International Journal of Plant & Soil Science

Volume 35, Issue 19, Page 1700-1706, 2023; Article no.IJPSS.106203
ISSN: 2320-7035

Chemical Synthesis of Sulphur Nanoparticles and Their Characterization

G. Priyadharshan [a], R. Rajeswari [a*], S. Maragatham [a], S. K. Rajkishore [b], C. Sharmila Rahale [c] and D. Pradeep [c]

[a] Department of Soil Science and Agricultural Chemistry, Tamilnadu Agricultural University, Coimbatore, India.
[b] Department of Environmental Science, Tamil Nadu Agricultural University, Coimbatore, India.
[c] Centre for Agricultural Nanotechnology, Tamil Nadu Agricultural University, Coimbatore, India.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/IJPSS/2023/v35i193717

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/106203

Original Research Article

Received: 02/07/2023
Accepted: 05/09/2023
Published: 07/09/2023

ABSTRACT

This study focuses on the synthesis and comprehensive characterization of sulphur nanoparticles (S-NPs) using a precipitation method. The synthesis involved sodium thiosulphate and cetyl trimethyl ammonium bromide surfactants in a concentrated hydrochloric acid medium. The resulting S-NPs were thoroughly characterized using various advanced techniques. X-ray diffraction (XRD) analysis confirmed the crystalline nature of the nanoparticles, revealing distinctive diffraction patterns. Transmission electron microscopy (TEM) provided high-resolution images that elucidated the size and morphological aspects of the S-NPs, which exhibited a uniform size distribution. Scanning electron microscopy (SEM) further supported the morphological information, showcasing the surface features of the nanoparticles. Additionally, Fourier-transform infrared spectroscopy (FT-IR) analysis enabled the identification of functional groups and surface chemistry changes

**Corresponding author: E-mail: rrajeswaritnau@gmail.com;*

associated with the S-NPs. The comprehensive utilization of XRD, TEM, SEM, and FT-IR analysis provides a detailed understanding of the structural, morphological, and chemical attributes of the synthesized sulphur nanoparticles, paving the way for their potential applications in various fields.

Keywords: Sulphur Nanoparticles (nano-S); TEM; SEM; XRD; FT-IR; CHNS analyzer.

1. INTRODUCTION

Nanotechnology is a creative, inventive, and scientific method for designing, manipulating, and developing usable nanoparticles. It creates materials with nanometer-scale dimensions between 1 and 100 nm. Because of their tiny size, nanomaterials have a higher surface-area to-volume ratio compared to bulk forms. This improves the biological reactivity and physical properties [1]. Some nutrients are provided by nano fertilizers in a nano form, promoting plant growth and productivity. Nano-fertilizers with a diameter of 100 nm can spread like a powder or liquid [2]. A large amount of inorganic fertilizer supplied to the soil is lost and becomes inaccessible to plants. As a result, additional fertilizers are being added to the soil to compensate the fertilizer losses. It influence the soil nutrient balance severely [3].

The Indian Council of Agricultural Research (ICAR) has established a unique platform to focus on Nanotechnology Applications in Agriculture. “At present, in India, the ongoing research is mainly concentrated on nanoparticle synthesis, smart release of nutrients from nano-fertilizers, nano-induced polysaccharide powder for moisture retention/soil aggregation, controlled release of herbicide active components from nano-encapsulated products, nano-seed stimulation, and gradual and steady pesticide release” [4]. “Nano-S has been synthesized through the utilization of physical, chemical, and biological methods. The top-down approach was employed in the physical method, where elemental sulfur was powdered and ground in a high-energy ball mill for one hour” [5]. There are numerous methodologies and strategies employed in the synthesis of nano-particles to achieve the desired size and shape. Several methods have been utilized for the production of nano-S, including reverse micro-emulsion [6,7], electro-chemical method [8], water-in micro-emulsion system [9], ultra-sonication [5], and super-saturated solvent method [10]. In addition, attempts have been made to achieve green synthesis of nano-S using fruit extracts from *Albizia julibrissin*, but the recovery of nano-S is relatively low [11]. All these techniques, however, are expensive and difficult to expand, in addition to requiring large amounts of surfactants and being damaging to the environment [12].

2. MATERIALS AND METHODS

2.1. Nanoparticle Synthesis

The mixture of sodium thiosulphate pentahydrate ($Na_2S_2O_3.5H_2O$) and CTAB was made by adding 30 ml of 0.93 mM CTAB to 50 ml of 1M sodium thiosulphate pentahydrate at room temperature. The mixer was mechanically stirred at 120 rpm and heated in a continuous bath at 40°C. After that, 100 ml of 2M HCl solution was gradually added to the mixture under stirring conditions. The reaction was stopped after 40 minutes with the immediate appearance of a yellow precipitate. The generated yellow precipitate was collected, cleaned with distilled water, and dried.

2.2 Characterization of Nanoparticles

1 mg of nano-S particles were dispersed in 10 ml of deionized water and sonicated for 10 minutes with a water bath sonicator, and the particle size was determined with a particle size analyzer (Nanopartica SZ-100, Horiba Scientific, Japan). Simultaneously, the zeta potential was assessed with the aim of evaluating the particle's stability.

The dimensions and shape of the nano-S particles were determined using a scanning electron microscope (FEI, Quanta 250, Netherlands) at 7.00 kV. The sample for TEM analysis was made by dispersing a solution of the nano sulphur product in 70% ethanol in a water bath and using copper grids that had been coated with carbon.

Fourier Transform Infrared Spectroscopy (FT-IR) is a strong analytical method used to determine the molecular composition and structure of materials. The functional group in the nano-S fertilizer was analyzed using Fourier transform infrared spectroscopy (FT-IR). Nano-S particles were crushed with potassium bromide (KBr) in a ratio of 2:1 in a pestle and mortar for 30 minutes before being directly pressed into a hard disc.

The 0.5 to 1.0 mm disc was scanned after being put in a transmission holder. A Bio-Rad Excalibur 3000 MX FT-IR spectrometer and a helium-purged MTEC 300 photoacoustic cell were used for collecting the spectral data.

The Raman Spectra of nano-S were collected under dark circumstances at room temperature using a Raman apparatus (R-3000-QETM, Germany). The samples were measured using the Raman system's solid probe. One to two grams of powdered solid sample were put in a glass tube and placed into the sample holder before opening the RSIQ software in the system and turning on the laser light source in the equipment to collect the Raman spectrum of a sample using Raman spectroscopy.

The X-ray diffractometer (XRD) is used to determine the surface area and the phase of crystalline structure in materials. X-ray diffraction involves X-rays interacting with a crystalline sample and producing a diffraction pattern that reveals information about the placement of atoms in the crystal structure. Approximately 1 g of nano-S was used for XRD measurement.

2.3 Nano-fertilizer Sulphur Content (CHNS Analyzer)

A CHNS analyzer is a laboratory apparatus that measures the amounts of carbon (C), hydrogen (H), nitrogen (N), and sulphur (S) and their elemental composition. The prepared sample was subsequently placed in the ignition chamber of the CHNS analyzer. The sample is frequently placed in a tiny crucible or container. Oxygen is delivered to the combustion chamber for the sample to burn fully. During burning, the carbon, nitrogen, hydrogen, and sulphur in the sample mix with oxygen to generate carbon dioxide (CO_2), water vapor (H_2O), nitrogen oxides (NO_2, NO_3), and sulphur dioxide (SO_2). These gaseous byproducts were transported out of the ignition chamber. The analyzer output data showed the proportions of carbon, hydrogen, nitrogen, and sulphur that were present in the original sample.

3. RESULTS AND DISCUSSION

3.1 Synthesis and Characterization

It is evident from the TEM images (Fig. 1) that the nanoparticles formed during water precipitation combined with CTAB, had particle sizes ranging from 24 to 40 nm. Utilizing a sonicator, the particles were homogenized and their internal structure was examined through SEM technology (Fig. 2). From this figure, it is clear that sulphur particles are almost spherical in shape.

Zeta potential analysis is a valuable technique for accurately determining the surface charge of nanoparticles in solution (colloids). The nano-sulfur particles were characterized by a zeta potential of -34.5 mV, indicating an increased level of stability of the nano-S (Fig. 3). This data clearly shows that synthesized nano sulphur is a nano size, homogenous and stable. This result shows almost similar results as was found in a previous study [13].

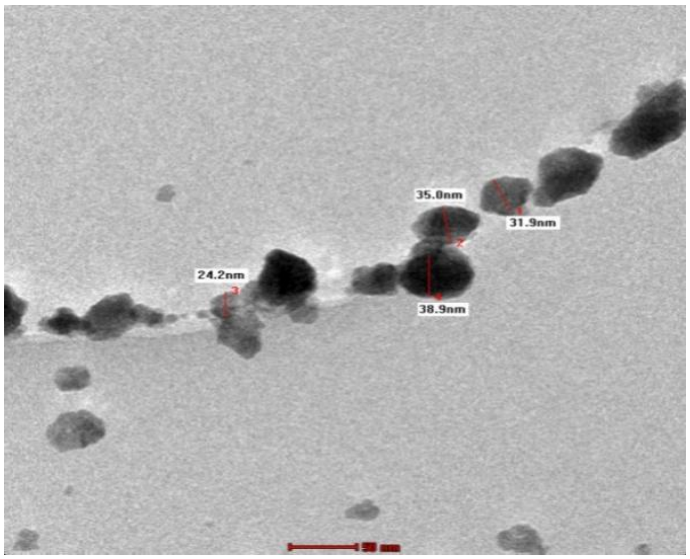

Fig. 1. TEM image of nano-S

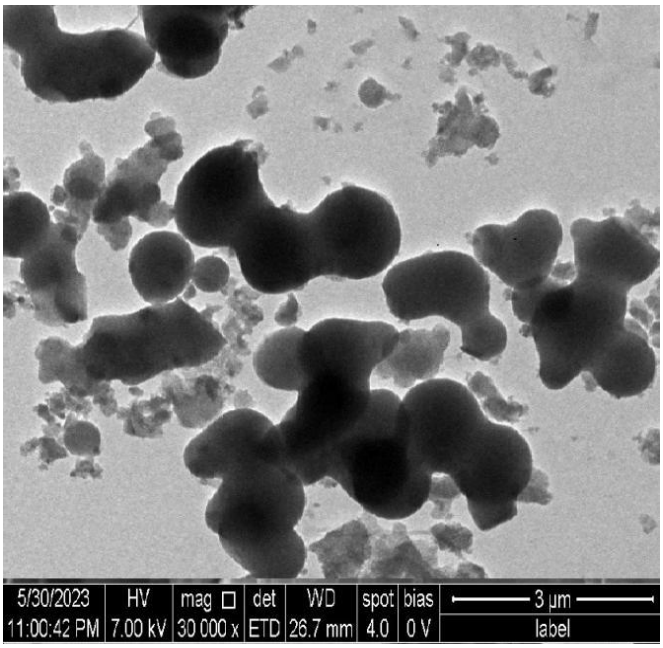

Fig. 2. SEM image of nano-S

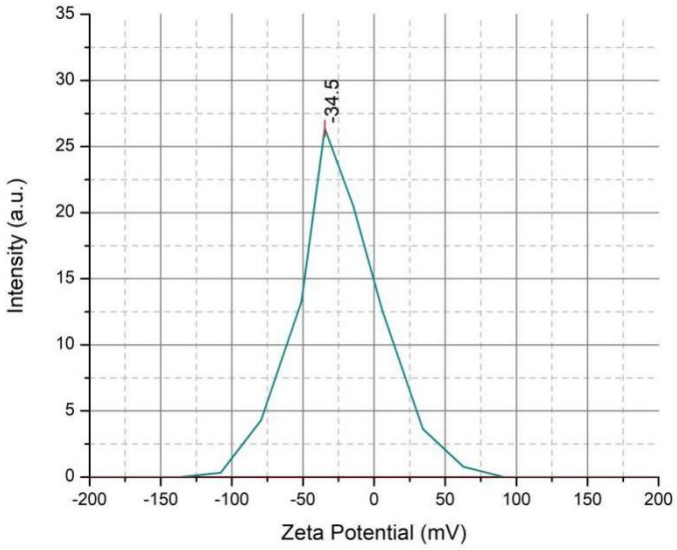

Fig. 3. Zeta potential of nano-S

A CHNS analyzer is a laboratory apparatus that provide information regarding the amounts of carbon (C), hydrogen (H), nitrogen (N), and sulphur (S) and their elemental composition in percentage. The analyzer output data revealed the proportions of carbon (0.033%) and sulphur (99.58%).

The surface area and crystalline phase of the nano-S particles were determined through X-Ray diffraction (XRD) analysis. The XRD pattern of the nano-S particles is depicted in Fig. 4. The analysis revealed that the nano-S sample consisted of a single crystalline phase, and the XRD pattern exhibited distinct peaks at 2θ values of 23.129, 25.885, 26.769, and 27.783. Among these, the peak at 2θ = 27.783 is attributed to sulphur, confirming the presence of sulphur in the nanoparticle sample. The XRD profile of the nano-S particles closely resembled the findings from a previous study [14].

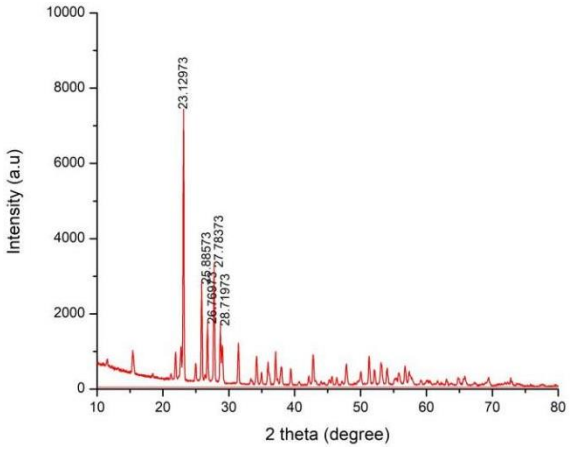

Fig. 4. XRD characterization of nano-S

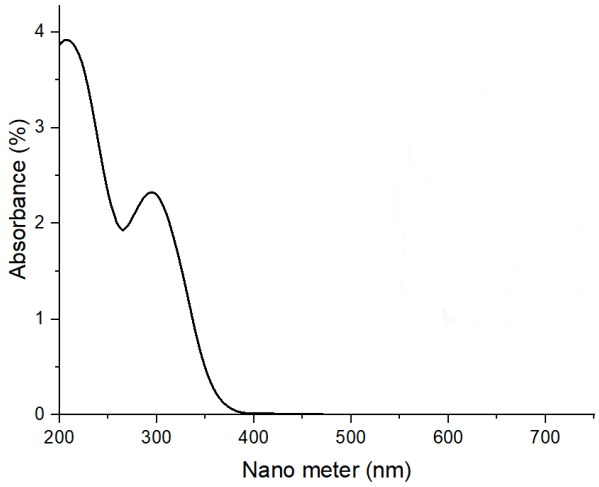

Fig. 5. UV-VIS spectra of nano-S

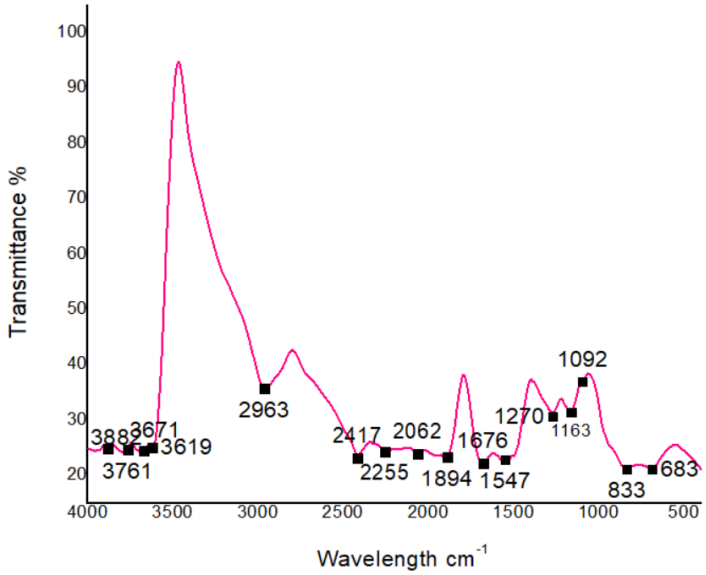

Fig. 6. FT-IR characterization of Nano Sulphur

The confirmation of the synthesized nano-S particles involved employing UV-visible spectrophotometer analysis. This technique enabled the determination of the nanoparticles' highest absorption point. The absorption peak, visible at 292nm- 294nm in Fig. 5, exhibited a similarity to findings of a previous study [15].

Nano-S confirmation was achieved using FT-IR spectra (Fig. 6), covering a range from 683 to 3900 cm^{-1}. The spectra displayed distinctive peaks at wave numbers of 683.24, 833.34, 1092.35, 1163.19, 1270.61, 1547.46, 1676.20, 1894.00, 2062.12, 2417.01, and 2963.96 cm^{-1}. Notably, the presence of peaks at 1062.94 cm^{-1} (associated with sulphur vibrations) provided conclusive evidence of the successful synthesis and characterization of nano-S. The FT-IR peaks observed from the nano-S particles were found to be highly similar to the results reported in a previous study [14].

4. CONCLUSION

The synthesis of sulphur nanoparticles was effectively achieved through a precipitation method utilizing ($Na_2S_2O_3.5H_2O$) with CTAB as a stabilizer, mixed in concentrated HCl at 40 degree Celsius. This procedure gave sulphur nanoparticles with a remarkably crystalline structure and a uniform size range of 24-45 nm. The confirmation of the nanoparticles' structural morphology was carried out using XRD, SEM, and TEM analyses, further validating their nanoscale characteristics.

ACKNOWLEDGEMENT

I would like to acknowledge the Department of Soil Science and Agricultural Chemistry and Center for Agricultural Nanotechnology, Tamilnadu Agricultural University, Coimbatore-641003 for their support and resources that greatly contributed to the completion of this article. Their expertise and facilities were invaluable in advancing our research. Grateful for their contribution to our research programme.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Mali SC, Raj S, Trivedi R. Nanotechnology a novel approach to enhance crop productivity. Biochemistry and Biophysics Reports. 2020;24:100821.
2. Jampílek J, Kráľová K. Application of nanotechnology in agriculture and food industry, its prospects and risks. Ecological Chemistry and Engineering S. 2015; 22(3):321-361.
3. Baruah S, Dutta J. Nanotechnology applications in pollution sensing and degradation in agriculture: A review. Environmental Chemistry Letters. 2009; 7:191-204.
4. Elizabath A, Babychan M, Mathew AM, Syriac GM. Application of nanotechnology in agriculture. Int. J. Pure Appl. Biosci. 2019;7(2):131-139.
5. Siddiqui MH, Al-Whaibi MH, Firoz M, Al-Khaishany MY. Role of nanoparticles in plants. Nanotechnology and plant sciences: Nanoparticles and their impact on plants. 2015;19-35.
6. Ghosh Chaudhuri R, Paria S. Core/shell nanoparticles: Classes, properties, synthesis mechanisms, characterization, and applications. Chemical reviews. 2012; 112(4):2373-2433.
7. Mani PK, Mondal S. Agri-nanotechniques for plant availability of nutrients. Plant nanotechnology: Principles and practices. 2016;263-303.
8. Deshpande AS, Khomane RB, Vaidya BK, Joshi RM, Harle AS, Kulkarni BD. Sulfur nanoparticles synthesis and characterization from H2S gas, using novel biodegradable iron chelates in aqueous surfactant systems. MRS Online Proceedings Library. 2008;1103(1):1.
9. Guo Y, Zhao J, Yang S, Yu K, Wang Z, Zhang H. Preparation and characterization of monoclinic sulfur nanoparticles by water-in-oil microemulsions technique. Powder technology. 2006;162(2):83-86.
10. Shamsipur A, Kashani-Bozorg SF, Zarei-Hanzaki A. The effects of friction-stir process parameters on the fabrication of Ti/SiC nano-composite surface layer. Surface and Coatings Technology. 2011; 206(6):1372-1381.
11. Soleimani M, Aflatouni F, Khani A. A new and simple method for sulfur nanoparticles synthesis. Colloid Journal. 2013;75:112-116.
12. Khairan K, Jalil Z. Green synthesis of sulphur nanoparticles using aqueous garlic extract (Allium sativum). Rasayan Journal of Chemistry. 2019;12(1).

13. Suleiman M, Al-Masri M, Al Ali A, Aref D, Hussein A, Saadeddin I, Warad I. Synthesis of nano-sized sulfur nanoparticles and their antibacterial activities. J Mater Environ Sci. 2015; 6(2):513-518.
14. Subramanian KS, Rajeswari R, Yuvaraj M, Pradeep D, Guna M, Yoganathan G. Synthesis and Characterization of nano-sulfur and its impact on growth, yield, and quality of sunflower (*Helianthus annuus* L.). Communications in Soil Science and Plant Analysis. 2022;53(20):2700-2709.
15. Baloch H, Siddiqua A, Nawaz A, Latif MS, Zahra SQ, Alomar SY, Elsayed TM. Synthesis and characterization of sulfur nanoparticles of citrus limon extract embedded in nanohydrogel formulation: *In vitro* and *In vivo* studies. Gels. 2023;9(4): 284.

© 2023 Priyadharshan et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:
The peer review history for this paper can be accessed here:
https://www.sdiarticle5.com/review-history/106203