribution of all samples. The mean particle size for the unirradiated sample was calculated to be approximately 21.75 nm, with most particles falling within the 1-20 nm size range. This reflects the natural size distribution of ZnO NPs without external modification (~~P.~~Sabel et al., 2022).

After 15 minutes of blue laser irradiation (G15), the FESEM images show observable microstructural changes, including a slight increase in surface roughness and particle dispersion (~~P.~~ Mahamuniet al, 2019). This shows the initiation of surface modifications and defect formation. The O: Zn ratios increase from 0.81 to 0.94, suggesting enhanced oxygen incorporation or surface oxidation (Mazar et al., 2022). These changes are caused by the interaction of laser energy with the ZnO lattice, leading to structural rearrangements and surface energy variations (Bayram et al,2019). After 15 minutes of irradiation, the mean particle size decreases slightly to 17.95, with a significant portion of particles still within the 1-20 nm range. This reduction suggests that the laser energy induces partial fragmentation of the larger particles or modifies their morphology, creating smaller and more uniform particles (Jayachandran et al., 2021).

Prolonged irradiation for 30 minutes (B30) results in more pronounced surface roughness and morphological changes. The particles exhibit increased disorder and surface defects due to the cumulative effects of laser energy. These modifications suggest enhanced structural activity, which can influence the material's optical and electronic properties (Jayachandran et al., 2021). Thus decreased the O: Zn ratio to 0.78. For the G30 sample, the mean particle size increases slightly to 19.70 nm, likely due to particle agglomeration caused by prolonged irradiation. Although some particles remain small, others merge into larger aggregates, which is reflected in the

increased particle count in higher size intervals (Bayram et al., 2019).

The particle size distribution and the creation of defects directly correlate with enhanced optical activity. Smaller particles with higher surface areas exhibit increased light absorption, while the oxygen vacancies and surface modifications further enhance the visible light absorption, making the material suitable for applications like photocatalysis or optoelectronics.

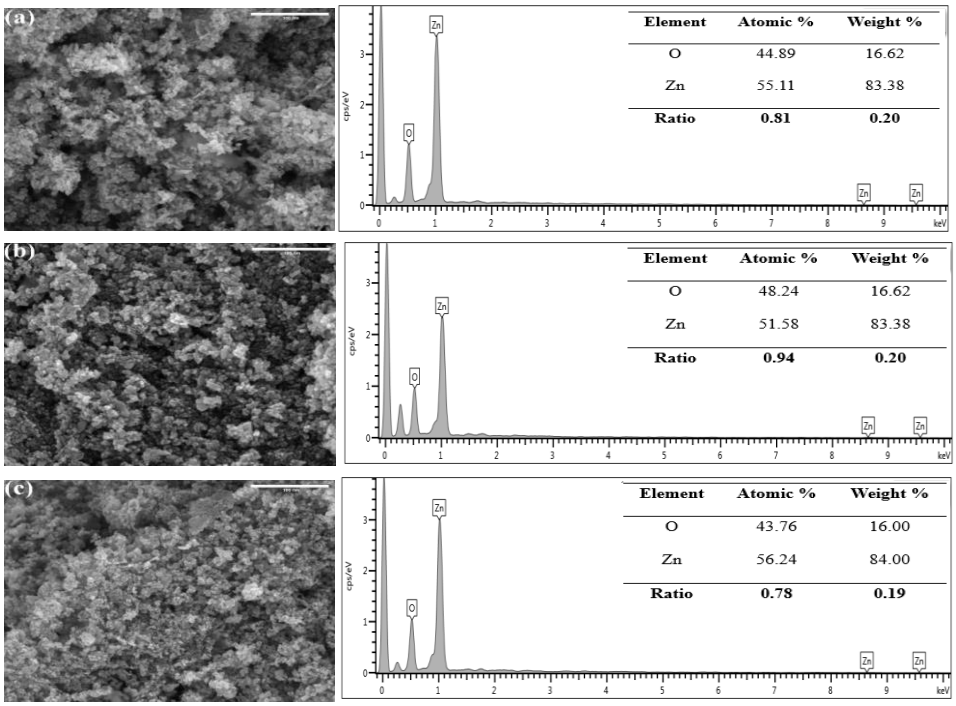


Figure 6: The figure elucidates the FESEM and EDX of non-irradiated and irradiated ZnO NPs

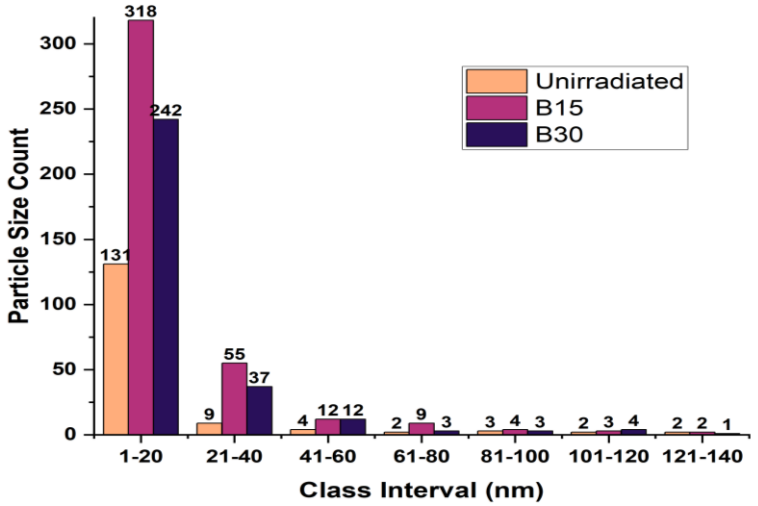


Figure 7: Shows the distribution of particle sizes and defect creation

X-Ray Diffraction (XRD)

The XRD (Bruker A8 Advance, Germany) patterns showed the crystalline structure analysis of ZnO nanoparticles under different blue laser exposure times. The diffraction peaks at (100), (002), (101), (102), (110), (103), (200), (112), and (201) planes correspond to the typical hexagonal wurtzite structure of ZnO (Farooq et al., 2013). The average crystallite sizes show a decreasing trend with increased laser exposure time, which were 16.08 nm, 15.65 nm, and 15.45 nm for unirradiated samples, B15, and B30, respectively. This reduction in crystallite size indicates that blue laser irradiation causes slight structural modifications in the ZnO NPs due to attribute of the thermal effects induced by laser

irradiation, which leads to slight deformation and restructuring of the crystal lattice (Abdelghani et al., 2022). The high-intensity peaks with reduced full width at half maximum (FWHM) suggest good crystallinity of the samples (Khorsand et al., 2011).

Peak intensity of the XRD patterns demonstrates that the peak positions remain unchanged across all samples, confirming the preservation of the wurtzite crystal structure. Peak intensities increase with longer exposure times, suggesting enhanced crystallinity. The sharpness of the peaks indicates good crystallinity in all samples, with the strongest peaks corresponding to (100), (002), and (101) planes. The consistent peak position but varying intensities suggest that while the blue laser treatment affects the crystal growth, it does not alter the fundamental crystal structure of the ZnO NPs. The slight variations in crysatllite size after different durations of laser exposure indicate that the laser-induced modifications are time-dependent (Abdelghani et al., 2022).

Table 6: XRD patterns demonstrating the crystalline structure analysis of ZnO Nps.

ZnO NPs Samples	Average Cryatallite Size, D (nm)
Unirradiated	16.08
B15	15.65
B30	15.45

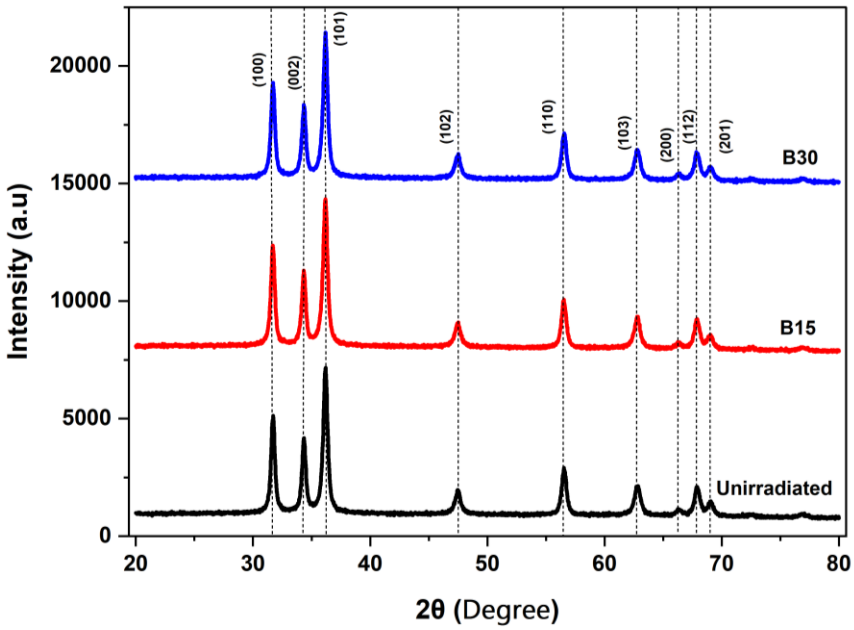


Figure 8: XRD patterns showing their peak intensity

CONCLUSION

The weevils were subject to various treatments of the laser-irradiated ZnO NPs, and there was a significant difference in the mortality rate, especially in the 15-minute irradiated Zinc Oxide Nanoparticles. Weevils subjected to the treatments with the 15mins irradiated ZnO Nps mortality recorded at the first, second, and third days of about 33.33%, 26.67%, and 36.67% mortality rate recorded respectively. This was monitored hourly. The 30mins irradiated ZnO Nps showed a low mortality rate, quite below the 15-minute irradiated ZnO Nps. While the control had a mortality rate slightly above the 30 minutes irradiated ZnO Nps.There was significant difference in the mortality rate between the treatments of 15mins and 30minutes irradiated ZnO Nps and the control. The study has therefore shown that modified Zinc Oxides Nps using the appropriate wavelength and power can be efficient for weevil control.

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