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THE SYNTHESIS OF POLYLACTIC ACID POLYMER COATED WITH Ag_2O-TiO_2 NANOPARTICLES AND ITS PHOTO-CATALYTIC ACTIVITY

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ABSTRACT

Interest in the green synthesis of PLA-Ag_2O-TiO_2 nanoparticles has exploded in recent decades due to the need to develop cost-effective and environmentally friendly processes. A novel method to develop different kinds of nanomaterials is green synthesis. This study employed an eco-friendly synthesis method that produced Ag_2O-TiO_2 nanoparticles (NPs) using polylactic acid (PLA). The XRD pattern of TiO_2 powder containing 1 mmol of silver nitrate with leaf extract, the crystal phase is found to be anatase in all samples. The FTIR spectra show peaks for O-H stretching vibrations, bending vibrations, and Ti-OH surface groups. Co-doped TiO_2 intensity reduces, with efficient dispersion of silver, and no clusters. The morphology and structure of the prepared samples were examined using Scanning Electron Microscopy (SEM), revealing a spherical Ag_2O-TiO_2 nanocomposite with slightly agglomerated powder particles. The size was determined using transmission electron microscopy (TEM). The size of leaf extract Ag_2O-TiO_2 nanoparticles were30 ± 5 nm. The study investigated the photocatalytic properties of pesticide residues in water, with a nanocatalyst. The samples were exposed to sunlight and filtered through a 0.45µm PTFE membrane filter. The findings revealed that the presence of a catalyst significantly reduced the samples' half-life, indicating that nanoparticles are an effective photocatalyst for removing pesticide residues.

Keywords: Ag_2O-TiO_2 Nanoparticles, Polylactic acid, *Catalytic Activity*, Green synthesis, XRD, FTIR, FE-SEM, TEM.

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INTRODUCTION

PLA can decompose into carbon dioxide, lactic acid, and water under certain composting conditions.[1] It is commonly used in 3D printing, medical implants, food packaging, and disposable cutlery.[2] PLA has a low melting point, high strength, and good layer adhesion. However, it is brittle and has poor heat resistance.[3,4] Ag_2O-TiO_2 nanoparticles are a composite nanomaterial that combines silver oxide and titanium dioxide, with improved properties and potential applications in photocatalysis, electronics, and the environment.[5] They are effective at degrading organic pollutants under UV light, have unique electrical properties, and are used in air and water purification systems due to their antimicrobial and photocatalytic properties. Sol-gel, sonochemical, and hydrothermal treatments are common synthesis methods.[6] Polylactic acid (PLA) is an excellent method for producing environmentally friendly Ag_2O-TiO_2 nanoparticles.[7] PLA is biodegradable and derived from renewable resources, making it an ideal choice for green chemistry. This method is popular because it is inexpensive, uses few toxic chemicals, and is environmentally friendly.[8] Common techniques include mixing with precursors, sonication or heating, and characterizing the nanoparticles with UV-Vis spectroscopy, XRD, and SEM.[9] Green nanoparticles have high photocatalytic activity and strong antimicrobial properties.[10] Photocatalytic activity is the acceleration of a photoreaction in the presence of a catalyst.[11-14] This catalyst, typically a semiconductor, absorbs light and aids in the transformation of chemical compounds.[15] It is a critical process in water purification, air purification, and energy conversion.[16-17] For example, when light strikes the photocatalyst, it produces electrons and holes.[18] These electrons and holes then react with water and oxygen to produce reactive oxygen species, which can degrade pollutants or drive chemical reactions.[19-20] Triallate is a pre-emergent herbicide that is widely used to control grassy weeds like wild oats in crops such as barley, wheat, lentils, peas, and sugar beets.[21] It

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works by preventing the growth of weed seedlings before they emerge from the soil. The degradation of triallate herbicide in water is a critical step toward reducing its environmental impact.[22] According to studies, triallate can be degraded into less harmful substances via a variety of pathways, including microbial degradation and chemical reactions. One study realized that triallate can degrade into its metabolite, 2,3,3-trichloro-prop-2-en-sulfonic acid (TCPSA), which has a higher leaching tendency and is easier to remove from water. Water pH, temperature, and the presence of specific microorganisms can all have an impact on the rate of degradation.[23] Coating polymers with Ag_2O-TiO_2 nanoparticles improves their photocatalytic activity, making them useful in applications like wastewater treatment and air purification. The Ag_2O nanoparticles improve TiO_2's visible light absorption, which is typically only responsive to UV light.[24-25] This combination allows for more efficient use of sunlight, which increases the degradation of pollutants.

EXPERIMENTAL

Synthesis of Ag_2O-TiO_2 Nanoparticles (NPs)

Briefly, 50 milliliters of absolute ethanol were mixed with 0.05 mol tetrabutyl orthotitanate drop by drop to create a solution. The mixture was then vigorously stirred for 20 minutes at room temperature before three drops of concentrated HNO_3 were added. After that, 0.01 mol of silver nitrate was added to the reaction mixture as needed, and it was constantly stirred for 60 minutes to dissolve the Ag. Then, 3.0 mL of deionized water was added to the solution that had been mentioned. We then let the mixture sit at room temperature for two hours while stirring it constantly. This made a gel, which we let sit at room temperature for twelve hours. were made by drying them at 70ºC for 24 hours and then annealing them at 300ºC for 3 hours. We also made a sample of TiO_2 (anatase) that wasn't doped by following the same steps but leaving out the silver nitrate, which is pure TiO_2. The doping levels are given in mmol of titanium atoms.

Synthesis of PLA Coated Ag_2O-TiO_2 NPs

A 100 ml glass beaker was filled with 25 ml of 4% PLA (PLA 1.0 g was dissolved in 25 ml of acetone) and 1 gram of Ag_2O-TiO_2 nanoparticles. The beaker was stirred for 2 hours with a magnetic stirrer. We used a 1 M NaOH solution to change the pH of the solution to 10.0, which made a white precipitate. To make the PLA-Ag_2O-TiO_2 nanoparticles used in this study, the precipitate was filtered and washed four times with distilled water. It was then put in a glass petri dish and put in the oven at 70°C for five hours.

Characterization of PLA Coated Ag_2O-TiO_2 NPs

We used different methods to describe the synthesized nanoparticles. One of these was X-ray diffraction (Rigaku Smartlab SE Multipurpose XRD), which measured the phase composition, lattice parameters, and crystallite size. Fourier transform infrared spectroscopy (Agilent 4300-FTIR) is a tool that helps find the functional groups and bonds in precursors and products. Scanning electron microscopy (SEM) can show the size, shape, distribution, and morphology of PLA-Ag_2O-TiO_2 NPs. Transmission electron microscopy (Tescan-TEM) looks at the size, shape, and crystal structure of PLA-Ag2O-TiO_2 NPs.

Tap Water Collection

The tap water was collected at Mahatma Gandhi University, Nalgonda, Telangana - 508 254. The latitude is 17.1429° N and the longitude is 79.2163° E.

HPLC Conditions

The triallate residues was determined using High Performance Liquid Chromatography (HPLC) using specific instrument conditions. The instrument was a Shimadzu with a PDA detector, a 20:80 v/v mobile phase, a Phenomenex C18 column (250 mm x 4.6 mm, 5µ), a 30°C oven temperature, a 1.2 ml/minute flow rate, 10 µL injection volume, a run time of 10 minutes, and a retention time of approximately 4.8 minutes.

Method Specificity

We examined the specificity of the method on untreated control samples of tap water extract, acetonitrile, 0.1% ortho-phosphoric acid, working standard, and test solutions.

Linearity of Response

Weighing 10.06 mg of reference standard into a 50 mL volumetric flask and bringing it to volume with acetonitrile produced a stock solution of triallate standard stock. The correct volume of stock solution was then diluted into various 10 mL volumetric flasks, and acetonitrile was added to bring the flasks to volume

in order to create a series of calibration solutions. HPLC was used to analyze the prepared calibration solutions, which were 0.01 µg/mL (L1), 0.1 µg/mL (L2), 1.0 µg/mL (L3), 2.0 µg/mL (L4), 5.0 µg/mL (L5), and 10.0 µg/mL (L6). The correlation coefficient was calculated by plotting a linear curve for the standard concentration against the observed peak area.

Assay accuracy and Precision

Fortified samples and an untreated (blank) sample are analyzed as part of the validation process. After adding a known amount of triallate and sample workup, fortified samples were created. The HPLC method was then used to extract and determine the amount of triallate present in the tap water. The concentration levels of the fortified samples were 1xLOQ = 0.01 µg/mL and 10x LOQ = 0.1 µg/mL. Five replicates were used for method validation at each level of fortification. The response area of the fortified samples was used to compute the percentage recovery and the percentage relative standard deviation.

Limit of Quantification (LOQ)

The lowest validated level with adequate recovery is known as the limit of quantification (LOQ). Five injections of 0.01 µg/mL fortification level recovery samples of triallate were used to determine the LOQ. For LOQ, low-level recovery solutions were employed.

Photolytic and Photocatalytic Studies

A concentration of 0.5 µg/mL of each was added in order to study the photocatalysis of triallate residues in water. At every fortification level, single replications were carried out in addition to control samples for comparison. For the experiments, two sets of spiked concentrations are made. One set of samples was tested with the catalyst (PLA Coated Ag_2O-TiO_2 NPs), and the other set was not. The samples were placed in direct sunlight. At specified intervals, aliquots of the sample were taken. During this time, water samples were taken at temperatures between 26 and 42°C. The samples obtained at different sampling times were filtered using a 0.2 m PTFE membrane filter. After that, the filtrates were gathered into vials with an amber hue. Each sample was stored in the dark at 5°C prior to HPLC analysis. A Beckman cooling centrifuge with 3000 rotations per minute was used to centrifuge the PLA-coated Ag_2O-TiO_2 NP-fortified samples for five minutes at 5°C. The supernatants were moved to amber-colored bottles and kept at 5°C in the dark until analysis to stop the residues from degrading any further.

Sample Extraction

A vacuum rotary evaporator was used to concentrate the representative homogenized 5 ml of water sample until it was completely dry, and then acetonitrile was added until the desired level was reached. The HPLC was filled with the solution.

RESULTS AND DISCUSSION

Characterization of PLA Coated Ag_2O-TiO_2 NPs

FTIR Analysis

Fourier Transform Infrared Spectroscopy (Fig.-1) is used to determine the chemical structure of PLA coated with Ag_2O-TiO_2 nanoparticles. FTIR analysis aids in the identification of functional groups as well as chemical structure changes resulting from the coating process. PLA coated with Ag_2O-TiO_2 nanoparticles exhibits distinct absorption bands, including O-H stretch (3200-3600 cm^{-1}), C=O stretch (1700 cm^{-1}), and Ti-O-Ti (1300-1400 cm^{-1}).

XRD Analysis

The nanoparticles' XRD patterns are shown in Fig.-2. There are no crystalline phases in the diffraction pattern of alginate. PLA, however, exhibits a broad and weak diffraction peak at $2\theta = 20.08°$. The (101), (004), (200), (105), (211), (116), (220), (215), and (224) crystal planes are represented by the diffraction peaks at 25º, 30º, 48º, 50º, 54º, 62º, 68º, 74º, and 82º. This XRD pattern did not show up in rutile or brookite form and is in accordance with the standard JCPDS values of anatase TiO_2 (JCPDS Card No. 21-1272)[16,17] with a tetragonal structure.

SEM Analysis

Larger clusters are produced when particles in specific regions of the sample are more connected to one another, as seen in Fig.-3. This suggests that certain particles in the sample serve as seed particles, drawing

in more particles through condensation. The sample consequently agglomerates in particular regions. Additionally, SEM can show how nanoparticles group together. Since alginate inhibits aggregation, nanoparticles can disperse more efficiently.

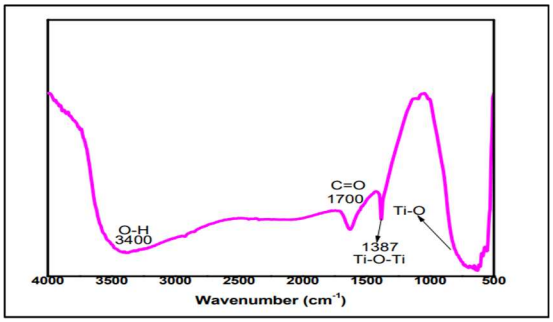

Fig.-1: FTIR Spectra of PLA Coated Ag_2O-TiO_2 NPs

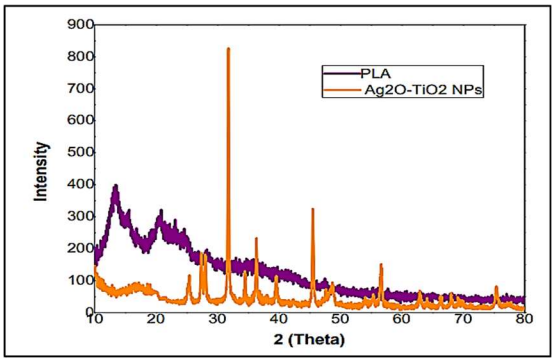

Fig.-2: XRD of PLA and PLA Coated Ag_2O-TiO_2 NPs

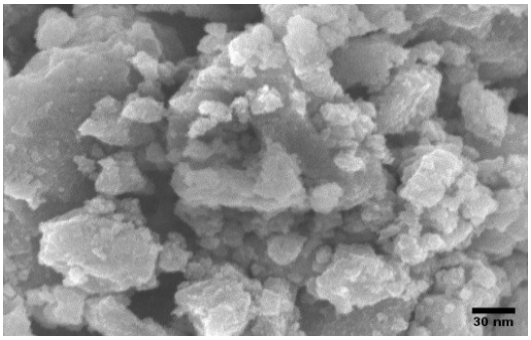

Fig.-3: SEM image of PLA Coated Ag_2O-TiO_2 NPs

TEM Analysis

Figure-4 reveals a TEM image of PLA Coated Ag_2O-TiO_2 NPs ranging from 30 to 130 nm. The sample has a high level of crystallinity, particle aggregation, and a distinctive cubic structure. PLA Coated Ag_2O-TiO_2 NPs nanoparticles exhibit distinct structure and shape.

Method Validation

Specificity

The analytical method was determined to be specific. There was no interference detected at the retention times of the Triallate peaks. The difference in retention time between test items and reference standards was found to be within ± 5.0%.

Linearity

The linearity of the method was established by injecting six different concentrations of Triallate reference standard into HPLC and plotting the standard concentrations (µg/mL) against the respective peak areas. Table-1 shows the results of area concentrations. The linearity curve is shown in Fig.-5. Figure-6 shows a representative chromatogram.

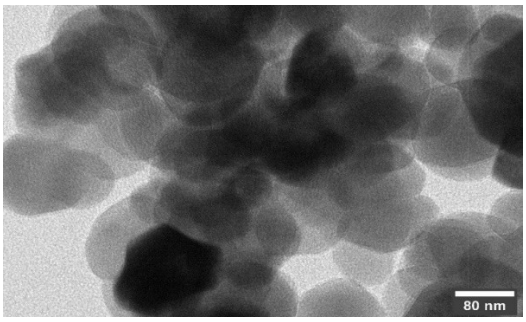

Fig.-4: TEM image of PLA Coated Ag_2O-TiO_2 NPs

Table-1: Detector Linearity Test

Standard Code	Std. Concentration (µg/mL)	Triallate Std. Area
Linearity-1	0.01	234
Linearity-2	0.10	2412
Linearity-3	1.0	23987
Linearity-4	2.0	46147
Linearity-5	5.0	115409
Linearity-6	10.0	225682
Intercept		831.38
Slope		22577.73
Correlation of Coefficient (r)		0.9999
Coefficient of determination (r^2)		0.9999

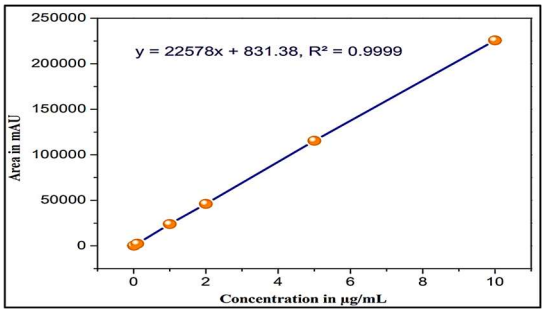

Fig.-5: Linearity Curve of Triallate Standard

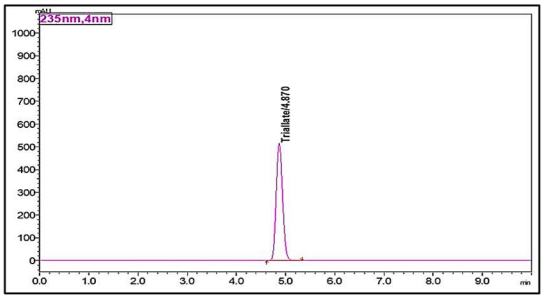

Fig.-6: Representative Triallate Standard Chromatogram of Linearity -6

Recovery and Repeatability

There were two recovery control samples (n=2) at each of the two fortification levels, which correspond to 0.03 µg/mL and 0.3 µg/mL for water. HPLC was used to analyze the triallate in the finished solution. Table-2 presents the results.

Limit of Quantitation (LOQ)

The lower-level recovery test in tap water yielded a limit of quantification (LOQ) of 0.03 µg/mL.

Table-2: Recovery and Repeatability of Triallate in Tap Water

Sample Code	Recovery (%) of Triallate in Tap Water	Average	Standard Deviation	%RSD
LOQ Level_R1	85.76	84.89	1.08	1.27
LOQ Level_R2	83.54			
LOQ Level_R3	84.89			
LOQ Level_R4	86.12			
LOQ Level_R5	84.15			
LOQ X10 Level_R1	90.13	91.39	0.97	1.06
LOQ X10 Level_R2	92.34			
LOQ X10 Level_R3	90.89			
LOQ X10 Level_R4	92.37			
LOQ X10 Level_R5	91.23			
Average	88.64			
Standard Deviation	2.19			
%RSD	2.47			

Photolytic Studies and Photocatalytic Studies

Table-3 and Fig.-7 demonstrate that Triallate's half-life in tap water without a catalyst was 4.41 days. In contrast, the half-life of Triallate in tap water with a catalyst was found to be 5.30 hours; the findings are displayed in Table-4 and Fig.-8.

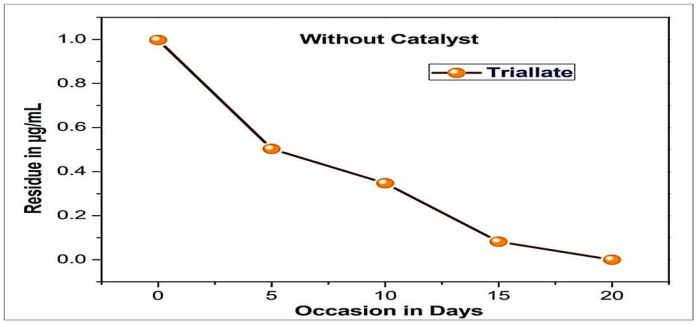

Fig.-7: Photolysis Curve of Triallate in the absence of PLA Coated Ag_2O-TiO_2 NPs in Tap Water (without catalyst)

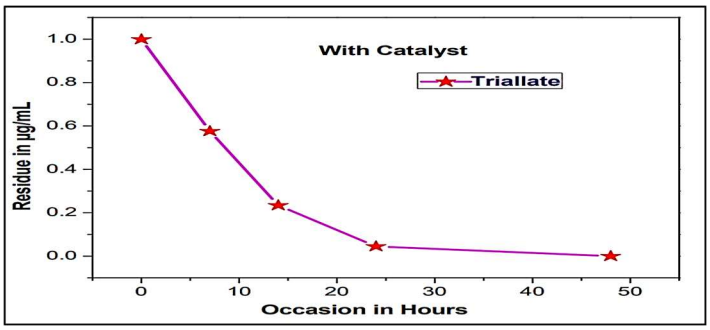

Fig.-8: Photocatalysis Curve of Triallate in the presence of PLA Coated Ag_2O-TiO_2 NPs in Tap Water (With Catalyst)

Table-3: Photolysis of Triallate under Direct Sunlight in Tap Water (without catalyst)

Occasion (Days)	Residue Level	Log	Triallate	
0	0.997	-0.0013	Slope	-0.068
5	0.503	-0.2984	Half-life (DT50)	4.41
10	0.347	-0.4597		
15	0.082	-1.0862		
20	BDL	BDL	Intercept	0.051
			CC	0.928

Table-4: Photocatalysis of Triallate in the Presence of PLA Coated Ag_2O-TiO_2 NPs Under Direct Sunlight in Tap Water

Occasion (Days)	Residue Level	Log	Triallate	
0	0.999	-0.0004	Slope	-0.057
7	0.576	-0.2396	Half-life (DT50)	5.30
14	0.234	-0.6308		
24	0.045	-1.3468		
48	BDL	BDL	Intercept	0.085
			CC	0.920

CONCLUSION

The study found that triallate residues, a significant environmental and public health concern, are successfully removed from water by PLA-coated Ag_2O-TiO_2 NPs. Easy recovery and reuse are made possible by the nanomaterial's superior adsorption performance and stability. Studies on photocatalysis reveal higher efficiency and quicker reactions, and the DT50 value, or half-life, is significant in environmental chemistry. This study proposes novel applications for PLA-coated Ag_2O-TiO_2 nanoparticles in environmental remediation and wastewater treatment.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-6: Clean Water and Sanitation*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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