Curcuma caesia rhizome extract – Mediated Green synthesis of Titanium Dioxide nanoparticles and their Characterisation

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Abstract:

This study reports the green synthesis of *Curcuma caesia* rhizome extract with Titanium dioxide (TiO_2) nanoparticles. The rhizome extract biosynthesized gives Amber colour or reddish brown colored solution was formed. UV–Vis spectroscopy revealed a sharp absorption peak at 334 nm, characteristic bioactive compounds present in rhizome extract.. FTIR spectra showed phytochemical functional groups of bioactive compounds of rhizome extract, including O–H (3523 and 3265 cm^{-1}), C–H (2925 cm^{-1}), and C=O (1720 cm^{-1}), along with Ti–O–Ti vibrations below 800 cm^{-1}, confirming TiO_2 formation. X-ray diffraction patterns exhibited distinct peaks at 27.4°, 36.1°, 41.2°, 54.3°, and 69.0° (2θ), corresponding to the rutile phase (JCPDS 21-1276), with an average crystallite size of 26–30 nm calculated by the Scherrer equation. SEM images revealed aggregated particles with a size range of 50–150 nm, while EDS confirmed the elemental composition with a Ti:O atomic ratio close to 1:2. The results establish green synthesis as a sustainable and efficient approach for producing biosynthesized product with potential applications in photocatalysis, antimicrobial activity, anticancer, anti inflammatory, antioxidant etc.

Keywords: *Curcuma caesia* rhizome, Titanium dioxide NPs, UV, IR, XRD, SEM.

Introduction:

Nanotechnology is one of the advanced sciences of the twenty-first century, having applications in diverse fields including medicine, textiles, pharmaceuticals, agriculture, horticulture, electronics, cosmetics, and material development [1-3]. Now, the use of nanomaterials in healthcare is considered one of the most promising approaches. As the nanoparticles are biocompatible, highly bioavailable, and more precise, it has been drawing huge attention in the field of biomedical sciences, specifically in bioimaging, drug delivery, and cancer therapy [4,5]. However, the chemical synthesis of nanoparticles is discouraged by researcher due to their toxic effects on the environment. It also poses not only hazards to mankind but also serious environmental problems, including those affecting soil, water, and the atmosphere [6-8]. Therefore, alternative methods such as green synthesis of nanoparticles are widely accepted due to their eco-friendly and environmentally sound technologies [9]. Among different techniques of synthesis, the green method has gained wider acceptance as it is cost-effective, eco-friendly, stable, and easy to store [10]. Plant extracts contain bioactive compounds that can act as reducing and capping agents in nanoparticle synthesis [11].

TiO_2 nanoparticles become a new generation of advanced materials due to their brilliant and interesting optical, dielectric, and photo-catalytic characteristics from size quantisation. It is one of the most widely used nanostructures in various Areas [12]. Titania is the only titanium oxide that occurs naturally [13,14,15,16]. TiO_2 is an odourless, brilliantly white powder that, under normal conditions, is hydrophobic in nature. It is a highly stable material that also works well as an opacifier. Some researches were focused on its effect on bacteria, algae, plankton, fish, mice, and rats [17,18], but its impact on fungi or plants' growth was unclear.

This study demonstrates the synthesis of TiO_2NPs using *Curcuma caesia* Roxb. Rhizome extract, commonly known as black turmeric, is reported for the first time from these regions. Black turmeric *(Curcuma caesia* Roxb.) of family Zingiberaceae, an industrially important plant, is now categorised as a critically endangered species [19,20]. Black turmeric is an erect rhizomatous herb belonging to the Zingiberaceae family, consisting of a bluish-black rhizome, which is why it is known as black turmeric. It has an intense camphoraceous odour and many medicinal properties and is used in the pharmaceutical industry. Black turmeric has been used as a folk medicine since ancient times. The Adi tribe of Arunachal Pradesh uses the rhizome of black turmeric as an anti-diuretic. In contrast, the Khamti tribe, belonging to the Lohit district of Arunachal Pradesh, uses the paste of fresh black turmeric rhizome to treat scorpion and snake bites. Its rhizome is also used as a muscle relaxant, and it possesses anti-asthmatic activity. The advantages of curcumin present in the leaves and rhizome of *Curcuma caesia* are one of the most powerful antioxidants, which will inhibit the formation of reactive oxygen species, have anti-cancer, anti-inflammatory, anti-microbial, and wound healing effects.

Several studies reported the use of plant extracts such as *Solanum lycopersicum* [21], *Plantago asiatica* [22], *Eclipta prostrate* [23], *Plumbago zeylanica* [24], *Punica granatum* [25], *Camellia sinensis* [26], etc. for the synthesis of nanoparticles. However, there is no report of the use of *Curcuma caesia* Roxb. (black turmeric) rhizome extract for the synthesis of TiO_2NPs.

Materials and methods:

Sample collection: (Materials)

The Rhizome powder of *Curcuma caesia,* used as the green source in this synthesis process (Fig. 1), was procured from Holy Naturals online. It was taxonomically authenticated by Dr Dande Swana Sree, Department of Botany (specimen code: DA 101), and a voucher specimen was deposited in the Herbarium of Cluster University, Silver Jubilee Government College (A), Kurnool. The collected rhizome powder was stored in an airtight container at room temperature until further use. The chemicals were used as received from the vendor without further purification.

Fig. 1 *Curcuma caesia rhizomes* **Soxhlet rhizome extract** **Biosynthesized** **TiO_2NPs**

Preparation of the rhizome extract:

The ethanolic rhizome extract of *Curcuma caesia* was prepared by taking 20 g of powdered root, which was placed in a Soxhlet apparatus (Fig. 1) and extracted with ethanol (95%) for about 6 hr at 35°C. The ethanolic rhizome extract of *Curcuma caesia* was stored in a refrigerator at 4°C for further use. The rhizome extract colour was dark brown.

Biosynthesis of *Curcuma caesia* rhizome extract with Ethanolic solution TiO_2 NPs:

The prepared rhizome extract was utilized for the biosynthesis of TiO_2 NPs. We first prepared 100 mL of a 1 mM ethanolic solution of TiO_2. A partial turbidity solution was formed, so 10 mL of HCl was added for solubility. Then, 20 mL of isolated rhizome extract was placed into a conical flask. The flask was then placed on a magnetic stirrer. 50 mL (1 mM) of TiO_2 nanopowder solution was added dropwise to the rhizome extract. The biosynthesis of *Curcuma caesia* rhizome extract dark brown colour changes to amber-like or reddish brown. The biosynthesis of the product solution was further analysed for characterisation of UV, IR, XRD, and SEM.

Results and discussion:

UV–Visible Spectroscopic Analysis:

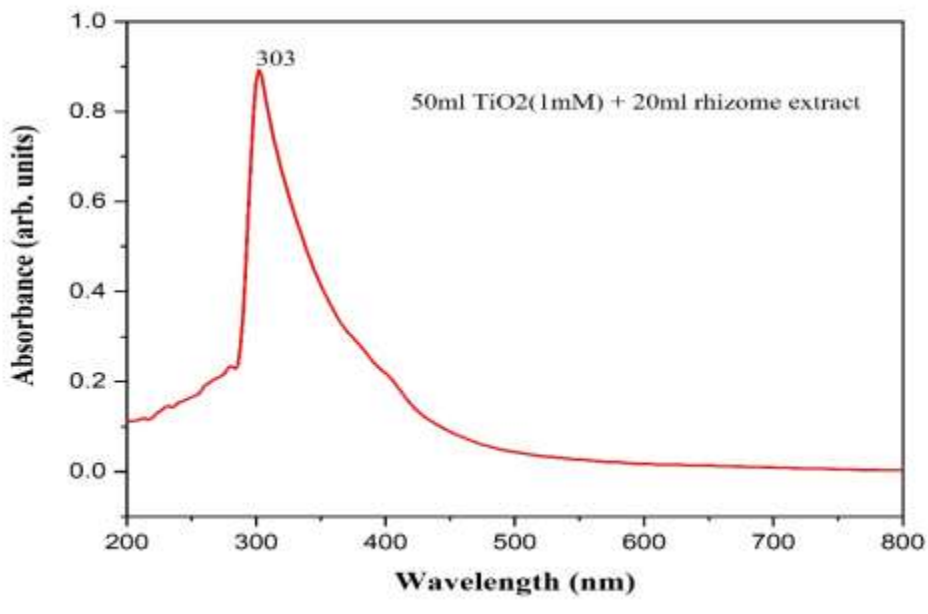


Fig. 2 UV–Vis spectrum of rhizome extract of *Curcuma caesia* biosynthesised with TiO2Nps

UV–Visible spectral analysis of rhizome extract of *Curcuma caesia* biosynthesised with TiO2Nps shows that the surface plasmon resonance (SPR) sharp absorption peak at 303 nm wavelength, which confirms the successful amber colour rhizome extract biosynthesis of TiO_2 NPs, which corresponds to the electron transition from valence band (O 2p) to the conduction band (Ti 3d). After the peak, the absorbance gradually decreases towards higher wavelengths (400-800 nm), forming a long tail (Blue shift), which suggests that particles are in the nanoscale range. The UV spectra show that additional peaks are not observed, which indicates the purity and stability of the biosynthesized rhizome extract.

Fourier Transform Infrared Spectroscopic Analysis (FTIR):

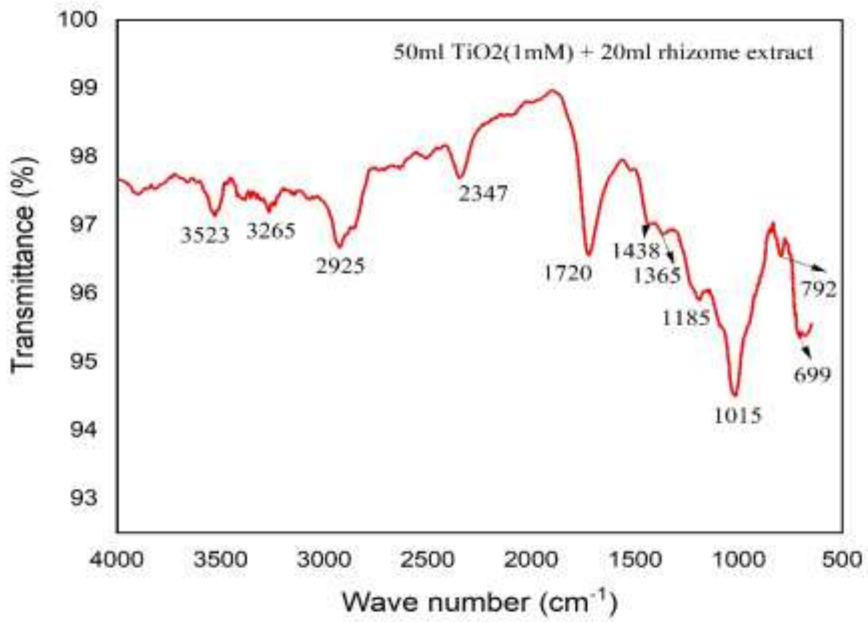
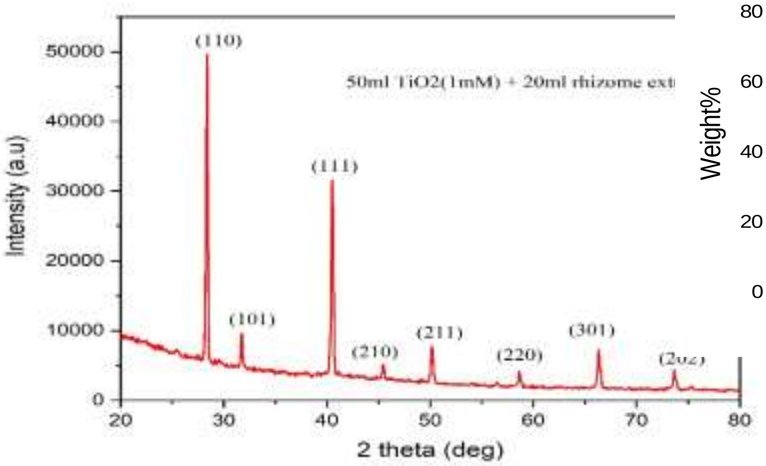


Fig. 3 FTIR spectrum of rhizome extract of *Curcuma caesia* biosynthesised with TiO2 Nps

The FTIR spectrum of the rhizome extract of *Curcuma caesia* biosynthesised with TiO2 Nps was shown in Fig.3. The FTIR spectrum of biosynthesized rhizome extract with TiO2 Nps clearly shows different bioactive compounds present in the green synthesized rhizome extract of *Curcuma caesia.* The FTIR spectrum exhibited a broad absorption band at 3523 cm-1 & 3265 cm^{-1} corresponding to the hydroxyl (-OH) group in phenols and alcohols, and at 2925 cm^{-1} corresponding to the C-H stretching of alkanes from bioactive compounds (flavonoids, alkaloids, tannins, terpenoids, saponins, glycosides) in the rhizome extract. The peak at 2347 cm^{-1} shows possible CO2 asymmetric stretching, and a sharp peak at 1720 cm^{-1} corresponds to C=O stretching of carboxylic acids in plant metabolites that act as reducing/stabilizing agents. The peaks at 1185 cm^{-1}& 1015 cm^{-1} indicate C – O stretching of alcohols, ethers, or esters present in phytochemicals. The peaks at 792 cm^{-1} & 699cm^{-1} correspond to Ti–O–Ti stretching vibrations, which confirms the formation of TiO_2 nanoparticles [27].

X-ray Diffraction (XRD):



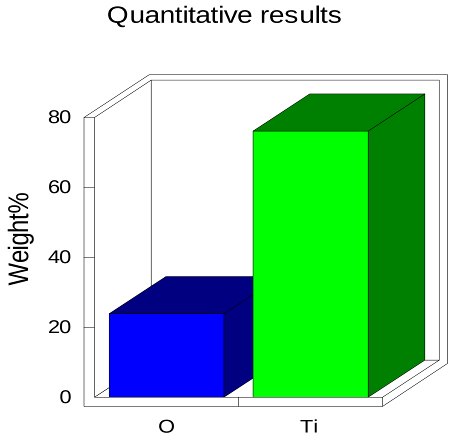


Fig. 4 XRD pattern rhizome extract of *Curcuma caesia* biosynthesised with TiO2 Nps

The analysis of the X-ray diffraction of the rhizome extract of *Curcuma caesia* with green-synthesised TiO_2 nanoparticles is shown in Fig. 4. The sharp and intense diffraction peaks at (110) and (111) confirm the formation of highly crystalline nanoparticles. The Bragg diffraction angle and XRD peaks have Miller indices of 2θ = 28.49, 31.75, 40.58, 45.41, 50.24, 58.74, 66.41, and 73.74 for (110), (101), (111), (210), (211), (220), (301), and (202) respectively, which verifies the polycrystalline structure of the rhizome extract biosynthesized TiO_2 NPs. The absence of additional impurity peaks indicates phase purity of the biosynthesized nanoparticles. The average crystallite size was found to be 26.4 nm, and the diffraction pattern revealed the rutile phase of the developed TiO_2 nanoparticles.

Scanning Electron Microscope (SEM):

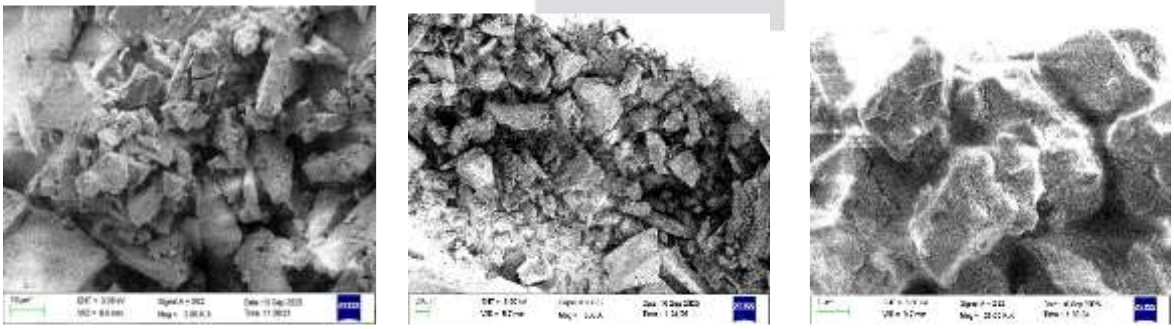


Fig. 5 SEM images of rhizome extract of *Curcuma caesia* biosynthesised with TiO2 Nps

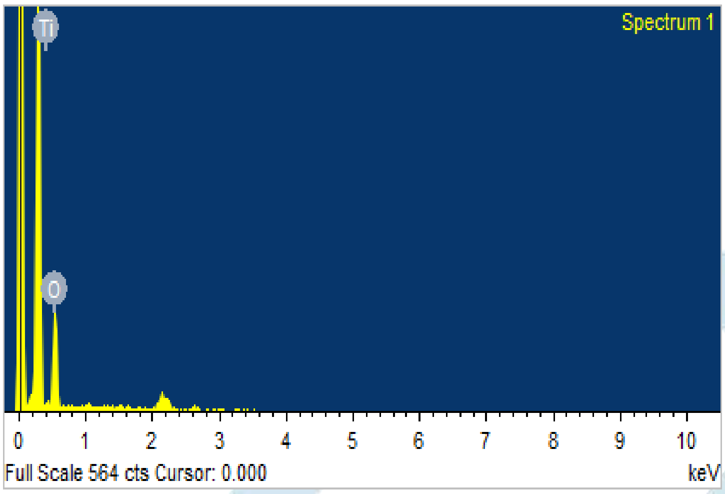


Fig. 6 EDS (Energy Dispersive X-ray Spectroscopy)

Field Emission Scanning Electron Microscopy (FESEM) was employed to examine the morphological characteristics of rhizome extract of *Curcuma caesia* biosynthesised with TiO2 NPs at various magnifications, as shown in Fig. 5. At lower magnification, the particles appeared as irregularly shaped agglomerates. However, upon closer inspection at a higher magnification, they were found to be made up of compact, crystalline-like grains with rough surfaces. This morphology indicates aggregated nanostructures with particle sizes between 50 to 150 nm. The nanoparticles' tendency to cluster is likely due to their high surface energy, a common trait in green-synthesised oxides. The observed characteristics confirm the successful formation of nanoparticles with a varied particle size distribution.

The elemental composition was confirmed by Energy Dispersive X-ray Spectroscopy (Fig. 6). The spectrum showed two major peaks corresponding to titanium (Ti) and oxygen (O), with no additional impurity peaks detected, confirming the purity of the synthesized material. Quantitative EDS analysis revealed Ti (76.11 wt%, 51.56 at%) and O (23.89 wt%, 48.44 at%), giving an approximate atomic ratio of 1:2 (Ti:O), which is consistent with stoichiometric TiO_2. The high titanium weight percentage is attributed to its greater atomic mass compared to oxygen. Overall, the combined SEM and EDS results confirm that the green synthesis approach successfully produced pure TiO_2 nanoparticles with crystalline morphology and correct elemental composition.

Conclusions:

In this study, the rhizome extract of *curcuma caesia* biosynthesized with TiO_2 nanoparticles were successfully synthesized via a green route. The present work successfully demonstrated an eco-friendly, cost-effective, and sustainable approach for the biosynthesis of titanium dioxide nanoparticles using rhizome extract of *Curcuma caesia* as a natural reducing and stabilizing agent. The nanoparticles were confirmed by UV–Vis, FTIR, XRD, SEM, and EDS analyses. The surface plasmon resonance (SPR) sharp absorption peak at 303 nm wavelength, which confirms the successful amber colour rhizome extract biosynthesis of TiO_2 NPs. The FTIR spectrum of biosynthesized rhizome extract with TiO2 Nps clearly shows different bioactive compounds (flavonoids, alkaloids, tannins, terpenoids, saponins, glycosides) present in the green synthesized rhizome extract of *Curcuma* *caesia.* FTIR confirmed nanoparticle formation and the role of phytochemicals in stabilization. XRD showed rutile-phase TiO_2 with an average crystallite size of ~26–30 nm. SEM revealed aggregated nanostructures with particle sizes ranging from 50 to 150 nm, while EDS confirmed elemental purity with a Ti:O atomic ratio close to 1:2. The findings demonstrate that green synthesis is an eco-friendly, cost-effective method for producing pure TiO_2 nanoparticles. Biosynthesized rhizome extract with TiO_2 adapt to various biomedical applications.

References:

1. Giannousi, K., Avramidis, I., & Dendrinou-Samara, C. (2013). Synthesis, characterization, and evaluation of copper-based nanoparticles as agrochemicals against *Phytophthora infestans*. *RSC Advances, 3*(44), 21743–21752.

2. Jayarambabu, N., Akshaykranth, A., Rao, T. V., Rao, K. V., & Kumar, R. R. (2020). Green synthesis of Cu nanoparticles using *Curcuma longa* extract and their application in antimicrobial activity. *Materials Letters, 259*, 126813.

3. Chauhan, N., Thakur, N., Kumari, A., Khatana, C., & Sharma, R. (2023). Mushroom and silk sericin extract mediated ZnO nanoparticles for the removal of organic pollutants and microorganisms. *South African Journal of Botany, 153*, 370–381.

4. Salem, S. S. (2023). A mini review on green nanotechnology and its development in biological effects. *Archives of Microbiology, 205*, 128.

5. Ventola, C. L. (2012). The nanomedicine revolution: Part 1: Emerging concepts. *Pharmacy and Therapeutics, 37*(9), 512–525.

6. El-Batal, A. I., El-Sayyad, G. S., Mosallam, F. M., & Fathy, R. M. (2020). *Penicillium chrysogenum*-mediated mycogenic synthesis of copper oxide nanoparticles using gamma rays for in vitro antimicrobial activity against some plant pathogens. *Journal of Cluster Science, 31*(1), 79–90.

7. Lee, H. J., Song, J. Y., & Kim, B. S. (2013). Biological synthesis of copper nanoparticles using *Magnolia kobus* leaf extract and their antibacterial activity. *Journal of Chemical Technology and Biotechnology, 88*(11), 1971–1977.

8. Panda, M. K., Singh, Y. D., Behera, R. K., & Dhal, N. K. (2020). Biosynthesis of nanoparticles and their potential application in the food and agricultural sector. In *Green Nanoparticles: Synthesis and Biomedical Applications* (pp. 213–225).

9. Thakur, N., Nigam, M., Mann, N. A., Gupta, S., Hussain, C. M., Shukla, S. K., & Khan, S. A. (2023). Host-mediated gene engineering and microbiome-based technology optimization for sustainable agriculture and environment. *Functional & Integrative Genomics, 23*(1), 57.

10. Das, A. K., et al. (2023). Papaya latex-mediated synthesis of prism-shaped proteolytic gold nanozymes. *Scientific Reports, 13*, 5965.

11. Ningthoujam, R., Jena, B., Pattanayak, S., Dash, S., Panda, M. K., Behera, R. K., Dhal, N. K., & Singh, Y. D. (2021). Nanotechnology in food science. In *Bio-nano interface: Applications in food, healthcare and sustainability* (pp. 59–73). Springer Singapore.

12. Seabra, A. B., & Duran, N. (2015). Nanotoxicology of metal oxide nanoparticles. *Metals, 5*(2), 934–975.

13. Mondal, K., & Sharma, A. (2016). Recent advances in the synthesis and application of photocatalytic metal–metal oxide core–shell nanoparticles for environmental remediation and their recycling process. *RSC Advances, 6*, 83589–83612.

14. Gupta, S. M., & Tripathi, M. (2011). A review of TiO_2 nanoparticles. *Chinese Science Bulletin, 56*, 1639–1657.

15. Nabi, G., Aain, Q. U., Khalid, N. R., Tahir, M. B., Rafique, M., Rizwan, M., Hussain, S., Iqbal, T., & Majid, A. (2018). A review on novel eco-friendly green approach to synthesis of TiO_2 nanoparticles using different extracts. *Journal of Inorganic and Organometallic Polymers and Materials, 28*, 1552–1564.

16. Ziental, D., Czarczynska-Goslinska, B., Mlynarczyk, D. T., Glowacka-Sobotta, A., Stanisz, B., Goslinski, T., & Sobotta, L. (2020). Titanium dioxide nanoparticles: Prospects and applications in medicine. *Nanomaterials, 10*, 387.

17. Mahmoodzadeh, H., Nabavi, M., & Kashefi, H. (2013). Effect of nanoscale titanium dioxide particles on the germination and growth of canola (*Brassica napus*). *Journal of Ornamental Horticultural Plants, 3*, 25–32.

18. Jesline, A., John, N. P., Narayanan, P. M., Vani, C., & Murugan, S. (2015). Antimicrobial activity of zinc and titanium dioxide nanoparticles against biofilm-producing methicillin-resistant *Staphylococcus aureus*. *Applied Nanoscience, 5*(2), 157–162.

19. Behar, N., Tiwari, K. L., & Jadhav, S. K. (2014). A review on non-conventional turmeric: *Curcuma caesia* Roxb. *Current Trends in Biotechnology and Pharmacy, 8*(1), 91–101.

20. Borah, A., Kumar, D., Paw, M., Begum, T., & Lal, M. (2020). A review on ethnobotany and promising pharmacological aspects of an endangered medicinal plant, *Curcuma caesia* Roxb. *Turkish Journal of Botany, 44*(3), 205–213.

21. Batool, M., & Masood, B. (2017). Green synthesis of copper nanoparticles using *Solanum lycopersicum* (tomato aqueous extract) and study characterization. *Journal of Nanoscience and Nanotechnology Research, 1*, 1–5.

22. Nasrollahzadeh, M., Sajadi, S. M., & Khalaj, M. (2014). Green synthesis of copper nanoparticles using aqueous extract of the leaves of *Euphorbia esula* L. and their catalytic activity for ligand-free Ullmann-coupling reaction and reduction of 4-nitrophenol. *RSC Advances, 4*(88), 47313–47318.

23. Chung, I. M., Rahuman, A. A., Marimuthu, S., Kirthi, A. V., Anbarasan, K., Padmini, P., & Rajakumar, G. (2017). Green synthesis of copper nanoparticles using *Eclipta prostrata* leaves extract and their antioxidant and cytotoxic activities. *Experimental and Therapeutic Medicine, 14*(1), 14–18.

24. Jamdade, D. A., Rajpali, D., Joshi, K. A., Kitture, R., Kulkarni, A. S., Shinde, V. S., Bellare, J., Babiya, K. R., & Ghosh, S. (2019). *Gnidia glauca*- and *Plumbago zeylanica*-mediated synthesis of novel copper nanoparticles as promising antidiabetic agents. *Advances in Pharmacological Sciences, 2019*, 1–11.

25. Padma, P., Banu, S., & Kumari, S. (2018). Studies on green synthesis of copper nanoparticles using *Punica granatum*. *Annual Research and Review in Biology, 23*(1), 1–10.

26. Ahmed, A., Usman, M., Liu, Q. Y., Shen, Y. Q., Yu, B., & Cong, H. L. (2019). Plant-mediated synthesis of copper nanoparticles by using *Camellia sinensis* leaves extract and their applications in dye degradation. *Ferroelectrics, 549*(1), 61–69.

27. Ul-Hamid, A., Aljebab, H. H., Aldaoudeyeh, A. I., Al-Shorman, M. M., & Almasoudi, A. S. (2023). Using biologically synthesized TiO_2 nanoparticles as antimicrobial and anticancer agents. *Saudi Journal of Biological Sciences, 30*(12), 103743.