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ORIGINAL PAPER

Production of Biogenic Silica Nanoparticles by Green Chemistry Approach and Assessment of their Physicochemical Properties and Effects on the Germination of *Sorghum bicolor*

Rajiv Periakaruppan[1] · Renuga Devi N[2] · Salwan Ali Abed[3] · P. Vanathi[4] · J. Senthil Kumar[1]

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Abstract

The synthesis of phyto-extract-assisted nanomaterials is very popularity as the process is simple and inexpensive. *Euphorbia thymifolia* L. belongs to family Euphorbiaceae and it is well-known herb species. The aim of the present research is a green synthesis of silica nanomaterials using the aqueous extract of *E. thymifolia.* The synthesized silica nanoparticles were characterized by Ultraviolet-visible (UV-Vis) spectrophotometer, Fourier Transform Infrared Spectroscopy (FTIR), X-Ray diffraction analysis (XRD), Scanning Electron Microscope (SEM) with Energy Dispersive X-ray Analysis (EDAX), Dynamic Light Scattering (DLS) and Thermogravimetric analysis (TGA). These results confirmed the successful formation of nanoparticles, which are spherical and amorphous in nature. EDAX analysis determined the purity of the silica nanoparticles, which are composed of Si and O elements with no other impurities. XRD spectroscopy illustrates that characteristic diffraction peaks for silica nanoparticles were observed at 2ϴ range 20° corresponding to 101 planes. The average size of synthesized silica nanoparticles is 17 nm. The surface charge and stability of silica nanomaterials were analysed using dynamic light scattering (DLS), which revealed that the synthesized nanomaterials have a negative charge (-2.00 mV). The results obtained from this investigation confirm that the aqueous extract of *E. thymifolia* can play a vital role in the capping and stabilization of Tetra Ethyl Ortho Silicate to silica nanoparticles. In addition, the effect of bio-synthesized silica nanoparticles on the germination of *Sorghum bicolor* was determined, and it was concluded that silica nanoparticles improved the percentage of seed germination and that it would be useful for agricultural application.

Keywords Biologcial method · *E. thymifolia* · Silica nanoparticles · Physicochemical properties · Seed germination

1 Introduction

Nanotechnology signifies an innovative route to technical progress that concerns the administration of material at the nano-scale level. Nanotechnology aims to design and characterize the particles by controlling their structure and size at the nanometre level. Nanotechnology is primarily concerned with fabrication into various sizes and shapes and their potential use for humans [1]. During the past few years, nanomaterials have been utilized in various applications such as medicine, pharmaceuticals, cancer diagnosis, cosmetics, and food and textile industries, etc. Even though physical and chemical methods are utilized for the synthesis of nanoparticles, these methods are expensive and release more toxic materials into the environment. Hence, currently, the green chemistry approach i.e. usage of biological materials like plant extracts, microorganisms, etc. is followed for fabricating nanoparticles owing to their properties like eco-friendliness, low toxicity, and cost-effectiveness [2].

Silica nanoparticles promise a wide range of new technological applications in various fields such as drug delivery, tissue engineering, cancer diagnostics, enzyme immobilization, cell imaging, sensor development, etc. These nanoparticles are used for the production of

✉ Rajiv Periakaruppan
rajivsmart15@gmail.com

1 Department of Biotechnology, PSG College of Arts & Science, Coimbatore 641014, Tamilnadu, India

2 Department of Biotechnology, Karpagam Academy of Higher Education, Coimbatore 641021, Tamilnadu, India

3 College of Science, University of Al-Qadisiyah, Al Diwaniyah, Iraq

4 Department of Biotechnology, Sri Ramakrishna College of Arts & Science, Coimbatore, Tamil Nadu, India

multifunctional nanostructure materials for various applications. Silica nanoparticles are synthesized by both top-down and bottom-up approaches. They are also synthesized by different physical and chemical methods such as the sol gel method [3], chemical vapour condensation [4], photo-ablation [5], micro emulsion, etc. However, these physical and chemical methods for the synthesis of nanoparticles have some drawbacks like the need for costly raw materials, very high temperature, and production of more toxic agents like Nickel tetra carbonyl, Diborane, Silicon tetrachloride, etc. [6].

The green synthesis of silica nanoparticles has several benefits and is free from the disadvantages of nanoparticles synthesized by physical and chemical methods. Silica nanoparticles synthesized by the green chemistry approach are used in various applications such as in medicines, pharmaceutical industries, paints, cosmetics, etc. In the biological synthesis method, the toxic chemical is replaced by eco-friendly nontoxic materials [7]. Nowadays, silica nanoparticles are predominantly used because of their unique properties like larger surface area, excellent thermal stability, ease of surface modification, admirable zeta potential activity, etc. Several natural precursors like clay, rock, and agricultural wastes such as rice husk, straw, sugarcane bagasse, *Bambusa vulgaris* residues, and weed plants are used for the synthesis of silica nanoparticles [8]. The extract of certain leaves and fruits and ash of some plants are used for the synthesis of silica nanoparticles. Currently, the green synthesis method used for the synthesis of various nanoparticles includes ZnO [9], CuO [10, 11], CeO_2 [12] FeO [13], Au [14], and titanium oxide [15] for various applications. The research related to the synthesis of silica nanoparticles was limited, hence these nanoparticles were used in this study to assess their efficiency against various applications. Different types of biological materials are utilized for the synthesis of silica nanoparticles.

Euphorbia thymifolia (Fig. 1) belongs to the family Euphorbiacea. It is frequently found in wastelands, road sides, and wall side sunder humid conditions. It is popular for its medicinal use predominantly in Africa. *Euphorbia thymifolia* is used for treating various ailments that include skin infection, parasitic infection, menstrual disorders, urinary tract infection, leprosy, dysentery, eye disease, and measles [16, 17]. This plant contains some low phytochemicals like flavonoids, phenols, gallotannins, isomallotinic acid, hexahydroxy diphenic acid, and gallic acid [16].

In this study, the *Euphorbia thymifolia* was used for the synthesis of silica nanoparticles without using harmful reducing or capping agents. *Euphorbia thymifolia*-mediated silica nanoparticles were characterized by different techniques. In addition, the effect of bio-synthesized silica nanoparticles on the germination of *Sorghum bicolor* was determined.

Fig. 1 *Euphorbia thymifolia*

2 Materials and Methodology

All chemicals and reagents (99.9% pure and of analytical grade) were obtained from Sigma Aldrich for this investigation. Fresh and healthy *E. thymifolia* L. was collected from Dharapuram District, Tamilnadu, India in January 2021. The plant has been authenticated by the Botanical Survey of India, Tamilnadu Agricultural University (TNAU), Coimbatore, Tamilnadu, India. The authentication number is BSI/SRC/5/23/2021/Tech./38.

2.1 Preparation of the Extract

10 grams of fresh plantlets of *E. thymifolia* were weighed and ground by using a mortar and pestle with 250 mL of distilled water. Then, the extract was boiled at 65°C for 30 minutes. After boiling, the mixture was filtered with a filter paper. This step was repeated three times to get a pure extract. Finally, the obtained extract was stored in the refrigerator for further use. The phytochemicals of *E. thymifolia* were assessed according to the methods of Harborne [18].

2.2 Production of Silica Nanoparticles and Characterization of Silica Nanoparticles

A 250 mL of Tetra Ethyl Ortho Silicate (TEOS) was prepared using de-ionized water. Aqueous extract of *E. thymifolia* was mixed with precursor solution. The mixture of extract and TEOS solution was stirred at room temperature for 15 minutes. Later, 10 mL of ethanol was added to the above solution mixture at the same condition. Next, the 1 M HCl was mixed into that reaction mixture and incubated for 20 minutes at room temperature. A precipitation-like jelly form was obtained at the end and

Table 1 Phytochemicals screening for aqueous extract of *E. thymifolia*

S.NO	Phytochemicals	Aqueous extract of *E. thymifolia*
1	Steroids	Absent
2	Alkaloids	Absent
3	Tannins	Present
4	Saponins	Absent
5	Tri terpenoids	Absent
6	Glycosides	Present
7	Flavonoids	Present
8	Reducing sugar	Absent

it was dried at 100 °C for 12 h. Finally, the fine white powder was achieved and stored in a sterile container for characterization.

Different spectroscopic and microscopic equipment were used to assess the physicochemical properties of green synthesized silica nanoparticles. The optical properties of as-synthesized silica nanoparticles were done using UV–vis spectroscopy. The nature and the average size of nanoparticles were determined by XRD analysis. FT-IR analysis was utilized to know the functional groups of phytochemicals from *E. thymifolia* for capping and stabilization of silica nanoparticles. EDX analysis was utilized to comprehend the purity and elemental composition of nanoparticles. The stability of nanoparticles was predicted through Zeta potential analysis. The morphology of nanoparticles was determined by the SEM analysis.

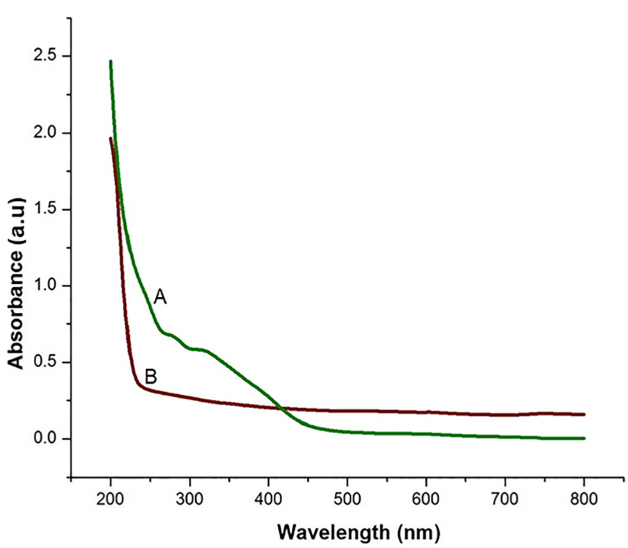

Fig. 2 UV spectra, where A = Silica nanoparticles and B = Extract of *Euphorbia thymifolia*

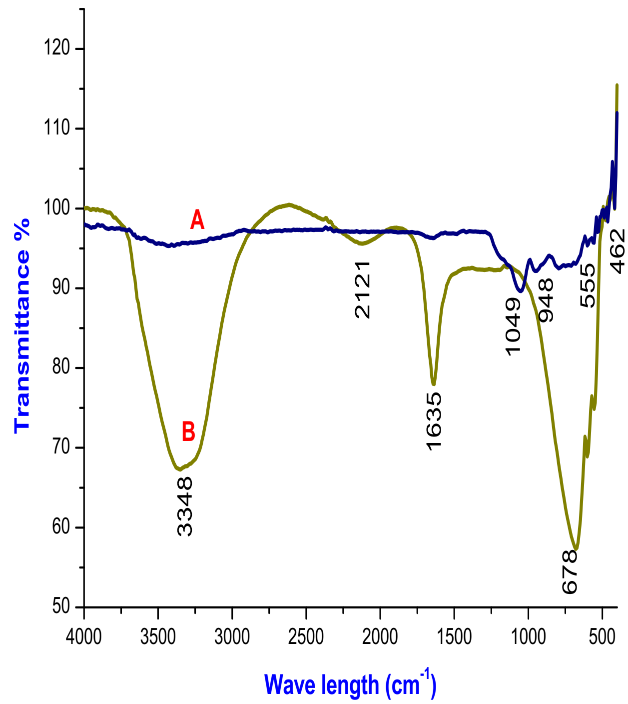

Fig. 3 FT-IR spectra, where A = Silica nanoparticles and B = Extract of *Euphorbia thymifolia*

2.3 The Effects of Silica Nanoparticles on the Germination of *Sorghum Bicolor*

Seeds of *Sorghum bicolor* were collected from the local market, Coimbatore, Tamilnadu, India. The effect of silica

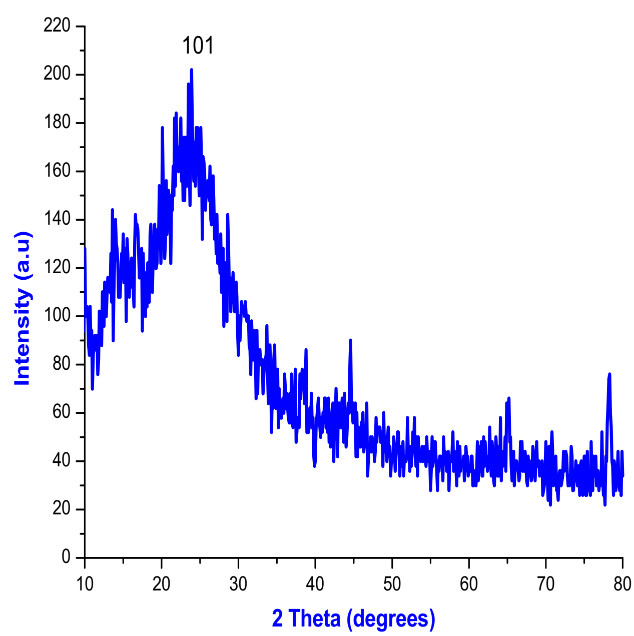

Fig. 4 XRD spectra of *E. thymifolia* mediated Silica nanoparticles

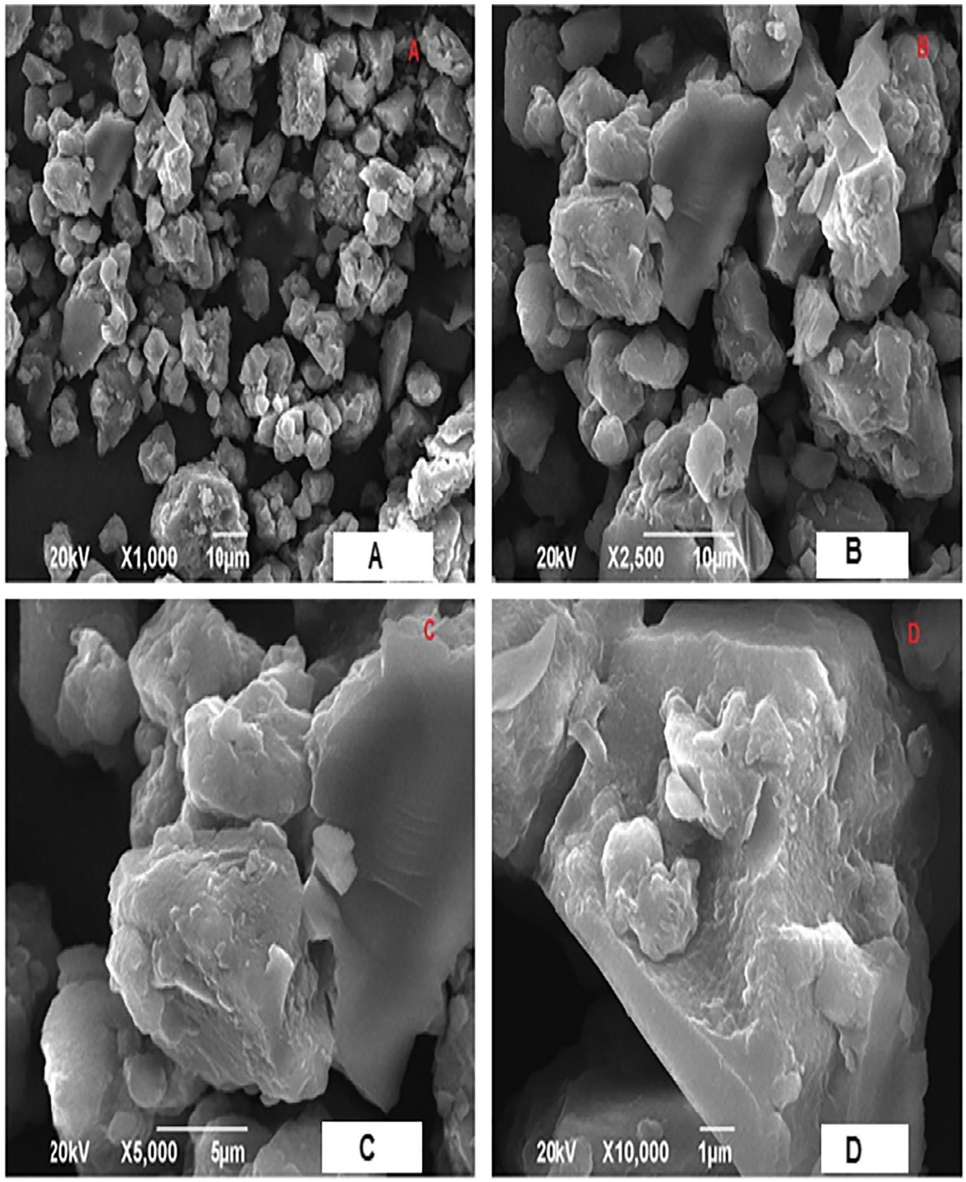

Fig. 5 SEM images of *E. thymifolia* mediated Silica nanoparticles

nanoparticles on the germination of *Sorghum bicolor* was studied using the protocol with minor modification of Maroušek et al. [19].

3 Results and Discussion

Phytochemicals in *E. thymifolia* were investigated through stranded techniques, which are presented in Table 1. The aqueous extract of *E. thymifolia* exhibited the presence of tannins, glycosides, and flavonoids. Similarly, Singh et al. [20] have reported the presence of alkaloids, polypenoids, tannins, flavonoids, and glycosides in the methanolic extract of *Azadiracta indica* leaves.

Tetra Ethyl Ortho Silicate (TEOS) is a primary precursor to the preparation of silica nanoparticles. In the presence of ethanol, plant extract, and HCl undergo hydrolysis and condensation reaction to produce silica nanoparticles through a continuous stirring process. HCl is used as a catalyst to precipitate the silica nanoparticles. The formation of Si-OH occurs by the replacement of (-OR) group with (OH) group from plant extracts and ethanol. The highly formed Si-OH is dehydrated and dealcoholized to form Si-O-Si particles [21–25].

Figure 2A and B show the UV spectra of green-synthesized silica nanoparticles and aqueous extract of *E. thymifolia.* Silica nanoparticles show peaks between 300 and 400 nm. Similarly, Periakaruppan et al. [26] synthesized the silica nanoparticles using the leaf extract of *Punica granatum* and assessed its optical properties using the UV spectral study. They got absorption peaks between 300 and 370 nm in UV spectra for silica nanoparticles.

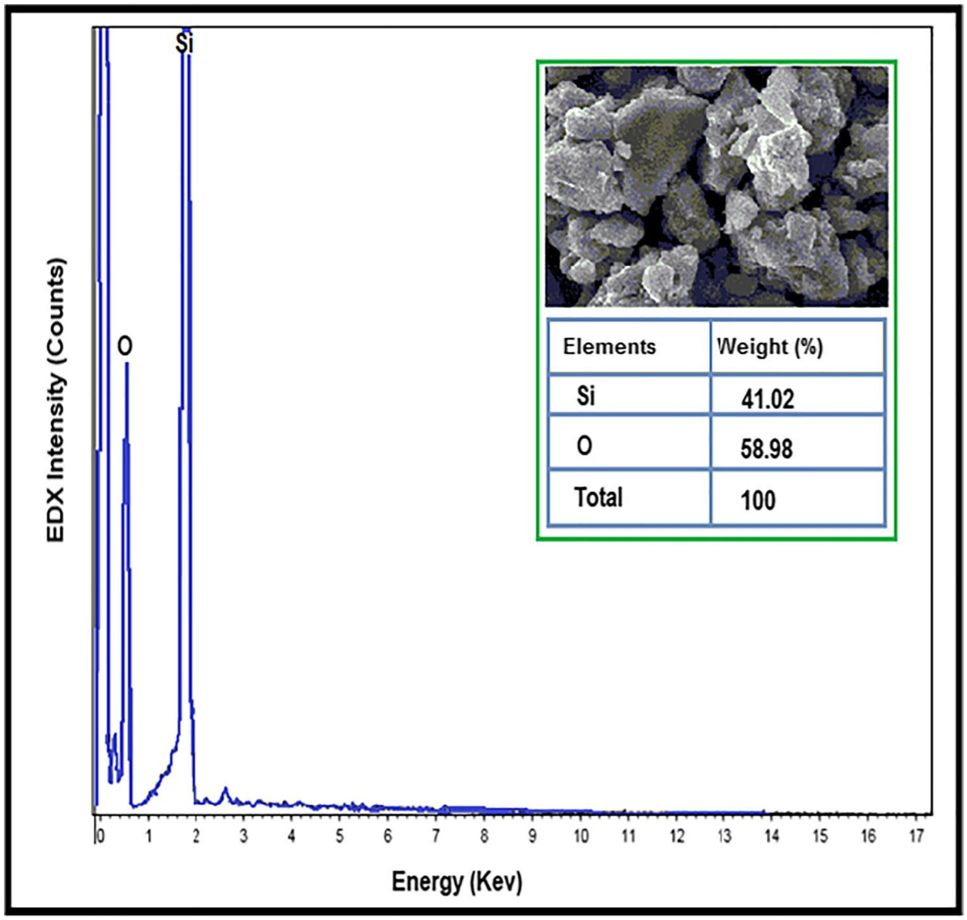

Fig. 6 EDX spectra of *E. thymifolia* mediated Silica nanoparticles

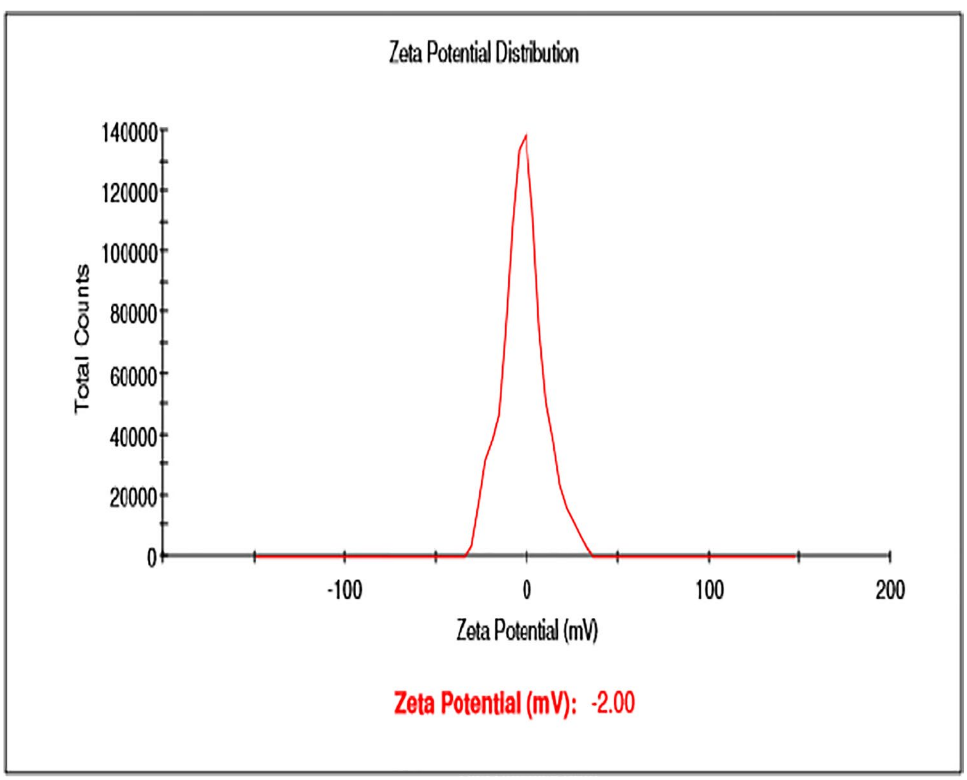

Fig. 7 Zeta Potential analysis of *E. thymifolia* mediated Silica nanoparticles

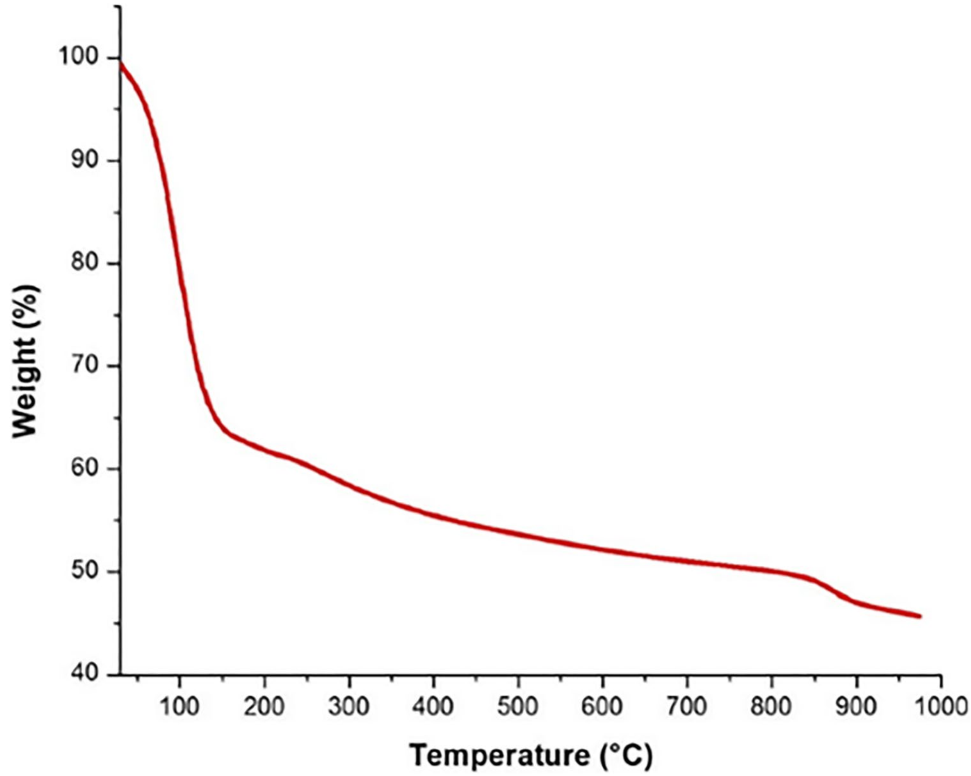

Fig. 8 TGA analysis of *E. thymifolia* mediated Silica nanoparticles

The functional groups of synthesized silica nanoparticles and extract of *E. thymifolia* were evaluated and the spectra are shown in Fig. 3A and B. The strong peaks were displayed at 462, 555, 948, and 1049 cm^{-1}. All the peaks indicate the presence of Si–O elements and symmetric Si–O bonds (Silanol). The functional group of O-H stretching and O–H bending occurred at peaks of 3348, 2121, 1635, and 678 cm^{-1}. Our result of FT-IR spectra is similar to the one obtained by Sankareswaran et al. [27], who bio-fabricated the biogenic silica nanomaterials using the extract of a medicinal plant (*Bryophyllum pinnatum)* and determined its functional groups and surface chemical moiety through FT-IR analysis.

Based on Fig. 4, *E. thymifolia*-mediated silica nanoparticles are found to have an amorphous pattern and are detectable by a peak at 2θ (Theta) = 28° in XRD spectra. The average size of the synthesized silica nanoparticles was calculated, and it was found to be 17 nm.This pattern is in agreement with other investigations [26, 28].

SEM analysis was used to find out the shape of the synthesized nanoparticles. The SEM images (Fig. 5A -D) of green synthesized silica nanoparticles display the surface and spherical shape. A few of the nanoparticles were in aggregated form. EDX analysis was conducted with SEM analysis to reveal the purity and composition of silica nanoparticles. EDX spectra (Fig. 6) show the atomic percentage of Silica (41.02) and Oxygen (58.98). Maroušek et al. [19] produced spherical-shaped silica nanoparticles using lignin from coir pith via the acidic sol-gel method. They detected the shape and purity of the silica nanomaterials using SEM with EDX analysis.

The stability of green synthesized nanomaterials is important for its practical applications. The stability is related to the surface electrical charge of the nanoparticles Uda et al. [29]. *E. thymifolia*-assisted silica nanoparticles

Table 2 Comparison of green synthesis and chemical synthesis of silica nanoparticles

S.NO	Parameters	Green synthesis	Chemical synthesis
1	Procedures/Steps	Simple	Complicated
2	Usage of hazardous chemicals	Less	High
3	Toxicity	Less	High
4	By products	Easley degradable	Partially /difficult to degradable
5	Biological activity	High	Moderate

Table 3 Effects on Silica nanoparticles on germination of *Sorghum bicolor*

Treatments	Concentrations	Germination percentage (%)
Control	Distilled water alone	98
T1	200 ppm of silica nanoparticles	98
T2	400 ppm of silica nanoparticles	95
T3	600 ppm of silica nanoparticles	90
T4	800 ppm of silica nanoparticles	87
T5	1000 ppm of silica nanoparticles	80

showed a minimum zeta potential of −2.00 mV (Fig. 7). The silica nanoparticles have a negative charge of zeta potential. Hence, it clearly reveals that the particles are stable because of the electrostatic repulsion.

Weight loss, crystallization temperature, melting point, sintering behaviour, and glass transition temperature of nanomaterials are investigated using the thermogravimetric analysis (TGA) [30]. The thermal stability of the prepared green-synthesized silica nanoparticles was characterized using thermogravimetric analysis (TGA) as shown in Fig. 8. TGA spectra of biosynthesized silica nanoparticles displayed a steady weight loss at the temperature range of 30 – 1000°C.A 35% of weight loss was observed up to 200°C due to the loss of moisture by the silica nanoparticles. Afterward, 25% of weight loss occurred until 900°C due to the decomposition of heat-resistive phyto-compounds in *E. thymifolia*-assisted silica nanoparticles [31]. Table 2 explains the comparison of green synthesis and chemical synthesis of silica nanoparticles.

3.1 Analysis of Seed Germination

The seed germination analysis was performed using various concentrations of as-silica nanoparticles. Table 3 determines the effect of green-synthesized silica nanoparticles on the germination of *Sorghum bicolor.* The highest percentage of seed germination was observed at 200 ppm of silica nanoparticles as compared to the control of distilled water-treated seeds. The concentration of 500 ppm did not improve the germination percentages. Our finding is more similar to the one made in a previous research study [19]. Maroušek et al. [19] reported that a higher concentration of silica nanoparticles seemed to block the biochemical metabolism during the germination of seeds.

4 Conclusion

The present study makes out the best way to understand the green approach method to synthesize silica nanoparticles without using harmful chemicals. *E. thymifolia*-based silica nanomaterials were produced by a green chemistry approach. Phytochemical screening of *E. thymifolia* (aqueous extract) shows the presence of tannins, flavonoids, and glycosides. Silica nanoparticles were successfully characterized using UV visible spectroscopy, XRD, SEM, EDAX, FTIR, zeta potential analysis, and TGA. All the characterization reveals that synthesized silica nanoparticles were amorphous in nature with average size of 17 nm, pure and thermo-stable. This study concludes that the aqueous extract of *E. thymifolia* acts as a reducing and capping agent for the synthesis of silica nanoparticles. The lowest concentration of silica nanoparticles was found to improve the seed germination percentage. It may play a vital role in the production of nano-fertilizers.

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Data Availability Not applicable

Declarations

Ethics Approval Not applicable

Consent to Participate Not applicable

Consent for Publication Not applicable

Competing Interests The authors declare no competing interests.

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