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M MADHUKARA NAIK (✉ madhukara@mvjce.edu.in)

MVJCE: MVJ College of Engineering <https://orcid.org/0000-0002-0135-1035>

M Vinuth

NIE Institute of Technology

V. Udaya Kumar

MVJ College of Engineering

K. H. Hemakumar

Cambridge Institute of Technology

G Preethi

MVJ College of Engineering

M Prathap Kumar

MVJ College of Engineering

G Nagaraju

Siddaganga Institute of Technology

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A Facile Green Synthesis of Nickel Ferrite Nanoparticles using *Tamarindus Indica* Seeds for Magnetic and Photocatalytic Studies

M. Madhukara Naik^{a*}, M. Vinuth^{b*}, V. Udaya Kumar^a, K.H. Hemakumar^{c*}, G. Preethi^a,
M. Prathap Kumar^a, G. Nagaraju^d

^aDepartment of Chemistry, MVJ College of Engineering, Bengaluru 560 067 Karnataka, India

^bDepartment of Chemistry, NIE Institute of Technology, Mysuru 570 018, Karnataka, India

^cDepartment of Chemistry, Cambridge Institute of Technology, Bengaluru 560 036, India

^dEnergy Materials Research Laboratory, Department of Chemistry, Siddaganga Institute of Technology, Tumakuru-572 103, India

*Corresponding Authors email ID: madhukara@mvjce.edu.in; vinuthm@nieit.ac.in
khhemakumar@gmail.com

Abstract:

Magnetic NiFe₂O₄ nanoparticle (NFNPs) was synthesized by the microwave-assisted method using *Tamarindus indica* seeds as a green reducing agent. The identification of NFNPs was carried out by XRD, FTIR, SEM with EDAX analysis, UV-Visible Spectroscopic and luminescence techniques. Spinel structure of NFNPs with a single phase has been confirmed by XRD with an average crystallite size of 21 nm. FTIR confirms the presence of tetrahedral and octahedral sites of prepared NFNPs. SEM with EDAX and TEM gives the information of agglomeration of magnetic nanoparticles with elemental composition present in the NFNPs and spherical nature of nanoparticles with a particle size of 29 nm. The prepared NFNPs are visible active with band gap of 1.92 eV. NFNPs show effective photocatalytic activity under visible light irradiation towards the degradation of anionic Alizarin red S dye and cationic Methylene Blue dye. NFNPs show good magnetic property in VSM studies. The prepared NFNPs can be useful for wastewater treatment.

Keywords: NiFe₂O₄, *Tamarindus Indica* seeds, Microwave method, VSM analysis, Anionic Alizarin red S dye, Methylene blue dye

1. Introduction

In industrial wastewaters, degradation of dyes has generated a great attention due to low decoloration, slow biodegradation, high toxicity and high volume of production. Every year dyes are produced in large scale and are naturally resistant towards sunlight, water, detergents and other basic chemicals which make them basically difficult to treat [1-2]. These dyes applied to various types of industries including paper, textile, leather, cosmetic, nutrition and pharmaceutical industries. Annually over 700,000 tons of dyes will be produced off which nearly 100,000 different type of dyes are commercially available, during dying process 15% of which are discharged into the water sources. Azo dyes constitute more than 50% of these globally produced dyes. These complex aromatic dyes cause severe impact on the human health and aquatic life. These concerns lead to develop new technologies for waste water treatment [2-3].

Recently, due to their optical, magnetic and photocatalytic applications nickel ferrite (NiFe_2O_4) nanoparticles have attracted very much interest in scientific society. NiFe_2O_4 is a soft magnetic material with saturation magnetization ($M_s=40.8$ emu/g), coercive field ($H_c=98$ Oe), remanance magnetization and low electrical resistivity [4]. Generally, in nanoparticles crystallinity, morphology and band gap play an important role in magnetic studies and the photocatalytic applications. Hence, it is a suitable material for magnetic, gas and humidity sensing, catalytic and magneto-optical applications [5]. For the synthesis of NiFe_2O_4 nanoparticles several methods have been used which are co-precipitation, sol-gel, combustion, microwave, hydrothermal, and sol-gel auto-combustion methods [6-7]. Among these methods, microwave-assisted method has extended much attention because it is environmentally benign, less reaction time, simple process, and relatively lowers the processing time and temperature which permits to prepare the nanocrystalline ferrite nanoparticles [8]. Table 1 gives the comparative study of green/biosynthesis of NiFe_2O_4 NPs.

Table 1 Biosynthesis of NiFe₂O₄ NPs

Method of synthesis	Green materials	Calcination temperature (°C)	Morphology	Ref.
Hydrothermal	<i>Urtica</i> extract	-	Rod like platelet	[9]
Sol-gel combustion	Honey-mediated	1100	Octahedron	
Modified sol-gel	<i>Aloe vera</i> extract	900	Agglomerated	[10]
Simple sol-gel auto-combustion	Onion extract	750	Agglomerated	[11]
Reduction	<i>Desmodium gangeticum</i> (Linn) DC roots	-	-	[12]
Hydrothermal	<i>Aloe vera</i> extract	-	Nanoparticles	[12]
Microwave-assisted green synthesis	<i>Tamarindus indica</i> seeds	600	Spherical	Present work

From the literature, it can be observed that NiFe₂O₄ played a vital role in the field of magnetic and photocatalytic applications. Few authors reported the magnetic and photocatalytic studies of NiFe₂O₄ NPs. Hirthna et al. has described in the work that NiFe₂O₄ NPs synthesized by chemical co-precipitation method for photocatalytic degradation of methyl orange dye (~72.66% within 5 h). [13]. Andris sutka et al. have prepared the anatase-NiFe₂O₄ heterostructures (co-precipitation method) for photocatalytic activity (methyl orange: 96% degradation after 3 h) [14]. D. Li et al. has synthesized spinel NiFe₂O₄ ferrite by sol-gel method for magnetic studies with saturation magnetization (Ms=66.6 emu/g), remanent magnetization (Mr=15.9 emu/g) and coercivity (Hc=161.6) [15].

In the present study, using *Tamarindus indica* seed powder as a reducing agent, green synthesis of NiFe₂O₄ NPs has been carried out by microwave-assisted method. The as prepared microwave-assisted NiFe₂O₄ NPs were characterized by different methods such as XRD, SEM with EDAX, FTIR, TEM, UV-Visible and Luminescence Spectroscopy for photocatalytic (anionic Alizarin red S dye and cationic Methylene blue dye) and magnetic studies.

2. Experimental

2.1 Materials

The *Tamarindus indica* seeds were obtained from a local market of Shivamogga, Karnataka, India. The precursors used are $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were obtained from HIMEDIA, India which are used without additional purification and of analytical grade. Throughout the experiment Deionized water was used.

2.2 Preparation of *Tamarind* seeds powder

The collection of dried seeds of *Tamarindus indica* were washed in tap water to remove the dust particles and then followed by the doubled distilled water for two-three times. After washing, seeds were shaded and dried at room temperature for 10-15 days. After air-dried, seeds were crushed using electric mixture. After crushing, the seeds powder was stored in refrigerator for further analysis.

2.3 Synthesis of NiFe_2O_4 NPs

NiFe_2O_4 NPs were prepared by taking $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with the ratio of 2:1 (Fe:Ni) in extracted *Tamarindus indica* seed powders with metal nitrates to extract 1:1 ratio in 50 ml deionized water. To get the homogeneous solution the reaction mixture was stirred for about 1 h and a domestic microwave oven (frequency of 2.54 GHz at 900 W output power) was used. The solution of reaction mixture was irradiated for 15 min and the attained product was annealed at 600 °C for 4 h.

2.4 Characterization techniques:

Rigaku Smart Lab XRD (Tokyo, Japan) with $\text{Cu-K}\alpha$ radiation source ($\lambda=1.5406 \text{ \AA}$) was used for X-ray diffraction (XRD) measurements. To study the two major bond frequencies of nickel ferrite NPs like tetrahedral and octahedral sites was analyzed in the range $4000\text{-}350 \text{ cm}^{-1}$ by using Fourier transform infrared spectrum (FTIR) (Bruker alpha-P infrared spectrophotometer). Zeiss electron microscope was used to observe the surface morphologies of the samples like scanning electron microscopy (SEM) and elemental analysis. For shape and morphological observation Field Emission Gun-Transmission Electron Microscope 300 kV was used. Shimadzu UV-Visible spectroscopy was used for optical studies. During degradation,

Agilent technology Cary-60 spectrophotometer was used for the absorbance of the organic dye. Agilent technology Cary Eclipse Spectrofluorometer was used for luminescence studies.

2.5 Photocatalytic degradation procedure:

Photodegradation of anionic Alizarin red S (ARS) dye and cationic Methylene blue (MB) dye under visible light irradiation in presence of microwave-assisted NiFe_2O_4 NPs was evaluated. In a photoreactor, 50 mg of NiFe_2O_4 photocatalyst was added to a quartz tube containing 100 mL of 20 ppm anionic ARS dye and cationic MB dye aqueous solution. In dark condition to attain the adsorption/desorption equilibrium the reaction mixture was stirred in dark for 30 min. At room temperature, the solution (reaction mixture) was irradiated under visible light. The degradation residual was collected every 30 min and was tested by UV-Vis absorption spectra at the absorbance of 525 nm (ARS) and 663 nm (MB). By the following relation the photocatalytic degradation percentage of dyes was measured,

$$\text{percentage of degradation} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

Where, C_o is the initial absorbance of aliquot and C_t is the absorbance of anionic ARS dye aliquot after time t in min, respectively.

3. Results and Discussion

3.1 XRD analysis

Fig. 1 XRD pattern of microwave-assisted NiFe_2O_4 NPs

XRD pattern of microwave-assisted NiFe_2O_4 nanoparticles was shown in Fig. 1 and the spinel structure with single phase material was confirmed with JCPDS No. 86-2267. Debye-Scherrer's formula was used to determine the average crystallite size of NiFe_2O_4 NPs and was estimated as 21 nm,

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (2)$$

Where, λ is wavelength of radiation source ($1.5406 \text{ \AA}$) and β is the full width half maximum.

By the following formula it was calculated that Dislocation density of NiFe_2O_4 NPs was found to be $2.2675 \times 10^{15} \text{ lines/m}^2$,

$$\delta = 1/D^2 \quad (3)$$

Microstrain of green synthesized NiFe_2O_4 NPs was 4.96×10^{-2} and was found by following relation,

$$\mu = \frac{\beta \cos \theta}{4} \quad (4)$$

3.2 Morphological analysis

Fig. 2 (a) & (b) SEM images and (c) EDAX pattern of microwave-assisted NiFe_2O_4 NPs

Fig. 3 TEM images of microwave-assisted NiFe_2O_4 NPs

Fig. 2a & 2b showed the SEM micrograph of microwave-assisted NiFe_2O_4 NPs where the agglomerated with uniform distribution of NPs and also narrow size distribution of NPs observed. During microwave combustion process the high energy generated leads to the agglomeration of NiFe_2O_4 NPs. TEM micrograph (Fig. 3) showed the uniform formation spherical NF nanoparticles. The chemical elemental compositions of prepared NiFe_2O_4 NPs was observed in EDAX spectrum. The characteristic peaks of elements Ni, Fe and O are present in the Fig. 2c and also it showed that there is no impurities present in the prepared NiFe_2O_4 NPs.

3.3 FTIR analysis

Fig. 4 FTIR Spectrum of microwave-assisted NiFe_2O_4 NPs

FT-IR spectrum of microwave-assisted NiFe_2O_4 NPs (Fig. 4) recorded in the range between $4000\text{--}350\text{ cm}^{-1}$. Spinel ferrite have two main frequencies of absorption bands in those

two the absorption band at $\sim 598\text{ cm}^{-1}$ assigned between Ni-O in tetrahedral sites which occurs due to intrinsic stretching vibration of bonds. The weakest absorption peak observed at $\sim 399\text{ cm}^{-1}$ assigned to the stretching vibration of bonds between Fe-O in octahedral sites. The weak band at 2928 and 1398 cm^{-1} corresponds to stretching vibration of C-H group. The band at 3384 and 1631 cm^{-1} is attributed to the stretching vibration of H-O-H groups of water molecules adsorbed. The corresponding absorbed Carbon dioxide on the surface of NiFe_2O_4 NPs was observed at 1105 cm^{-1} [16]. Based on the overhead results, the ferrite structure expected can be concluded.

3.4 Optical studies

Fig. 5 UV-Vis absorbance and band gap of microwave-assisted NiFe_2O_4 NPs

Fig. 5 showed the optical absorption spectrum of NiFe_2O_4 NPs. The absorption edge of the NiFe_2O_4 NPs was observed at 460 nm. The fundamental absorption calculations was used for the optical energy band gap calculation and was calculated by the relation [17]

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (5)$$

Where A is a constant, E_g is the band gap of the material and the exponential n depends on the transition type. For direct allowed transition the parameter n with value 2 can be used and for indirect allowed transition $\frac{1}{2}$ can be used. Tauc plot between $(\alpha h\nu)^2$ and energy (hν) are plotted and the linear straight line which meets the energy axis was extrapolated to obtain the energy bandgap (Fig 5). The optical energy band gap of NiFe_2O_4 NPs was found to be 1.92 eV. The obtained result matched nearly with the literature and the materials is visible active [18].

Fig. 6 Luminescence spectrum of microwave-assisted NiF_2O_4 NPs

The luminescence spectrum of the microwave-assisted NiF_2O_4 NPs can be observed in Fig. 6 at an excitation wavelength of 230 nm. In the visible region it exhibits violet, blue, green and orange emission at 449, 489, 532 and 604 nm. The sharp peaks in the spectra are assigned to the transfer of charges at octahedral sites between Fe^{3+} and surrounded O^{2-} ions. The peak at 532 nm attributed to the recombination of photo-generated holes from nickel interstitials and oxygen vacancies which are originated from the near band gap emission with ionized charged species. The blue green emission of NiF_2O_4 NPs can be confirmed by electron transition from deep donor level oxygen vacancies to the valence band [19-20].

3.5 Magnetic studies

Fig. 7 Magnetization hysteresis loop of microwave-assisted NiF_2O_4 NPs

The magnetic properties NiF₂O₄ NPs were characterized using a vibrating sample magnetometer (VSM) with an applied magnetic field -15000 of +15000 Oe at room temperature. The microwave-assisted NiF₂O₄ NPs confirmed as ferromagnetic (soft magnetic) from Fig. 7 which shows the plot of magnetization versus applied field (M–H) loop. The remanent magnetization (M_r), saturation magnetization (M_s) and coercivity (H_c) of NiFe₂O₄ nanoparticles are 12.27 emu/g, 35.13 emu/g, 1230 Oe, respectively [21, 22]. These results confirmed that the prepared NPs will become a renewable photocatalyst because by using an external magnetic field the photocatalyst can be removed effectively from the aqueous solution of reaction mixture.

3.6 Photocatalytic activity

The photodegradation of anionic ARS dye ($\lambda = 525$ nm) and cationic MB dye ($\lambda = 663$ nm) in the presence of microwave-assisted NiF₂O₄ NPs has been assessed under visible light (Fig. 8). The absorbance of anionic ARS dye solution was decreased with increasing visible light irradiation time. The absorbance of anionic ARS dye cationic MB dye has drastically decreased and gives 83% and 82% of degradation in 120 min.

Microwave-assisted NiF₂O₄ nanoparticles mainly depends crystalline nature, charge separation and on the distinctive surface morphology (SEM and TEM). The degradation of anionic ARS dye and cationic MB dye follows the pseudo first order kinetic from the kinetic studies which was confirmed by the relation,

$$C_t = C_0 e^{-Kt} \quad (6)$$

Alternatively

$$\ln\left(\frac{C_0}{C_t}\right) = Kt \quad (7)$$

Where, C_0 is the initial concentration, C_t is the concentration of aqueous solution of anionic ARS dye at time t and K is the rate constant (min^{-1}). The obtained first-order rate constant of NiF₂O₄ photocatalyst was $6.02 \times 10^{-3} \text{ min}^{-1}$.

Fig. 8 Photocatalytic absorbance spectrum of anionic ARS dye and cationic MB dye in presence of microwave-assisted NiFe₂O₄ NPs

3.7 Photocatalytic degradation mechanism

Following equations shows the degradation mechanism of anionic ARS dye cationic MB dye solution in the presence of NiFe₂O₄ photocatalyst,

Fig. 9 Photocatalytic degradation mechanism of anionic ARS dye cationic MB dye in presence of microwave-assisted NiFe_2O_4 NPs.

In the photodegradation process of the anionic ARS dye cationic MB dye $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ are the notable reactive species (Fig. 9). Photocatalytic degradation efficiency of anionic ARS dye of microwave-assisted NiFe_2O_4 NPs compared with some other metal oxide NPs given in Table 2.

Table 2 Photocatalytic degradation efficiency (anionic ARS dye) of microwave-assisted NiFe_2O_4 nanoparticles compared with some other metal oxide NPs

Sample	Source	Degradation efficiency (%)	Ref.
ZnO	UV	77	[23]
ZnO	Sunlight	51.62	[24]
SnO_2	Sunlight	46.29	[24]
ZnO (prismatic tip)	UV light	66	[25]
ZnO (nanobuds)	UV light	70	[25]
ZnS	Sunlight	50	[26]
TiO_2	Visible light	50	[27]
3% Bi doped TiO_2	Visible light	78	[27]
5% Bi doped TiO_2	Visible light	75	[27]
NiFe_2O_4	Visible light	83	<i>Present work</i>

4. Conclusion

Microwave-assisted green method was used to synthesis the NiFe_2O_4 NPs using *Tamarindus indica* seed powder as an reducing agent. XRD confirmed the spinel structure with single phase of NiFe_2O_4 nanoparticles with an average crystallite size of 21 nm. The presence of tetrahedral (598 cm^{-1}) and octahedral (399 cm^{-1}) sites in ferrite NPs was observed in the prepared sample by FTIR analysis. The agglomeration of magnetic nanoparticles and the presence of elemental compositions were observed in SEM images and EDAX spectrum. TEM image showed the spherical nature of NiFe_2O_4 nanoparticles with particle size of 29 nm. It was confirmed that the sample was visible active because the optical band gap was 1.92 eV and green emission around 532 nm was observed in luminescence spectrum. Microwave-assisted NiFe_2O_4 nanoparticles showed significant photocatalytic (anionic ARS dye and cationic MB dye) and Magnetic studies. Biosynthesized NiFe_2O_4 NPs are the appropriate material for optical studies, wastewater treatment and magnetic studies.

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Figures

Figure 1

XRD pattern of microwave-assisted NiFe₂O₄ NPs

Figure 2

(a) & (b) SEM images and (c) EDAX pattern of microwave-assisted NiFe_2O_4 NPs

Figure 3

TEM images of microwave-assisted NiFe₂O₄ NPs

Figure 4

FTIR Spectrum of microwave-assisted NiFe₂O₄ NPs

Figure 5

UV-Vis absorbance and band gap of microwave-assisted NiF2O4 NPs

Figure 6

Luminescence spectrum of microwave-assisted NiF2O4 NPs

Figure 7

Magnetization hysteresis loop of microwave-assisted NiFe₂O₄ NPs

Figure 8

Photocatalytic absorbance spectrum of anionic ARS dye and cationic MB dye in presence of microwave-assisted NiFe₂O₄ NPs

Figure 9

Photocatalytic degradation mechanism of anionic ARS dye cationic MB dye in presence of microwave-assisted NiFe₂O₄ NPs.