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From Garden to Guardian: *Tagetes erecta*-derived Photoluminescent Zinc Oxide Quantum Dots (ZnO-QD) as Eco-Catalysts for Aquatic Decontamination

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Abstract

This study presents an eco-innovative procedure of photoluminescent zinc oxide quantum dots (ZnO-QDs) utilizing *Tagetes erecta* (marigold) leaf extract as an ecological reducing and capping agent, offering a sustainable alternative to orthodox chemical synthesis routes. ZnO-QDs were fabricated by rapid amalgamation of marigold leaf extract with zinc acetate solutions at varying molar concentrations (1, 3, and 5 mM) under ambient stirring conditions for 5 minutes. The instantaneous emergence of a pale-yellow coloration signaled quantum dot nucleation, subsequently verified through UV-visible spectroscopy exhibiting characteristic absorption maxima within the 300-350 nm range. The synthesized QDs demonstrated remarkable photoluminescence under UV irradiation, with emission spectra peaking at 330 nm excitation, confirming their quantum-confined optical properties. Comprehensive physico-chemical characterization was executed using Fourier-transform infrared spectroscopy (FT-IR) to identify phytochemical functional groups mediating QD stabilization, while field-emission scanning electron microscopy (FE-SEM) elucidated surface morphological features and crystalline structure. The photocatalytic efficacy of the biogenic ZnO-QDs was assessed through solar-driven degradation experiments employing methylene blue as model organic pollutant, revealing differential degradation kinetics-moderate photodegradation efficiency for methylene blue. Furthermore, the multifunctional potential of these quantum dots was demonstrated through antibacterial assays via the well-diffusion method and antioxidant capacity evaluation using DPPH radical scavenging assays, positioning marigold-derived ZnO-QDs as promising compound for integrated eco-waste remediation and bio-medical applications.

Keywords: Green synthesis; Zinc oxide quantum dots; *Tagetes erecta*; Dye degradation; antibacterial

Introduction

Nanotechnology has emerged as a powerful tool in addressing environmental pollution, particularly in water purification and wastewater treatment. Quantum dots (QDs) are nanosized semiconductor materials with unique physical and chemical properties, among

which size-dependent photosensitive and electronic properties are predominantly important. Quantum dots show strong catalytic activity, making them attractive photocatalysts for breaking down organic pollutants. In addition to their remarkable luminescent and electrical characteristics, QDs have prospective uses in the biological sciences. Because of their ultrasmall size and ultrahigh surface-to-volume ratio, semiconductor QDs with diameter 2-10 nm, have recently become promising tools for single-particle and single-molecule imaging in living cells and animals[1].

Green chemistry experiments are based on a set of principles, aimed at minimizing or eliminating the use of hazardous materials in the design, execution, and application[2]. In plant mediated synthesis, plant biomolecules such as proteins, and metabolites served as reducing, capping as well as stabilizing agents[3]. ZnO-QDs has a wide and strong absorption in the ultraviolet region and thus they are widely used as sensors, transistors, UV detectors, and optoelectronic devices. ZnO quantum dots typically exhibit two distinct emission bands: near-band-edge emission in the ultraviolet region and defect-related emission in the visible region, the latter commonly appearing as blue, green, or yellow fluorescence[4]. ZnO quantum dots are particularly effective in removing organic pollutants and act as appealing as eco-catalysts[5]. Here, the green synthesis of Zinc oxide quantum dots (ZnO-QDs) was done using Tagetes erecta (marigold) leaf extract.

Experimental

Zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$] purchased from Sigma-Aldrich Chemicals (India). *Tagetes erecta* (African Marigold) is a natural herbicide were collected from local area. UV-Visible spectrometer-SHIMADZU UV-1800, FTIR spectrometer-SHIMADZU IR Prestige-21 in the wavenumber range 600-4000 $cm^{-1}$is used for study. HORIBA Fluorescence Spectrometer with Integrating Sphere & Lifetime Detector is used to luminescent studies. Field Emission Scanning Electron Microscope (FE-SEM) with EDS-TESCAN BRNO s.r.o., Czech Republic is used to study surface morphology.

Tagetes erecta holds a mixture of terpenes, monoterpenes, flavonoids and other essential oils. It is also known for its antimicrobial, and antioxidant properties in local medicine and used pest and weed control in organic agriculture due to the presence polyphenols[6].The fresh leaves of the *Tagetes erecta* (marigold) were taken, properly cleaned, 20 g of leaves were chopped into tiny pieces. An aqueous extract was prepared with 100 mL of Distilled water. On heating with Zinc acetate solution in the ratio 1:1 the colour turned pale yellow. Zinc acetate solutions of different concentrations (1 mM, 3 mM, and 5 mM) were tried.




Figure 1. (a) Leaves of *Tagetes erecta* (b) Leaf extract

Antimicrobial activity

The antimicrobial activities of ZnO-QDs were assessed against Gram-positive (*Staphylococcus aureus*-ATCC 25923) and Gram-negative (*E. coli* -ATCC 25922) cells using agar well diffusion technique. Using a well cutter wells of approximately 10 mm was bored and added different concentrations (25µL, 50µL and 100µL) of samples. The samples are allowed to diffuse out into the medium and interacted with the test organisms depending on their antimicrobial activity. The resulting circular zones of inhibition were measured in millimeters. Streptomycin used as control.

Antioxidant activity

The free radical scavenging activity of different samples was determined by using DPPH assay[7]. DPPH assay uses 1, 1-diphenyl-2-picryl hydrazyl (DPPH) is a stable free radical with pink colour which turns yellow when scavenged. The free radical scavenging reaction between (DPPH) and an antioxidant (H-A) can be written as,

$$\mathrm{DPPH} + [\mathrm{H\text{–}A}] \rightarrow \mathrm{DPPH\text{–}H} + (\mathrm{A})$$

Antioxidant samples react with DPPH and reduce it to DPPH-H and as consequence the absorbance at 517 nm decreases. The absorbance measurements are carried out using SHIMADZU(UV-1900i) UV-VIS spectrophotometer. The percentage inhibition is calculated as, Inhibition (%) =

$$\text{Inhibition } (\%) = \frac{\text{control} - \text{test}}{\text{control}} \times 100$$

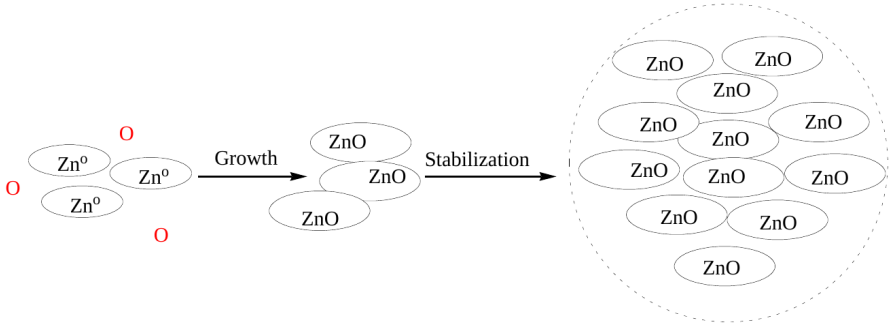
Catalytic Activity

The catalytic properties of ZnO-QDs enable the efficient degradation of organic pollutants, such as dyes and nitroaromatic compounds, in water. ZnO-QDs catalyst supports degradation of the toxic dye methylene blue into less harmful products facilitating its removal. The fall in the intensity of peak at 664 nm is studies using UV-visible spectroscopy.

Results and Discussion

Synthesis and characterization of ZnO-QDs

A slight colour change from pale yellow to light yellow was observed, indicating the formation of ZnO quantum dots. Plant chemicals reduce Zn^{2+} to Zn^{0}. From the reaction conditions oxygen combines with Zn^{0} to form ZnO. After the growth process in the quantum dot region Phytochemicals took the role of capping agents and stable ZnO-QD formed. The proposed mechanism is as shown in Scheme 1.



Scheme 1. Mechanism of ZnO-QD formation

The formation of ZnO-QD show localized surface plasmon resonance (SPR) using UV–Visible (UV-vis.) Spectroscopy in the range of 300–500 nm[8]. The absorption maximum observed at 309 nm confirms the formation of ZnO and reflected their optical behaviour due to quantum confinement.

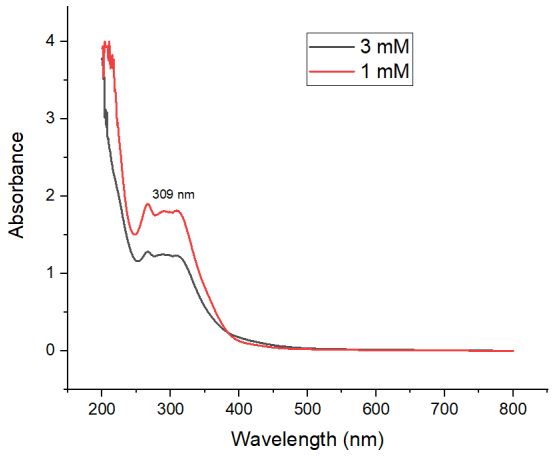


Figure 2. UV–Visible Spectrum of ZnO-QD

The light-emitting nature of ZnO-QD is proved from their excellent photoluminescence spectra on an excitation of 330 nm. Photoluminescence (PL) emission spectroscopy can used recognize and compute the defect states[9]. Visual and notable fluorescence effect was observed in ZnO-QDs from *Tagetes erecta* in contrast to the non-fluorescent effects of ZnO[10]. Nature-inspired generation of ZnO-QDs is a promising alternative for

sustainable development. The prominent emission from ZnO-QDs confirms its luminescent properties.

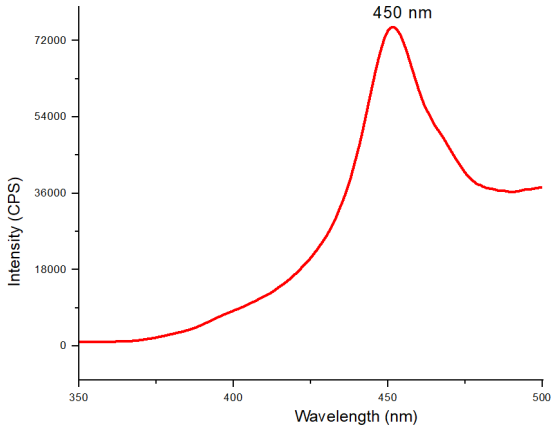


Figure 3. Photoluminescence (PL) emission by ZnO-QDs

FT-IR spectroscopy identified the functional groups present in the ZnO-QD and revealed the main functional groups of *Tagetes erecta* which stabilize them. The characteristic IR band at 3344 cm^{-1} and 1664 cm^{-1} is attributed to the O–H stretching vibrations in polyphenols[11]. This analysis helped in confirming the formation of Zn–O bonds and also showed the presence of biomolecules or stabilizing agents attached to the quantum dots.

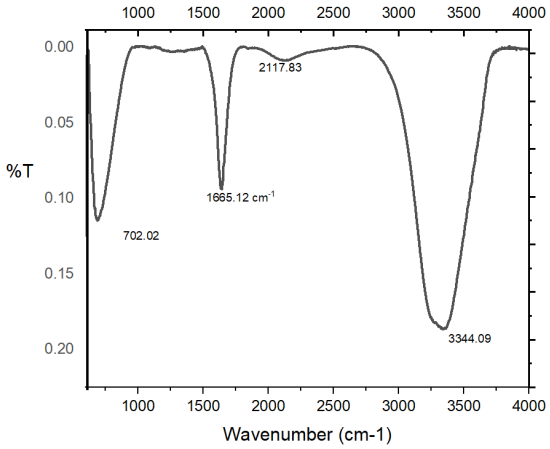


Figure 4. FTIR spectrum of ZnO-QDs

The surface morphology, size etc of the synthesized ZnO-QDs were examined using field emission scanning electron microscopy (FE-SEM). The FE-SEM images showed the particle shape, surface texture, and overall distribution of the quantum dots, supporting the successful formation of nanoscale ZnO.

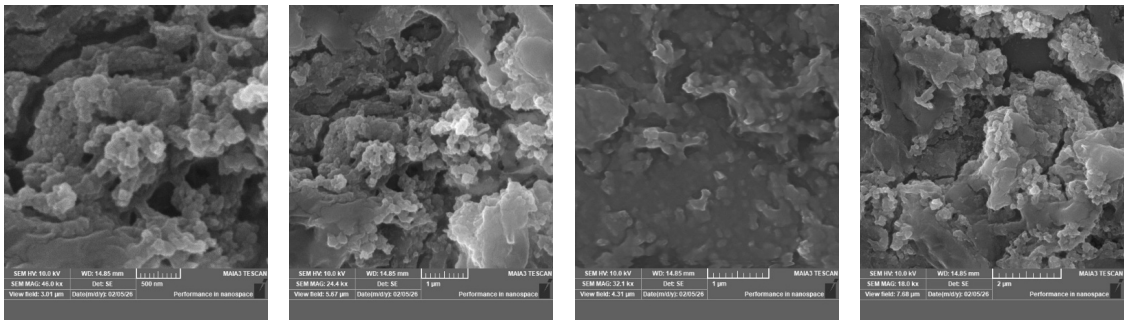


Figure 5. FE-SEM images of ZnO-QD

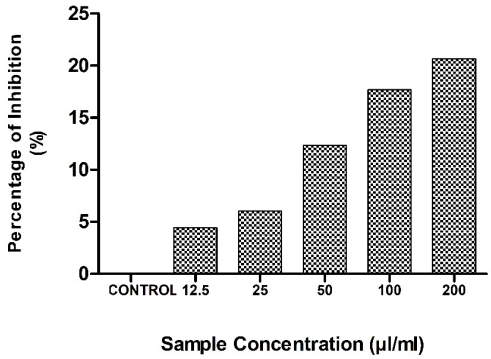


Figure 6. DPPH Radical scavenging capacity of different concentrations of ZnO-QD.

IC_{50} stands for the concentration of a substance needed to inhibit a biological process by 50% compared to an untreated control. The lower IC_{50} higher will be the activity. IC_{50} value shown by ZnO-QD: 469.71 µl/mL confirms its moderate antioxidant activity (ED 50 PLUS V1.0 Software).



Figure 7. Antimicrobial activity of ZnO-QDs against *E. coli* and *S. aureus* (Agar well diffusion method)

Photographs of Mueller Hinton Agar plates showing zones of inhibition produced by 25 µL, 50 µL, and 100 µL of ZnO-QD samples (1 mg mL^{-1}) and a positive control

(Streptomycin, 50 µL, 10µg mL^{-1}). The inhibitory effects of ZnO-QDs against two different bacterial strains were given in Figure 8. The antimicrobial activity of ZnO-NPs is a size-dependent property[12].

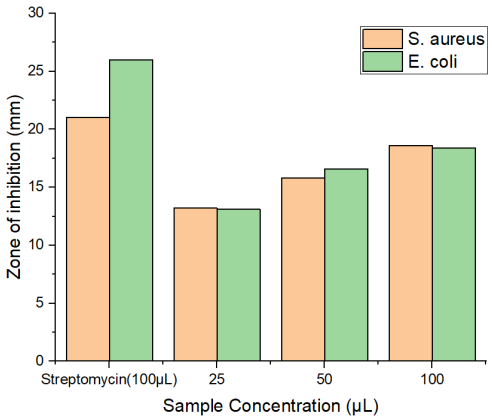


Figure 8. Plot of inhibition (%) of ZnO-QD for the different microorganisms

Microbial infections pose significant challenges to public health, and the emergence of antibiotic resistance has become a major concern in healthcare systems. As shown in Figure 8, E. coli exhibited a larger zone of inhibition than S. aureus, indicating greater susceptibility of E. coli to ZnO-QDs under the tested experimental conditions. Disruption of the bacterial cell membrane, inhibition of protein synthesis, and alterations in gene expression etc. are the main mechanisms underlying reasons for antibacterial activity[13]. It developing unique antimicrobial agents, adjuvants to conventional therapies and natural food preservatives.

Photocatalytic activity of synthesized ZnO-QDs was evaluated using methylene blue dye under UV light. In the case of methylene blue, a gradual decrease in the absorption peak was observed with time, confirming dye degradation. Photocatalytic degradation of methylene blue happens within 5 minutes in the presence of catalyst ZnO-QDs[14]. This property makes ZnO-QDs ideal candidates for treating wastewater from textile and chemical industries.

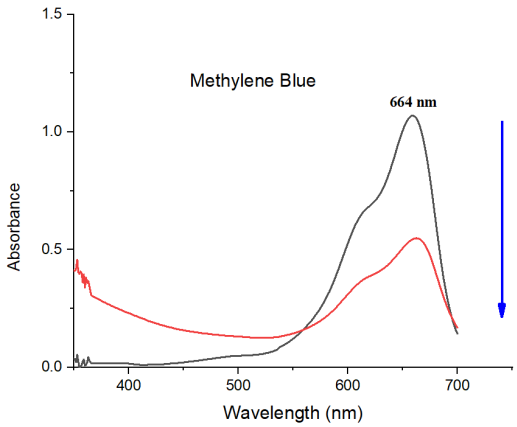


Figure 9. Photocatalytic degradation of methylene blue in the presence of catalyst ZnO-QDs

Conclusions

Green synthesis of ZnO-QDs using *Tagetes erecta* leaf extract successfully produced photoluminescent nanomaterials with confirmed quantum confinement. The synthesized ZnO-QDs demonstrated moderate antioxidant activity (IC_{50}: 469.71 µl/mL), notable antibacterial activity against *S. aureus*, and effective photocatalytic degradation of methylene blue, establishing them as promising eco-friendly candidates for biomedical and environmental remediation applications.

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