Research Article

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Green Synthesis of Barium Sulphate Nanostructures Using *Azadirachta indica* Leaf Extract

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ABSTRACT

Green synthesis of nanostructures is a growing technology owing to its potential applications in various fields. The method is feasible, simple and non-toxic; it is a low-cost strategy. It meets the standards of green chemistry, high crystalline nature and morphological structures. In this work, green synthesis of barium sulphate nanostructure was carried out by using *Azadirachta indica* (neem) leaf extract, barium chloride dehydrates and anhydrous sodium sulphate as source materials, by co-precipitation method. The as-synthesized barium sulphate nanostructures were subjected to different characterization techniques for their structural, functional, morphological and elemental studies by using XRD, FTIR, SEM and EDX. XRD reveals the orthorhombic crystal phase with a sharp diffraction peaks phase. SEM studies revealed the rice grain-like structures with an average diameter of 71.36 nm. Furthermore, a better understanding of this biological phenomenon may provide new insights for enhancing nanomaterial usage in the future.

Keywords: Green synthesis; $BaSO_4$; Nanoparticles; *Azadirachta indica*.

1. INTRODUCTION

Green synthesis of nanomaterials is garnering huge attention at nanoscale-level engineering (Huston *et al.* 2021). Recently, nanomaterials and structures have been widely demonstrated in medicine, biology and life science research fields. It is useful in drug delivery (designing & carriers). Nanoparticles majorly affect cellular and biological activity and cytotoxicity, owing to its large surface area. The different physical and chemical methods are useful for the preparation of barium sulfate nanoparticles; moreover, various researchers reported a number of synthetic strategies like chemical co-precipitation, spray pyrolysis, sol-gel, sono-chemical and microemulsion (Nagajyothi *et al*. 2016; Saravanan *et al.* 2022; Sivanandan and Saravanan *et al.* 2023). However, green synthesis-based nanoparticles are eco-friendly and less expensive. Majorly, green-synthesized nanoparticles are the best candidates for use in medical applications, since they are devoid of toxic reducing agents. The prospect of commercial-based applications (pigment, printing ink, cosmetics, etc.) has been majorly accelerated for the growing demand of multifunctional barium sulphate ($BaSO_4$) nanoparticles. Meenakshi *et al.* (2019) synthesized highly crystalline and thermally stable $BaSO_4$ nanoparticles by using *Azadirachta indica* (neem) leaf extract at room temperature. XRD revealed the orthorhombic phase with an average crystallite size of 55.6 nm. Meenakshi *et al.* 2019 confirmed the strong barium, sulfur and oxygen elements by EDX; moreover, nanorod-like structures were noticed using Field Emission Gun-Scanning Electron Microscopy (FEG-SEM). Gupta *et al.* (2010) prepared $BaSO_4$ nanoparticles using the precipitation method. The structure, absorption and morphology properties were studied by XRD, FTIR and TEM. This method could be employed to synthesize a higher yield of $BaSO_4$ nanoparticles (Asha *et al*. 2020). Pawar *et al.* (2022) employed silver nanoparticles using the green synthesis method; they were synthesized using *Azadirachta indica* leaf extract and characterized by SEM, FTIR and UV-Visible spectroscopy. The prepared particles were impregnated onto a cotton cloth and antimicrobial studies were investigated. These green synthesized Ag nanoparticles on the cotton cloth were found to have potential applications, including bandages (for wounds), medical textiles and sports clothing (Pawar *et al*. 2022). Similarly, Saravanan has investigated the functional (FTIR), structure (XRD) and morphological (SEM) properties of Ag nanoparticles, green synthesized using *Azadirachta indica* leaf extract (Saravanan *et al.* 2021). In the world, there is always a constant demand to establish new, safe, effective and low-cost drugs with fewer side effects on the human immune system. *Jagannath and Manjunath* explored the solution combustion of porous nature β-$BaSO_4$ nanopowder using ionic liquids. The ionic liquid, benzene sulfonyl methyl imidazolium chloride, is used as a fuel and sulfonating agent. Further, the characterization was carried out by using XRD, TEM, SEM, BET and FTIR techniques (Jagannath and Manjunath, 2019). Gupta *et al.* (2010) demonstrated the preparation of $BaSO_4$ nanoparticles by precipitation method. Here, sodium hexametaphosphate was used as a stabilizing agent. XRD revealed an orthorhombic structure and TEM confirmed the average size as 40 nm (around). The FTIR absorption indicated the formation of $BaSO_4$ nanoparticles (Gupta *et al*. 2010). In this work, the focus was laid on the green synthesis and characterization of $BaSO_4$ nanorods using *Azadirachta indica* leaf extract. XRD, FTIR, SEM and EDX characterization studies were carried out to investigate their crystalline nature, structure and functional groups; morphological studies were also carried out.

2. EXPERIMENTAL APPROACH

2.1. Materials

Fresh leaves of *Azadirachta indica*, barium chloride ($BaCl_2.2H_2O$), and sodium sulphate (Na_2SO_4) were procured; ethanol and distilled water used in this experiment were of industrial grade. *A. Indica* leaves were collected from Sri YN College campus, Narsapur, West Godavari Dt., A.P., India. Glassware was cleaned with distilled water and acetone.

2.2. Co-Precipitation Method

First, fresh leaves of *A. indica* were washed several times with distilled water to remove contaminants from the surface and shade-dried at room temperature. After one week, the dried leaves were crushed into small pieces. Initially, 30 g of fine *A. indica* leaves were added in 40 ml of ethanol with the mixture and refluxed at 30 °C for 60 min. After cooling, the leaf extract was filtered through Whatmann filter paper and cooled for 30 min. Further, 20 ml of filtrate was taken in an ultrasonic probe sonicator and 40 ml of 0.05 mol l^{-1} $BaCl_2$ solution was added dropwise during sonication. After 10 min, 40 ml of 0.05 mol l^{-1} Na_2SO_4 was added dropwise; a green-colored precipitate was obtained. This green-colored precipitate produced during the reaction solutions was separated from Whatmann filter paper and kept at 100 °C for 2 h. This co-precipitation method intends to prepare BaSO4 for a comparative study of the size and shape of the samples. After the preparation, we dried the precipitate at a low temperature (100 °C) for 2 h. Fig. 1 shows the schematic diagram of the experimental procedural steps for the preparation of $BaSO_4$ nanoparticles.

2.3. Characterization

The synthesized and calcinated samples were characterized by various techniques. The crystalline nature and structural properties were tested by X-ray diffractometer (XRD, Bruker D8, Venture), while their functional groups were identified by Fourier transform infrared (FTIR, Perkin Elmer-Lamda 35) spectroscopy. The morphological structures and size of the particles were confirmed by Scanning electron microscopy (SEM, VEGA3 TESCAN); the elemental studies were done using Energy dispersive X-ray spectroscopy (EDX, Broker-XFlash 6130).

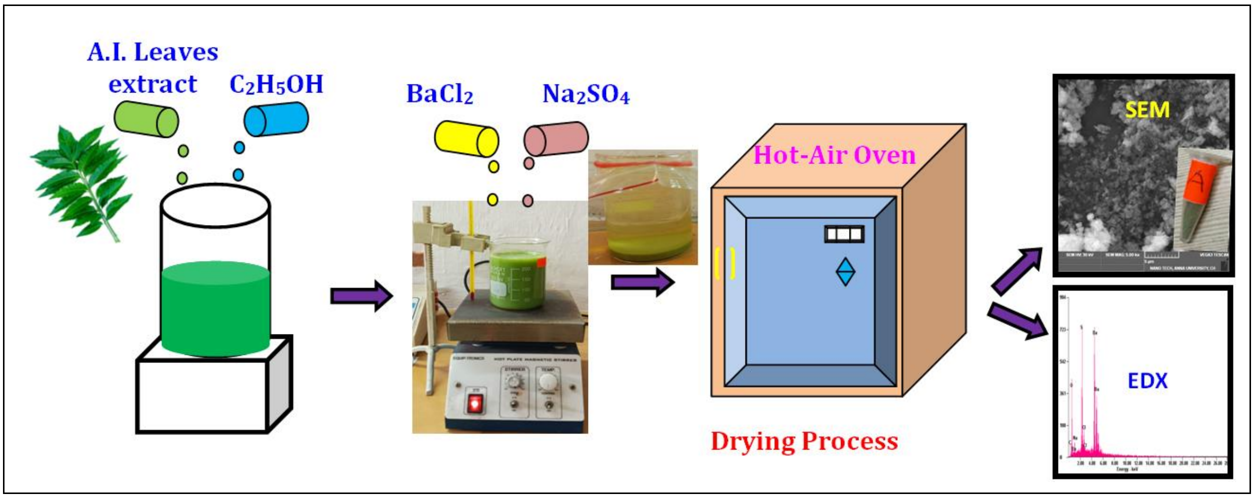

Fig. 1: Experimental procedure for synthesis of $BaSO_4$ nanoparticles

3. RESULTS AND DISCUSSION

3.1 Structural Analysis: XRD

The crystallographic phases of the synthesized nanostructures were verified by the XRD technique. The nature of crystallinity and phase composition of $BaSO_4$ nanorods were determined by X-ray diffraction (XRD) using Cu-Kα radiation. Data was collected at the scan rate of 1°/min with a step size of 0.02°. Here, the two theta range varies from 10 to 65°. In Fig. 2, indexed X-ray diffraction patterns of $BaSO_4$ nanostructures and diffracted lines are very sharp, not showing any Debye-Scherrer broadening. The $BaSO_4$ crystallized as orthorhombic crystals (*Sifontes et al.* 2015). The diffraction peaks are 31.4, 36.9, 39, 51.06 and 61.5 corresponding to the planes (211), (221), (022), (400) and (332). All the diffracted lines indexed to the orthorhombic structure agree with that reported in the literature (JCPDS, 24-1035) (Patel *et al*. 2014; Meagher *et al*. 2013; Gupta *et al*. 2010).

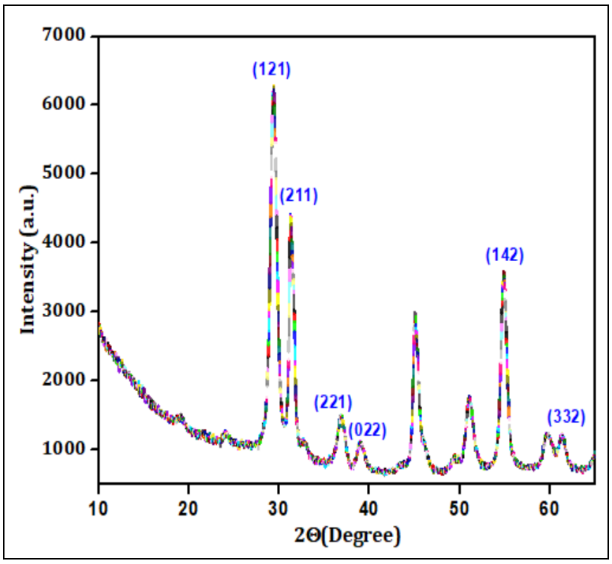

Fig. 2. XRD patterns of $BaSO_4$ powder

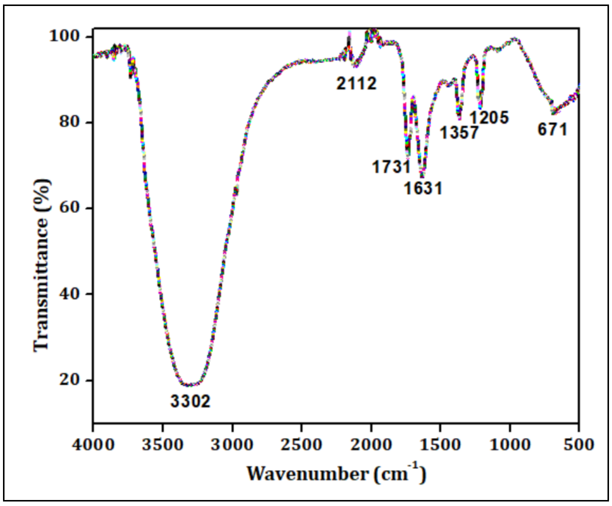

Fig. 3: FTIR spectrum of $BaSO_4$ nanostructures

3.2 Functional Group Study: FTIR

Fig. 3 shows the FTIR spectra of the green-synthesized $BaSO_4$ nanoparticles. Sifontes *et al.* reported that sulphate group has four basic vibration modes which are attributed to one non-degenerate mode (υ_1), doubly degenerate mode (υ_2) and two triply degenerate modes (υ_3 and υ_4). Here, a few prominent wave numbers are observed such as 3302, 2112, 1731, 1631, 1357, 1205, and 671 cm^{-1}. The two intense bands are related to asymmetric stretching and bending vibration modes are υ_3 and υ_4. The weak modes are υ_1 and υ_2 which correspond to symmetric and bending modes[15-16]. 1631 (υ_3) and 637 cm^{-1} (υ_4) are attributed the stretching vibration; SO_4^{-2} group was identified. The absorption peak around 3302 cm^{-1} is present due to the antisymmetric stretching vibration of O-H molecules (υ_4) located on a vacant site of barium (Ba) ion. Further, the peak at 2112 cm^{-1} represents the sulphur-oxygen combination of stretching and bending vibration modes (Sifontes *et al.* 2015; Prameena *et al.* 2013).

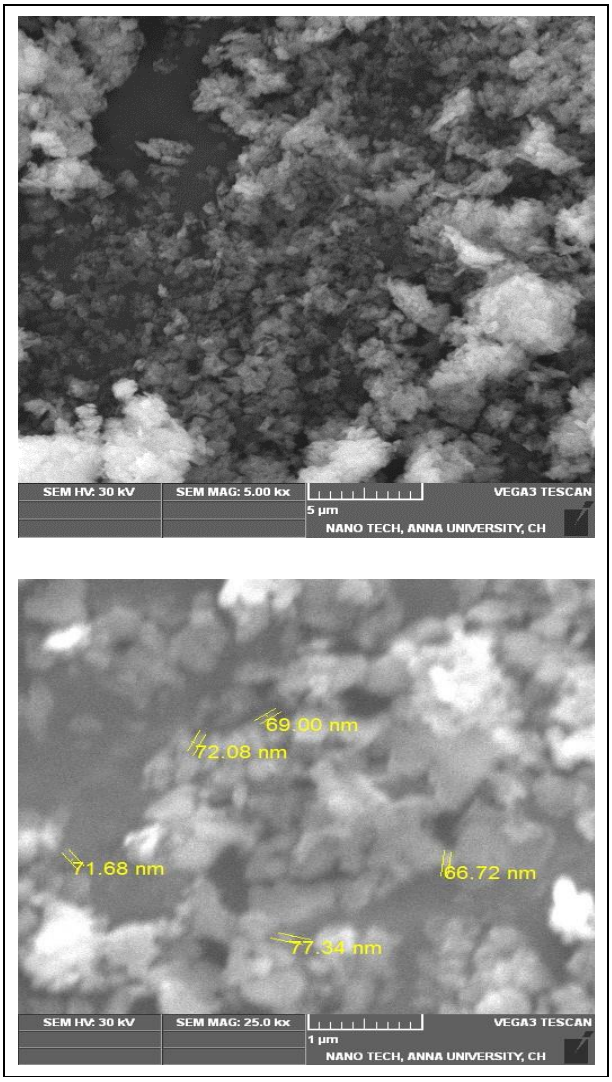

Fig. 4: SEM morphological images of $BaSO_4$ nanorods

3.3 Morphological Studies: SEM

The synthesized $BaSO_4$ samples were collected and found to be less agglomerated nanostructures. The particles obtained with neem leaf extracts were also like rice grain or rod-shaped $BaSO_4$ nanostructures. The morphological images of the synthesized nanostructures are shown in Fig. 4 (a) and Fig. 4 (b) by using scanning electron microscopy. Fig. 4 (a) displays the microstructure of rice grain, nanorod-like structures. The calculated diameter varied from 66.72 to 77.34 nm as depicted in Fig. 4 (b); the average size was found to be 71.34 nm. Similarly, the orange extracts influenced rod-like $BaSO_4$ particles with the size varying to a few hundred nanometers, as reported by Long *et al.* (2016). The soluble biomacromolecules such as acidic proteins, glycoproteins and polysaccharides are the key elements (parameters) in the biological systems for nucleators, anchoring units and growth (or shape) modifiers of the prepared materials. It was accepted in the previously reported works. Because of barium ions (Ba^{2+}) may be complex to solve with the biomolecules from fruits, plant extracts and vegetables. It makes more stable and agglomeration forms in solution (Long *et al.* 2016; Berman *et al.* 1993). These biological parameters helped to change the shape of the nanomaterials. Similar results were carried out and reported by Meenakshi *et al.* (2019).

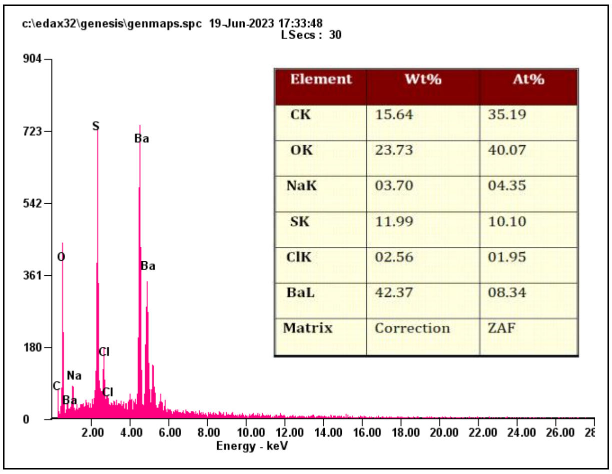

Fig. 5: The EDX spectrum of $BaSO_4$ nanostructures

3.4 Elemental Studies: EDX

Energy-dispersive X-ray (EDX) spectroscopy is a powerful technique to study the elemental composition of the prepared nanostructures. Further, the chemical composition and purity of the prepared samples are shown in Fig. 5. The EDX testing revealed the strong signal of Ba, S and O. The inset figure represents the weight and atomic percentage. The elemental studies are confirmed by Energy-dispersive X-ray (EDX) spectroscopy.

In this work, XRD, FTIR, SEM and EDX characterization results proved that the barium sulphate nanostructures can be prepared in the presence of neem (*A. Indica*) leaf extract by employing a simple method. Moreover, these nanostructures have applications for optical fillers, production of high-performance polymers, coatings and paints due to their unique physical and chemical properties.

4. CONCLUSIONS

In this work, the barium sulphate ($BaSO_4$) nanostructures were synthesized by using a co-precipitation method. After the preparation, the optical, structural, morphological and elemental studies were carried out using various characterization techniques. XRD results revealed that diffracted lines were well-matched with the standard JCPDS file and confirmed the orthorhombic crystal phase. The FTIR transmittance spectrum showed a strong absorption peak and evidenced the presence of Ba and SO_4 molecules. The SEM results have shown the low-agglomerated nanostructures of as-synthesized $BaSO_4$ and the average diameter was found to be 71.36 nm. The highest consistency in the elemental presence with atomic and weight percentages was confirmed by EDX. These $BaSO_4$ nanostructures are useful for various applications such as optical fillers and oil paints.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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