Volume - 13 | Issue - 04 | April - 2024 | PRINT ISSN No. 2277 - 8179 | DOI : 10.36106/ijsr

INTERNATIONAL JOURNAL OF SCIENTIFIC RESEARCH

SYNTHESIS AND CHARACTERIZATION OF CHITOSAN-COATED Fe2O3-Ag2O-TiO2 NANOPARTICLES AND PHOTOCATALYTIC DEGRADATION OF PESTICIDE RESIDUES IN DIFFERENT PH WATERS UNDER NATURAL CLIMATIC CONDITIONS

Chemistry

K. Ramaraju	Department of Chemistry, Mahatma Gandhi University, TS, Nalgonda–508254.
Tentu Nageswara Rao	Department of Chemistry, Krishna University, Machilipatnam, Andhra Pradesh, India.
Tentu Manohra Naidu	Department of Physics, Raghu Engineering College, Dakamarri, Visakhapatnam, AP, India.
Y. Prashanthi*	Department of Chemistry, Mahatma Gandhi University, TS, Nalgonda–508254. *Corresponding Author

ABSTRACT

The study focuses on the synthesis and characterization of chitosan-coated Fe2O3-Ag2O-TiO2 nanoparticles for environmental remediation. These nanoparticles have been identified as promising due to their high surface area and reactivity. Chitosan, a biocompatible polymer, is used to stabilize and enhance the photocatalytic activity of iron oxide, silver oxide, and titanium dioxide nanoparticles. The research, conducted in borosil glass bottles under sunlight, aims to determine optimal conditions for the degradation of pollutants. The efficiency of the process is highlighted by using a 0.1 percent concentration of catalyst for complete degradation. High-Performance Liquid Chromatography with a Photodiode Array detector (HPLC-PDA) is used to analyze the thiophanate in different pH waters, allowing for precise calculations of the rate constant and the time it takes for 50% of the compound to degrade (DT50).

KEYWORDS

Chitosan-Coated Fe2O3-Ag2O-TiO2 Nanoparticles, pH waters, thiophanate, DT50, HPLC-PDA.

INTRODUCTION

The synthesis and characterization of chitosan-coated Fe_2O_3-Ag_2O-TiO_2 nanoparticles represent a significant advancement in the field of environmental nanotechnology [1]. These nanoparticles are engineered to harness the unique properties of each component: the magnetic responsiveness of Fe_2O_3, the antibacterial effects of Ag_2O, and the photocatalytic activity of TiO_2. When combined with the biopolymer chitosan, known for its film-forming ability and biocompatibility, the resulting composite material exhibits enhanced stability and functionality [2]. The coating of chitosan not only prevents the agglomeration of nanoparticles but also introduces a functional surface that can interact with various contaminants, including pesticide residues [3].

The photocatalytic degradation of pesticide residues is a critical process for ensuring the safety of water resources. The chitosan-coated nanoparticles can be dispersed in waters of different pH levels, where they act as catalysts under natural sunlight to break down harmful organic compounds [4]. This process is influenced by the pH of the water, which affects the charge and reactivity of the photocatalyst surface, as well as the structure and solubility of the pesticide molecules. In acidic conditions, the protonation of functional groups on chitosan can lead to increased adsorption of certain pesticide residues, thereby enhancing degradation rates. Conversely, in alkaline waters, deprotonation can occur, potentially reducing the interaction between the catalyst and the pesticides [5].

Under natural climatic conditions, the efficiency of photocatalytic degradation can vary significantly. Factors such as sunlight intensity, temperature, and the presence of other organic or inorganic materials in the water can impact the degradation kinetics [6]. The chitosan coating can provide some level of protection against these variables, ensuring more consistent performance of the nanoparticles [7]. Moreover, the magnetic properties of Fe_2O_3 allow for the easy recovery of the nanoparticles from the water after treatment, facilitating their reuse and reducing waste [8].

The characterization of these nanoparticles typically involves a range of analytical techniques. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) are used to determine the crystalline structure and elemental composition, respectively. Fourier transform infrared spectroscopy (FTIR) can identify functional groups and confirm the presence of the chitosan coating [9]. Scanning electron microscopy (SEM) provides insights into the morphology and size distribution of the nanoparticles. Dynamic light scattering (DLS) and thermal gravimetric analysis (TGA) offer additional information on particle size in solution and thermal stability [10].

The potential applications of chitosan-coated Fe2O3-Ag2O-TiO2 nanoparticles extend beyond the degradation of pesticides [11]. They could be used in a variety of water treatment processes, including the removal of heavy metals, organic dyes, and other pollutants [12]. Their biocompatibility makes them suitable for applications in biomedical fields, such as drug delivery and bioimaging [13]. As research progresses, the scalability of synthesis methods and the long-term stability of these nanoparticles will be key factors in determining their commercial viability and environmental impact [14]. The ongoing development of such multifunctional materials holds promise for addressing some of the most pressing environmental challenges of our time.

Experimental

Preparation of Fe_2O_3.Ag_2O-TiO_2 nanocomposite

In brief, 0.02 mol tetrabutyl orthotitanate were added drop wise into 50 ml absolute ethanol to give a solution which was then vigorously stirred for 20 min at room temperature and add 3 drops of Conc. HNO_3. The desired amounts, 1.0 mmol of ferric nitrate and 1.0 mmol of silver nitrate (the molar ratio of Fe to Ag was 1:1) were added to the reaction mixture while stirring continuously for 60 min until the Fe and Ag were dissolved. 2.0 mL of deionized water was then dropped into the above solution. Afterwards, the resultant solution mixture was maintained at room temperature with continuous stirring for 2 h to form a gel which was then aged for 12 h at room temperature. After being dried at 80 $^{\circ}$C for 24 h were obtained and then annealed at 400 $^{\circ}$C for 3 h. An un-doped TiO_2 (anatase) sample was also prepared by adopting the above procedure without adding the ferric nitrate and silver nitrate which is pure TiO_2. The doping concentrations are expressed as mmol of titanium atom.

Preparation of chitosan-coated Fe_2O_3.Ag_2O-TiO_2 nanoparticles

C-Fe_2O_3.Ag_2O-TiO_2 NPs were prepared using the chemical precipitation method with typically; 0.5 g Fe2O3-Ag2O-TiO2 NPs were dissolved in 100 ml of 1% acetic acid solution, then, 1.0 g of chitosan was added in the solution and the mixture sonicated. The pH value of 9 of the solution was maintained at 10 by adding a dropwise solution of 0.1 M NaOH. The solution was heated in a water bath for 1 h at 100°C. After that, the solution was repeatedly centrifuged at 3500 rpm for 20 mins using distilled water so that the particles settled down in the bottom. The solution was filtered and dried in a vacuum oven at 50°C.

Chitosan-coated Fe_2O_3.Ag_2O-TiO_2 nanoparticles

X-ray diffraction study

The XRD study was conducted by a D8 X-ray Diffractometer model with Cu Kα radiation for the structural analysis of ZnO nanoparticles.

PRINT ISSN No. 2277 - 8179 | DOI : 10.36106/ijsr

The scanning rate of 0.02□ per second with the 2 degrees and the scanning range was 20-80°.

Transmission electron microscopy (TEM)

The C-Fe_2O_3.Ag_2O-TiO_2 NPs particle size was measured by Transmission electron microscopy (FEI, TECNAI G2 TF20-ST).

Scanning Electron Microscopy

C-Fe_2O_3.Ag_2O-TiO_2 NPs NPs and the surface morphology of the char residues which were obtained after performing thermo-gravimetric analysis was examined by scanning electron microscope (SEM) at 3000 magnification. Before SEM examination, a conductive gold layer was used for sputter-coating of the char residue surface. 15 kV accelerating voltage was applied for the examination.

Photocatalytic Study

The photocatalysis of thiophanate methyl in water was studied by spiking thiophanate methyl 10% SC formulation at 1 mg L^{-1} level. The study was conducted in aqueous buffer solutions of pH 4.0, 7.0 and 9.0. Three replications were made at each fortification level along with control samples for comparison. Two sets of spiked concentrations are prepared for the studies. To one set of samples, the catalyst (chitosan-coated Fe_2O_3.Ag_2O-TiO_2) was added, and the other set was studied without the addition of a catalyst. The samples were exposed to direct sunlight. Aliquots of samples were collected at pre-determined intervals. The temperature of water samples during the period was 25 to 42°C. The samples collected on different sampling occasions were filtered using 0.2 µm PTFE membrane filter and collected the filtrates in to amber-colored vials. All the samples were stored in the dark at < 5° C before being subjected to HPLC-DAD analysis. The samples fortified with chitosan-coated Fe_2O_3.Ag_2O-TiO_2 nanoparticles were centrifuged using a Beckman cooling centrifuge at 10000 rotations per minute for 4 minutes at 5°C. Transferred the supernatant in to the amber colored bottles and stored in dark at < 5° C until analysis to avoid further degradation of residues.

RESULTS

A D8 X-ray diffractometer model with Cu Kα radiation for the structural analysis of chitosan-coated Fe_2O_3.Ag_2O-TiO_2 NPs conducted the XRD study. The scanning rate of 0.02◦ per second and a current of 30 mA over a 2θ range of 20°–80°. The XRD of chitosan-coated Fe2O3-Ag2O-TiO2 NPs presented in **Figure 1**.

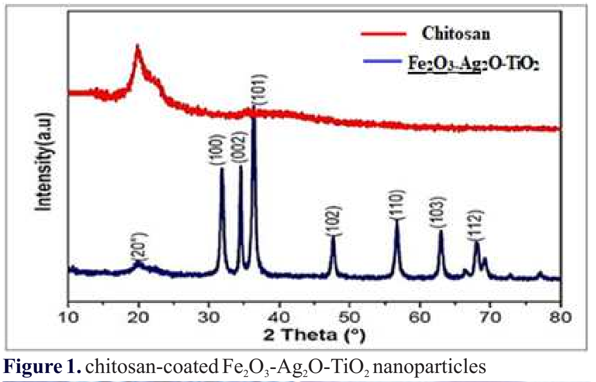

Figure 1. chitosan-coated Fe_2O_3-Ag_2O-TiO_2 nanoparticles

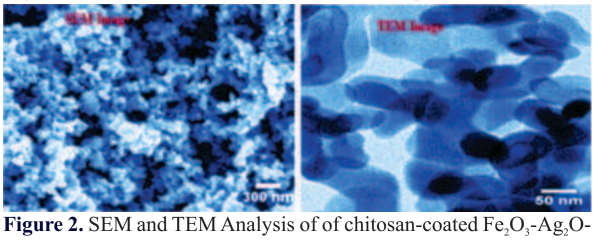

Figure 2. SEM and TEM Analysis of of chitosan-coated Fe_2O_3-Ag_2O-TiO_2 nanoparticles

SEM And TEM Analysis of chitosan-coated Fe_2O_3-Ag_2O-TiO_2 nanoparticles

The surface morphology of the acquired chitosan-coated Fe_2O_3.Ag_2O-TiO_2 nanoparticles) was documented using SEM The SEM image indicated that the chitosan-coated Fe_2O_3.Ag_2O-TiO_2 nanoparticles NPs have a smooth surface and the agglomeration of NPs is also visible there. The SEM and TEM images of chitosan-coated Fe_2O_3-Ag_2O-TiO_2 NPs are shown **(Figure 2).** The figure indicates that chitosan-coated Fe_2O_3-Ag_2O-TiO_2 NPs are uniform and cylindrical. The average particle size was calculated using Image-J software and the particle size is ranged from about 50 nm.

Photolytic And Photocatalytic Study

The degradation results of Thiophanate methyl in water showed the residues are highly stable, the stability decreased with decreasing pH. The half-life of Thiophanate methyl was 33.47, 42.17 and 58.12 days in acidic, neutral and basic pH's respectively. The half life of thiophanate methyl in the presence of a catalyst in different aqueous buffers was recorded to be 12.05 hours in acidic water, 20.47 hours in neutral water and 35.12 hours in basic water.

The representative curves were present in **Figure 3.**

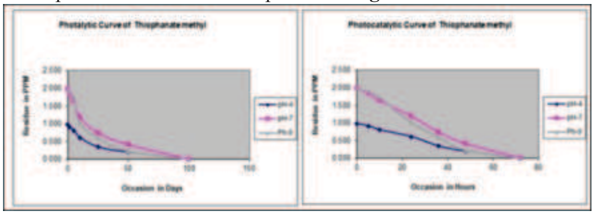

Figure 3: The representative photolytic and Photocatalytic Curves.

CONCLUSIONS

Synthesis of chitosan-coated nanoparticles: Combining Fe2O3, Ag2O, and TiO2 to create a compound with high surface area and reactivity. Chitosan as a stabilizer: Utilizing the biocompatible polymer to enhance the photocatalytic activity of the nanoparticles. Environmental remediation application: Employing the nanoparticles to degrade pollutants under sunlight in borosil glass bottles. Catalyst concentration: Using a 0.1 percent concentration of the nanoparticles to achieve complete degradation of pollutants. Analytical techniques: Implementing High-Performance Liquid Chromatography with a Photodiode Array detector (HPLC-PDA) for the analysis of thiophanate in various pH waters. Rate constant and DT50 calculations: Determining the rate at which thiophanate degrades and the time required for 50% degradation (DT50) to assess efficiency.

REFERENCES

1. Kashyap, J.; Riaz, U. Facile Synthesis of Novel Polypyrrole Dispersed AgFeO2 Nanohybrid with Highly Efficient Photocatalytic Activity towards 2,4,6-Trichlorophenol Degradation. *RSC Adv.* **2018**, *8*, 13218–13225, doi:10.1039/c8ra00754c.
2. Daqa, W.M.; Alshoaibi, A.; Ahmed, F.; Rao, T.N. Synthesis and Characterization of Nanoformulation of the Broad-Spectrum Enzyme Inhibitor Mancozeb by Polyethylene Glycol Capping and Its Dissipation Kinetics in Water Using TiO2 Nanoparticles. *Processes* **2022**, *10*, doi:10.3390/pr10122733.
3. Sarathi, R.; Devi, L.R.; Sheeba, N.L.; Esakki, E.S.; Sundar, S.M. Photocatalytic Degradation of Malachite Green Dye by Metal Oxide Nanoparticles-Mini Review. *J. Chem. Rev.* **2023**, *5*, 15–30, doi:10.22034/jcr.2023.359935.1187.
4. Raghavendra, G.M.; Jung, J.; Kim, D.; Seo, J. Chitosan-Mediated Synthesis of Flowery-CuO, and Its Antibacterial and Catalytic Properties. *Carbohydr. Polym.* **2017**, *172*, 78–84, doi:10.1016/j.carbpol.2017.04.070.
5. Inamuddin; Mohammad, A.; Asiri, A.M. *Inorganic Pollutants in Wastewater: Methods of Analysis, Removal and Treatment*; 2017; Vol. 16; ISBN 978-1-945291-63-0.
6. Taghizade Firozjaee, T.; Mehrdadi, N.; Baghdadi, M.; Nabi Bidhendi, G.R. Application of Nanotechnology in Pesticides Removal from Aqueous Solutions - A Review. *Int. J. Nanosci. Nanotechnol.* **2018**, *14*, 43–56.
7. Nageswara Rao, T.; Prashanthi, Y.; Ahmed, F.; Kumar, S.; Arshi, N.; Rajasekhar Reddy, G.; Manohra Naidu, T. Photocatalytic Applications of Fe–Ag Co-Doped TiO2 Nanoparticles in Removal of Flumioxazin Pesticide Residues in Water. *Front. Nanotechnol.* **2021**, *3*, 1–11, doi:10.3389/fnano.2021.652364.
8. Daqa, W.M.; Alshoaibi, A.; Ahmed, F.; Rao, T.N. Potential Applications of Chitosan-Coated Zinc Oxide Nanoparticles for Degrading Pesticide Residues in Environmental Soils. *Crystals* **2023**, *13*, doi:10.3390/cryst13030391.
9. Ahmed, F.; Rao, T.N.; Arshi, N.; Prashanthi, Y.; Kumar, S.; Alshoaibi, A. Fe2O3-Ag2O/TiO2 Nanocatalyst-Assisted LC-MS/MS-Based Detoxification of Pesticide Residues in Daphnia Magna and Algae Mediums. *Crystals* **2023**, *13*, doi:10.3390/cryst13040644.
10. Sharma, S.; Umar, A.; Mehta, S.K.; Ibhadon, A.O.; Kansal, S.K. Solar Light Driven Photocatalytic Degradation of Levofloxacin Using TiO2/Carbon-Dot Nanocomposites. *New J. Chem.* **2018**, *42*, 7445–7456, doi:10.1039/c7nj05118b.
11. Mohapatra, M.; Anand, S. Synthesis and Applications of Nano-Structured Iron Oxides/Hydroxides – a Review. *Int. J. Eng. Sci. Technol.* **2011**, *2*, 127–146, doi:10.4314/ijest.v2i8.63846.
12. Of, H.E.F. Synthesis and Characterization of Ag Doped TiO2, CdS, ZnS Nanoparticles for Photocatalytic, Toxic Ions Detection, and Antimicrobial Application. **2014**, doi:10.1201/9781420039283.fmatt.
13. Dobson, P.J. *Bionanomaterials for Environmental and Agricultural Applications*; 2022; Vol. 63; ISBN 9780750338639.
14. Naseem, T.; Durrani, T. The Role of Some Important Metal Oxide Nanoparticles for Wastewater and Antibacterial Applications: A Review. *Environ. Chem. Ecotoxicol.* **2021**, *3*, 59–75, doi:10.1016/j.enceco.2020.12.001.