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Green synthesis of multifunctional zinc oxide (ZnO) nanoparticles using *Cassia fistula* plant extract and their photodegradative, antioxidant and antibacterial activities

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ABSTRACT

The present study involves green synthesis of ZnO nanoparticles (Nps) using aqueous *Cassia fistula* plant extract as fuel by solution combustion synthesis. The ZnO Nps were characterized by Powder X- ray diffraction (PXRD), UV–visible studies and Transmission electron microscopy (TEM). The Nps were evaluated for photodegradative, antimicrobial and antioxidant activities. The extract was found to contain reducing components such as polyphenols (11%) and flavonoids (12.5%). The Nps were found to have a hexagonal wurtzite structure. UV–visible absorption of ZnO Nps showed absorption band at 370 nm which can be assigned to the intrinsic band-gap absorption of ZnO due to the electron transitions from the valence band to the conduction band. TEM image confirms the formation of nanoparticles and the average crystallite sizes were found to be ~5–15 nm. Methylene blue (MB) dye was effectively degraded under UV and Sun light illumination in the presence of ZnO Nps. Significant antioxidant activity was exhibited by Nps through scavenging of 1, 1-Diphenyl-2-picrylhydrazyl (DPPH) free radicals. Excellent bactericidal activity was shown by the Nps on *Klebsiella aerogenes*, *Escherichia coli, Plasmodium desmolyticum* and *Staphylococcus aureus*. Synthesis of multifunctional ZnO Nps using naturally occurring plant products has been advocated as a possible environment friendly alternative to chemical methods.

1. Introduction

Dye contaminants from fabric, printing, manufacture and many other industries show a vital role to damage the environment. These wastes enter into water ecosystem and create many environmental and health risks. Some methods like osmosis, adsorption, flocculation and others have been used for dye elimination from river, but each method has its own benefits and limitations. Photocatalytic treatment offers a capable, relatively low cost and eco friendly method to resolve this problem [1]. In past few years, ZnO has been most frequently used for degradation of many organic pollutants [2]. Along with this, microbial contamination is a thoughtful matter in healthcare and nutrition industry. Development of

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antimicrobial agents and external coatings has been given significant attention in recent years [3–5]. Antimicrobial properties with nano sized particles are of substantial interest in the recent past [6,7]. It was specified that nanosized semiconductors act as an effective photocatalytic agent resulting from either large surface area or quantum confinement effects of charge carriers for the degradation of organic contaminants in water under UV light and Sun light irradiation [8–10]. Photocatalytic function is very similar to that of chlorophyll in the photosynthesis. Photo-induced molecular reactions take place at the surface of the catalyst in a photocatalytic system. The simplest mechanism of photocatalytic reaction is the generation of electron–hole pair on the surface of the semiconductor and its endpoint is as follows. When a photocatalyst is exposed to the light which possess stronger energy than its band gap energy, then electron–hole pairs diffuse out to the surface of the photocatalyst and partake in the chemical reaction with the electron acceptor and donor [11]. These free holes and electrons convert to the neighboring oxygen and water molecules into $OH^{\cdot}$ free radicals and super oxides and these act as strong oxidizing agents for the degradation of dyes [11]. ZnO is a well known n-type wide-ranging band gap oxide semiconductor (~3.37 eV) and it has high binding energy (60 meV) [12,13]. ZnO is one of the hardest materials, hence it does not suffer from dislocation degradation during the course of operation [14]. Several approaches have been engaged to synthesize ZnO nanocrystals such as sol–gel solvothermal, direct precipitation and hydrothermal etc., [15–18]. Most of these approaches require tedious processes, expensive substrates, sophisticated equipments and rigorous experimental circumstances. Solution combustion synthesis is one of the best and easy methods for the synthetic approach towards the uniform mixing with combustible fuel. During solution combustion, exothermic reaction between oxidizing and reducing agent takes place. Generally metal nitrates are used because of their unique solubility to form homogeneous solution. Metal nitrates act as oxidizer agents and fuel acts as reducing agents for the synthesis of ZnO nano crystals [19–21].

In this paper, we are the first to report the green synthesis of ZnO nanoparticles via solution combustion synthesis using *Cassia fistula* leaf extract. Green synthesis is more environmental friendly with less side effects when compared to chemical methods. The leaf mainly contains (−) epiafzelechin, (−) epiafzelechin-3-Oglucoside, (−) epicatechin, procyanidin B2, biflavonoids, triflavonoids, rhein, Rheinglucoside, sennoside A, sennoside B, chrysophanol, and physcion [22]. It is widely used for its medicinal properties such as mild laxative for children and pregnant women. It is also a purgative owing to the wax aloin and a tonic [23]. It is also used for many other intestinal disorders like healing ulcers [24]. It is also known to exert antipyretic, analgesic, anti-inflammatory and hypoglycemic activities [25]. This study attempts to exploit *C. fistula* extract as fuel for the green synthesis of ZnO nanoparticles. This procedure involves a self-sustained reaction in homogeneous solution of Zinc nitrate and *C. fistula* leaf extract.

2. Materials and methods

C. fistula leaves were sourced from Devarayana Durga forest area of Tumkur district, Karnataka, India. The plant material was shade dried and powdered into 100 mesh size and was stored at room temperature in an airtight container.

2.1. Preparation of the extract

1:10 proportion of the coarsely powdered plant material to water was taken in a round bottomed flask and the extraction was carried out at 100 °C with a reflux arrangement for 5 h with constant stirring. The extract was filtered and centrifuged to remove any un-dissolved material. The extract was then concentrated, dried using roto evaporator and stored in airtight bottles at 4 °C.

2.2. Polyphenol assay

Folin ciocalteu reagent (FC reagent) (0.1 N) was prepared by diluting (1:20) commercially available FC reagent with distilled water. Sodium carbonate (7.5%) was prepared by dissolving 7.5 g of sodium carbonate in 100 ml of de-ionized water. Gallic acid (standard) Stock I (conc. 0.1 mg ml^{-1}) was prepared by dissolving 1 mg of Gallic acid in 10 ml with 50% methanol. For making standard graph of Gallic acid, concentration range of 2–20 μg/mL was used. The assay was carried out by using a Singleton and Rossi method [26]. In a typical process, 1000 μl of FC reagent was added to 200 μl of 50% methanol/standard/test sample with various concentrations, mixed and incubated at RT for 5 min. 800 μl of 7.5% sodium carbonate solution was added, mixed and incubated at 37 °C for 30 min. The absorbance was recorded at 750 nm against blank using spectrophotometer. Color correction was given with the same concentration of the test sample in 50% methanol without FC reagent.

2.3. Flavonoids assay

Vanillin, an aromatic aldehyde condenses with the flavon-3-ols and oligomers to form soluble pigments in acidic medium with an absorbance maximum at 500 nm, which can be detected by a UV–visible spectrophotometer. Vanillin Reagent (1%) was prepared by dissolving 1 g of crystallized vanillin in 100 ml of 70% Conc. H_2SO_4. Conc. H_2SO_4 (70%) was prepared by diluting 70 ml on Conc. H_2SO_4 in 100 ml de-ionized water. Methanol (50%) was prepared by diluting 1:1 with de-ionized water. 10 mg of Phloroglucinol was dissolved and made up to a volume of 10 ml with 50% methanol, followed by centrifugation at 12,000 rpm for 10 min and labeled as Stock I. Stock II was prepared by diluting Stock I to a Conc. of 0.1 mg ml^{-1} with 50% methanol. For making standard graph of Phloroglucinol, 1–10 μg/mL concentration range was used. The flavonoid assay was carried out using a Swain and Hillis method [27]. In a typical experiment, to a 400 μl of distilled water/positive control/test sample with various concentrations, 800 μl of 1% vanillin reagent was added, mixed and incubated at RT for 15 min. The absorbance was recorded at 500 nm against blank using the spectrophotometer. Color correction was given with the same concentration of the test sample in distilled water without vanillin reagent. The flavonoid content in the plant extract was measured with reference to the standard Gallic acid values.