

# Green synthesis of Fe<sub>3</sub>O<sub>4</sub> nano particles using Camellia angustifolia leaf extract and their enhanced visible-light photocatalytic activity

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## ABSTRACT

Green synthesis using biological molecules derived from plant sources in the form of extracts exhibiting superiority over chemical methods. In this attempt, we have synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles using Camellia angustifolia leaf extract. The synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles were characterized by UV-Visible Spectroscopy, Infrared spectroscopy (IR), Scanning Electron Microscopy (SEM) and Zeta potential analyzer. A SPR band at 405 nm in the UV-vis spectrum confirms the formation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles. FTIR analysis confirms the formation of Fe-O bond. As evident from SEM, the green synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles are spherical in shape with 5-10 nm in size. Zeta potential analysis reveals that the green synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles are stable due to the electrostatic repulsion. The photocatalytic activity of Fe<sub>3</sub>O<sub>4</sub> nanoparticles was evaluated for degradation of Methyl Orange and Malachite Green under sunlight.

**Keywords:** Green synthesis, Fe<sub>3</sub>O<sub>4</sub> nanoparticles, Camellia angustifolia, Dye degradation.

## 1.INTRODUCTION

A dye is a colored substance that has an affinity to the substrate to which it is being applied. Dyes are applied to numerous substrates for example to textiles, leather, plastic, paper, food etc. The necessity of preventing the dyestuff effluent from entering the ecosystem cannot be exaggerated. Both international and national regulations for industrial wastewater require substantial elimination of the dyestuff content from the effluent. The effluent treatment systems develop several approaches, but none of them is still sufficiently effective and a combination approach seems to be so far the most efficient.

Metal oxides/ Mixed metal oxides have wide applications [1-5]. Recently, metal oxides are found to be active catalyst for photodegradation and can be a cheaper alternative to noble metal catalysts [6-8].

Plants are nature's "chemical factories". They are cost efficient and require low maintenance. Plant-mediated synthesis of nanoparticles is a green chemistry approach that connects nanotechnology with plants [9, 10].

In this study, we proposed rapid, non-toxic, facile and green synthesis route to synthesize Fe<sub>3</sub>O<sub>4</sub> nanoparticles in only one step reaction.

## II. MATERIALS AND METHODS

### 2.1. Chemicals used

Ferric Chloride, Sodium hydroxide, Methyl Orange, Malachite Green was purchased from Aldrich Chemicals and used as such.

### 2.2. Preparation of *Camellia angustifolia* leaf extract

6g of *Camellia angustifolia* leaves were taken in a 250ml beaker along with 100ml distilled water and boiled at 60°C for 1hr. After boiling, the colour of the aqueous solution was changed from watery to brown colour and allowed to cool at room temperature. The aqueous extract of *Camellia angustifolia* leaves was separated by filtration with Whatman No.1 filter paper.

### 2.3. Green synthesis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles

*Camellia angustifolia* extract was condensed into half by placing in a rotary evaporator. About 15ml of *Camellia angustifolia* leaf extract was taken in a beaker and placed in a hot magnetic stirrer at 60°C, pH 7.5 and 220rpm for 30 minutes. About 5ml of 0.25M Ferric Chloride was added drop by drop into the beaker and then heated for 2 hours in a hot magnetic stirrer. The synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles were collected by centrifugation using research centrifuge for 15 minutes at 10,500 rpm and dried in a hot air oven at 50°C. Synthesized Magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles were identified by placing the magnetic bar at the each corner of the beaker with slow movement.



Figure 1. Magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles

## 2.4. Dye degradation using Fe<sub>3</sub>O<sub>4</sub> nano particles

To study the degradation of dye using Fe<sub>3</sub>O<sub>4</sub> nanoparticles, we have used Methyl Orange (MO) and Malachite Green (MG). The dye solutions were prepared by dissolving 0.1g dye in 100ml distilled water. About 0.1g or 0.01 g of Fe<sub>3</sub>O<sub>4</sub> nanoparticles and 10ml of dye solution were taken in a beaker and kept in sunlight. After 24 hours and 48 hours, the solution in the beaker was centrifuged using research Centrifuge for 20 minutes at 8000 rpm. The supernatant of the each centrifuged solution was collected using micro pipette and diluted in 1:2 ratio with water and the OD (Optical Density) was taken in a UV-Visible spectrometer.

## 2.5. Preparation of standard dye solutions and determination of OD value

Dye solutions of various concentrations were prepared by diluting the stock solution. The UV-visible spectra of MO and MG solutions show peaks at 565nm and 620nm respectively. The OD of the standard dye solutions was measured at maximum wavelength of 565nm for MO dye and 620nm for MG dye.

## III. RESULTS AND DISCUSSION

### 3.1. UV-Vis Spectroscopic analysis

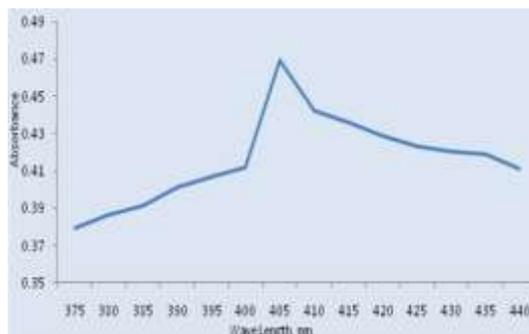


Figure 2. UV/Visible spectrum of green synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles

Formation and stability of Fe<sub>3</sub>O<sub>4</sub> nanoparticles in aqueous colloidal solution was confirmed by using UV-vis spectral analysis. UV-vis spectrum of synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles is shown in figure 2. Characteristic surface plasmon absorption band is observed at 405 nm for the black colour Fe<sub>3</sub>O<sub>4</sub> nanoparticles synthesized by Green Method.

### 3.2. FTIR analysis

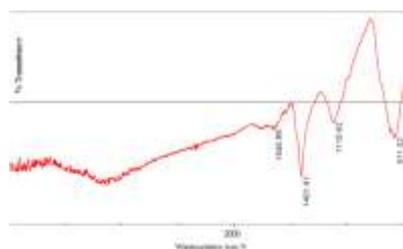


Figure 3. FTIR spectrum of green synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles

The various band obtained in the FTIR of green synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles have been utilized in the characterization of  $\text{Fe}_3\text{O}_4$  nanoparticles using reported values. In the FTIR spectra (figure 3), band at 1110.62 is attributed to  $-\text{C}-\text{O}-\text{C}$  stretching vibration. The band observed at 1401.47 has been attributed to aromatic C-H group/heteroatom containing C-C group. A strong band occurring at  $1646.99\text{cm}^{-1}$  in the spectrum corresponds to the carbonyl/ amine group. The band obtained at  $571.32\text{ cm}^{-1}$  is the characteristic band of Fe-O.

### 3.3. Scanning electron microscopic analysis (SEM)

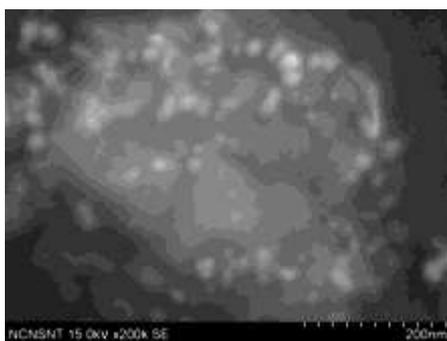


Figure 4. SEM image of green synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles

The scanning electron micrograph for green synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles is shown in figure 4. Most of the  $\text{Fe}_3\text{O}_4$  nanoparticles are within 5-10 nm in size. The shape of the nanoparticles is spherical. Therefore the  $\text{Fe}_3\text{O}_4$  nanoparticles were successfully synthesized by this green method.

### 3.4. Zeta potential analysis

The zeta potential analysis is used to measure the electrophoretic mobility of each nanoparticle sample. Zeta potential is a parameter that is used in the study of the surface charges and stability of NPs. A high absolute zeta potential value indicates a high electric charge on the surface of the  $\text{Fe}_3\text{O}_4$  nanoparticles. It describes strong repellent forces among the particles, which prevent aggregation and lead to stabilizing the NPs in the medium.

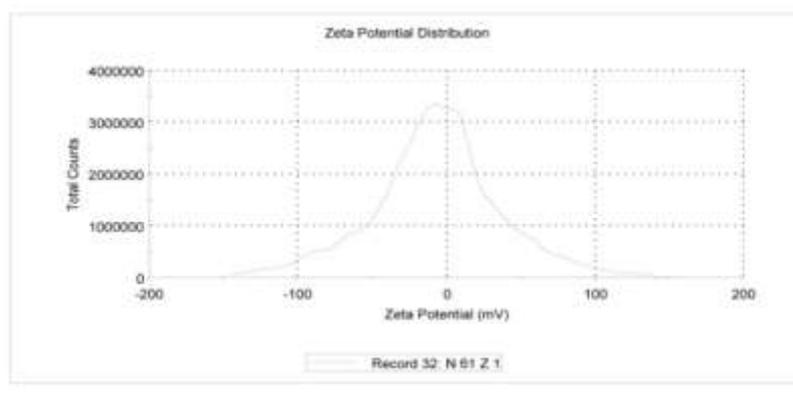


Figure 5. Zeta potential distribution of green synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles

Zeta potential of most of the green synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles is  $-8.87$  mV. This result reveals that the green synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles are stable due to the electrostatic repulsion.

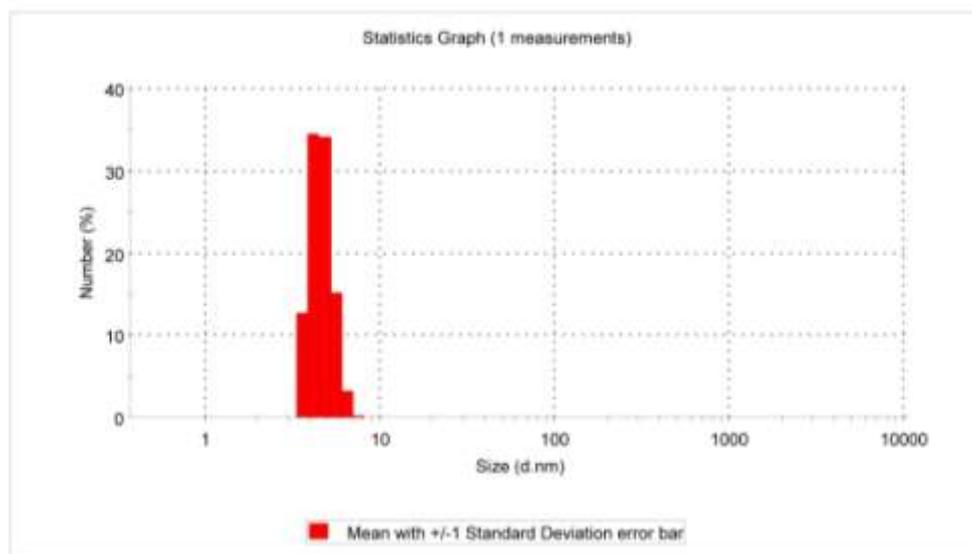


Figure 6. Size distribution of green synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles

The above graph indicates that 34.6% of green synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles have average diameter of 4.187 nm. 34.2 % of green synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles have average diameter of 4.849 nm. Green synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles are in the diameter range of 3.165 to 7.531 nm.

### 3.5. Dye degradation of green synthesized $\text{Fe}_3\text{O}_4$ nanoparticles

When the weight of  $\text{Fe}_3\text{O}_4$  nanoparticles used for dye degradation is 0.01g, the OD values of MO dye solution after 24hours and 48 hours are 1.245 and 0.435 respectively. When the weight of  $\text{Fe}_3\text{O}_4$  nanoparticles used for dye degradation is 0.1g, the OD values of MO dye solution after 24hours and 48 hours are 0.23 and 0.163 respectively.

When the weight of  $\text{Fe}_3\text{O}_4$  nanoparticles used for dye degradation is 0.01g, the OD values of MG dye solution after 24hours and 48 hours are 0.850 and 0.849 respectively. When the weight of  $\text{Fe}_3\text{O}_4$  nanoparticles used for dye degradation is 0.1g, the OD values of MG dye solution after 24hours and 48 hours are 0.850 and 0.847 respectively.

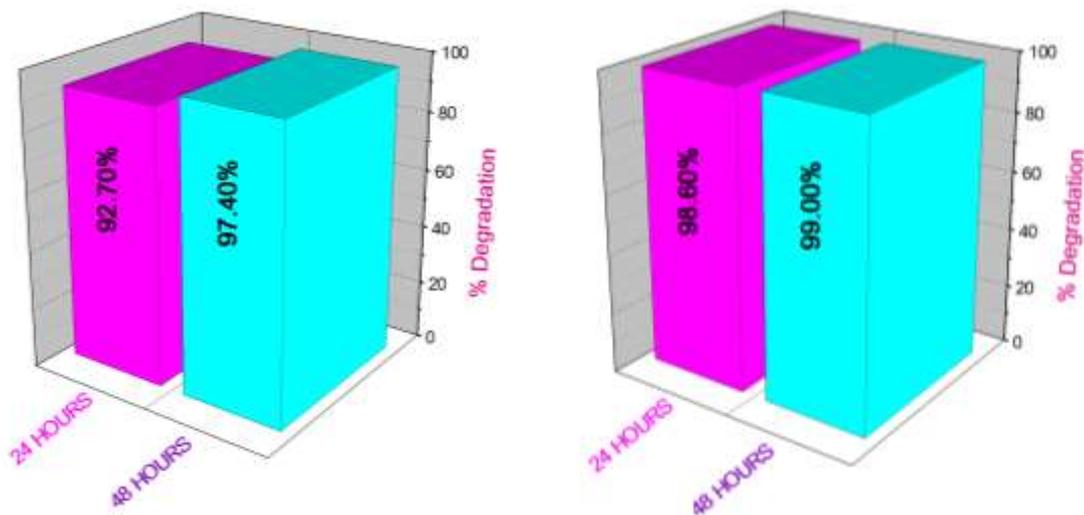


Figure 7. % degradation of MO dye using (a) 0.01g Fe<sub>3</sub>O<sub>4</sub> nanoparticles (b) 0.1g Fe<sub>3</sub>O<sub>4</sub> nanoparticles

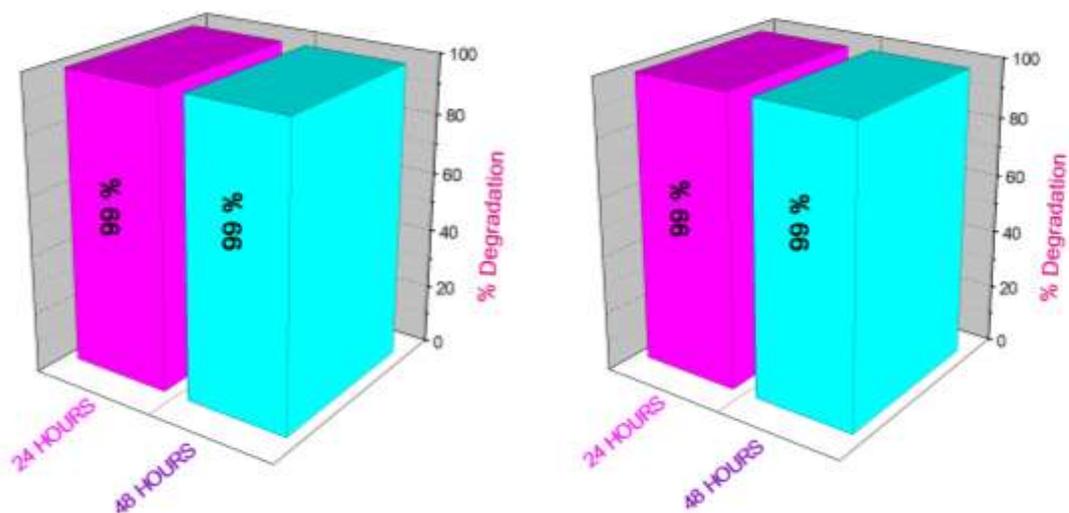


Figure 8. % degradation of MG dye using (a) 0.01g Fe<sub>3</sub>O<sub>4</sub> nanoparticles (b) 0.1g Fe<sub>3</sub>O<sub>4</sub> nanoparticles

In the case of MO dye, % dye degradation increases with increase in the amount of Fe<sub>3</sub>O<sub>4</sub> nanoparticles and increase in time. Thus more than 24 hours time interval and large amount of Fe<sub>3</sub>O<sub>4</sub> nanoparticles are required for the effective degradation of MO dye.

In the case of MG dye, % dye degradation did not change with increase in the amount of Fe<sub>3</sub>O<sub>4</sub> nanoparticles and increase in time. Thus 24 hours time interval and small amount of Fe<sub>3</sub>O<sub>4</sub> nanoparticles are enough for the effective degradation of MG dye.

#### IV. CONCLUSION

In conclusion, green method was used to synthesize high efficiency visible light  $\text{Fe}_3\text{O}_4$  nano photocatalyst. The results presented in this study indicated that  $\text{Fe}_3\text{O}_4$  nanoparticles is a very promising candidate for development of visible light driven photocatalysts for the degradation of dyes like Methyl Orange, Malachite Green, etc.

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