Titanium dioxide (TiO2) nanoparticles were synthesised and characterized in order to test their effectiveness against two predatory insects

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Abstract- Nanosciences and microbiology are the research of extremely small objects on a nm scale. Tribolium Castaneum and Trogoderma Granarium isolates of various ages have been reported from the Lahore commodity market. For each of the two insects, the population had been acclimated to the laboratory. To maintain a homogenous population, pupa of the same age were collected during insect development and placed in separate plastic jars until adult emergence (2 weeks). Following the extraction of plant components, the biosynthesis of titanium-particles was carried out according to the standard technique. Toxicity Bioassays were conducted using three different plant extract concentrations (5, 10%, and 15%) (For both of the basic plant oils as well as nano-particles). After 24, 48, and 72 hours of care, mortality was determined. Tribolium Castaneum has the highest mortality rate (15.10%) and the lowest mortality rate (15.10%). (46.12%). The highest death rates were 40.40 and 33.68 percent for TiO2 nanoparticles, respectively. Repellency bioassays using the area preference method (TiO2) revealed 86.10% and 72.64 percent repellency against Tribolium Castaneum and Trogoderma Granarium, respectively. The data from all bioassays were analyzed using a factorial design with a CRD statistical design.

I. INTRODUCTION

Nanosciences is a rapidly emerging and technologically advanced field of study that encompasses fundamental elements and recognizes and advances the evolving process of processing materials that include only one component. This has the ability to control individual molecules and atoms. This is one of the most significant technological advancements of the previous few decades [1]. Nanoparticles (Nanopowder, Nano ring, Nanocrystal) are the Nanoscience small building block [2]. It also used as a biomedical, optical and electronic field. The nanoparticle has been work very successfully in the field of medicine, environmental sciences and food processing [3]. Owing to its modern use such as environmental protection, data management, genetics, beauty products, medicines owing to their electronic, physical and magnetic properties, nanoparticles have recently been commercial[4]. In fact, the biosynthesis of nanoparticles is environmentally sustainable, because it can shape the toxic, costly chemicals without the use of them [5]This has also been used as a highly conductive and semi-conductor, medical equipment, sensor insulation, catalytic agents and as a pesticide as well. Nanocarriers are designed to reduce the amount of operation and delay the kinetics of agrochemicals releases [6].

Store grains and their products are attacked by a variety of insects, resulting in significant losses [7]. Crop storage accounted for about 9 percent of losses in industrialized countries and 20 percent in more emerging countries[8].All stored grain insect pests most disreputable is red flour beetle *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae), which is a pervasive pest of the store commodities like wheat flour and crushed cereals, is also the cosmopolitan and most destructive insect pest [9]. *T. granarium* serious pest in the product which retained in the hot and dry conditions, with high relative humidity gives an acute effect on the population and building-up the sound grain pest[10]. Their adults are not dangerous but their larvae are most destructive but their adults are very harmless [11].These larvae feed on sound grain and consume the entire kernel, leaving behind empty grains and husks. The quality of grains reduced due to frass and excreta in damage grains, it can create a negative effects on the atmosphere including infested grain have an adverse impact on human safety [12].

T. Granarium prevents grain from germinating by absorbing different nutrients while it feeds on larvae [13]. Other chemicals like pyrethroids are being also used for the control of stored grains insect-pests, but consistent use of theses insecticides may lead to serious problems related to biochemical and hematological changes in human beings[14]. Conventional insecticides also pose a hazardous effect on non-target organisms including beneficial insects [15]. Due to the potential insecticidal properties botanical is the possible alternative source of pest control[16]. The effect of plant products showed insecticidal, repellent and antifeedant effects against insect pests[17]. In the past years, *T. castaneum* pest can be controlled by Polyethalyen glycol and diatomaceous earth but garlic essential oil can be act as a reducing agent [18].

Preparation of Titanium oxide Nano-particles

To begin, we can prepare the silver nanoparticles in the following manner: Take the powdered leaves of R.communis, Jatropha curcus, and Citrus paradisi acquired at a local market. Deionized water used in all experiments, I took 10g of *R. communis, Jatropha curcus,* and *Citrus paradise* extracts by using weight balance, which can be boiled in 100ml distilled water in 250ml conical flask. Then this extract was cooled at room temperature, Filter into the No. 1 filter paper of Whatman. It filtrate was an act of minimizing and stabilization agent for the preparation of nanoparticles of titanium oxide. Ammonium solution will be added to Titanium oxide (solution followed by the addition of plant material extract 1-10ml) as described in [19].

Bioassay of TiO2 nanoparticles

We can employ a green synthesis method to create titanium nanoparticles. 10ml of plant oil from the stock solution cooked for 30 minutes at 90°C in 50ml double distilled water. Following that, we can filter this extract using Whattman filter paper. We can prepare the 1mM solution of the TiO_2 aqueous solution which can boil at 25°C for 2 hours. Add 10ml of aqueous plant extract into the 20 ml of 1mM TiO2 solution at 25°C heated with 200rpm stirring for 4hours. After 4 hours, the colors of the solution will be changed into lite green and then converted into colorless form. Then we can put the extract for 24 hours in oven for drying at 80°C. Then these precipitates were drying and stored for further analysis [20].

Figure 1.1 *(Titanium-Dioxide Dried nano-composites)*

Table 1: Change in solution color when forming Titanium dioxide nanoparticles using Jatropha curcus, Citrus paradise, and R the herb extracts of Communis.

| Solution	Before Reduction	After Reduction	Color intensity	Time
Jatropha curcus	Dark Yellow			
1mM solution of TiO_2	Transparent	Yellow	+	Immediately
		Pale Yellow	++	After 7 hours
		Off white	+++	After 24 hours
Citrus paradise	Lite Yellow			
1mM solution of TiO_2	Transparent	Green	+	Immediately
		Yellowish	++	After 7 hours
		Pale yellow white	+++	After 24 hours
R. communis				
1mM solution of TiO_2	Transparent	Yellow	+	Immediately
		Pale Yellow	++	After 7 hours
		Off white	+++	After 24 hours
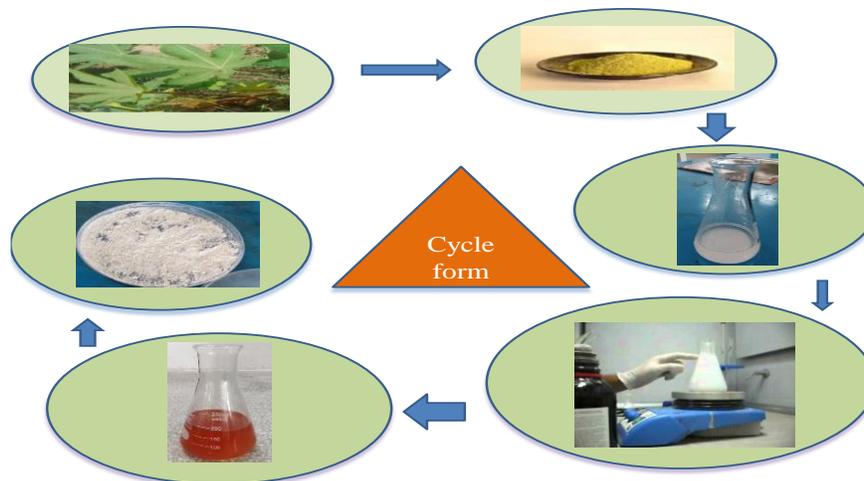
Figure 1.2: Sketch Explanation

CHARACTERIZATION OF NANOPARTICLES

We will use absorption spectra to determine the optimal output of silver nanoparticles. Through the use of a UV-visible spectrophotometer (HITACHI, Model U-2800) we will detect the wavelength of SNP; deionized water serves as a blank solution. The ultimate top point of silver nanoparticle will be in an air-dried shape and atomic-force-microscopy (Model-Nanosurf easy scan 2 AFM, Switzerland) as defined in [21] will be able to classify it.

TOXICITY BIOASSAY

Three herb extracts can be dissolved in the stock solution by using four solvents, their concentration is (15, 10 and 5 %). The concentration is to be hands-on smashed seeds, shook for better concentration delivery. This will allow air to be dried and placed into small plastic bottles. Both species, adults, will be released as defined in a controlled diet that includes jars [22].

Repellency

The mean percentage of repellence was calculated by using a preferential approach. After the filter paper was divided into two parts, one half of each paper was prepared with the extracts from the plants and acetone. After some time, the solution would evaporate, so two halves were inserted and put in a Petri bowl. 20 Tribolium castanium and Trogoderma granarium adults were re-allocated to a filter paper that was screened in the middle. Repellency data were reported respectively after 24, 48 and 72 hours [23].

Results and discussion

The studies have been repeated in thrice along with the control factor under different designs Fully Randomized Design (CRD) with all the various treatments. Plant extracts have been used at three different concentration levels, i.e. 5, 10 and 15 %, mortality results should be observed after 24, 48 and 72 hours of application of medication. At the same product type/rate of plant extracts, we had independently performed the experiments on repellence and growth inhibition. The data were collected about larval inhibition, pupa; inhibition and adult inhibition at daily intervals, while the repellency data was reported at 24 hrs.

WITH Titanium dioxide NANO-PARTICLES against *Tribolium castanium*

II. MORTALITY DATA AFTER EXPOSURE OF 24 HRS

To measure T-mortality. Castaneum, homogeneous adults were introduced into small plastic jars on a controlled diet. Adults were required to feed on controlled diets, and mortality data were reported. Wheat grains were used as diet and three concentrations of each plant extract were used viz., 5, 10 and 15%. Mortality data were recorded for 24, 48 and 72 h of the exposure period. Insects were held at 30 ± 2^0 C and 60 ± 5 per cent RH in incubators for mortality assessment. They repeated each operation and control three times.

Table 2.1 Reveals the variance analysis (ANOVA) of data on mean T percent mortality. Castaneum at various Jatropha curcus, Citrus paradise, and R concentrations. Commons.

Data showed that main effects, plants (F=4.66; df=1: p<0.05) and concentration (F=11.10 df=;2 p<0.05) were significant regarding mortality values of *T. castaneum* after an exposure period of 24 hours.

Table 2.1 Analysis of variance (ANOVA) of the data concerning % mortality of *Tribolium castaneum* (Herbst) for Titanium dioxide-based nano-particles

S.O.V	DF	SS	MSS	F value
Plant	2	555.807	277.904	38.4000**
Concentration(Conc.)	2	480.691	240.345	33.2103**
Plant*Concentration	4	65.422	16.355	2.2600
Error	18	130.267	7.237	
Total	26	1232.187		

Table 2.2 Comparison of the mean percentage mortality of *Tribolium castaneum* after exposure to different concentrations of plant extracts after 24 hrs

Concentrations (%)	Mean percentage of mortality ± SE
5	5.81±1.49
10	14.18±2.30
15	22.58±4.77

Data in table 2.1 Represents the insecticidal effect of different concentrations of 3 different oil against *Tribolium castaneum*. The experimental data revealed that maximum mortality (22.58%) at 15% was recorded. The mean mortality was 14.18 per cent at 10 per cent concentration and 5.81 per cent death at 5 per cent plant extract concentration was observed. From this, it is inferred that mortality only increased with a rise in concentrations of the 3 different plant oil and shows also that concentration has a major impact on the mean percent mortality rate of T. castaneum.

2.3 Comparison of the mean percentage mortality of *Tribolium castaneum* after exposure to different plant extracts after 24 hrs

Concentrations (%)	Mean percentage of mortality ± SE
P1	6.67±1.44
P2	11.12±1.82
P3	24.80±4.48

Table 2.3. For percent mean mortality values of different plant extracts at different concentration levels showed that extracts of *R. communis* and *Jatropha curcus* gave mortality values 24.80 and 11.12%, correspondingly. While the least mortality 6.67 % was given by extract of *Citrus paradise.*

2.4 Comparative mean percentage mortality of *Tribolium castaneum* after exposure to different concentrations of plant extracts after 24 hrs

Plant extracts x Concentrations (%)	(%) Mean Mortality ± SE
Citrus paradise x 5	1.67±1.67 g
Citrus paradise x 10	8.34±1.67 efg
Citrus paradise x 15	10.00±0.00 def
Jatropha curcus x 5	5.00±0.00 fg
Jatropha curcus x 10	11.67±1.67 cd
Jatropha curcus x 15	16.67±1.67 bc
Ricinus communis x 5	10.77±1.68 de
Ricinus communis x 10	22.56±1.68 b
Ricinus communis x 15	41.07±1.68 a

Table 2.4 showed the interaction between different concentrations (5, 10 and 15%) and different exposure periods. Mean mortality of *T. castaneum* was given in percentage by the application of an extract of *Ricinus communis*, *Jatropha curcus*, *Citrus paradise* oil along with the standard error in table 2.4.

The mean comparison of percentage mortality values of *T. castaneum* at different concentrations of selected plant extract was highest at maximum concentration. Extract of *Ricinus communis* gave the highest mean mortality revealed that maximum mortality (41.07 %) at 15% was recorded. The mean mortality was 22.56% at 10% concentration and 10.78% mortality was detected at 5 percent of the plant extract concentration. Extract of *Jatropha curcus* gave the mean mortality revealed that maximum mortality (16.67%) at 15% was recorded. The mean mortality was 11.67% at 10% concentration and 5.00% mortality was observed at 5 per cent plant extract concentration. Extract of *Citrus paradise* gave the mean mortality revealed that maximum mortality (10.00%) at 15% was recorded. The mean mortality was 8.34% at 10% concentration and 1.67% mortality of the plant extracts was estimated at 5 percent. The result given showed substantial correlation between exposure time and concentration. From the results, we inferred that mortality values were rising slowly, with a rise in plant extract concentration.

III.   MORTALITY DATA AFTER EXPOSURE OF 48 HRS

Table 3.1 Analysis of variance (ANOVA) of the data concerning % mortality of *Tribolium castaneum* (Herbst) for Titanium dioxide-based nano-particles

S.O.V	DF	SS	MSS	F value
Plant	2	1608.555	804.278	123.0181**
Concentration(Conc.)	2	1265.198	632.599	96.7590**
Plant*Concentration	4	457.108	114.277	17.4792*

S.O.V	DF	SS	MSS	F value
Error	18	117.682	6.538	
Total	26	3448.543		

Table 3.2 Comparison of the mean percentage mortality of *Tribolium castaneum* after exposure to different concentrations of plant extracts after 48 hrs

Concentrations (%)	Mean percentage mortality ± SE
5	5.81±1.49
10	14.18±2.30
15	22.58±4.77

Data in table 3.1. Represents the insecticidal effect of different concentrations of 3 different oil against *Tribolium castaneum*. The experimental data revealed that maximum mortality (22.58%) at 15% was recorded. The mean mortality was 14.18 % at 10% concentration and 5.81% mortality was observed at 5 per cent plant extract concentration. Through this, it is inferred that mortality only increased with a rise in concentrations of the 3 separate plant oil and indicates also that concentration has a major impact on the mean percent mortality rate of T. Castaneum.

3.3 Comparison of the mean percentage mortality of *Tribolium castaneum* after exposure to different plant extracts after 48 hrs

Concentrations (%)	Mean percentage of mortality ± SE
P1	6.67±1.44
P2	11.12±1.82
P3	24.80±4.48

Table 3.1 For percent mean mortality values of different plant extracts at different concentration levels showed that extracts of *R. communis* and *Jatropha curcus* gave mortality values 24.80 and 11.12%, correspondingly. While the least mortality 6.67 % was given by extract of *Citrus paradise*.

3.4 Comparative mean percentage mortality of *Tribolium castaneum* after exposure to different concentrations of plant extracts after 48 hrs

Plant extracts x Concentrations (%)	(%) Mean Mortality ± SE
Citrus paradise x 5	1.67±1.67 g
Citrus paradise x 10	8.34±1.67 efg

Plant extracts x Concentrations (%)	(%) Mean Mortality ± SE
Citrus paradise x 15	10.00±0.00 def
Jatropha curcus x 5	5.00±0.00 fg
Jatropha curcus x 10	11.67±1.67 cd
Jatropha curcus x 15	16.67±1.67 bc
Ricinus communis x 5	10.77±1.68 de
Ricinus communis x 10	22.56±1.68 b
Ricinus communis x 15	41.07±1.68 a

Table 3.4 showed the interaction between different concentrations (5, 10 and 15%) and different exposure periods. Mean mortality of *T. castaneum* was given in percentage by the application of an extract of *Ricinus communis*, *Jatropha curcus*, *Citrus paradise* oil along with the standard error in table 3.4

The mean comparison of percentage mortality values of *T. castaneum* at different concentrations of selected plant extract was highest at maximum concentration. Extract of *Ricinus communis* gave the highest mean mortality revealed that maximum mortality (41.07 %) at 15% was recorded. The mean mortality was 22.56% at 10% concentration and 10.78% mortality concentration of plant extracts was observed at 5 per cent. Extract of *Jatropha curcus* gave the mean mortality revealed that maximum mortality (16.67%) at 15% was recorded. The mean mortality was 11.67% at 10% concentration and 5.00% mortality the plant extract concentration was measured at 5 per cent. Extract of *Citrus paradise* gave the mean mortality revealed that maximum mortality (10.00%) at 15% was recorded. The mean mortality was 8.34% at 10% concentration and 1.67% mortality the concentration of plant extracts was measured at 5 per cent. The result given showed substantial correlation between exposure time and concentration. From the results, we concluded that mortality values were rising slowly, with a rise in plant extract concentration.

IV.   MORTALITY DATA AFTER EXPOSURE OF 72 HRS

Table 4.1 Analysis of variance (ANOVA) of the data concerning % mortality of *Tribolium castaneum* (Herbst) for Titanium dioxide-based nanoparticles

S.O.V	DF	SS	MSS	F value
Plant	2	967.452	483.726	94.106**
Concentration	2	1575.647	787.823	153.266**
Plant*Concentration	4	275.269	68.817	13.388*
Error	18	92.525	5.140	
Total	26			

Table 4.2. Comparison of the mean percentage mortality of *Tribolium castaneum* after exposure to different concentrations of plant extracts after 72 hrs

Concentrations (%)	Mean percentage of mortality ± SE
5	9.04± 0.87c
10	19.65± 2.41b
15	27.69± 3.45a

Data in table 4.1. Represents the insecticidal effect of different concentrations of 3 different oil against *Tribolium castaneum*. The experimental data revealed that maximum mortality (27.69%) at 15% was recorded. The mean mortality was 9.04 % at 5% concentration and 19.65% mortality was found at a plant extract concentration of 10 per cent. From this, it is concluded that Mortality increased even with a rise in concentrations of the three different plant oil and also indicates that concentration has a major impact on the mean percent mortality rate of T. castaneum.

4.3 Comparison of the mean percentage mortality of *Tribolium castaneum* after exposure to different plant extracts after 72 hrs

Concentrations (%)	Mean percentage of mortality ± SE
P1	11.89± 1.70c
P2	18.00± 2.29b
P3	26.49± 4.34a

Table 4.3. For percent mean mortality values of different plant extracts at different concentration levels showed that extracts of *R. communis* and *Jatropha curcus* gave mortality values 26.49 and 18.00%, corresponding. While the least mortality 11.89% was given by extract of *Citrus paradise.*

Comparative mean percentage mortality of *Tribolium castaneum* after exposure to different concentrations of plant extracts after 72hrs

Plant extracts x Concentrations (%)	(%) Mean Mortality ± SE
Citrus paradise x 5	6.334±1.34g
Citrus paradise x 10	12.00±1.15efg
Citrus paradise x 15	17.34±1.20def
Jatropha curcus x 5	9.67±0.34fg
Jatropha curcus x 10	19.00±0.57cd
Jatropha curcus x 15	25.34±0.67bc

Plant extracts x Concentrations (%)	(%) Mean Mortality ± SE
Ricinus communis x 5	11.12±1.16de
Ricinus communis x 10	27.94±2.04b
Ricinus communis x 15	40.40±2.10a

Table 4.2. Showed the interaction between different concentrations (5, 10 and 15%) and different exposure periods. Mean mortality of *T. castaneum* was given in percentage by the application of an extract of *Ricinus communis*, *Jatropha curcus*, *Citrus paradise* oil along with the standard error in table 4.2.

The mean comparison of percentage mortality values of *T. castaneum* at different concentrations of selected plant extract was highest at maximum concentration. Extract of *Ricinus communis* gave the highest mean mortality revealed that maximum mortality (40.40%) at 15% was recorded. The mean mortality was 27.94% at 10% concentration and 11.12% mortality was observed at 5 per cent plant extract concentration. Extract of *Jatropha curcus* gave the mean mortality revealed that maximum mortality (25.34%) at 15% was recorded. The mean mortality was 19.00% at 10% concentration and 9.67% mortality of the plant extracts was observed at 5 percent. Extract of *Citrus paradise* gave the mean mortality revealed that maximum mortality (17.34%) at 15% was recorded. The mean mortality was 12.00% at 10% concentration and 6.34% mortality was observed at 5 percent of the plant extract concentration. The result given showed substantial interaction between exposure time and concentration. From the analysis, we observed that mortality values were rising slowly, with a rise in plant extract concentration.

WITH Titanium dioxide NANO-PARTICLES against *Trogoderma granarium*

V.   MORTALITY DATA AFTER EXPOSURE OF 24 HRS

To evaluate the mortality of *T. granarium*, homogenous adults were released on the treated diet in small plastic jars. We found from the study that mortality values were increasing gradually, with a rise in concentration of plant extracts. Wheat grains were used as diet and three concentrations of each plant extract were used viz., 5, 10 and 15%. Mortality data were recorded for 24, 48 and 72 h of the exposure period. Insects were held at 30±2 oC and 60±5 per cent RH in incubators for mortality assessment. They repeated each treatment and control three times.

Table 5.1 reveals the analysis of variance (ANOVA) of data regarding the mean percentage mortality of *T. granarium* at different concentrations of *Jatropha curcus, Citrus paradise, and R. communis.* Data showed that main effects, plants (F=4.66; df=1: p<0.05) and concentration (F=11.10 df=;2 p<0.05) were significant regarding mortality values of *T. castaneum* after an exposure period of 24 hours.

Table 5.1. Analysis of variance (ANOVA) of the data concerning % mortality of *T. granarium* (Herbst) for Titanium dioxide-based nanoparticles

S.O.V	DF	SS	MSS	F value
Plant	2	871.817	435.909	114.508 **
Concentration	2	970.047	485.023	127.409 **
Plant*Concentration	4	180.138	45.035	11.830 *
Error	18	68.523	3.807	
Total	26	2090.525		

Table 5.2 Comparison of the mean percentage mortality of *Trogoderma granarium* after exposure to different concentrations of plant extracts after 24 hrs

Concentrations (%)	Mean percentage of mortality ± SE
5	6.36±1.01
10	16.41±2.36
15	20.66±3.00

Data in table 5.1. Represents the insecticidal effect of different concentrations of 3 different oil against *Trogoderma granarium*. The experimental data revealed that maximum mortality (20.66%) at 15% was recorded. The mean mortality was 6.36% at 5% concentration and 16.41% mortality was observed at a concentration of 10 per cent of plant extracts. From this, it is inferred that mortality only increased with a rise in concentrations of the 3 different plant oil and shows also that concentration has a major impact on the mean percent mortality rate of T. granarium.

5.3 Comparison of the mean percentage mortality of *Trogoderma granarium* after exposure to different plant extracts after 24 hrs

Concentrations (%)	Mean percentage of mortality ± SE
P1	7.23±1.12
P2	15.12±2.20
P3	21.09±3.29

Table 5.2. For percent mean mortality values of different plant extracts at different concentration levels showed that extracts of *R. communis* and *Jatropha curcus* gave mortality values 21.09 and 15.12%, corresponding. While the least mortality 7.23% was given by extract of *Citrus paradise.*

5.4 Comparative mean percentage mortality of *Trogoderma granarium* after   exposure to different concentrations of plant extracts after 24 hrs

Plant extracts x Concentrations (%)	(%) Mean Mortality ± SE
Citrus paradise x 5	3.34±1.67g
Citrus paradise x 10	8.34±0.34efg
Citrus paradise x 15	10.00±0.00def
Jatropha curcus x 5	7.00±1.00fg
Jatropha curcus x 10	17.00±1.52cd
Jatropha curcus x 15	21.34±0.89bc

Plant extracts x Concentrations (%)	(%) Mean Mortality ± SE
Ricinus communis x 5	8.75±0.89de
Ricinus communis x 10	23.90±1.78b
Ricinus communis x 15	30.63±0.67a

Table 5.5 showed the interaction between different concentrations (5, 10 and 15%) and different exposure periods. Mean mortality of *T. granarium* was given in percentage by the application of an extract of *Ricinus communis*, *Jatropha curcus*, *Citrus paradise* oil along with the standard error in table 5.5.

The mean comparison of percentage mortality values of *T. granarium* at different concentrations of selected plant extract was highest at maximum concentration. Extract of *Ricinus communis* gave the highest mean mortality revealed that maximum mortality (30.63%) at 15% was recorded. The mean mortality was 23.90% at 10% concentration and 8.75% mortality was observed at 5 per cent plant extract concentration. Extract of *Jatropha curcus* gave the mean mortality revealed that maximum mortality (21.34%) at 15% was recorded. The mean mortality was 17.00% at 10% concentration and 7.00% mortality concentration of plant extracts was observed at 5 per cent. Extract of *Citrus paradise* gave the mean mortality revealed that maximum mortality (10.00%) at 15% was recorded. The mean mortality was 8.34% at 10% concentration and 3.34% mortality was observed at 5% concentration of the plant extracts. The given outcome showed that the interaction of exposure time and concentration was significant. From the findings, we observed that mortality values were rising slowly, with a rise in plant extract concentration.

VI.   MORTALITY DATA AFTER EXPOSURE OF 48 HRS

Table 6.1 Analysis of variance (ANOVA) of the data concerning % mortality of *T. granarium* (Herbst) for Titanium dioxide-based nanoparticles

S.O.V	DF	SS	MSS	F value
Plant	2	580.743	290.371	80.454**
Concentration	2	717.708	358.854	99.429**
Plant*Concentration	4	159.210	39.802	11.028*
Error	18	64.964	3.609	
Total	26	1522.625		

Table 6.2 Comparison of the mean percentage mortality of *Trogoderma granarium* after exposure to different concentrations of plant extracts after 48 hrs

Concentrations (%)	Mean percentage of mortality ± SE
5	5.14±0.72
10	13.40±1.92

Concentrations (%)	Mean percentage of mortality ± SE
15	17.53±2.65

Data in table 6.1. Represents the insecticidal effect of different concentrations of 3 different oil against *Trogoderma granarium*. The experimental data revealed that maximum mortality (17.53%) at 15% was recorded. The mean mortality was 5.14% at 5% concentration and 13.40% mortality was observed at 10% concentration of the plant extracts. From this, it is inferred that mortality only increased with a rise in concentrations of a 3 different plant oil and shows also that concentration has a major impact on the mean percent mortality rate of T. granarium.

6.2 Comparison of the mean percentage mortality of *Trogoderma granarium* after   exposure to different plant extracts after 48 hrs

Concentrations (%)	Mean percentage of mortality ± SE
P1	7.23±1.21
P2	10.56±1.55
P3	18.29±3.04

Table 6.3 For percent mean mortality values of different plant extracts at different concentration levels showed that extracts of *R. communis and Jatropha curcus* gave mortality values 18.29 and 10.56%, correspondingly. While the least mortality 7.23% was given by extract of *Citrus paradise.*

6.4 Comparative mean percentage mortality of *Trogoderma granarium* after   exposure to different concentrations of plant extracts after 48 hrs

Plant extracts x Concentrations (%)	(%) Mean Mortality ± SE
Citrus paradise x 5	3.34±1.67g
Citrus paradise x 10	8.34±1.67efg
Citrus paradise x 15	10.00±0.00def
Jatropha curcus x 5	5.00±0.00fg
Jatropha curcus x 10	11.67±1.67cd
Jatropha curcus x 15	15.00±0.00bc
Ricinus communis x 5	7.07±0.00de
Ricinus communis x 10	20.20±1.014b
Ricinus communis x 15	27.60±1.22a

Table 6.4 showed the interaction between different concentrations (5, 10 and 15%) and different exposure periods. Mean mortality of *T. granarium* was given in percentage by the application of an extract of *Ricinus communis*, *Jatropha curcus*, *Citrus paradise* oil along with the standard error in table 6.4.

The mean comparison of percentage mortality values of *T. granarium* at different concentrations of selected plant extract was highest at maximum concentration. Extract of *Ricinus communis* gave the highest mean mortality revealed that maximum mortality (27.60%) at 15% was recorded. The mean mortality was 20.20% at 10% concentration and 7.07% mortality concentration of plant extracts was observed at 5 per cent. Extract of *Jatropha curcus* gave the mean mortality revealed that maximum mortality (15.00%) at 15% was recorded. The mean mortality was 11.67% at 10% concentration and 5.00% mortality was observed at 5% concentration of the plant extracts. Extract of *Citrus paradise* gave the mean mortality revealed that maximum mortality (10.00%) at 15% was recorded. The mean mortality was 8.34% at 10% concentration and 3.34% mortality was observed at 5 per cent plant extract concentration. The result given showed substantial association between exposure time and concentration. From the findings, we estimated that mortality values were rising slowly, with a rise in plant extract concentration.

VII.   MORTALITY DATA AFTER EXPOSURE OF 72 HRS

Table 7.1 Analysis of variance (ANOVA) of the data concerning % mortality of *T. granarium* (Herbst) for Titanium dioxide-based nanoparticles

S.O.V	DF	SS	MSS	F value
Plant	2	619.787	309.894	55.938**
Concentration	2	1246.537	623.268	112.504**
Plant*Concentration	4	186.387	46.597	8.411*
Error	18	99.719	5.540	
Total	26			

Table 7.2 Comparison of the mean percentage mortality of *Trogoderma granarium* after exposure to different concentrations of plant extracts after 72 hrs

Concentrations (%)	Mean percentage of mortality ± SE
5	7.69±0.73
10	15.63±1.69
15	24.34±3.02

Data in table 7.1. Represents the insecticidal effect of different concentrations of 3 different oil against *Trogoderma granarium*. The experimental data revealed that maximum mortality (24.34%) at 15% was recorded. The mean mortality was 7.69% at 5% concentration and 15.63% mortality was observed at a concentration of 10 per cent of plant extracts. From this, it is inferred that mortality only increased with a rise in concentrations of the 3 different plant oil and shows also that concentration has a major impact on the mean percent mortality rate of T. granarium.

7.3 Comparison of the mean percentage mortality of *Trogoderma granarium* after   exposure to different plant extracts after 72 hrs

Concentrations (%)	Mean percentage of mortality ± SE
P1	9.67±1.32
P2	16.67±2.41
P3	21.34±3.72

Table 7.4 for percent mean mortality values of different plant extracts at different concentration levels showed that extracts of *R. communis and Jatropha curcus* gave mortality values 21.34 and 16.67%, correspondingly . While the least mortality 9.67% was given by extract of *Citrus paradise.*

7.5 Comparative mean percentage mortality of *Trogoderma granarium* after   exposure to different concentrations of plant extracts after 72 hrs

Plant extracts x Concentrations (%)	(%) Mean Mortality ± SE
Citrus paradise x 5	5.00±0.00g
Citrus paradise x 10	10.00±0.00efg
Citrus paradise x 15	14.00±0.57def
Jatropha curcus x 5	9.00±0.00fg
Jatropha curcus x 10	15.67±0.34cd
Jatropha curcus x 15	25.34±1.34bc
Ricinus communis x 5	9.091±1.01de
Ricinus communis x 10	21.22±1.74b
Ricinus communis x 15	33.68±3.21a

Table 7.6. Showed the interaction between different concentrations (5, 10 and 15%) and different exposure periods. Mean mortality of *T. granarium* was given in percentage by the application of an extract of *Ricinus communis*, *Jatropha curcus*, *Citrus paradise* oil along with the standard error in table 7.6.

The mean comparison of percentage mortality values of *T. granarium* at different concentrations of selected plant extract was highest at maximum concentration. Extract of *Ricinus communis* gave the highest mean mortality revealed that maximum mortality (33.68%) at 15% was recorded. The mean mortality was 21.22% at 10% concentration and 9.091% mortality was observed at 5 per cent plant extract concentration. Extract of *Jatropha curcus* gave the mean mortality revealed that maximum mortality (25.34%) at 15% was recorded. The mean mortality was 15.67% at 10% concentration and 9.00% mortality was observed at 5% concentration of the plant extracts. Extract of *Citrus paradise* gave the mean mortality revealed that maximum mortality (14.00%) at 15% was recorded. The mean mortality was 10.00% at 10% concentration and 5.00% mortality of the plant extracts was observed at 5 percent. The given outcome

showed that the interaction of exposure time and concentration was significant. From the findings, we estimated that mortality values were rising slowly, with a rise in plant extract concentration.

Titanium Nano-composites

VIII.   UV-VIS SPECTRA ANALYSIS

The UV-Vis spectra were analysed to validate the presence of nanoparticles in the resulting solutions. UV-Vis absorption spectroscopy is an important technique for controlling the composition and consistency of aqueous solution in metal NPs. Metal NP's absorption range is susceptible to several variables like particle size, shape, and nano-particle interaction (agglomeration) with the media. Maximum absorption (ÿmax) depends on nanoparticles, thickness, and form. The UV-VIS absorption spectrum for TiO2 nanoparticles between 200 and 400 nm is shown in Figure 4.3 TiO2 absorption occurs at 280 nm, and its absorbance in UV – Vis spectroscopy will be 0.004. (Aryal et cetera, 2006).
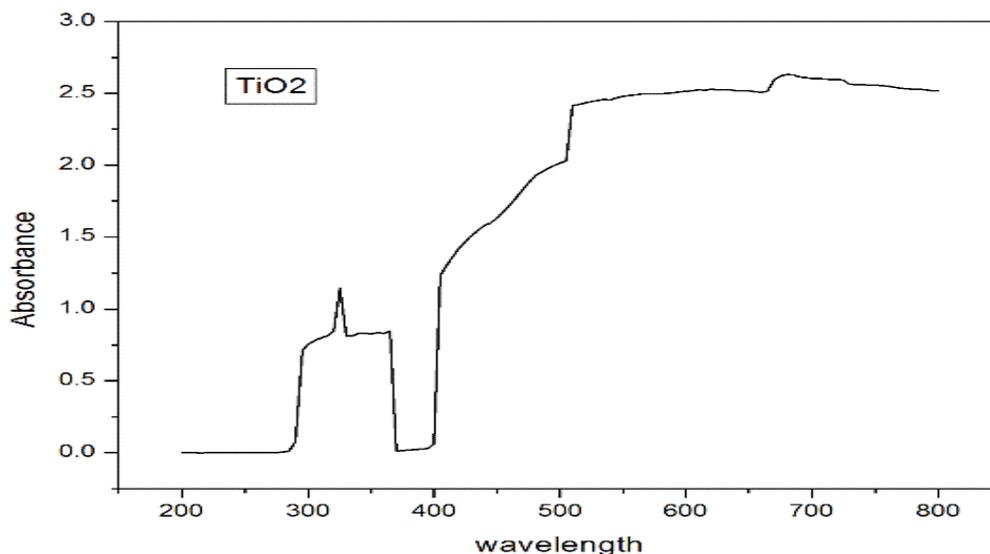
Figure 8.1: UV-Vis absorption spectra of titanium nanoparticle synthesized

IX.   FOURIER TRANSFORMS INFRARED SPECTROSCOPY (FTIR)

FTIR spectroscopy was used to classify various groups on Ricinus communis powder and to estimate their role in the formulation of nanoparticles. Figure 6 reveals the bands are at 3320 cm-1, 1590 cm-1, 1385 cm-1, 1024 cm-1. And 431-1 cm. The TiO2 nanoparticles FTIR spectrum showed characteristic 1024 cm-1 bands which indicate the presence of C-O stretching alcohols, carboxylic acids, esters, and ethers. The peak at 1385 cm-1 indicates C-H rock alkenes while the peak at 1590 cm-1 indicates the presence of saturated hydrocarbon signature C = C. The 3320 cm-1 band correlates to O-H, as do the alcohols and phenols bonded with H-. Such bonds are related to the Ricinus communis chemical composition. In addition, the structure of Ricinus communis contains such compounds as caffeic acid, quinic acid and chlorogenic acid. It also contains free-form, glycosidally bound flavonoids (quercetin, kaempferol, rutoside, luteolin, apigenin, isorhamnetin), and essential oil. The peak at 431 cm-1 shows TiO2 nanoparticles are present.
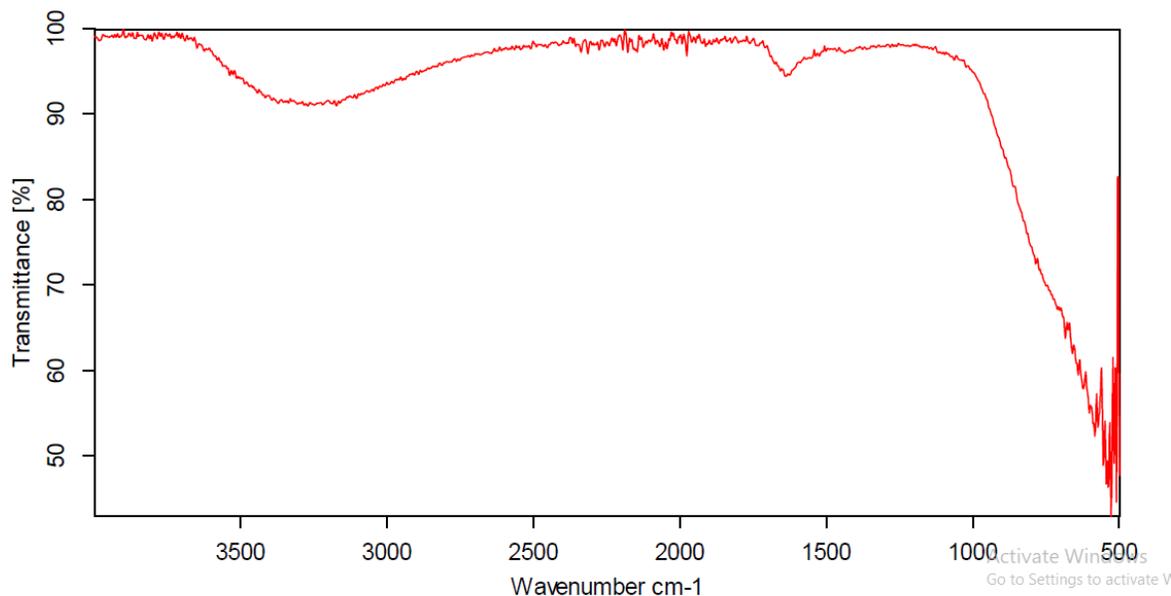
Figure 9.1 FTIR spectra of titanium dioxide nanoparticles

X.   CONCLUSION

The present data demonstrate that green synthesis can also be used to prepare modern nanotechnology. These nanoparticles were synthesised with a variety of solvents derived from plant extracts. The pests Tribolium castanium and Trigoderma granarium have a significant impact on soil fertility and growth. In recent years, specific plant extract oil has been utilised to help manage these effects, although it will not work adequately. As a result, we can now monitor the enormous reproduction sickness in our country using nanoparticles. Our investigations demonstrate that the nanoparticles perform really effectively, and that the oil extracts quite simply as a result. The results presented will demonstrate that this is correct. Then we may conclude that nanoparticles are suggested for use at the farm level due to their low cost, availability, eco-friendliness, and effectiveness as an alternative method of pest management.

REFERENCES

[1]   1.   Hao, Y., et al., Characterization of a major QTL for adult plant resistance to stripe rust in US soft red winter wheat. Theoretical and applied genetics, 2011. 123(8): p. 1401-1411.

[2]   2.   Ramezani, H. and G.A. Mansoori, Diamondoids as molecular building blocks for nanotechnology, in Molecular Building Blocks for Nanotechnology. 2007, Springer. p. 44-71.

[3]   3.   Peng, J., et al., Graphene quantum dots derived from carbon fibers. Nano letters, 2012. 12(2): p. 844-849.

[4]   4.   Dagdeviren, C., et al., Conformal piezoelectric energy harvesting and storage from motions of the heart, lung, and diaphragm. Proceedings of the National Academy of Sciences, 2014. 111(5): p. 1927-1932.

[5]   5.   Trindade, T., P. O'Brien, and N.L. Pickett, Nanocrystalline semiconductors: synthesis, properties, and perspectives. Chemistry of Materials, 2001. 13(11): p. 3843-3858.

[6]   6.   Pérez-de-Luque, A. and D. Rubiales, Nanotechnology for parasitic plant control. Pest Management Science: formerly Pesticide Science, 2009. 65(5): p. 540-545.

[7]   7.   Ahmedani, M.S., et al., Khapra beetle (Trogoderma granarium Everts): A serious threat to food security and safety. Pak. J. Agri. Sci, 2007. 44(3): p. 481-493.

[8]   8.   Phillips, T.W. and J.E. Throne, Biorational approaches to managing stored-product insects. Annual review of entomology, 2010. 55.

[9]   9.   Lu, H., et al., Effects of low-intensity microwave radiation on Tribolium castaneum physiological and biochemical characteristics and survival. Journal of insect physiology, 2010. 56(9): p. 1356-1361.

[10]   10.   Ramzan, M. and B. Chahal, Effect of interspecific competition on the population build-up of some storage insects. Indian Journal of Ecology, 1986. 13(2): p. 313-317.

[11]   11.   Parashar, M., Post harvest profile of black gram. Govt. India, Ministry of Agric. Deptt. Agric. and Coop. Directorate of Marketing and Inspection, Nagpur-440001, 2006.

[12]   12.   Arain, A., et al., Epilepsy and the impact of an epileptology clinic for patients with mental retardation and associated disabilities in an institutional setting. Epilepsia, 2006. 47(12): p. 2052-2057.

[13]   13.   Jood, S. and A. Kapoor, Effect of storage and insect infestation on protein and starch digestibility of cereal grains. Food chemistry, 1992. 44(3): p. 209-212.

[14]   14.   Khan, Z., J.I. Hussain, and A.A. Hashmi, Shape-directing role of cetyltrimethylammonium bromide in the green synthesis of Ag-nanoparticles using Neem (Azadirachta indica) leaf extract. Colloids and Surfaces B: Biointerfaces, 2012. 95: p. 229-234.

[15]   15.   Miller, R., I. Tegen, and J. Perlwitz, Surface radiative forcing by soil dust aerosols and the hydrologic cycle. Journal of Geophysical Research: Atmospheres, 2004. 109(D4).

[16]   16.   Taheriniya, S. and Z. Behboodi, Comparing green chemical methods and chemical methods for the synthesis of titanium dioxide nanoparticles. International Journal of Pharmaceutical Sciences and Research, 2016. 7(12): p. 4927.

[17] 17. Ali, K., et al., Medicinal response of Moringa olifera and Nicotiana tabacum as repellent and toxicant against Trogoderma granarium and Rhyzopertha dominica. ZEITSCHRIFT FUR ARZNEI-& GEWURZPFLANZEN, 2017. 22(3): p. 132-135.

[18] 18. Yang, F.-L., et al., Structural characterization of nanoparticles loaded with garlic essential oil and their insecticidal activity against Tribolium castaneum (Herbst)(Coleoptera: Tenebrionidae). Journal of agricultural and food chemistry, 2009. 57(21): p. 10156-10162.

[19] 19. Mirjalili, F., S. Manafi, and I. Farahbakhsh, Preparation and Characterization of TiO2 Nanoparticles Prepared by Sol-Gel Method. Advanced Ceramics Progress, 2017. 3(3): p. 38-47.

[20] 20. Dobrucka, R., Synthesis of titanium dioxide nanoparticles using Echinacea purpurea herba. Iranian journal of pharmaceutical research: IJPR, 2017. 16(2): p. 756.

[21] 21. Kasthuri, J., S. Veerapandian, and N. Rajendiran, Biological synthesis of silver and gold nanoparticles using apiin as reducing agent. Colloids and Surfaces B: Biointerfaces, 2009. 68(1): p. 55-60.

[22] 22. Rehman, K., et al., Prevalence of exposure of heavy metals and their impact on health consequences. Journal of cellular biochemistry, 2018. 119(1): p. 157-184.

[23] 23. Girshick, R., et al., Region-based convolutional networks for accurate object detection and segmentation. IEEE transactions on pattern analysis and machine intelligence, 2015. 38(1): p. 142-158.

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