

Biogenic Synthesis of Iron Oxide Nanoparticles using leaf

Extract of *Clitoria Ternatea*

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ABSTRACT

Nanocrystalline iron oxide was synthesized through green chemistry using the leaf extract of *Clitoria ternatea* (Linn). The Bragg reflection peaks with respective d -values in x -ray diffraction pattern were found to be in accordance with face centered cubic lattice of iron oxide (Fe_3O_4) with cell parameter equal to 8.394 Å. The average crystallite size was estimated to be 73 nm using Debye-Scherrer equation. Raman bands were observed corresponding to the crystalline phase of Fe_3O_4 . Further, the fluorescence emission studies revealed the existence of radiative recombination process inside the sample.

Keywords: Iron oxide nanoparticles, White Clitoria flower, *Clitoria ternatea* (Linn), fluorescence emission etc

I. INTRODUCTION

Green synthesis using various plant extracts has now become the usual tool for the synthesis of zero valent metals as well as metal oxide nanoparticles [1, 2]. Synthesis of iron oxide nanoparticles is particularly important due to their significant applications in biomedical field [1, 2]. Among various plant parts, the leaves are highly significant because of the rich content of antioxidants. As evidenced from toxicology center, Parakulangara, Kottayam, Kerala, the White Clitoria flower plant is coming under the Family Fabaceae. The Botanical name is *Clitoria ternatea* (Linn). In Sanskrit, the plant is called by names such as Sankapushpam, Aparajita, Girikarnika etc. In English, the plant is known as White Clitoria flower, Butterfly Pea, Winged-leaved Clitoria etc. In Hindi, the names such as Aparajit and Hajin are used. In Malayalam, the plant is popularly known by the name Vella Samkupushpam. White Clitoria flower is a perennial herbaceous plant. Its leaves are elliptic and obtuse. It grows as a vine or creeper, doing well in moist neutral soil. The most striking feature about this plant is its vivid deep blue flowers. They are solitary, with light yellow markings. They are about 4 cm long by 3 cm wide. There are some varieties that yield white flowers. The fruits are 5 – 7 cm long, flat pods with 6 to 10 seeds in each pod. They are edible when tender. White Clitoria flower is an important component of the medicine that is used to neutralize the poison from the bite of Cobra. The white colored clitoria is more powerful than the blue one. This paper deals with the collection of data recorded for the nanoparticle sample obtained after the reduction of iron nitrate hepta hydrate ($FeSO_4 \cdot 7H_2O$) using the leaf extract of White Clitoria flower.

II. EXPERIMENTAL DETAILS

Fresh and matured leaves of sangupushpam (figure 1(a)) were collected from nearby area of Punalur during March 2017. They were washed several times with running tap water and after that with distilled water and then allowed for air dry in room temperature. The dried leaves were then cut into fine pieces. The weighed leaves were then added with de-ionized water in the ratio 6 g :100 ml, and stirred well till boiling. The extracts were filtered first with ordinary filter paper and then using whatmann filters paper and kept cool for further use (figure 1 (b)).

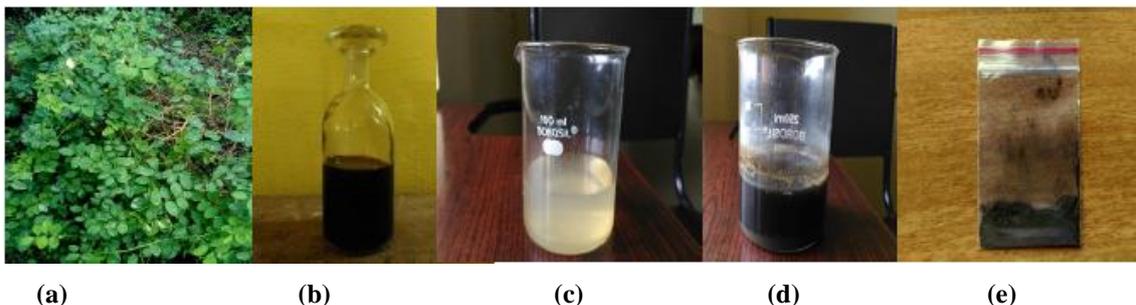


Figure 1: Different stages in the preparation of sample (a) image of the leaves (b) leaf extract (c) 0.05 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (d) formation of nanoparticles (d) annealed and finely crushed nanoparticles

0.05 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ precursor salt solution was prepared by dissolving appropriate amount of hepta hydrated iron sulphate in de-ionized water (figure 1(c)). In 2:3 ratio the precursor salt was mixed with the leaf extract under constant stirring and heating at about 90 °C for one hour. The pH and colour of solution were also noted frequently. Initially pH was low at 2; added a few drops of 0.1M NaOH solution to adjust pH above 5. The deep black solution indicative of the formation of iron oxide nanoparticles were identified (figure(d)). The solution was then kept overnight and the residue obtained is washed thoroughly with de-ionized water. For proper aging the residue was annealed at 130 °C for 1 hr and then crushed into fine powder (figure 1(e)). The sample has been labelled as Fe-NP-WCF for further reference.

III. RESULTS AND DISCUSSION

Figure 2 shows the x-ray diffraction pattern recorded for Fe-NP-WCF sample, using XPERT-PRO Diffractometer system having type 0000000083005153 with continuous scan mode of step size 0.0170 in the goni axis in the 2θ range 10° to 89.9°, installed at National Centre for Earth Science Studies (NCESS), Thiruvananthapuram. X-rays from the Cu anode material including K-alpha1, K-alpha2 and K-beta radiations with respective wavelengths, 1.54060 Å, 1.54443 Å, and 1.39225 Å with K-alpha2 to K-alpha1 ratio equal to 0.50000 were allowed to impinge on the sample. The 240 mm goniometer radius having 100 mm distance focus-diverg-slit was used with generator settings 30 mA, 40kV. The Bragg reflection peaks with respective d-values were found to be in accordance with JCPDS data No: ICDD PCPDF WIN #PDF 790416, corresponds to the face centered cubic lattice of iron oxide (Fe_3O_4) with cell parameter equal to 8.394 Å.

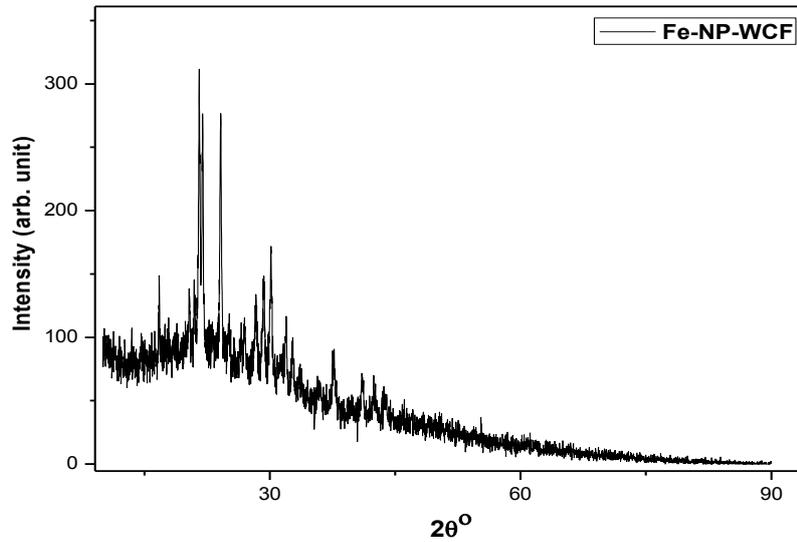


Figure 2: X-ray diffraction pattern recorded for Fe-NP-WCF

Considerably broadened x-ray reflection peaks from various crystallographic plane surfaces indicate the distribution of crystallite size in nanometric regime. The average crystallite size was evaluated using Debye-Scherrer equation [3]:

$$D = \frac{k\lambda}{\beta \cos \theta_B}$$

where D is the thickness (diameter) of the particle, λ is the X-ray wavelength (1.5406 Å), β is the full width at half maximum (FWHM) of the main peak under consideration, k is the shape factor and θ_B is the Bragg angle of reflection. The main intense peak at 21.5471° was taken for analysis to obtain the size estimation using Scherer formula. Accordingly, the estimated crystallite size is 73 nm.

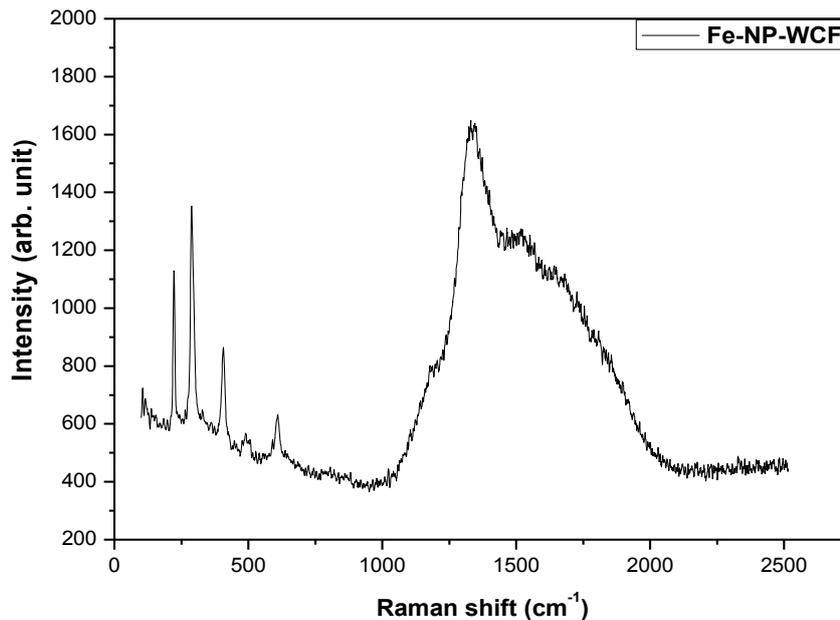


Figure 3: Raman spectrum recorded for Fe-NP-WCF

Raman studies were carried out at the National Facility for Geo fluids Research and Raman Analysis of the NCESS, Government of India, Thiruvananthapuram, using Reflex Raman Spectrometer. The instrument uses a diode laser exciting at a wavelength of 785 nm (300 mW, CW, Model. No. HPNIR 92E371, Class 3 B laser product, Renishaw plc, UK). Instrument calibration performed by measuring Raman spectra of the internal and external silicon sample shows a sharp peak at a full-width half-maximum (FWHM) of $520 \pm 0.5 \text{ cm}^{-1}$. The spectral range of the equipment is from 50 to 3000 cm^{-1} shift from the laser line, accomplished with an edge filter. The Raman scattered light is dispersed with a grating of 1200 lines/mm.

Figure 4 shows the graphical depict of the result obtained after recording Raman spectrum of the sample Fe-NP-WCF. The intensity of the scattered light is plotted against each of the energy (frequency) of the light. The frequency is traditionally measured in a unit called the wave number. Six peaks were observed respectively at frequencies 223 cm^{-1} , 306 cm^{-1} , 448 cm^{-1} , 501 cm^{-1} , 666 cm^{-1} and 1337 cm^{-1} . Metal oxides do not always occur in the crystalline form. When in an amorphous state, the Raman bands are quite absent, but often can be derived from one of the crystalline forms of the same material. The transition from amorphous to crystalline form (devitrification) can be an important phenomenon in terms of the performance of the ceramic. Metal oxides occur in crystals in which the oxygen anions are often in close-packed sites and the metal cations fit into tetrahedral or octahedral sites, with two tetrahedral sites per oxygen ion and one octahedral site per oxygen. To a large extent, this follows from the fact that the ionic radii of anions are significantly larger than that of cations. The stoichiometry of the oxide will determine how many metal cations will be present and the details regarding the electronic states will play a role in determining the overall symmetry of the lattice. Raman spectrum of bulk iron (III) oxides features with a_{1g} , e_g and $3t_{2g}$ optical phonon modes [4]. Here, the peaks at 223 cm^{-1} and 448 cm^{-1} are assigned to t_{2g} mode. The one at 306 cm^{-1} is assigned to e_g mode and that at 666 cm^{-1} is assigned to a_{1g} mode. In comparison with the Raman modes of bulk Fe_3O_4 , one t_{2g} around 540 cm^{-1} is missing and which is attributed to the reduced size of the present system. However, an additional peak observed at 501 cm^{-1} is attributed to $\alpha\text{-Fe}_2\text{O}_3$ phase generated in the sample. Nevertheless, the broad peak observed at 1337 cm^{-1} represents the umbrella mode vibrations corresponding to the methyl group present in the organic capping around the nanoparticles. This type of organic capping is usual in green synthesized nanoparticles wherein the flavonoids in the leaf extract act as reductant as well as capping agent.

The fluorescence emission studies were carried out using Reflex Raman Spectrometer offering automated alignment. The spectrum stabilized laser module at 405 nm excitation (20 mW, CW, Model.no. I0405SR0050B, Class 3B laser product, Innovative Photonic Solutions, USA) is used for the study. The system is fully automated and self-validating with auto aligning and optimization of input laser.

A laser beam of 10mW is directed on the sample to generate, capture, and then record emitted fluorescence at a wavelength range of 406–750 nm with a 1 nm spectral resolution. The entire spectrum is captured from 406 to 750 nm in one acquisition window with an acquisition time of 10 s. The gratings used in the study are 2400 l/mm (UV), and the laser spot size is $4\mu\text{m}$.

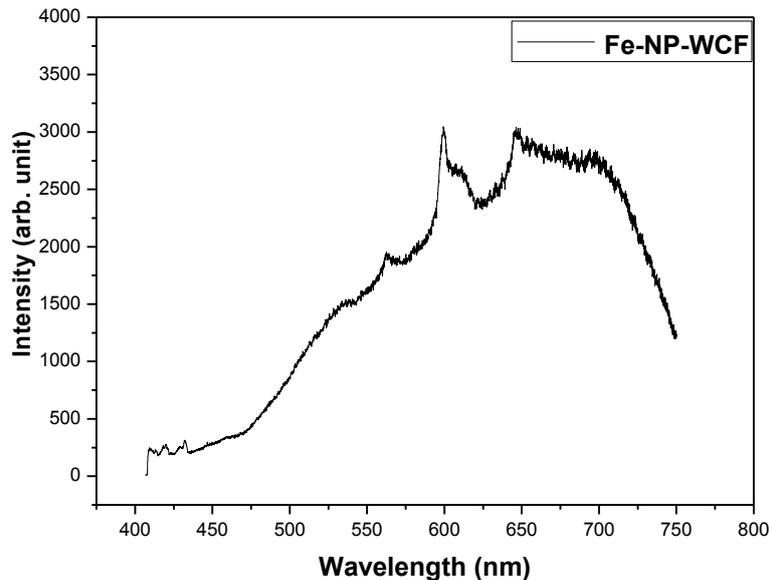


Figure 4: Fluorescence spectrum recorded for Fe-NP-WCF

The emission peaks were observed at 563 nm, 600 nm and 646 nm respectively (Figure 4). The excitation was made at wavelength 405 nm using a laser source. The emissions corresponding to higher wavelengths are indicative of fractional radiative recombination processes inside the sample. A single excitation giving rise to multiple emissions suggest that the radiative recombination takes place from different excited levels including the defect states in the crystal.

IV. CONCLUSIONS

Face centered cubic lattice of iron oxide (Fe_3O_4) nanoparticles with average crystallite size equal to 73 nm and cell parameter equal to 8.394 Å could be successfully synthesized through green synthesis method using the leaf extract of *Clitoria ternatea* (Linn). In agreement with the XRD result, Raman spectroscopic studies confirmed the formation of iron oxide phase in the sample. Existence of radiative recombination process inside the sample was observed from fluorescence emission study.

V. ACKNOWLEDGEMENTS

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