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ZnS semiconductor quantum dots production by an endophytic fungus *Aspergillus flavus*

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ABSTRACT

The development of reliable and eco-friendly processes for the synthesis of metal sulphide quantum dots has been considered as a major challenge in the field of nanotechnology. In the present study, polycrystalline ZnS quantum dots were synthesized from an endophytic fungus *Aspergillus flavus*. It is noteworthy that apart from being rich sources of bioactive compounds, endophytic fungus also has the ability to mediate the synthesis of nanoparticles. TEM and DLS revealed the formation of spherical particles with an average diameter of about 18 nm and 58.9 nm, respectively. The ZnS quantum dots were further characterized using SEM, EDAX, XRD, UV–visible spectroscopy and FTIR. The obtained results confirmed the synthesis of polycrystalline ZnS quantum dots and these quantum dots are used for studying ROS activity. In addition this paper explains kinetics of metal sorption to study the role of biosorption in synthesis of quantum dots by applying Morris-Weber kinetic model. Since *Aspergillus flavus* is isolated from a medicinal plant Nothapodytes foetida, quantum dots synthesized from this fungus may have great potential in broad environmental and medical applications.

1. Introduction

Quantum dots are the semiconductor nanoparticles which have gained significance due to their unique quantum confinement effects. Amidst II–VI semiconductors, zinc sulphide has immense consideration due to its specific band structure, wide band-gap energy and large exciton binding energy [24,38]. These properties capacitate the utility of ZnS QDs in diverse fields such as catalyzators, chemical sensors, biosensors, UV light sensors, nanogenerators, field emitters and field effect transistors [9,28]. In addition ZnS nanoparticles find its applications in remediation of environment pollutants by absorption and acts as a photo-catalyst in the degradation of organic pollutants such as dyes, halogenated derivatives, and p-nitrophenol [8,43].

Recent years have evinced the integration of nanomaterials of biological origin in nano-engineered devices. The biogenic synthesis of quantum dots have been preferred over the traditional chemical methods due to their nontoxic nature and the inherent biocompatibility rendered to the quantum dots in a microbial assisted synthesis procedure [19,36]. Moreover, according to literature, chemical methods limit the applications of nanoparticles in the field of medicine and environment [15,41]. In biogenic synthesis, yield of nanoparticles produced from fungi is high compared to plants and bacteria [37]; this is due to the fact that fungi secrete more amounts of proteins which directly translate to higher productivity of nanoparticles formation [33]. Further, good monodispersity, minimal media requirements, intracellular metal uptake capabilities and well defined dimensions can be obtained by fungal nanoparticle synthesis [26,34]. Moreover, fungal biomass is easy to handle which makes the scale up process accessible [5].

In this context, endophytic fungi which are known to secrete structurally diverse bioactive compounds were explored for the synthesis of nanoparticles [8,11,12]. Interference of endophytes and nanomaterials is a relatively new research area that has attracted unequivocal attention. In the current study an endophytic fungus *Aspergillus flavus* was selected for the synthesis of ZnS quantum dots due to antioxidant property [40]. To the best of our knowledge this is the first report on ZnS semiconductor quantum dots production using endophytic fungi *Aspergillus flavus* (Family: Trichocomaceae) which has been isolated from leaves of *Nothapodytes foetida*.

2. Experimental details

2.1. Isolation and identification of endophytic fungi

Endophytic fungi were isolated from leaf segments of *Nothapodytes Foetida* located at 13°30″N and 75°2″E in the

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Western Ghats, Daksina Karnataka, India. These leaf segments were surface sterilized and cut into minute pieces and placed on petri plates (containing Potato Dextrose Agar (PDA) media amended with 0.5 g/L streptomycin sulphate) such that the internal tissues were in contact with the media [1,30]. The petri plates were examined after the completion of incubation period and individual pure fungal colonies were streaked onto other PDA plates. The isolated fungi were sent for identification at Agharkar Research Institute, Pune, India. Further studies were conducted based on growth and tolerance potential of endophytic fungi.

2.2. Tolerance studies

The most tolerant fungal isolate was subjected to tolerance studies in potato dextrose broth medium (PDB) amended with Zinc Heptahydrate in a concentration range of 0.5–3 mM and media without metal solution is considered as control. PDB containing the respective concentrations of the metals were inoculated with 1 ml of freshly prepared spore suspension of the fungal isolate and put on shaker at 115 rpm at 28 °C for 5 days. Fungal growth was harvested after 5 days through filtration using Whatman filter No. 42. The harvested fungal biomass was rinsed with double distilled water 3–4 times and dried in hot air oven at 70 °C. The dry weight of the biomass was calculated and compared with control.

2.3. Kinetics of metal sorption

In order to analyze kinetics of Zn biosorption onto mycelium of *Aspergillus flavus*, pseudo-first order [18] and Morris-Weber kinetic models [42] were applied. The Morris-Weber equation was expressed as follows:

$$q_t = k_{id} t^{1/2} + C$$

where q_t (g/kg) is the metal uptake at time t (day), k_{id} (g kg^{-1} day$^{-0.5}$) is the intra particle diffusion rate constant, and C is a constant (g/kg).

The pseudo-first-order rate equation by the Lagergren's is given as:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303}$$

where q_e (g/kg) and q_t (g/kg) are the metal uptake on 5th day and at any given time t (day), respectively and k_1 is the rate constant (day^{-1}). Using the experimental data on metal uptake q_t vs t and the equilibrium uptake q_e (the constant value of uptake reached during experiments), a graph of $\log(q_e - q_t)$ vs t were plotted for metal under study. The validity of first order kinetic model to represent the experimental data were tested by the linear nature of the plot [44].

2.4. Extracellular synthesis and characterization of Zinc Sulfide quantum dots

The mycelial discs (2 mm × 5 mm) from an actively growing source culture of Aspergillus flavus were aseptically transferred into 250 ml PDB and grown for two days at 28 °C and 115 rpm. Thereafter, the media components were drained off and the fungal biomass was harvested, and was added to a flask containing (100 ml) 3 Mm Zinc Sulfate Heptahydrate solution in order to facilitate the biosynthesis of ZnS nanoparticles [14,35].

The biosynthesized product was characterized using based on Transmission Electron Microscopy (TEM), Dynamic light scattering (DLS), Scanning Electron Microscopy (SEM), Energy Dispersive Analyses of X-rays (EDAX), X-ray diffraction (XRD), UV–vis and Fourier Transfer Infra-Red (FTIR) Spectrometer. The band gap was determined by Tauc plot and the crystallite size was calculated based on Scherrer equation.

2.5. Zinc Sulfide quantum dots-induced ROS activity study based on antimicrobial activity

Antimicrobial activity was determined by using sterile filter paper discs (Whatman No. 3: 10 mm square) dipped in 50 μL of the ZnS quantum dots solution were placed on E. coli culture agar plates and based on zone of inhibition average percent inhibition was calculated. Each plate had a set of controls which are compared with zone of inhibition [21,32].

For cell viability test, E. coli growth in the culture media was monitored by measuring its optical density (O.D) at 600 nm. E. coli culture was retrieved and was supplemented with different concentrations of ZnS quantum dots of concentration ranging between 10 and 100 mL/100 mL of media. All the flasks were then incubated at 37 °C in an orbital shaker at 150 rpm. The bacterial growth was monitored after 24 h by measuring the O.D of the culture media at λ = 600 nm [13].

3. Results and discussion

3.1. Tolerance potential and biosorption kinetics Aspergillus flavus

Results on the analysis of the fungal growth in the presence and absence of Zn show a decrease in biomass content with increase in the concentration of $ZnSO_4$ from 0.5 to 3 mM as represented in Fig. 1. Observations on the fungal growth and morphology on PDA plates with and without Zn stress affirm the tolerance of this fungus to this metal (Fig. 2).

The experimental data on kinetic studies fitted well with the intra particle diffusion model with R^2 value 0.992 which indicates that the intra particle diffusion process is one of rate controlling step [17]. The intercept, '*C*' is proportional to the boundary layer thickness for external film mass transfer and estimated to be −0.4 (negative) which indicates that other processes like surface chemical reaction and transportation into cell interior may contribute to the overall rate of metal uptake, apart from intra particle diffusion and external film mass transfer. The calculated value of intra particle diffusion rate constant (k_{id}) is 0.9 (Fig. 3a). Lagergren's pseudo first-order model equation was used to explain the kinetics of metal uptake by the organism *Aspergillus flavus* [22]. The straight line fit of the experimental data to the model was tested based on the value of the coefficient of determination (R^2) and rate constants (k_1). The

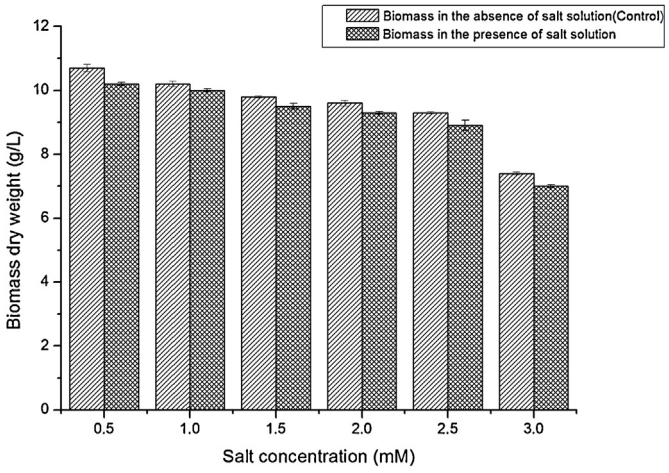

Fig. 1. Effect of concentrations of $ZnSO_4$ on *Aspergillus flavus* growth.