

Photocatalytic degradation of synthetic dyes using iron (III) oxide nanoparticles (Fe_2O_3 -Nps) synthesised using *Rhizophora mucronata* Lam

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Abstract: Biosynthesis of nanoparticles through plant extracts is gaining attention due to the toxic free synthesis process. The environmental engineering applications of many metal oxide nanoparticles have been reported. In this study, iron oxide nanoparticles (Fe_2O_3 -Nps) were synthesised using a simple biosynthetic method using a leaf extract of a mangrove plant *Rhizophora mucronata* through reduction of 0.01 M ferric chloride. Fe_2O_3 -Np synthesis was revealed by a greenish colour formation with a surface plasmon band observed close to 368 nm. The stable Fe_2O_3 -Np possessed excitation and emission wavelength of 368.0 and 370.5 nm, respectively. The Fourier-transform infrared spectral analysis revealed the changes in functional groups during formation of Fe_2O_3 -Np. Agglomerations of nanoparticles were observed during scanning electron microscopic analysis and energy-dispersive X-ray spectroscopic analysis confirmed the ferric oxide nature. The average particle size of Fe_2O_3 -Np based on dynamic light scattering was 65 nm. Based on transmission electron microscopic analysis, particles were spherical in shape and the crystalline size was confirmed by selected area electron diffraction pattern analysis. The synthesised Fe_2O_3 -Np exhibited a good photodegradation efficiency with a reduction of 83 and 95% of phenol red and crystal violet under irradiation of sunlight and florescent light, respectively. This report is a facile synthesis method for Fe_2O_3 -Np with high photodegradation efficiency.

1 Introduction

Nanotechnology is a tool of the recent decade to resolve many issues related to environment and health care. The nano-scale particles have numerous advantages and are widely explored for its new functionalities. The metal nanoparticles production is usually carried out using physical and chemical methods. An array of chemicals is required for the metal nanoparticles production, which is very reactive and toxic reducing agents. This brings about many deleterious effects during its application in health care and environmental engineering. In the meantime, many facile and reliable green technologies were adopted for the production of these nanoparticles. Among the green technologies, various organisms act as precursors to produce the stable and well-functionalised nanoparticles, which include bacteria, actinomycetes, fungi, yeast, viruses, plants and so on [1, 2]. Plant-mediated nanoparticle synthesis is more reliable in terms of its monodispersed nature, stability and fast synthesis compared to other precursors [3, 4]. Various part of plants can be used for the metal nanoparticle synthesis and the process is the simplest and most cost-effective [5].

The environmental engineering applications of many metal oxide nanoparticles, especially iron oxide nanoparticles (Fe_2O_3 -Nps) have been reported. Recently, metal nanoparticles and metal oxide nanoparticles are used as nano-adsorbents, nano-catalysts, nano-filtration and nano-biocides for remediation of water and wastewater pollutants. Among them, potential of iron nanoparticles was found suitable for environmental remediation. The nanoscale zero-valent iron has a large surface area to volume ratio, which enhances their reactivity especially in the environmental applications [6].

In the present work, we used *Rhizophora mucronata* a common mangrove plant for the synthesis of Fe_2O_3 -Nps. The mangrove plants such as *R. mucronata* and *R. apiculata* were used for metal Np synthesis through bio-reduction method [7], which were proved to have antimicrobial [8] and anti-larvicidal activity [9]. However,

there are no reports pertaining to the Fe_2O_3 -Np synthesis using *R. mucronata* and hence this form the first report on the Fe_2O_3 -Np synthesis to the best of our knowledge.

The dye decolourisation using biological system is a complex process requiring a suitable enzyme system in bioremediation of such effluents. Such dye rich effluents can be treated through metal oxide nanoparticle by the photocatalytic degradation process. Photocatalytic reactions are induced by the illumination of nano-sized semiconductors such as TiO_2 , ZnO, ZnS, WO_3 and Fe_2O_3 in a suspension and they are most promising for the wastewater treatment [10] because of their high stability, low costs, high efficiency and no toxicity [11]. Among various semiconductors used in photocatalysts, iron oxide nanomaterials exhibit promising photocatalytic activities [12–14]. However, ‘combinational’ nanoparticle systems were used previously for the dye photocatalytic degradation activity. In the present study, we focused on the application of Fe_2O_3 -Nps alone in the photocatalytic degradation activity of some selected synthetic dyes.

2 Materials and methods

2.1 Extract preparation

Rhizophora mucronata Lam. leaves were collected from Mangalavanam mangrove ecosystem, Kerala, India. The leaves were washed well to remove excess salt and dust particles. A 5 g of leaves was weighed and chopped into small pieces and an extract was made by boiling in millipore water for 5 min. The leaves were removed by filtration and the filtrate was used for nanoparticle synthesis.

2.2 Synthesis of Fe-nanoparticles

FeCl_3 (Sigma Aldrich) solution of two different concentrations (0.1 M and 0.01 mM) was made using millipore grade water. This solution was added to an equal amount of plant extract (1:1 v/v)

while mixing. The colour change was observed while adding the solutions which confirmed the $\text{Fe}_2\text{O}_3\text{-Np}$ synthesis.

2.3 Characterisation of Fe-nanoparticles

Based on the colour change, the nanoparticle synthesis was initially screened and the sample was subjected to scanning in the range of 200–800 nm using UV–Vis spectrophotometer (Spectronic-200, Thermo Scientific, USA). The absorbance maximum of the nanoparticle solution was noted. The nanoparticle sample and plant extract were subjected to Fourier-transform infrared (FTIR) analysis (FTIR Prestige 21 Shimadzu) in the range of 4000–400 cm^{-1} for understanding the functional groups involved. Particle size of the synthesised nanoparticle was determined by dynamic light scattering (Malvern Instruments Ltd.). The sample was further centrifuged and dried overnight for scanning electron microscopy (SEM) (JEOL Model JSM – 6390LV), energy-dispersive X-ray spectroscopic analysis (EDAX) and X-ray diffraction (XRD) analysis using X-ray diffractometer (Bruker AXS D8 Advance). Excitation and emission properties of the $\text{Fe}_2\text{O}_3\text{-Np}$ synthesised were analysed by spectrofluorometric analysis using spectrofluorometer (SL-174, Elico, India). Further characterisation was carried out using high-resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction (SAED) pattern.

2.4 Photocatalytic degradation of synthetic dyes using Fe-Np

The photocatalytic degradation activities of synthesised $\text{Fe}_2\text{O}_3\text{-Np}$ samples were analysed using various concentrations of synthetic dyes under different light sources. For the experiment, four synthetic dyes namely phenol red (PR), rhodamine B (RB), acridine orange (AO) and crystal violet (CV) were used. Three different conditions were applied to the photo-catalysis reaction by illumination through fluorescent light, sunlight and UV light. The solution was stirred well before the illumination. The vials containing dyes + $\text{Fe}_2\text{O}_3\text{-Np}$ were incubated under illuminated conditions for 30 min and absorbance was measured at 554, 525, 590 and 570 nm for RB, AO, CV and PR, respectively, using UV–Vis spectrophotometer. The decolourisation efficiency was calculated using the formula: $(A_0 - A_t)/A_0 \times 100$, where A_0 is the absorbance before irradiation and A_t is the absorbance at time t [15]. The absorbance contributed by nanoparticles was subtracted from test solution (kept as control) in the experiment.

3 Results and discussion

3.1 Spectroscopic analysis of $\text{Fe}_2\text{O}_3\text{-Nps}$

The colour change of the extract from colourless to greenish-black was observed immediately after mixing, which indicated the formation of $\text{Fe}_2\text{O}_3\text{-Nps}$. The time required for the bio-reduction of the metal ions varied from a few minutes as in *Euphorbia milli* to about 24 h as in lemon grass tea. When the *R. mucronata* leaf extract and FeCl_3 solution was mixed, a colour change was observed from yellowish brown to finally dark green, almost blackish green colour indicating the formation of $\text{Fe}_2\text{O}_3\text{-Np}$. In a previous work on $\text{Fe}_2\text{O}_3\text{-Np}$ synthesis using neem leaves extract also, a similar change in colour was noticed [16]. During the excitation of surface plasmon resonance (SPR), there was a visible change in colour which was characterised by UV–Vis spectroscopy that could be due to the formation of $\text{Fe}_2\text{O}_3\text{-Np}$ [17]. Generally, the $\text{Fe}_2\text{O}_3\text{-Nps}$ have been prepared by strong hydrolysis of iron salts at elevated temperature [18]. The plant-mediated $\text{Fe}_2\text{O}_3\text{-Nps}$ were prepared at room temperature in our study. Due to the high organic contents in the plant extracts, the mechanism study of $\text{Fe}_2\text{O}_3\text{-Nps}$ formation is bit difficult. However, the organic compound present in the plant extracts acts as a reducing as well as capping or binding agent to form $\text{Fe}_2\text{O}_3\text{-Nps}$ [19].

UV–Vis spectroscopy is the most widely used technique to investigate the optical properties of the particles. UV–Vis spectroscopy analysis was carried out in the range of 200–800 nm

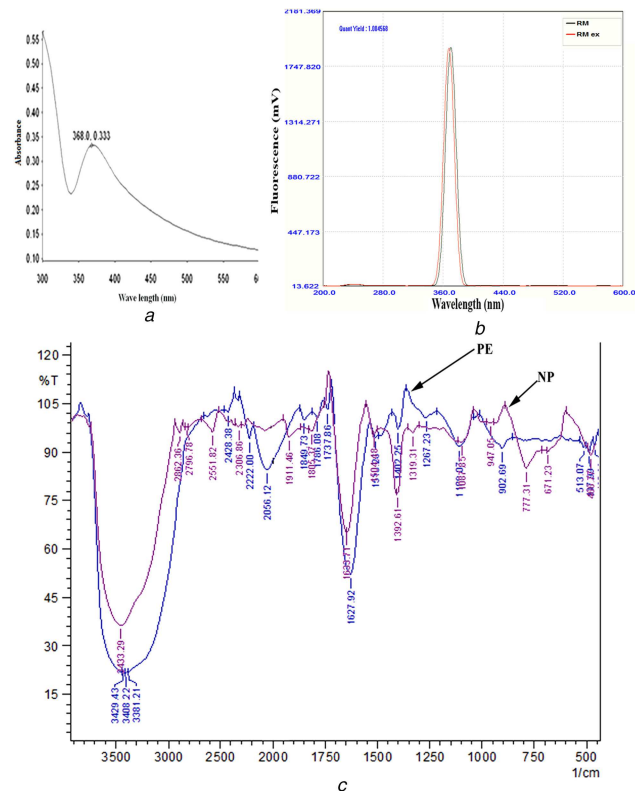


Fig. 1 Characterisation of iron nanoparticle synthesis by *Rhizophora mucronata* (a) UV–Vis spectrum, (b) Photoluminescence spectrum, (c) FTIR spectrum

and the maximum absorbance was observed at 368 nm that may be due to the formation of $\text{Fe}_2\text{O}_3\text{-Nps}$ due to the excitation of surface plasmon vibrations (Fig. 1a). UV–Vis spectrum, known as the surface plasmon absorption band, of the individual nanoparticles is different from that of nanoparticles aggregate. The SPR of a nanoparticle aggregate is shifted to a longer wavelength as compared with SPR of the individual particles [20]. The shorter UV absorption wavelength confirmed that no aggregation of Nps occurred during the synthesis. Metallic iron nanoparticles synthesised in the present work exhibited a relatively identical UV–Vis spectrum obtained from previous reports [21].

However, the UV–Vis spectrum of $\text{Fe}_3\text{O}_4\text{-Nps}$ in the aqueous *Sargassum muticum* extract had two absorption peaks at wavelengths of 402 and 415 nm indicating the formation of ferrous oxide nanoparticles [22]. Similarly, nanoparticle synthesised using *Eucalyptus globulus* leaf extract mixture exhibited an absorption maximum (λ_{max}) peak around 402 nm indicating the formation of low dimensional $\beta\text{-Fe}_2\text{O}_3$ [19]. UV–Vis spectrum was observed for the extract with 0.1 M and 0.01 mM of FeCl_3 solution exhibited similar λ_{max} . In the present study, the results depicted that 0.01 M was the optimum FeCl_3 concentration for the synthesis of $\text{Fe}_2\text{O}_3\text{-Np}$. Excitation and emission properties of the $\text{Fe}_2\text{O}_3\text{-Np}$ synthesised were analysed by spectrofluorometric analysis (Fig. 1b). The $\text{Fe}_2\text{O}_3\text{-Np}$ exhibited an excitation at 368 nm and emission at 370.5 nm with a quantum yield of 1.0045. This result shows the possible application of the synthesised $\text{Fe}_2\text{O}_3\text{-Np}$ in bio-imaging.

3.2 FTIR analysis of synthesised $\text{Fe}_2\text{O}_3\text{-Nps}$

The $\text{Fe}_2\text{O}_3\text{-Nps}$ synthesised by *R. mucronata* was subjected to FTIR analysis and compared with the plant extract (before reaction). The FTIR spectrum of $\text{Fe}_2\text{O}_3\text{-Np}$ (Fig. 1c) represents the major absorption bands. The bands/peak assignments from the FTIR spectrum of $\text{Fe}_2\text{O}_3\text{-Np}$ were: 3433.29-Br (OH) a characteristic N–H vibration region; 2862.36 – hydroxyl compounds; 2796.78 – C–H stretch of aldehyde; 2551.82 – SH

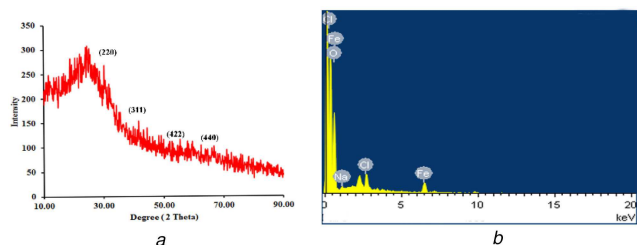


Fig. 2 Characterisation of Iron (III) oxide nanoparticle synthesised by *Rhizophora mucronata* using X-ray spectroscopy (a) XRD spectrum of Fe₂O₃-Np, (b) EDAX

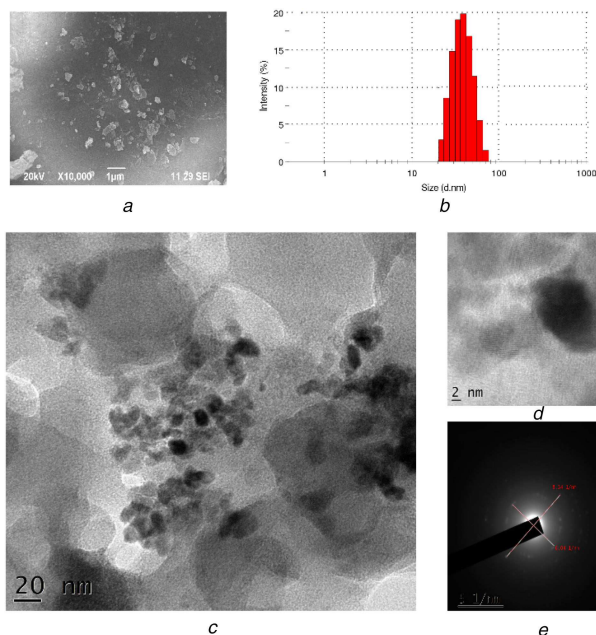


Fig. 3 Morphological and size characterisation of Fe₂O₃-Np synthesised by *Rhizophora mucronata* (a) SEM image, (b) Particle size distribution, (c) HR-TEM image, (d) Magnified Fe₂O₃-Np, (e) SAED

stretch; 2306.86-S=O stretching; 1911.46 – N=C=S stretching; 1805.37 – C=O stretching; 1633.71-C=C alkene; 1504.48-C=C stretching – alkenes; 1392.61 – C–H deformation due to alkynes; 1319.31 – NO₂ nitro compounds; 1087.85 – C–O stretching due to secondary alcohols; 777.31 – C–H alkenes; 671.23 – C–Br stretch of halogen groups and 466.77 – metal oxide or metal chloride. The bands at 466.77 cm⁻¹ were due to the formation of metal oxides or metal chlorides [23, 24]. Bands at 3429.43, 3408.22 and 3381.21 cm⁻¹ were not visible in the FTIR spectrum of nanoparticle. Similarly, bands at 2056.12 and 902.69 cm⁻¹ were disappeared. Moreover, there was visible shift of peaks during the nanoparticle formation that might be due to oxido-reductive reactions. The results were comparable with previous reports of Balamurugan *et al.* [19]. The presence of phenolic compounds and proteins might be responsible for the formation and stabilisation of synthesised Fe₂O₃-Nps [19].

3.3 XRD analysis of synthesised Fe₂O₃-Nps

The average size, the crystalline nature of the particles and quality of compounds were determined by XRD spectrum with CuK α radiation $\lambda = 1.504 \text{ \AA}$ over a wide range of Bragg angles using XRD patterns (Fig. 2a). The XRD spectrum showed different diffraction peaks at 12.02°, 23.83°, 31.92° and 45.81° corresponding to the crystal planes of (220), (311), (422) and (440) of crystalline Fe₂O₃. The obtained data matched with the Joint Committee on Powder Diffraction Standards (JCPDS) File No. (4-755). Previously, major characteristic peaks for prepared crystalline metallic nanoparticles were obtained at 2 θ values of

24.2°, 33.1°, 35.7°, 40.9°, 49.4°, 54.1°, 57.6°, 62.6° and 64.0° corresponding to (012), (104), (110), (113), (024), (116), (018), (214) and (300), respectively [19]. The average lattice size found for Fe₂O₃-Np ranged from 1.14 to 4.55 nm with a lattice strain of 0.0204 to 0.304. EDAX also supported the oxide nature of the nanoparticle (Fig. 2b).

3.4 SEM analysis of synthesised Fe₂O₃-Nps

The dry powdered sample was analysed for the structure and morphology of the synthesised Fe₂O₃-Np using SEM at different magnification levels (Fig. 3a). SEM images revealed that the synthesised Fe₂O₃-Np were aggregated as irregular sphere shapes with rough surfaces. The morphology of the nanoparticles mostly appeared to be porous and spongy. Based on the dynamic scattering light (DSL) method, the average particle size was about 65 nm. However, agglomerations were observed similar to the previous report of Balamurugan *et al.* [19]. However, larger Fe₃O₄-Np with an average diameter of 116 nm was also reported [25]. Stability of the Fe₂O₃-Np was carried out after 3 months, and the peak position was stable.

3.5 TEM analysis

In the present work, the TEM images of the synthesised Fe₂O₃-Np showed spherical morphologies with 5.58–9.02 nm size (Figs. 3c and d). This was in agreement with the SAED results (6.04–8.3 nm) (Fig. 3e). α -Fe₂O₃ nanoparticles synthesised by using green tea (*Camellia sinensis*) leaf extract resulted in spherical and highly porous particles with an average diameter of 60 nm based on the TEM images [26].

3.6 Photocatalytic degradation of synthetic dyes

The photocatalytic degradation of four dyes was carried out under three different illumination conditions. The Fe₂O₃-Np concentration when increased had enhanced the photocatalytic degradation of all dyes. RB, PR and AO exhibited maximum degradation at highest Fe₂O₃-Np concentration when incubated under sunlight (Fig. 4), whereas in the case of CV, maximum degradation was observed under fluorescent light followed by UV light source. CV showed minimal degradation under sunlight. The photo-oxidation of RB was carried out in the presence of H₂O₂/Fe²⁺ ion using UV light [27]. In a similar study, Alshehri *et al.* [28] observed that the Fe nanoparticles degraded more than 55% of Congo red within a short period of 30 min under UV irradiation. However, a better degradation was observed in our study with a reduction of 83 and 95% of PR and CV under irradiation of sunlight and florescent light, respectively. At high concentrations, most of the dye molecules, after being adsorbed on the surface of Fe nanoparticles, may block the active reaction sites and might result in a decrease in the photodegradation efficiency [29]. In a previous study, they obtained maximum photodegradation efficiency with a concentration of 60 $\mu\text{g ml}^{-1}$ [28]. However, the concentration required in our study was very minimum as 50 $\mu\text{g ml}^{-1}$.

4 Conclusion

Biogenic synthesis of Fe₂O₃-Np using *R. mucronata* was very fast and required no toxic chemicals. Synthesised Fe₂O₃-Np was confirmed by colour change, and based on UV–Vis spectroscopy analysis, where a λ_{max} of 368.0 nm was observed. The Fe₂O₃-Nps were stable up to 3 months and exhibited an excitation at 368.0 nm and emission at 370.5 nm. FTIR spectrum revealed the changes of functional groups during the formation Fe₂O₃-Nps. The average lattice size found for Fe₂O₃-Np ranged from 1.14 to 4.55 nm based on XRD analysis and mean particle size distribution in aqueous media was about 65 nm. TEM analysis revealed a smaller particle size of 5.58–9.02 nm that was in agreement with SAED analysis. The synthesised Fe₂O₃-Np exhibited a good photodegradation

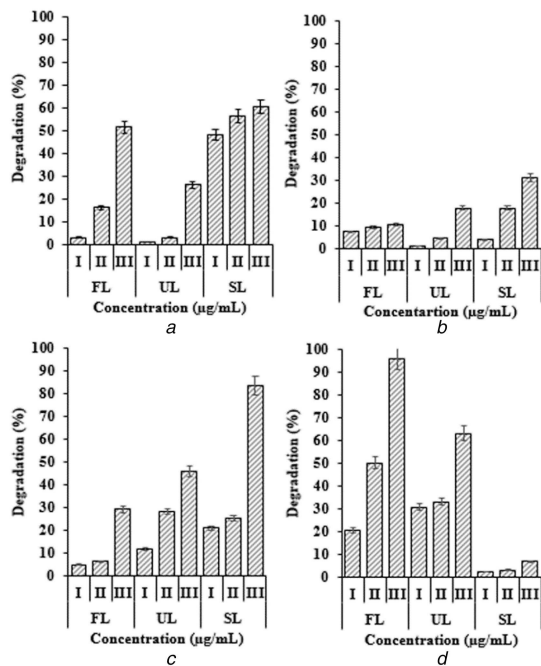


Fig. 4 Photocatalytic degradation of synthetic dyes

(a) Rhodamine, (b) Acridine orange, (c) Phenol red, (d) Crystal violet (I, 10 $\mu\text{g ml}^{-1}$; II, 25 $\mu\text{g ml}^{-1}$ and III, 50 $\mu\text{g ml}^{-1}$; FL, florescent light; UL, UV light; and SL, sunlight)

efficiency with a reduction of 83 and 95% of PR and CV under irradiation of sunlight and florescent light, respectively.

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