

REVIEW ON THE GREEN SYNTHESIS OF MAGNETIC IRON OXIDE NANOPARTICLES: METHODS, MECHANISMS, AND APPLICATIONS

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DOI: 10.63001/tbs.2025.v20.i03.S.I(3).pp806-810

KEYWORDS

Magnetic nanoparticles, iron oxide, green synthesis, plant-mediated, eco-friendly nanomaterials, biomedical applications

Received on:

12-07-2025

Accepted on:

10-08-2025

Published on:

17-09-2025

ABSTRACT

The synthesis of magnetic iron oxide nanoparticles has gained significant interest due to their wide-ranging applications in biomedical and environmental fields. While traditional physical and chemical methods pose ecological and toxicity concerns, green synthesis using plant extracts offers an eco-friendly and cost-effective alternative. This review comprehensively discusses chemical, microbial, and especially plant-mediated synthesis routes for iron oxide nanoparticles. Characterization, mechanisms of formation, and potential applications in catalysis, drug delivery, and wastewater treatment are also highlighted.

INTRODUCTION

Magnetic iron oxide nanoparticles have emerged as one of the most promising nanomaterials owing to their unique physical, chemical, and magnetic properties. These nanoparticles, particularly magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), exhibit superparamagnetism, large surface area-to-volume ratios, and high chemical stability, which make them suitable for diverse applications across biomedical, environmental, and industrial domains. Applications include magnetic resonance imaging (MRI) contrast enhancement, targeted drug delivery, cancer hyperthermia therapy, environmental remediation, catalysis, and magnetic data storage.

Traditionally, magnetic nanoparticles are synthesized using physical and chemical methods such as co-precipitation, hydrothermal synthesis, sol-gel processing, and thermal decomposition. However, these methods often involve toxic chemicals, high energy consumption, and hazardous by-products, posing serious environmental and biological safety concerns. This has led to a growing interest in developing alternative, sustainable synthesis approaches that align with the principles of green chemistry.

Green synthesis has recently gained attention as a clean, cost-effective, and environmentally benign method of producing nanoparticles. Among the biological agents employed, plant-mediated synthesis has shown particular promise due to its simplicity, availability, and the wide variety of phytochemicals

(e.g., polyphenols, flavonoids, alkaloids) that can act as both reducing and stabilizing agents. Despite these advantages, plant-based green synthesis of iron oxide nanoparticles remains relatively underexplored compared to gold or silver nanoparticles, and challenges remain in terms of reproducibility, particle uniformity, and scaling for industrial production.

Recent literature reveals a rapid expansion in green synthesis research, particularly in the last decade. However, gaps still exist regarding the mechanistic understanding of phytochemical interactions with iron salts, standardization of protocols, and comparative performance analysis of green-synthesized nanoparticles versus those from conventional methods.

This review aims to provide a comprehensive overview of the current progress in the synthesis of magnetic iron oxide nanoparticles with an emphasis on green synthesis using plant extracts. It also discusses the structural, magnetic, and functional characteristics of the synthesized nanoparticles, highlighting their potential applications and identifying key areas for future research.

2. LITERATURE REVIEW

Magnetic iron oxide nanoparticles (MIONPs), especially Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$, have gained extensive attention due to their superparamagnetic behavior, chemical stability, and biocompatibility. Traditional chemical and physical synthesis methods often involve hazardous substances and harsh conditions, prompting the need for eco-friendly alternatives. Green synthesis routes utilizing plant extracts, microbial agents,

and biowaste offer an environmentally benign and sustainable pathway for nanoparticle production [2], [6], [19].

Fruit waste like orange peel, papaya leaf, mango seed kernel, and pomegranate peel has also been employed in green synthesis. These materials serve both environmental and economic benefits [16], [24], [32], [25]. Rautela et al. [20] showed that green tea extract-based synthesis results in biocompatible Fe₃O₄ nanoparticles for biomedical use. Lakshmi and Nanda [25] reported that Punica granatum peel extract improved particle stability and morphology.

Although less common than plant-mediated methods, microbes like Lactobacillus sp., Bacillus subtilis, and fungi such as Aspergillus are capable of reducing metal ions enzymatically [2], [12]. Marimón-Bolívar and Toussaint-Jimenez [2] provided a comprehensive review of microbial-mediated synthesis of magnetite nanoparticles, particularly for environmental remediation.

Characterization is vital to evaluate structural and functional attributes.

- XRD and TEM confirm crystalline spinel structure and particle size range (10-50 nm) [10], [14].
- FTIR validates biomolecule capping from plant extracts [22], [28].
- VSM reveals superparamagnetic properties with slight saturation magnetization variations due to surface defects [13], [18].

Meena and Arora [14] synthesized Fe₃O₄ NPs using Aloe vera, reporting spherical shapes and excellent magnetic behavior. Mohammad et al. [19] confirmed enhanced stability and biocompatibility through FTIR and zeta potential measurements.

Green-synthesized MIONPs are explored for drug delivery, MRI contrast agents, and hyperthermia treatment due to their bio-safety and magnetism [14], [19], [21]. For instance, Wahab et al. [12] demonstrated antimicrobial efficacy using Hibiscus rosa-sinensis-derived nanoparticles. Fe₃O₄ NPs synthesized from guava and mango extracts are capable of adsorbing dyes and heavy metals such as Cr(VI), Pb²⁺, and methylene blue [30], [32], [23]. Choudhury et al. [23] utilized Azadirachta indica to prepare MIONPs, efficiently removing hexavalent chromium from wastewater. Khan et al. [33] reported effective dye degradation using nanoparticles synthesized from banana pseudostem extract. Green NPs act as heterogeneous catalysts in Fenton reactions and promote sustainable agriculture through enhanced nutrient delivery and pest control [7], [18], [27]. Shende et al. [7] reviewed their contribution to crop yield improvement and soil health.

Several researchers have compared different green synthesis methods:

- Bartwal et al. [8] analyzed sol-gel vs green routes, favoring plant-based methods for sustainability.
- Oluwatoyin et al. [1] reviewed nano-structured photocatalysts and highlighted the efficiency of green synthesis in photocatalytic degradation.
- Ikumapayi et al. [6], [34] presented an overview of advances in nanoparticle synthesis, reinforcing the cost and safety advantages of eco-friendly methods.

Subhan et al. [3] and Mohamad et al. [5] also discussed alternative laser and bimetallic synthesis routes, although these require more sophisticated instrumentation than green methods.

Table 1: Plant Sources Used for Green Synthesis of Fe₃O₄ Nanoparticles

Plant Source	Phytochemicals	Nanoparticle Type	Size (nm)	Applications	Reference
<i>Camellia sinensis</i> (Green Tea)	Polyphenols, catechins	Fe ₂ O ₃ / Fe ₃ O ₄	10-30	Fenton catalyst, dye degradation	[20]
<i>Azadirachta indica</i> (Neem)	Flavonoids, terpenoids	Fe ₃ O ₄	15-25	Chromium removal, antimicrobial	[11], [23]
Banana peel	Reducing sugars, polyphenols	Fe ₃ O ₄	~18	Antibacterial, dye degradation	[15], [33]
<i>Aloe vera</i>	Saponins, polysaccharides	Fe ₃ O ₄	18-25	Biomedical imaging	[14]
<i>Punica granatum</i> (Pomegranate)	Ellagitannins, polyphenols	Fe ₃ O ₄	~20	Biomedical coating, stability enhancer	[25]
<i>Moringa oleifera</i>	Phenolics, flavonoids	Fe ₃ O ₄	10-40	Catalysis, antibacterial	[18]

3. METHODOLOGY

3.1 Microbial Synthesis

Microorganisms such as bacteria (e.g., Bacillus subtilis, Lactobacillus sp.), fungi (e.g., Aspergillus niger), and algae can biosynthesize magnetic iron oxide nanoparticles through biologically mediated reduction mechanisms [2], [19].

These microbes secrete enzymes (e.g., reductases, hydrogenases) and chelator compounds that facilitate the transformation of metal precursors into nanoparticles. The method offers greater control over crystal structure, dispersion, and surface modification, and can be conducted under ambient conditions.

Microbial synthesis is often categorized into:

- Biologically induced mineralization (BIM)
- Biologically controlled mineralization (BCM)

These mechanisms contribute to uniform nanoparticle morphology and phase-pure magnetite formation.

3.2 Biopolymer-Assisted Synthesis

Natural biopolymers such as gelatin, starch, chitosan, cellulose, and alginate have been used as green templates and stabilizing agents in nanoparticle synthesis [5], [12]. These biopolymers offer:

- Biocompatibility and biodegradability
- Controlled surface charge
- Improved colloidal stability

The functional groups in these polymers (e.g., hydroxyl, carboxyl, amine) coordinate with iron ions, leading to better control over nucleation and growth processes. This method is particularly promising for biomedical applications due to enhanced biological compatibility.

4. CHARACTERIZATION OF GREEN SYNTHESIZED MIONPS

4.1 Structural Properties

Green-synthesized MIONPs typically exhibit the inverse spinel crystal structure, as confirmed by X-ray Diffraction (XRD). Sharp diffraction peaks correspond to planes of Fe₃O₄ or γ-Fe₂O₃ phases, indicating high crystallinity.

Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) analyses show nanoparticle sizes generally in the 5-30 nm range, with spherical or quasi-spherical morphology depending on the extract and synthesis parameters [10], [14].

4.2 Magnetic Properties

Vibrating Sample Magnetometry (VSM) is used to analyze the magnetic behavior of Fe₃O₄ nanoparticles. Most green-synthesized MIONPs exhibit superparamagnetism, meaning they show strong magnetization in an external magnetic field but negligible remanence.

However, their saturation magnetization (Ms) is slightly lower than chemically synthesized counterparts, due to surface defects and organic coatings from plant or microbial agents that reduce magnetic core density [19], [31].

4.3 Surface Functional Groups

Fourier-Transform Infrared Spectroscopy (FTIR) confirms the presence of various surface-bound organic functional groups such

as -OH, -COOH, and -NH₂, originating from the plant or microbial capping agents. These groups provide:

- Enhanced colloidal stability
- Better dispersion in aqueous systems
- Potential for targeted drug delivery or surface functionalization

These biomolecule-derived coatings play a critical role in the bioavailability and target specificity of MIONPs in environmental or biomedical systems.

5. APPLICATIONS OF GREEN-SYNTHESIZED MAGNETIC IRON OXIDE NANOPARTICLES (MIONPS)

5.1 Biomedical Applications

Magnetic iron oxide nanoparticles synthesized via green methods have demonstrated high biocompatibility and surface functionality, making them ideal candidates for biomedical applications:

- **Drug Delivery:** Surface-functionalized MIONPs can be conjugated with therapeutic agents and guided to specific tissues or tumor sites under an external magnetic field, enabling targeted and controlled drug release [12], [20].
- **MRI Contrast Agents:** Fe₃O₄ nanoparticles exhibit excellent T₂-weighted magnetic resonance imaging (MRI) contrast due to their strong magnetic susceptibility, enhancing image resolution without causing cytotoxicity [19], [28].
- **Hyperthermia Treatment:** Under an alternating magnetic field, MIONPs generate localized heat, which can be exploited in magnetic hyperthermia for non-invasive cancer therapy, selectively damaging tumor cells while sparing healthy tissues [6].

Table 2: Applications of Green-Synthesized MIONPs

Field	Application	Mechanism	Benefit
Biomedical	Drug delivery	Magnetic guidance and surface targeting	Site-specific delivery, reduced toxicity
	MRI contrast agent	T ₂ contrast enhancement due to magnetic susceptibility	Improved imaging resolution
	Hyperthermia therapy	Inductive heating under alternating magnetic field	Cancer cell destruction with low side effect
Environmental	Heavy metal adsorption (Pb ²⁺ , Cr ⁶⁺)	Surface complexation, ion exchange	Efficient pollutant removal
	Dye degradation (e.g., methylene blue)	Catalysis via Fenton-like reactions	Decolorization, COD reduction
	Oil spill remediation	Magnetic separation after hydrophobic coating	Reusability, eco-friendly cleanup
Catalysis	Advanced oxidation (Fenton reaction)	Generation of hydroxyl radicals	Breakdown of recalcitrant organics
Agriculture	Nano-fertilizers and pest control	Controlled nutrient release and pathogen inhibition	Enhanced crop yield, reduced pesticide use

5.2 Environmental Remediation

The unique magnetic and surface properties of green-synthesized MIONPs make them suitable for **eco-remediation** tasks:

- **Heavy Metal Adsorption:** MIONPs effectively remove toxic metal ions such as Pb²⁺, Cr⁶⁺, and As³⁺ through surface complexation and ion exchange processes [24], [30].
- **Dye and Pollutant Removal:** Their large surface area and catalytic activity enable adsorption and degradation of synthetic dyes and organic pollutants in wastewater.

- **Oil Spill Clean-Up:** Hydrophobic surface-modified MIONPs have been used to adsorb hydrocarbons, with easy magnetic separation, enabling reusability and reducing environmental footprint [2], [31].

5.3 Catalysis

MIONPs act as effective heterogeneous catalysts, particularly in Fenton and Fenton-like reactions used for oxidative degradation of organic pollutants. Their reactivity, stability, and magnetic retrievability make them ideal for advanced oxidation processes (AOPs) in wastewater treatment [3], [7], [23].

Table 3: Comparison of Chemical and Green Synthesis Methods for MIONPs

Synthesis Method	Precursors	Conditions	Advantages	Limitations
Co-precipitation	FeCl ₃ , FeCl ₂ + NaOH	Room temp, inert (N ₂) atmosphere	Simple, cost-effective	Needs pH control, may produce mixed phases
Sol-Gel	Iron nitrate, gelatin	Low temp, drying and calcination required	Homogeneous particles	Time-consuming, shrinkage upon drying
Hydrothermal	Fe salts in water	High temp and pressure (>100 °C, >1 atm)	Crystalline, well-shaped particles	Requires autoclave, pressure control
Thermal Decomposition	Iron pentacarbonyl + oleic acid	~100-200 °C, inert gas	Monodisperse, crystalline nanoparticles	Toxic precursors, flammable gases
Plant-mediated (Green)	Plant extracts + FeCl ₃ /FeCl ₂	Ambient or mild heating	Eco-friendly, biocompatible surface coating	Batch variability, lower crystallinity
Microbial synthesis	<i>Bacillus</i> , <i>Lactobacillus</i> , fungi	Incubation at optimal microbial growth	Precise morphology, biologically templated	Slow growth, sterilization required

CONCLUSION

The green synthesis of magnetic iron oxide nanoparticles (MIONPs) using plant extracts, microbes, and biopolymers presents a sustainable and biocompatible alternative to conventional chemical methods. Their applicability across medicine, environmental engineering, and catalysis highlights their multidisciplinary potential.

Despite significant advancements, challenges remain in scaling up these biosynthetic routes and ensuring reproducibility. Future research should emphasize:

- Standardization of green synthesis protocols
- Mechanistic understanding of plant/microbial interactions

- Development of multifunctional MIONPs for combined diagnostic and therapeutic (theranostic) applications

The fusion of green chemistry with nanotechnology holds transformative potential, paving the way for safer, environmentally responsible innovations across sectors.

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