Green synthesis and characterization of TiO_2 nanoparticles by using ornamental grass *Cynodon dactylon* (Doob grass)

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Abstract

Due to their wide-ranging applicability in numerous fields, nanoparticles (NPs) are in profitable demand. Traditional chemical synthesis procedures are employed to create metallic nanoparticles, and the chemicals utilised are frequently hazardous, volatile, and expensive. The development of dependable, long-lasting, and environmentally acceptable methods for creating metallic nanoparticles is now a key advancement in the field of nanotechnology. Plant extracts can replace the expensive and inefficient large-scale manufacturing of nanoparticles since they are environmentally benign and cost-effective. In the current study, we developed stable Titanium oxide nanoparticles utilising a unique method that involved using *Cynodon dactylon* leaf extract and experiencing a sudden decline in titanium ions.The titanium element is present in significant amounts in TiO_2 NPs, which is equivalent to a high oxygen concentration. Using the FT-IR spectrum, the functional group and chemical component contained in the produced TiO_2 NPs were located. The stretching and bending vibration of the -OH group is what causes the peaks at 3189.08 and 1634.22 cm^{-1} in the spectrum. The monodisperse character of the particles, with an average particle size of about 524 dnm, is revealed by the DLS results. Zeta potential was used to assess the stability of nanoparticles. It was discovered that the zeta potential value was strongly negative, or 31.7 mV, which suggests that the particles were well colloidal and steadily stable. The TiO_2 nanoparticles' TGA-DTA curve exhibits a progressive decline with increasing temperature under inert conditions.

Keywords: "*TiO_2 nanoparticles", "Cynodon dactylon", "XRD", "FTIR", "SEM", "TGA"*

Introduction

Many weed species in our environment are often highly effective therapeutic plants for many of our time's significant health problems. *Cynodon dactylon* (L.) Pers., a weed (the common name is derived from the Greek words "kuon" meaning dog and "odous" meaning tooth, while the specific name "daktulos" means finger - referring to the finger-shaped inflorescence), is one of ten auspicious herbs that comprise the group "Dasapushpam" in Ayurveda (science of life, prevention and longevity - system of medicine). oldest and most diverse economy). It is said to be India's holiest plant besides *Ocimum* sp. [1].

In the current period, nanotechnology and green chemistry, like other mechanism breakthroughs, are expected to rise in demand, and the amount of research being undertaken in this sector is rapidly increasing around the world. Nanotechnology is concerned with the creation of nanometre-sized materials. It has a broad field that includes several topics from applied and material science. Nanoparticles are particles with a size of up to 100 nm that exhibit completely unique properties due to their size, distribution, and shape. The nanoscale materials differ from their bulk counterparts due to the higher surface area of these nanoparticles, which is primarily responsible for their distinct chemical, optical, and mechanical capabilities [2].

Metallic nanoparticles (NPs) are distinguished by their optical, electrical, and photothermal properties. Researchers have spent the last few decades focusing on nano-sized particles due to their wide range of applications [3]. Among all the inorganic materials, a researcher is most interested in metal oxide nanoparticles because of their unique features and applications to the physical and chemical properties of TiO_2. Furthermore, these features may aid in the modification of particle size, surface morphology, crystalline phase, and dimension [4]. Nowadays, the production of nanoparticles by a synthetic approach using plants is applied in a wide range [5]. The green manufacturing of titanium oxide nanoparticles has greater advantages because it uses less chemicals [6].

TiO2 nanoparticles have mostly been employed as a catalyst in the organic reaction for organic waste degradation in water [7]. Plants can be more advantageous than other biological methods for nanoparticle synthesis because the process of maintaining cell cultures can be eliminated, and nanoparticle synthesis using plant leaf extracts can be more reasonable when compared to whole plants due to the practicability in the downstream processing steps. Although Bekele *et al* [3] reported the production of TiO_2 nanoparticles from numerous plants such as Cassia fistula, Hibiscus rosa sinensis, and others, the potential of plants as a biological source for nanoparticle synthesis remains unexplored.

In this research, we describe a low-cost, convenient, green synthesis method for producing large amounts of TiO_2 nanoparticles using *Cynodon dactylon* leaf extract. Burmuda grass is usually present at any nearby location. It is an attractive Horticulture lawn grass with a high commercial value. The cost-effective green production of Titanium dioxide nanoparticles from locally available grass will be extremely advantageous to the agriculture sector. Previously, other syntheses of Nano materials were attempted utilising this grass, but they were not cost efficient or sustainable, whereas we use a cost-effective method for the synthesis part. Phytochemical compounds in grass aid in salt reduction and act as a stabilising agent. According to Nallathambi and Bhargavan [8], this plant includes a significant number of phytochemicals that can act as a reducing and stabilising agent in the green synthesis of NPs (Scheme-2). In this study, we used aqueous extracts of the lawn grass *Cynodon dactylon* (Doob grass) to create titanium oxide nanoparticles. X-ray Diffraction (XRD), Fourier transforms infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), Zeta potential (DLS), and thermogravimetric analyses were used to evaluate the produced nanoparticles (TGA).

Materials and methods

Preparation of *Cynodon dactylon* extract

Cynodon dactylon leaves were taken from the lawn of the Bidhan Chandra Krishi Vishwavidyalaya campus in Mohanpur, West Bengal. The collected leaves were rinsed many times with deionized water. 50 g of finely chopped Cynodon dactylon leaves were cooked in 500 ml of double distilled water for 10 minutes before being filtered through Whatman No 1 filter paper. The filtrate was collected and kept at 4°C until needed.

Synthesis of TiO_2 NP

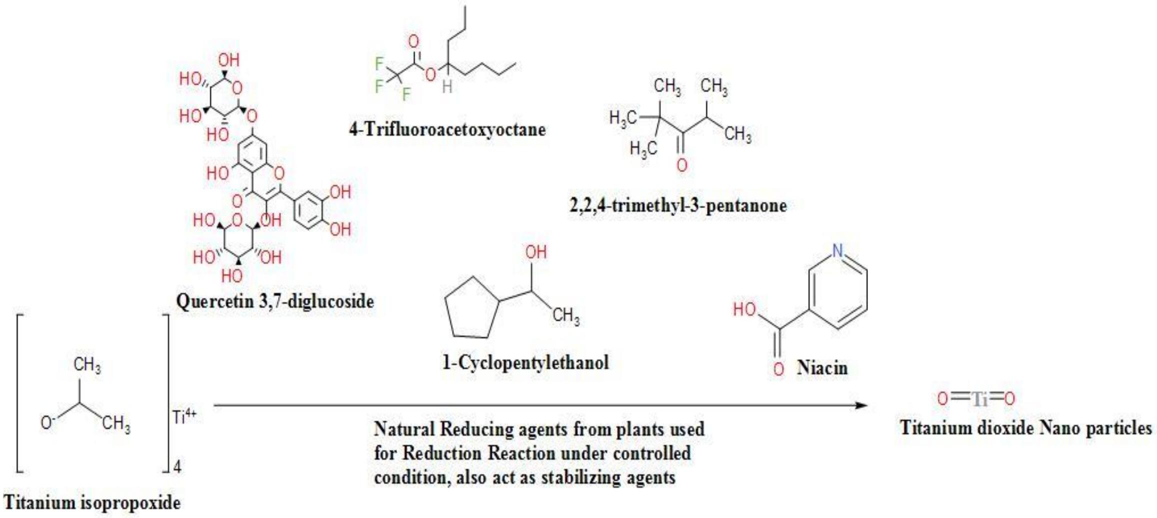
Titanium isopropoxide (TTIP, $C_{12}H_{28}O_4Ti$,97%) should be dissolved in 100 millilitre of Millipore water at 1.0 N. Drop by drop addition of grass extract while swirling steadily produced a pH of 7. The mixture was continuously stirred for five hours. In this procedure, nanoparticles were created. These nanoparticles were then separated using what-man filter paper, and the materials were repeatedly rinsed with water to get rid of the by-products. The nanoparticles were calcined at 500–600°C for two hours after being dried at 100°C overnight (Scheme-2).

Characterisation of TiO_2 NPs

Results from FT-IR, X-ray Diffraction, SEM, EDAX, TGA, and DLS were used to characterise the generated green based TiO_2 nanoparticles. We use an X-ray diffractometer to measure the size of nanoparticle crystals. This investigation was carried out using a BRUKER X-Ray Diffractometer (CIF, IACS, Jadavpur, Kolkata). This device operates at 30 kV and 40 mA with a 2 range of copper that ranges from 10.0 to 89.9. The FT-IR spectrum is captured using FT-IR (PERKIN ELMER) spectroscopy at a resolution of 4cm^{-1}. It has KBr optics with 0.5cm^{-1} resolution, 8,300-350 cm^{-1}, and KBr optics.

'JEOL', a field emission scanning electron microscope, is utilised to find the samples' SEM pictures. SEM and EDAX are both used to examine the size, shape, and elemental makeup of molecules and nanoparticles, respectively. The average size and zeta potential of the colloidal solution of metal nanoparticles are analysed in this research project utilising the Particle Size and Zeta Potential Analyzer "MALVERN." Thermogravimetric analysis "PERKIN ELMER" is used to examine how a sample's weight and mass vary as a result of a change in temperature when air O_2 is used as an inert environment [9,10].

Scheme1 Method for creating environmentally friendly TiO_2 nanoparticles by *Cynodon dactylon* (Doob grass)



Scheme2 The chemical reaction scheme for the synthesis of titanium dioxide nanoparticles from Cynodon dactylon.

Result and discussion

The extract of Cynodon dactylon was used to make white titanium dioxide nanoparticles, which were then analysed using XRD, SEM, FT-IR spectroscopy, TGA, and Zeta Potential size distribution.

XRD analysis

The 101, 110, 103, 004, 112, 200, 105 and 211 crystalline anatase and rutile structures of produced titanium dioxide nanoparticles are responsible for the green XRD patterns of TiO_2 nanoparticles found at 25.36, 26.54, 37.05, 37.78, 38.54, 48.12, and 54.02 degrees. By employing X-ray diffraction measurements, the synthesis of titanium dioxide nanoparticles using *Cynodon dactylon* leaves extract was examined. The results from Saranya et al [15], research is in favour of the conclusions. Scherrer's formula was used to calculate the average crystal size, which was estimated to be 12 nm.

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where D is crystalline size, λ is wavelength of X-ray (1.54 Å), β is full width half maxima, θ is Bragg angle, K is shape factor (0.9).

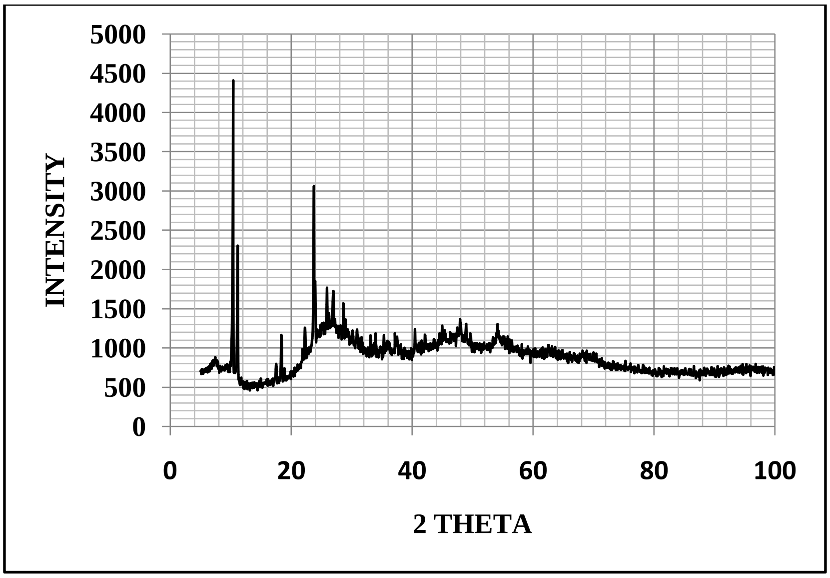


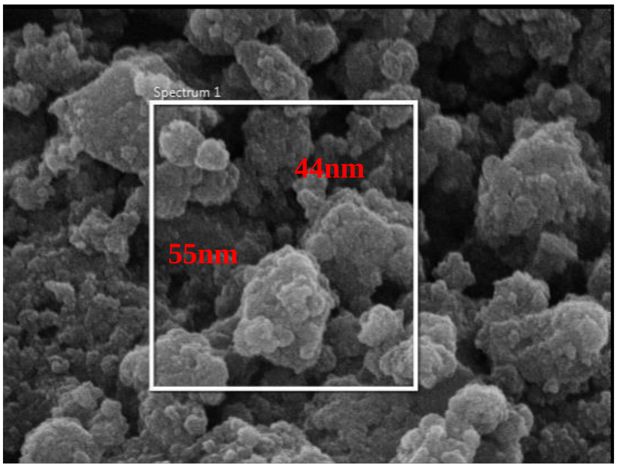
Fig1XRD of green TiO_2 NPs

SEM microscopy analysis

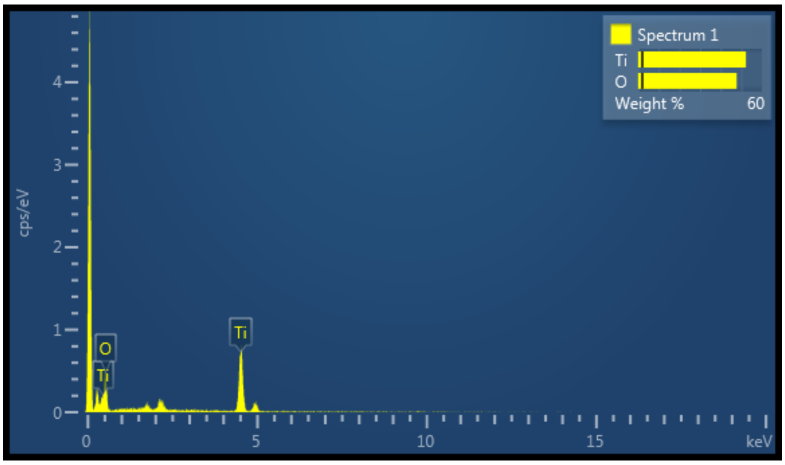
The SEM pictures of the ready TiO_2 NPs are shown in Fig. 2(a). Greenly synthesised TiO_2 nanoparticles have a spherical form in their SEM picture. As a result, the previous researcher claimed that metal oxides are the only substance that can provide these results [11]. TiO_2 NPs with a spherical shape were found to have an average particle size between 32 and 55 nm. In general, the relationship between the material's surface volume and the reduction in particle size is inverse.

Elemental dispersive spectrum

EDS spectra were used to examine the chemical compounds' constituent parts. The EDS spectra of green synthetic TiO_2 NPs are displayed in Fig. 2(b). Titanium (Ti) and oxygen are the ingredients in the synthetic TiO_2 NPs (O). The titanium element is present in significant amounts in TiO_2 NPs, which is equivalent to a high oxygen concentration. The TiO_2 NPs' atomic and weight percentages are listed in Table 1. It displays three strong peaks that are recognised as molecules of titanium and oxide [12].



(a)



(b)

Fig2 (a) SEM image (b) EDS- Elemental dispersive spectrum of TiO_2NPs

Table1 Elemental dispersive spectrum composition of TiO_2NPs

SPECTRUM 1	Wt%	Wt% SIGMA
O	47.77	2.05
Ti	52.23	2.05
TOTAL	100.00	

FTIR analysis

Using the FT-IR spectrum, the functional group and chemical component contained in the produced TiO_2 NPs were located. The FT-IR spectra of sol-gel-derived TiO_2 in the 400–4000 cm1 region are shown in Fig. 3. The stretching and bending vibration of the -OH group is what causes the peaks at 3189.08 and 1634.22 cm^{-1} in the spectrum. Peaks at 521.88 cm^{-1} and 1440 cm^{-1} in the spectra of pure TiO2 dnm (Table 2) indicate stretching vibrations of Ti-O and

Ti-O-Ti, respectively. The presence of amines is shown by peaks at 3810 cm^{-1}. Alkynes are present, as shown by peaks at 3287.11 $cm^{-1.}$ Aromatic rings may be seen in the peaks at 3011.35 cm^{-1}, The presence of pyridines is indicated by peaks at 1712.28 cm^{-1}. The majority of titanium dioxide in green synthesis is converted by these phytochemicals to stable TiO_2 [13].

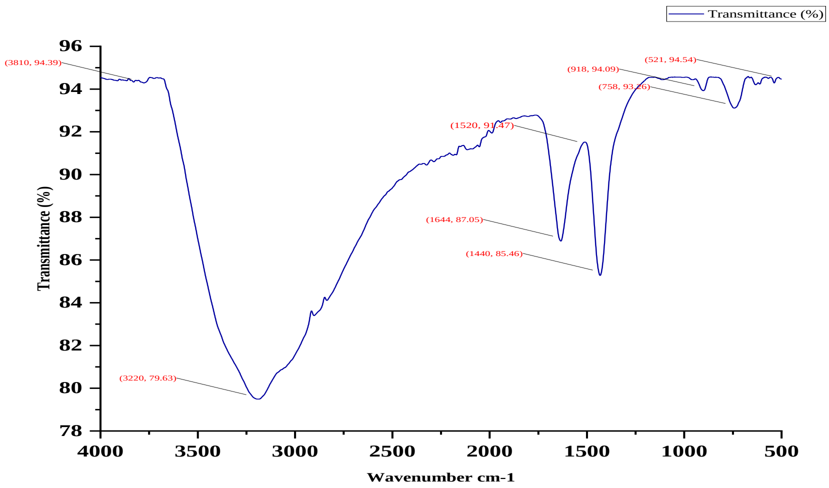


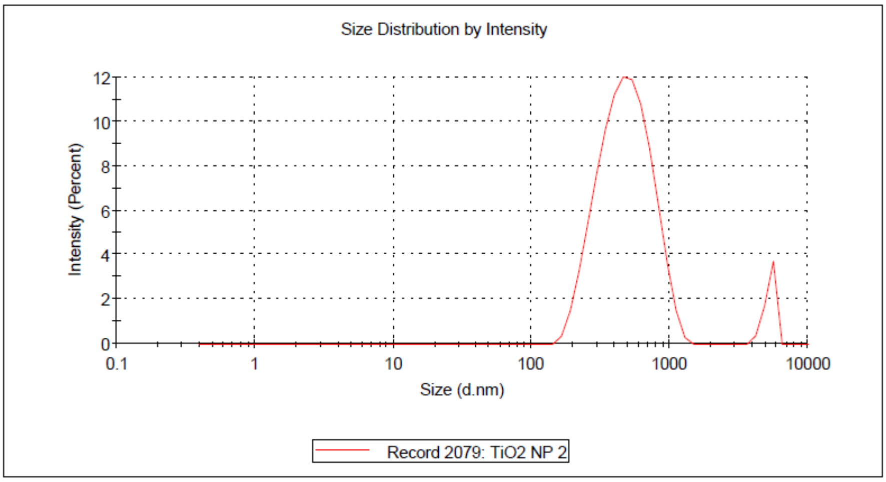
Fig3 FTIR Spectrum functional group and chemical compound present in the prepared TiO_2 NPs

Table2 FTIR peak table

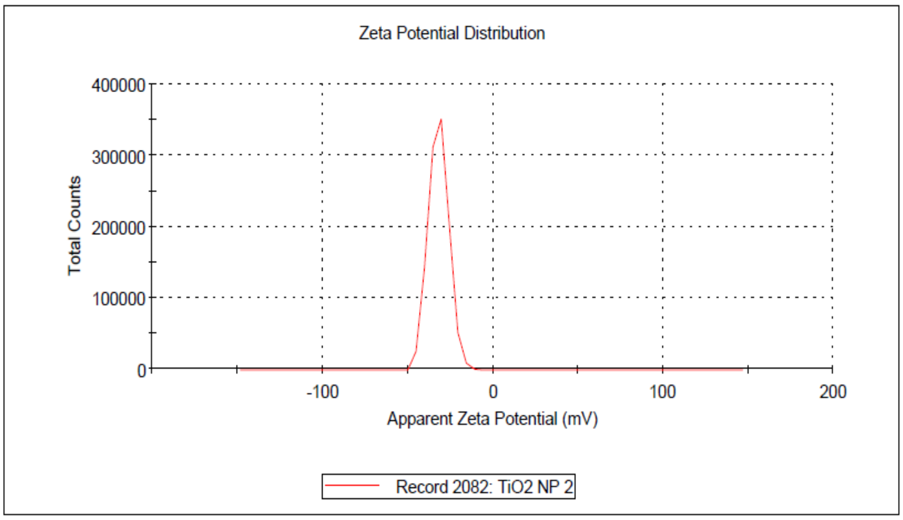
PEAK NUMBER	X (cm^{-1})	Y (%T)
1	3189.08	79.49
2	1634.22	86.89
3	1432.55	85.28

DLS and Zeta Potential

Green produced TiO_2 NPs were subjected to dynamic light scattering (DLS) analysis to determine the particle size distribution. Here, the sample was thoroughly dissolved in distilled water before DLS analysis. Results obtained as indicated in Fig. 4 (a) reveal that particles are monodisperse and that their average size is around 524 dnm (Table. 3). Zeta potential was used to assess the stability of nanoparticles, as shown in Fig. 4. (b). Zeta potential was determined to be strongly negative, or 31.7 mV, and conductivity was found to be 0.0327 mS/cm (Table 4), which suggests that the particles were well colloidal and steadily stable. [14]



(a)



(b)

Fig4 (a) Size distribution (b) Zeta Potential (mV) of TiO_2 NPs

Table3 Size Distribution Report by Intensity

Properties			**Size (dnm)**	**% Intensity:**	**St Dev**
Z-Average (d. nm):	555.5 (55.5nm)	**Peak 1:**	507.7	94.2	**210.6**
PdI:	0.355	**Peak 2:**	5242	5.8	**448.9**
Intercept:	**0.878**	**Peak 3:**	**0.000**	**0.0**	**0.000**

Table4 Zeta potential Report by area

			Mean (mV)	**Area (%)**	**St Dev (mV)**
Zeta Potential (mV):	-31.8	**Peak 1:**	-31.8	100.0	**5.81**

Zeta Deviation (mV):	5.81	**Peak 2:**	0.00	0.0	**0.00**
Conductivity(mS/cm):	**0.0327**	**Peak 3:**	**0.00**	**0.0**	**0.00**
Resultquality	**Good**				

Thermogravimetric analysis (TGA)

On the synthesised TiO_2 NPs, a thermogravimetric and derivative thermogravimetric analysis was anticipated. The TiO_2 nanoparticles' TGA-DTA curve is displayed in (fig-5). It is clear that the TG curve declines till a temperature of 250 ^{0}C before becoming static for a while and then declining once more. Two distinct zones may be seen in the TG-DTA traces. Due to their water dehydration, the first weight loss of approximately 65% is visible at temperatures below 100 ^{0}C. The breakdown of compounds in the TiO_2 NPs from 150-800 C is demonstrated by the DTA weight reduction of approximately >75%. This research was previously attested to for a sample of rice [15]. The proteins were tarnished and the organics were burned throughout the heating process, according to the TGA-DTA curves. [16]

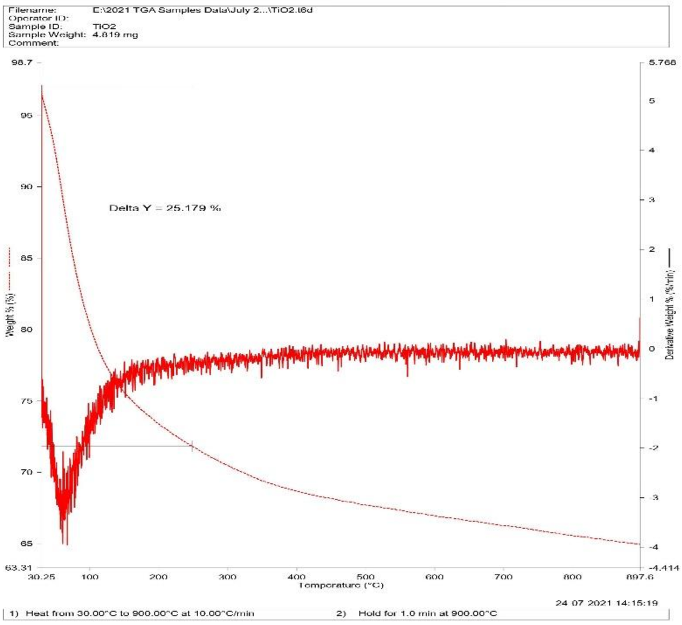


Fig5 TGA-DTA curves (Thermogravimetric and derivative thermogravimetric analysis)

Conclusion

In conclusion, *Cynodon dactylon* was used in a green synthesis technique to create TiO_2 nanoparticles (Doob grass). The TiO_2 NPs in the sample have an elemental composition of TiO_2, and the FTIR spectral data show that the nanoparticles were synthesised correctly. The XRD and SEM results also show that the particles are crystalline and almost spherical in shape. The heat accountability of the NPs is displayed by TGA-DTA. The zeta results from the DLS reveal that the particles are monodisperse, with an average particle size of about 524 dnm and a strong negative zeta potential value of 31.7 mV.

Scope in future

Nanoparticle green synthesis is not a new approach, although the steps and techniques differ from person to person. In order to improve production by quality and quantity, innovative nanotechnological approaches have been developed in the agricultural industry. Farmers are looking for technology and methods that are user-friendly, environmentally friendly, and sustainable. The technology of producing nanoparticles from grasses or decorative plants that are readily available locally will aid this industry and related industries in the future.

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