ABSTRACT
Ecofriendly green synthesis of titanium dioxide nanoparticles were carried out using Erythrina variegates leaves extract. The synthesis of the titanium dioxide nanoparticles was performed by adopting standard procedure. The titanium dioxide nanoparticles were characterized by UV, FT-IR, XRD and FESEM analysis. UV-Visible absorbance of titanium dioxide nanoparticles was observed at 270 nm. FT-IR stretching frequencies at 418.5 cm⁻¹ proved that these nanoparticles were bonded to the oxygen present in the bio-active constituents of Erythrina variegates and indicated the formation of Metal-oxygen bonds. XRD & FESEM analysis of titanium dioxide nanoparticles proved that they exist in spherical; face centred cubic (fcc) crystalline structure with size of 39 nm approximately.

KEYWORDS: Erythrina variegates, titanium dioxide nanoparticles, FT-IR and FESEM.

INTRODUCTION
Nanotechnology plays a very important role in modern research¹,² in the treatments of infection,³ cancer,⁴ allergy,⁵ diabetes⁶ and inflammation.⁷ Green chemistry is used to minimize the use of hazardous to environment.⁸⁻¹⁰ Many researchers used green synthesis methods for different metal nanoparticles due to their growing need of eco-friendly properties.¹¹,¹² In this method, the plant extract has been used as capping and reducing agent
for the synthesis of titanium dioxide nanoparticles due to their reducing properties of the bioactive constituents present in the leaves extract.\textsuperscript{[13, 14]} Titanium dioxide (TiO\textsubscript{2}) is a white solid inorganic substance that is thermally stable, non-flammable, poorly soluble and it occurs in nature as well-known minerals rutile, anatase and brookite.\textsuperscript{[15]} The most important application areas are paints and varnishes as well as paper and plastics, which account for about 80\% of the world's titanium dioxide consumption. It is also used to cleave protein that contains the amino acid proline.\textsuperscript{[16]} Titanium dioxide is also used as a material in the memristor, which can be employed for solar energy conversion based on Titanium dioxide solar cells using conjugated polymers as solid electrolytes.\textsuperscript{[17]} Synthetic single crystals and films of Titanium dioxide are used as a semiconductor.\textsuperscript{[18, 19]} Studies on phytochemical analysis of Erythrina variegated species have demonstrated that alkaloids and flavonoids were found to be major constituents.\textsuperscript{[20]} Alkaloid fraction from the bark showed several characteristic pharmacological effects such as neuromuscular blocking, CNS depressant and anticonvulsant effects. The leaves are used to stimulate lactation and menstruation. It is commonly mixed with castor oil to treat dysentery. The bark is used as a laxative, diuretic, and expectorant.\textsuperscript{[21, 22]} Different parts of E. Variegata have used in traditional medicine as nervine sedative, febrifuge and anti-asthmatic. Crude extract obtained from the E. variegated have potential effects for the treatment of convulsion, fever, inflammation, bacterial infection, insomnia, helminthiasis, cough, cuts and wounds.\textsuperscript{[23-27]}

Knowing the importance of Erythrina variegated leaves extract constituents and titanium dioxide nano particles biological importance, and in continuation of our work on bioactivity and stability prediction of phytoconstituents present in Erythrina variegated,\textsuperscript{[28-30]} we planned to synthesize titanium dioxide nano particles by greener method using Erythrina variegated leaves extract in an ecofriendly manner.

**EXPERIMENTAL METHOD**

a) Materials
The leaves of Erythrina variegated were collected from Sivakasi areas of virudhunagar district, Tamilnadu. Titanium isopropoxide of Merck grade was used.

b) Methods

**Preparation of Ethanol Extract of Erythrina variegated leaves**
About 5g of powdered plant leaves were taken into a 500 ml round bottomed flask along with 100 ml of ethanol in a soxhlet apparatus and allowed to boil at 60°C under reflux condition.
until a clear colourless solution was obtained and then it was cooled down to room
temperature. The filtrate was filtered through Whatmann No.1 filter paper to get clear
solution. The filtrate was stored at 4°C for the titanium dioxide nanoparticle synthesis.

**Synthesis and Separation of Titanium Dioxide Nanoparticles**
For the synthesis of titanium dioxide nanoparticles, the Erlenmeyer flask containing 40 ml of
0.4M of titanium tetraisopropoxide in 20 ml of ethanolic leaves extract were reacted together
under magnetic stirring at 50°C. After four hours of continuous stirring, the formed titanium
dioxide nanoparticles were acquired by centrifugation at 10000 rpm for 15 minutes. Then the
centrifuged particles were washed with ethanol and again subjected to centrifugation at
5000rpm for 10 minutes. Separated titanium dioxide nanoparticles were dried and grinded to
calcinate at 500°C in muffle furnace for about 3 hours. The calcined titanium dioxide
nanopowder was used for the nanoparticle characterization.

**Characterization of titanium dioxide Nanoparticles**
Characterisation of titanium dioxide nano particles was first carried out using UV-Visible
absorption spectrophotometer 2400PC with a resolution of 1nm between 300 and 900nm
possessing a scanning speed of 300nm/min. The characterization of functional groups on the
surface of titanium dioxide nanoparticles by leaves extract were investigated by FT-IR
spectra analysis using (Shimadzu FT-IR 8400S model) and the spectra was scanned in the
range of 4000-400cm⁻¹ range at a resolution of 4 cm⁻¹. The particle size and nature of the
titanium dioxide nano particles were determined using XRD PW 3050/60 X-pert PRO
operating at a voltage of 45 KV, a current of 40mA with Cu K alpha radiation at 20 angle
ranging from 5⁰ to 90⁰. A thin film of titanium dioxide nanoparticles was made by dipping a
glass plate in a solution and carried out for X-ray diffraction studies. FESEM analysis was
done by using a JSM6701F–6701 model.

**RESULTS AND DISCUSSION**

**UV-Visible Spectral Analysis**

**Figure 1** showed the UV absorption spectra of the titanium dioxide nanoparticles. The
absorbance of titanium dioxide nanoparticles appeared at 270 nm and this result was similar
with Curtis et al results for the titanium dioxide nanoparticles within the range of 220-450
nm. The peak value was found to be gradually decreased with increase in particle size.
Titanium dioxide Surface Plasmon Resonance effects decrease with the time because of the
oxidation of the synthesized titanium dioxide nanoparticles.
Fourier Transform-Infrared Spectral Analysis

The FTIR analysis was used to identify the capping, reducing and stabilizing capacity of the leaves extract. It was also used to determine the functional groups attached to titanium dioxide nanoparticles. FTIR spectra of Erythrina variegate leaves extract as given as Figure-2, showed the broad band between 3200 cm\(^{-1}\) - 3600 cm\(^{-1}\) indicated the presence of bonded –OH groups. The band at 1641 cm\(^{-1}\) indicated the presence of carbonyl group in the Erythrina variegate leaves extract. Figure-3 showed the FTIR spectrum of titanium dioxide nanoparticles in which titanium nano particles showed the IR stretching frequency at 418.5cm\(^{-1}\) (for metal oxygen binding). The diminished –OH stretching and the carbonyl stretching at 3200 cm\(^{-1}\) to 3600 cm\(^{-1}\) and at 1604 cm\(^{-1}\) of Erythrina variegate leaves extract assisted titanium nano particles FTIR spectra, on comparing FTIR spectra of Erythrina variegate leaves extract showed that titanium nano particles were formed by binding with the –OH oxygen and carbonyl oxygen of bio-active compounds present in Erythrina variegate leaves extract. The peaks at 441.70cm\(^{-1}\), 484.13 cm\(^{-1}\) to 700 cm\(^{-1}\) showed the bending and stretching mode of Ti-O-Ti.
Figure – 2 FT-IR Spectrum of the Erythrina Variegate leaves Extract.

Figure – 3 FT-IR Spectrum of The titanium dioxide nanoparticles

X-Ray Diffraction Spectroscopy

The powdered sample was used by a Cu Kα - X Ray Diffractometer for confirming the presence of titanium dioxide and analyzes the structure and it was shown in Figure-4. The diffraction peaks at 2θ with 25.3°, 38.3°, 48°, 54°, 62° corresponds to the crystal planes of (101), (004), (200), (105) and (204) respectively, indicating the formation of anatase phase of titanium dioxide as given in the Figure-4. The peaks of the graph were in good agreement with the literature report (Akarsuet al.). The location of the peaks was compared to literature values and the presence of Titanium dioxide nano particles was confirmed. The average size of the particles was calculated using Debye-Scherrer”s formula.

Figure–4 XRD Spectrum of Titanium dioxide nanoparticles
Field Emission Scanning Electron Microscopy Analysis
The FESEM analysis was used to determine the structure of the reaction products that were formed. Thin films of the sample were prepared on a carbon coated copper grid by just dropping a very small amount of the sample on the grid, extra solution was removed using a blotting paper and then the film on the SEM grid were allowed to dry by putting it under a mercury lamp for 5 min. SEM image was found to be roughly spherical spongy shape and agglomeration of nanoparticles were found as given in Figure-5. The size of the titanium nano particles were in the range of 39 – 53 nm.

![SEM Image](image.png)

**Analysis of Titanium dioxide nanoparticles**

**CONCLUSION**
Erythrina Variegate leaves extract assisted synthesis of Titanium dioxide nanoparticles in an Eco-friendly approach was carried out and the formation of Titanium dioxide nano particles were confirmed as per as the following observations:

- In UV-Visible spectroscopy, a strong absorption was observed at the wavelength 270 nm for titanium dioxide nano particles.
- The titanium nano particles showed the IR stretching frequency at 418.5cm⁻¹ (for titanium - oxygen bonding).
- XRD studies confirmed that the titanium nano particles formed by Erythrina variegate leaves extract were smaller in size in range of nanoscale.
- Field emission Scanning Electron Microscopy (FESEM) studies also confirmed the formation of Titanium dioxide nanoparticles and their sizes were in the range of 39 – 53 nm.
REFERENCES

