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Review

Harnessing plant extracts for eco-friendly synthesis of iron nanoparticle (Fe-NPs): Characterization and their potential applications for ameliorating environmental pollutants

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ABSTRACT

Iron-nanoparticles (Fe-NPs) are increasingly been utilized in environmental applications due to their efficacy and strong catalytic activities. The novelty of nanoparticle science had attracted many researchers and especially for their green synthesis, which can effectively reuse biological resources during the polymerization reactions. Thus, the synthesis of Fe-NPs utilizing plant extracts could be considered as the eco-friendly, simple, rapid, energy-efficient, sustainable, and cost-effective. The green synthesis route can be recognized as a practical, valuable, and economically effective alternative for large-scale production. During the production process, some biomolecules present in the extracts undergo metal salts reduction, which can serve as both a capping and reducing mechanism, enhancing the reactivity and stability of green-synthesized Fe-NPs. The diversity of species provided a wide range of potential sources for green synthesis of Fe-NPs. With improved understanding of the specific biomolecules involved in the bioreduction and stabilization processes, it will become easier to identify and utilize new, potential plant materials for Fe-NPs synthesis. Newly synthesized Fe-NPs require different characterization techniques such as transmission electron microscope, ultraviolet-visible spectrophotometry, and X-ray absorption fine structure, etc, for the determination of size, composition, and structure. This review described and assessed the recent advancements in understanding green-synthesized Fe-NPs derived from plant-based material. Detailed information on various plant materials suitable of yielding valuable biomolecules with potential diverse

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Abbreviations: NPs, nanoparticles; Fe-NPs, iron-nanoparticles; Fe, iron; Fe, Au, gold; Ag, silver; Pt, platinum; Pd, palladium; Ti, titanium; Sb, antimony; Cr, chromium; Cu, copper; Pb, lead; Zn, zinc; Ni, nickel; Hg, mercury; As, arsenic; Cd, cadmium; SEM, scanning electron microscopy; AFM, atomic force microscopy; DLS, dynamic light scattering,; EDS, X-ray energy dispersive spectroscopy; TEM, transmission electron microscope; UV–vis, ultraviolet-visible spectrophotometry; EDAX, energy dispersive X-ray spectroscopy; FTIR, Fourier transform infrared spectroscopy techniques; XRD, X-ray diffraction; EXAFS, X-ray absorption fine structure; HR-TEM, high resolution transmission electron microscope; XPS, X-ray photoelectron spectroscopy; GC-MS, ghromatography-mass spectrometer; GCG, gallocatechin gallate; EGCG, epigallocatechin gallate; EGC, epigallocatechin; EC, epicatechin; BET-method, Brunauer–Emmett–Teller isotherm; COD, chemical oxygen demand; NZVI, zero-valent Fe-NPs; AgO, silveroxide; SiO_2, siliconoxide; TiO_2, titanium oxide; ZnO, zinc oxide; FeO, iron oxide; EELS, electron energy loss spectroscopy; XANES, X-ray absorption near-edge structure spectroscopy.

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applications in environmental safety. Additionally, this review examined the characterization techniques employed to analyze Fe-NPs, their stability, accumulation, mobility, and fate in the environment. Holistically, the review assessed the applications of Fe-NPs in remediating wastewaters, organic residues, and inorganic contaminants. The toxicity of Fe-NPs was also addressed; emphasizing the need to refine the synthesis of green Fe-NPs to ensure safety and environmental friendliness. Moving forward, the future challenges and opportunities associated with the green synthesis of Fe-NPs would motivate novel research about nanoparticles in new directions.

1. Introduction

Nanotechnology, which refers towards the creation and regulation of matter especially at the microscopic level i.e., nanoscale, had gotten a lot of press recently because to its numerous applications in sectors including geology, biomedicine, chemistry, optics, catalysis, electronics, magnetics, ocean science, and agriculture (Ramanayaka et al., 2020; Samrot et al., 2020; Sani et al., 2023). Nanoparticles (NPs) size ranging from 1 to 100 nm are being recognized as key basic components of nanotechnology due to the large number of nanoscale materials and processes that have arisen (Kadzinski et al., 2018; Sobhy et al., 2023; Jafir et al., 2024). Generally, NPs with unique electronic, optical, thermal, electrical, chemical, mechanical, and magnetic properties are of particular interest, owing to their particularly small size and higher surface/volume ratio when associated to their bulk counterparts (Rai and Yadav, 2013; El-Abeid et al., 2024). In comparison to bulk materials, NPs require significantly less raw resources, cost, and energy to achieve the targeted goals (Raveendran et al., 2003; Sani et al., 2023).

Due to increasing anthropogenic activities, many pollutants originating from agricultural, municipal, and industrial sources are infiltrating the food production and natural ecological ecosystems (Haider et al., 2021). Interestingly, NPs have a strong potential to decontaminate the environment, as evidenced by their ability to interact effectively with pollutants in controlled lab trials (Ali et al., 2023; Alhaithloul et al., 2023; Khalid et al., 2023; Jalil et al., 2023). Specifically, the iron-NPs (Fe-NPs) such as zero-valent-iron (nZVI), iron-oxides (FeO), iron-phosphate ($FePO_4$), and bimetallic Fe-NPs (Fe/Pd, Fe/Ni, Fe/Ag, and Fe/Cu) have the most potential in this domain due to their better reactivity (Noubactep et al., 2012). This technique is now being commercialized in several countries and is achieving widespread popularity.

Generally, NPs can be produced via conventional physical and chemical methods such as electro-deposition, pyrolysis, sol-gel process, supercritical fluid, etching, chemical vapor-deposition, and laser ablation (Samrot et al., 2020; Sunny et al., 2022; Yasin et al., 2024). Although NPs produced are well-defined and pure, these strategies have several drawbacks, such as the utilization of harmful chemicals, elevated energy consumption, the need for complicated instruments, and superior conditions i.e., pH, pressure, and temperature, the formation of hazardous byproducts, and low production rates (Genuino et al., 2013; Aisida et al., 2020). The material and ecological costs of production are relatively expensive, and stability is also a major concern. Simultaneously, the rapid advancement of nanotechnology has increased public awareness of human health and environmental issues (Samrot et al., 2020). The negative consequences of NPs are currently unknown, and they could be more harmful than bulk compounds (Mondal et al., 2020). Several toxicological studies had revealed that NPs might be hazardous at the subcellular, cellular, and biomolecular levels under certain scenarios (Hong et al., 2011; Es'haghi et al., 2016). At present, the health and environmental impacts of indirect and direct NPs exposure are still poorly understood, and they may be significant in some circumstances, and these uncertainties require further assessment (Groiss et al., 2017; Bolade et al., 2019). Furthermore, when novel NPs with unique properties are developed, research groups and enterprises all over the world begin to use them at an uncontrollable rate (Aisida et al., 2020). As a result, their manufacturing and implementation, particularly in developing nations, lack an adequate control mechanism (Wardak et al., 2007). Furthermore, chemically generated NPs are undesirable used for biomedicine due to certain chemical components could be deposited onto the NPs' surface, potentially causing an adverse reaction in biomedical applications (Mondal et al., 2020). As a result, academics are currently focusing their study on finding a suitable alternative to physical and chemical approaches, with the goal of reducing or eliminating the usage and manufacture of dangerous materials while taking social, economic, and environmental concerns into account.

Green synthesis has seen a surge in popularity as researchers look for new ways to make NPs. Green synthesis has undeniable benefit because it can minimize NP toxicity and environmental implications by using environmentally benign and biodegradable biological sources (Kharissova et al., 2013; Maqsood et al., 2023). It is also simple, dependable, cost-effective, and environmentally friendly. Plant-based materials such as stem, seed, root, and leaf, are currently being investigated as sustainable and renewable biological feedstocks (Es'haghi et al., 2013; Samrot et al., 2020). Green synthesized NPs utilizing plant extracts seems to be more appealing and profitable than approaches involving whole microbes and plants since it is faster, simpler, and less expensive (Mittal et al., 2013; Makarov et al., 2014a, 2014b), allowing for commercial-scale production of NPs with better specified morphology and size (Raveendran et al., 2003). Plants are largely available and naturally benign (Kharissova et al., 2013). In fact, current green chemistry technique offers a noval and fascinating phase in the production of NPs that can both minimize plant waste and produce value-added compounds (Es'haghi et al., 2016; Bolade et al., 2019). These NPs are also ecologically friendly and biocompatible, making them ideal for biomedical, environmental, and agricultural purposes.

Though extracts synthesised from plant residues were used to minimize trace-metal contaminates for the first time in the beginning era of 1900s, yet the source of the capping and reducing representatives involved is unknown. Varied plant extracts have different amounts and components of capping and reducing agents, as is well known (Mittal et al., 2013). Plant extracts, along with their quantities, are found to alter the process of nanoparticle formation, as well as their number and properties (Dwivedi and Gopal, 2010). As a result, the precise mechanism governing the nature of the capping and reducing agents used in the manufacture of green-synthesised iron nanoparticles (Fe-NPs) must be elucidated. Some macromolecules in plant sources have been observed to act as both capping and reducing agents in the formation of Fe-NPs. Although certain reducing sources, i.e., (borohydride) is recognized as hazardous, and several regularly utilized capping agents are permanent contaminates which might build in the ecological ecosystem, hence means avoiding the use of extra reagents. This could endanger the environment or human health (Genuino et al., 2013).

The synthesis and application of Fe-NPs synthesized from various sources, i.e., plant extracts, algae, microorganisms, and their derivatives, have garnered significant attention in academic research (Fahmy et al., 2018; Kozma et al., 2015; Bolade et al., 2020). Despite the growing literature on using green-synthesized Fe-NPs for contaminant remediation, a crucial gap persists in understanding their synthesis mechanisms and intricate potential especially for remediation of organic and inorganic pollutants. Hence, this comprehensive review addresses this gap by intricately examining the mechanisms underlying green Fe-NPs synthesis with plant-based materials, providing insights crucial for developing more sustainable synthesis protocols. It synthesizes existing knowledge and identifies emerging opportunities for practical implementation in environmental remediation. Evaluating the environmental implications, particularly the toxicity of Fe-NPs on plants in water and soil interactions, provides critical insights for responsible deployment. The findings of this review provide a valuable resource for researchers and policymakers, offering insights into current challenges, proposing avenues for improvement in Fe-NPs synthesis, and inspiring further innovative research towards sustainable solutions in environmental remediation.

2. Data collection methodology

The methodology for data collection involved utilizing various research platforms like Google Scholar, Scopus, and Web of Science to gather literature relevant to this review. Keywords such as iron, Fe-NPs, Fe-NPs synthesis, characterization, heavy metal toxicity, organic contaminants, dyes, green synthesis of Fe-NPs, and Fe-NPs alleviating heavy metals toxicity were employed to search for pertinent literature. A systematic and comprehensive approach was adopted to identify and collect relevant literature, focusing on peer-reviewed sources, global studies, and studies published from 2000 onwards. Only studies published in English were considered, while studies in other languages were excluded from analysis.

3. The iron-nanoparticles synthesis route by plant-based materials extract

Green chemistry is a comparatively recent idea that aims to accomplish durability at the molecular scale (Anastas and Eghbali, 2010). It originally originated in the early 1990s (Collins, 1997). It seeks to keep intrinsic concerns to a minimal at all phases of the life cycle, lowering the risk of developing safer, more sustainable substances and processes (Mondal and Purkait, 2019). It has gotten a lot of press since it can leverage chemical innovation to achieve both ecological and financial aims. Green chemistry focuses on the application of the Twelve Principles, which include preventative measures, atom budget, lower dangerous substances production/synthesis, developing harmless/safer chemicals, solvent-based, and accessories, developing for higher energy efficacy, using sustainable feedstocks, reducing derivative products, catalysis, strategy utilized for deterioration, actual research for pollution control, and intrinsically secure chemistry to avoid accidents (Anastas and Eghbali, 2010; Madubuonu et al., 2019). Green chemistry primarily attempts to minimize or eradicate the use of chemical pollutants in the manufacture, strategy, and use of biochemical substances, and considers minimal hazard as an evaluation metric when developing new chemical processes (Varma, 2012; Samrot et al., 2020).

John Warner and Paul Anastas introduced the Twelve Principles in 1998 (Anastas and Warner, 1998). The Twelve Principles played an important part in sustainable design as a theoretical principle. The selection of raw organic biomass, the effectiveness and stability of the alteration, the toxicology and degradability of processes, and the implemented chemicals are all factors in the development of novel chemical products and processes (Amendola et al., 2011; Raji et al., 2019). Green chemistry approaches must be implemented in the establishment of developing NPs and their applications because: (i) this technology is expected to be widely used and spread globally, especially in its early stages (Iravani, 2011); (ii) because there is currently relatively little toxicological evidence on these developing NPs, identifying potential threats to ecosystem and human health is extremely difficult (Samrot et al., 2020); (iii) many commonly used compounds are poisonous and costly, and the preparation method is inefficient (Kadzinski et al., 2018). One of the most pressing concerns in nanoscience research work is the intersection of green chemistry concepts and nanotechnology (Makarov et al., 2014a, 2014b).

Several nanoscience researchers have applied these ideas to the nanoparticle synthesis for economic and environmental reasons, leading to the rapid growth of green synthesis (Mittal et al., 2013; Samrot et al., 2020). Because Fe-NPs, once produced using physical and chemical and processes, have various limits and downsides, the green method of synthesis is presently emerging as a promising solution for their manufacture (Raji et al., 2019; Bolade et al., 2019). Capping agents, for example, are important in the biochemical generation of NPs as they potentially influenced both the growth process and the morphology and size of NPs by absorption on the developing surface (Sharma et al., 2012). Nevertheless, various capping agents are natural/organics, and frequently utilized precursors in this procedure, i.e., $NaBH_4$, which are categorized as a noxious and highly expensive, creating severe ecological/environmental issues and ruling out biological applications (Genuino et al., 2013). Additionally, quick reaction or agglomeration/accumulation with the environment (such as water or oxygen in dissolved formed) results in decreased stability and reactivity. Thermal decomposition, for example, requires the use of costly and toxic reagents like $Fe(CO)_5$, as well as the elimination of by-products and the development of wastewater (Li et al., 2009). The essential elements for selecting a green synthesis approach are an environmentally ecofriendly reduction-agents, a nonhazardous capping-agents, and biologically consistent solvent/extract system (Nadagouda and Varma, 2006). As previously stated, biomolecules found in several biological resources that may be used as mutually capping and reducing agents in the generation of NPs, eliminating the demand for extra hazardous and expensive chemicals (Madubuonu et al., 2019; Aisida et al., 2020). As a result, green synthesis of Fe-NPs is explored since biological sources are cost-effective, environmentally benign, safe for people, and long-term for biomedical and commercial usage (Mondal and Purkait, 2019; Aisida et al., 2020). The biological resources used to make Fe-NPs are discussed in the sections below.

Much research has been reported on the green synthesis approach using microbes (Singh et al., 2016; Mondal et al., 2020), but plant-based resources are rarely described and have only recently become important. Plant-based resources are more favourable than microbes for synthesizing NPs as plant residues/resources are easily accessible and not necessitate a complicated procedure of sustaining cell-cultures (Manquián-Cerda et al., 2017). Plants are the primary photosynthetic autotrophs in the food supply chain, producing many plants in the terrestrial ecosystem (Saif et al., 2016). Even at very low concentrations, several heavy metals (HMs) are recognized to be harmful environmental pollutants. Plants may minimize trace-metal ions on the outer surface and in dissimilar tissues, indicating that they have a lot of potential in terms of heavy metal bioavailability and detoxification (Haider et al., 2021). Bioavailability of HMs is presently being widely used to remove harmful substances from contaminated locations since it is a cost-effective, environmentally acceptable, and efficient method (Varma, 2012; Bolade et al., 2019). Plants specifically, taken up low concentrations of trace-metals through soils/effluents and store them especially in specific portions of tissues, which are later retrieved after harvesting via smelting and sintering (Makarov et al., 2014a, 2014b). It was discovered that metals are finally provided in the form of NPs throughout the accumulation process (Gardea-Torresdey et al., 2002). In this situation, complete plants can be used to manufacture metal NPs in substantial quantities.

However, several current disadvantages restrict their practical implementation. Nanoparticles, for example, vary widely in shape and size, with their location depending on the existence of specific biomolecules in the plant, which may obstruct applications that require precise shape and size (Es'haghi et al., 2016; Samrot et al., 2021). It's really a difficult topic to solve in terms of enhancing nanoparticle extraction, purification, and separation from plants (Makarov et al., 2014a, 2014b). In this perspective, researchers are focusing their efforts on developing an in vitro technique for producing metal NPs using plant extracts. A little change in pH and reaction temperature can influence the size and structure of NPs (Rai and Yadav, 2013). This process happens instantly, unlike bioavailability, which requires a long spell to ingest and diffuse metal ions from the entire plant. Plant extracts have previously been used to generate a wide variety of metal NPs, including iron (Fe), copper (Cu), titanium (Ti), palladium (Pd), silver (Ag), and gold (Au) (Akhtar et al., 2013). Some published articles have reviewed the green synthesis and characterization of Ag-NPs and Au-NPs in particular (Sharma et al., 2012), so only Fe-NPs are to be emphasized. Based on plant-based materials NPs are classified as Fe-NPs, Fe-oxide NPs, and Fe-hybrid NPs which are presented in Table 1. In conclusion, the green synthesis of Fe-NPs using plant-based materials is a promising approach that aligns with the principles of green chemistry. The use of plant extracts as reducing and capping agents can lead to the production of stable and environmentally friendly Fe-NPs. However, further research is needed to address the challenges associated with the variability in NPs properties and the optimization of extraction and purification processes.

4. The molecular complexity associated with plant-derived residues and Fe-NPs synthesis process

Though several studies have investigated and discovered plants-residues capable of synthesizing NPs, the specific synthesis method has not been thoroughly investigated, necessitating further knowledge. Understanding the relevant organic molecules present in plant residues is crucial for fully identifying the actual methodology. This section describes research on the influence of biomolecules in plants and the mechanisms that underlying it. Polyphenolic chemicals, polysaccharides, alkaloids, terpenoids, and proteins in plant extracts were principally responsible for the decrease and stabilization of Fe-NPs (Mittal et al., 2013; Kavitha et al., 2013). Polyphenolic substances, such as stilbenes, tannins, flavonoids, and phenolic acids, as well as lignans, can be found in a variety of vegetables, fruits, and herbs. They belong to a vast class of bioactive compounds that have a high antioxidant activity and can actively chelate and decrease metal ions to NPs (Ignat et al., 2011). Researchers currently agree that polyphenolic chemicals present in plant extracts are predominantly for Fe-NPs production.

The Folin–Ciocalteu technique can be used to determine the total polyphenol content of the extract (Machado et al., 2013). Polyphenolic chemicals, which are widely observed in tea extracts, may act as capping and reducing agents in the formation of Fe-NPs. Nadagouda et al. (2010) reported that, (i) polyphenols produced complex-structure with trace-metal ions, lowering the trace-metals; and (ii) organic-molecules present in extract of green-tea had higher alcoholic-functional groups, facilitating reduction of NPs and its stability (Nadagouda et al., 2010). X-ray energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) were used by Shahwan et al. (2011) to indicate the existence of polyphenols in green tea extract. Polyphenols on the surface of the nanoparticles were also identified using the Fourier transform infrared spectroscopy technique (FTIR), with representative peaks at 1065, 1400, and 1600 cm^{-1} resulting from the extending vibration of C-O-C, in-plane bending vibration of -OH in phenols, and C═C extending in polyphenols-functional groups, respectively.

Benković et al. (2023) found that the capping and reducing factors in black-tea and oolong-tea were still polyphenols based on results from X-ray diffraction (XRD), EDS, and ultraviolet-visible spectrophotometry (UV-Vis). Polyphenolic chemicals found in eucalyptus (*Eucalyptus globulus* L.) leaf extract are still important in reducing and stabilizing NPs. According to Gupta et al. (2023), an XRD hump at $2\theta = 25^{\circ}$ correlated to organic compounds that worked as capping agents on the surfaces of synthesized-Fe-NPs. Specific biomolecules which regulated the stabilization and reduction of Fe-NPs largely contained -OH, C═C, and C-O-C functional-groups, according to results mentioned by FTIR. Because this result was comparable to that obtained with extract of green-tea, polyphenolic-functional groups components were significantly assumed as eucalyptus leaf extract's capping and reducing agents. Because most hydroxyl groups were oxidized to carboxyl groups throughout the production process, the following is a proposed method for the synthesis of Fe NPs utilizing eucalyptus leaves and green tea and extracts (Smuleac et al., 2011; Ovais et al., 2018);

$$nFe^{2+} + 2Ar\text{-}(OH)_n \rightarrow nFe^0 + 2nAr{=}O + 2nH^+$$

where Ar is the phenyl group and n are the number of hydroxyl groups oxidized by Fe^{2+}

In addition, to polyphenols, Other functional groups, or organic-molecules, are included in the formation of Fe-NPs. Saponins and tannins and worked as capping agents in the study with hopbush (*Dodonaea viscosa* L.) leaf extract, whereas polyhydroxy groups and flavonoids in satin (*Scindapsus pictus* L.) might reduce metal ions (Kumar et al., 2013). The potential of aromatic ring, phenolic oxygen, and C═O group of the p-benzoquinone present in the leaves aqueous-extract of henna tree (*Lawsonia inermis* L.) acts as stabilizing and reducing agents was demonstrated by Naseem and Farrukh (2015). Similarly, Prasad et al. (2014) discovered functional-groups (C═O, -OH, C═C, -NH, and C═N) in peppermint (*Mentha piperita* L.) leaves extract were involved in the synthesis process using FTIR analysis. Saif et al. (2016) used FTIR and gas chromatography-mass spectrometer (GC-MS) to discover phytols, terpenoids (δ sitosterols, β sitosterols, β amyrins, and α amyrins), and antioxidants (5-diene, vitamin E, and δ-stan-3) as capping and reducing agents. Makarov et al., (2014a), (2014b) suggested a method for Fe-NP establishment via plant extract by two processes in which: (i) biomolecules with an aldehyde or hydroxy group may minimize trace-metals; and (ii) carbonyl-groups existing in the included organic-molecules or acquired subsequently reduction can bind to the NPs, resulting in Fe-NPs stabilization. Using green tea extracts, Ahmmad et al. (2013) offered a more complete demonstration of the individual mechanisms of polyphenolic-chemicals and the formation process of α-Fe_2O_3. The critical characteristics of polyphenolic compounds, such as epicatechin (EC, 0.5–2.2 %), epigallocatechin gallate epigallocatechin (EGC, 0.7–2.3 %), (EGCG, 36–40 %), and gallocatechin gallate (GCG, >45 %) contributed to metal ion reduction and NPs stabilization (Chen et al., 2001; Ahmmad et al., 2013). The equivalent pathway for the synthesis of α-Fe_2O_3 utilizing green tea aqueous extract is shown briefly in Fig. 1. Furthermore, studies utilizing the sprouts of soybean (*Glycine max* L.) demonstrated that proteins were involved in the formation of Fe_3O_4-NPs (Cai et al., 2010). Amino acids/proteins may interact to trace-metals through carbonyl and amine groups. The FTIR analysis used in this investigation was as follows: (i) 1645 cm^{-1}, 1520, and 1235 cm^{-1} were directly featured to bands of amide I, amide II, and amide III respectively, owing to the combination of C-N, N-H, and C═O; (ii) 1460 cm^{-1} was related to the -COO group of amino acid remains in the proteins; (iii) 1082 cm^{-1} and 1402 cm^{-1} were related to C-O-C and C-OH of proteins; and (iv) 675 cm^{-1} was related to the N-H group of amino acid remains in the proteins (Cai et al., 2010). The presence of an organic acid, such as citric/oxalic acid, in barley (*Hordeum vulgare* L.) and garden-sorrel (*Rumex acetosa* L.) plant extracts proved their potential to stabilize NPs (Rao et al., 2013). Metal ions are known to be reduced by monosaccharides with an aldehyde group. As a result, it was hypothesized that a carbohydrate like glucose, which was a key factor of tridax-daisy (*Tridax procumbens* L.) leaves extract, would operate as a reducing agent (Lunge et al., 2014).

5. Characterization of the iron nanoparticles

For optimal application of Fe-NPs, specific information on their morphology and size, structure, composition, and other surface attributes is required. The following section describes the methods used to characterize these features.

Table 1
Green synthesis of iron nanoparticles by using plant-based material and characterizations.

Plant	Precursor	Nanoparticle type	Size (nm)	Characterization	References
Medicago sativa (alfalfa) biomass	$FeNH_4(SO_4)_2 12\ H_2O$	$Fe_{0.902}O$ and Fe_3O_4	1–10	TEM	Herrera-Becerra et al. (2007); Herrera-Becerra et al. (2008)
Green tea *(Camellia sinensis)*	$FeCl_3$	Fe NPs	5–15	UV spectra; TEM, XRD	Hoag et al. (2009)
Glycine max (soybean) sprouts	$FeNH_4(SO_4)_2 12\ H_2O$	Fe_3O_4	8	SEM, FTIR, TEM, XPS,	Cai et al. (2010)
Green tea *(Camellia sinensis)*	$Fe(NO_3)_3$	Fe NPs	40–50	UV spectra; TEM, XRD	Nadagouda et al. (2010)
Tannins	$FeNH_4(SO_4)_2.12\ H_2O$	Fe_2O_3	< 7	TEM	Herrera-Becerra et al. (2010)
Sorghum bicolor (sorghum) bran	$FeCl_3$	Fe NPs	50	XRD, SEM, FTIR, EDS	Njagi et al. (2011)
Green tea *(Camellia sinensis)*	$FeCl_3$	Fe NPs	20–30	XRD, SEM	Smuleac et al. (2011)
Green tea *(Camellia sinensis)*	$FeCl_2$	Fe NPs	40–60	XRD, SEM, TEM, FTIR	Shahwan et al. (2011)
Grape seed proanthocyanidin	$FeCl_3$	Fe_3O_4/Au	35	UV spectra, FTIR, TEM	Narayanan et al. (2012)
Green tea (*Camellia sinensis*)	$FeCl_3$	Fe NPs	-	XRF	Chrysochoou et al. (2012)
Tridax procumbens (tridax daisy) leaf	$FeCl_3$	Fe_3O_4	80–100	FTIR, TEM, XRD	Senthil and Ramesh, (2012)
Green tea (*Camellia sinensis*) leaf	$Fe(NO_3)_3$	α-Fe_2O_3	60	SEM, FTIR, XRD, TEM, XPS, EDS	Ahmmad et al. (2013)
Tata green tea (*Camellia sinensis*)	$Fe(NO_3)_3$	Fe NPs	59.08±7.81	XRD, SEM	Tandon et al. (2013)
Eucalyptus globulus (eucalyptus) leaf	$FeSO_4.7H_2O$	Fe NPs	50–80	UV spectra, FTIR, XRD, SEM	Madhavi et al. (2013)
Azadiracchta indica (neem) leaf	$FeCl_3$	Fe NPs	50–100	XRD, SEM	Pattanayak and Nayak, (2013)
26 tree leaves	$FeCl_3$	Fe NPs	10–20	TEM	Machado et al. (2013)
Black tea, grape marc, and vine leaf	$FeCl_3$	Fe NPs	15–45	TEM	Machado et al. (2013)
Dodonaea viscosa (purple hopbush) leaf	$FeCl_3$	Fe NPs	50–60	UV spectra, FTIR, TEM	Daniel et al. (2013)
Citrus sinensis (sweet orange) peel pith	$FeCl_3$	Iron nanorods	20–40	TEM, XPS, EDS	López-Téllez et al. (2013)
Punica granatum (pomegranate) leaf	$FeNH_4(SO_4)_2.12\ H_2O$	Fe^0/ Fe_3O_4	100–200	SEM, XRD	Rao et al. (2013)
Aloe barbadensis (Aloe vera)	$Fe(C_5H_8O_2)_3$	Fe_3O_4	6–30	XRD, SEM, TEM,	Phumying et al. (2013)
Terminalia chebula (Chebulic myrobalan) fruit	$FeSO_4.7\ H_2O$	Fe NPs	< 100	UV spectra, FTIR, XRD, TEM	Kumar et al. (2013)
Plantain peel	$FeCl_3$	Fe_3O_4	1–50	TEM, EDS, SEM, FRIR	Venkateswarlu et al. (2013)
Eucalyptus tereticornis (eucalyptus) leaf	$FeCl_3$	Fe NPs	40–60	XRD, TEM	Wang, (2013)
Mentha spicata (spearmint) leaf	$Fe(NO_3)_3$	Fe NPs	20–45	UV spectra, FTIR, TEM	Prasad et al. (2014)
Tea waste	$FeCl_3$	Fe_3O_4	5–25	TEM, FTIR, XRD	Lunge et al. (2014)
Passiflora tripartita (curuba) *var. mollissima* fruit	$FeCl_3$	Fe_3O_4	22.3±3	TEM, FTIR, XRD	Kumar et al. (2014)
Hordeum vulgare (barley) and *Rumex acetosa* (garden sorrel) extracts	$FeCl_3$	FeO-NPs	0.9–29.9, 9.9–39.9	TEM, XPS, EDS	Makarov et al., (2014a), (2014b)
Colocasia esculenta (taro) leaf	$FeCl_2$, $FeCl_3$	Iron oxide/reduced graphene oxide nanohybrid	-	XRD, TEM	Thakur and Karak, (2014)
Lawsonia inermis (henna tree) leaf	$FeSO_4.7\ H_2O$	Fe NPs	21	SEM, FTIR, XRD, TEM	Naseem et al. (2015)
Camellia sinensis, green tea, *Syzygium aromaticum* (clove), *Mentha spicata* (spearmint), *Punica granatum* (pomegranate) juice, and red wine	$FeCl_3$	Fe-NPs	< 59.9	TEM	Mystrioti et al. (2016)
Vitis vinifera (grape) leaf	$FeCl_2$	Fe NPs	15–100	XRD, SEM, FTIR, EDS	Saif et al. (2016), Manquián-Cerda et al. (2017)
Oolong, green, and black tea	$FeSO_4.7\ H_2O$	Fe NPs	20–40	XRD, SEM	Gautam et al. (2019)
Eucalyptus globulus (eucalyptus) leaf and green tea	$FeSO_4.7\ H_2O$	Fe NPs	20–80	XRD, SEM, FTIR, EDS	Patil and Chandrasekaran, (2020)
Vitis vinifera (grape) leaf	$FeCl_2$	Fe/Pd	10–100	SEM, FTIR, EDS	Bolade et al. (2020)
Eucalyptus globules (eucalyptus)	$FeNO3\cdot 9H_2O$	Fe-NPs	2–120	XRD, XPS, FTIR, BET, TEM	Litter (2022)
Oolong tea	$FeSO_4.7H_2O$	Fe NPs	40–50	XRD, SEM, TEM, FTIR	Ying et al. (2022)
Eucalyptus globules (eucalyptus)	$FeCl_3\cdot 6H_2O$, $NiCl_2\cdot 6H_2O$	Fe/Ni-NPs	60–85	SEM, EDS, XRD, FTIR	Kumar et al. (2023)
Loose-leaf green tea	$FeCl_3\cdot 6H_2O$, $NiCl_2\cdot 6H_2O$	Fe/Ni-NPs	40–80	SEM, EDS, XRD, FTIR	Cheng and Wen, (2022)
Eucalyptus tereticornis (eucalyptus), *Melaleuca nesophila* (pink melaleuca), *and Rosemarinus officinalis* (rosemary) *leaves*	$FeCl_3$	Fe NPs	40–60	XRD, SEM, TEM, FTIR, BET, EDS	Gupta et al. (2023)
Eucalyptus globules (eucalyptus)	$FeSO4.7H_2O$	Fe-NPs	70±20	SEM, EDS, FTIR, XRD	Ifthikar et al. (2023)
Oolong tea, green tea, and black tea	$FeSO_47H_2O$	Fe-NPs	39.5–50.5	XRD, SEM, TEM, FTIR, BET, EDS	Benković et al. (2023)

Note; Scanning electron microscopy= SEM; Atomic Force Microscopy= AFM; Dynamic light scattering= DLS; X-ray energy dispersive spectroscopy= EDS; transmission electron microscope= TEM; Ultraviolet-visible spectrophotometry= UV–vis; Energy Dispersive X-ray Spectroscopy= EDAX; Fourier transform infrared spectroscopy techniques= FTIR; X-ray diffraction= XRD; High resolution transmission electron microscope= HR-TEM X-ray photoelectron spectroscopy= XPS; Brunauer–Emmett–Teller isotherm = BET method.

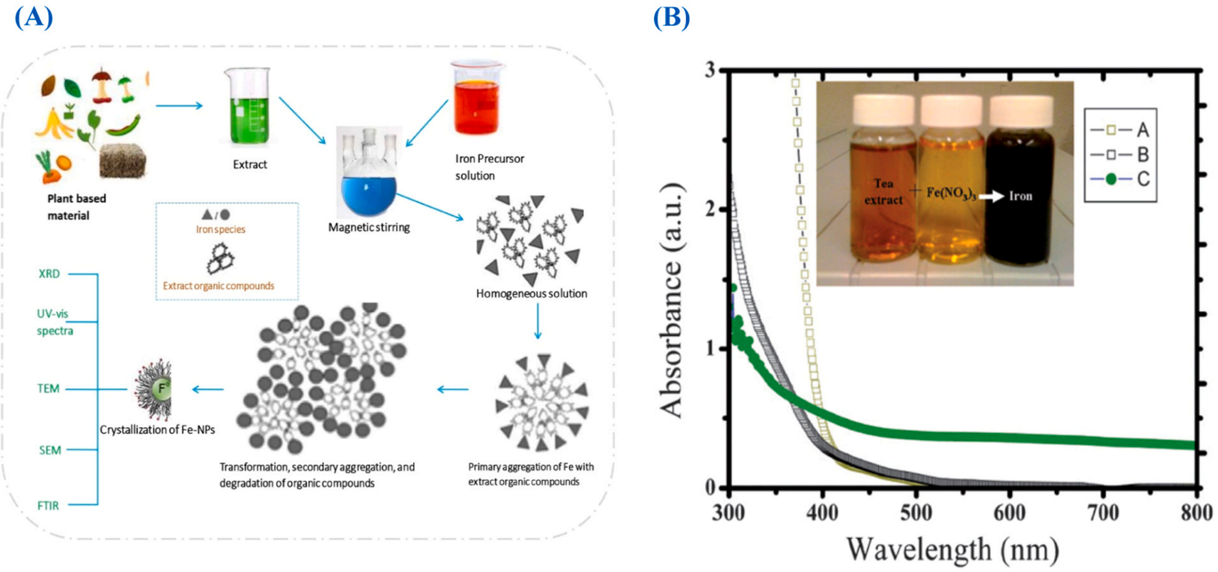

Fig. 1. (A) Schematic illustration of green-synthesis of iron-nanoparticles (Fe-NPs) by using plant-based material. Step 1. Preparation of plant-based extract. Step 2. Preparation of iron precursor solution. Step 3. Magnetic stirring. Step 4. Filtration. Step 5. Characterization. (B) Represents the ultraviolet–visible spectroscopy (UV-spectra) of ferric nitrate (A), tea extract (B), and ferric nitrate and tea extract reaction product (Hoag et al., 2009).

5.1. Morphology and size of the iron nanoparticles

The morphology and size of Fe-NPs can be determined using three different techniques i.e., atomic force microscopy (AFM), scanning electron microscopy (SEM) or field-emission SEM, and transmission electron microscope (TEM) (Manquián-Cerda et al., 2017). These approaches can obviously demonstrate particles with a widely dispersed or aggregated spherical morphology, as well as irregular aggregates with a range of sizes (Ifthikar et al., 2023). The size can also be determined via dynamic light scattering (DLS). SEM images of Fe-NPs made with

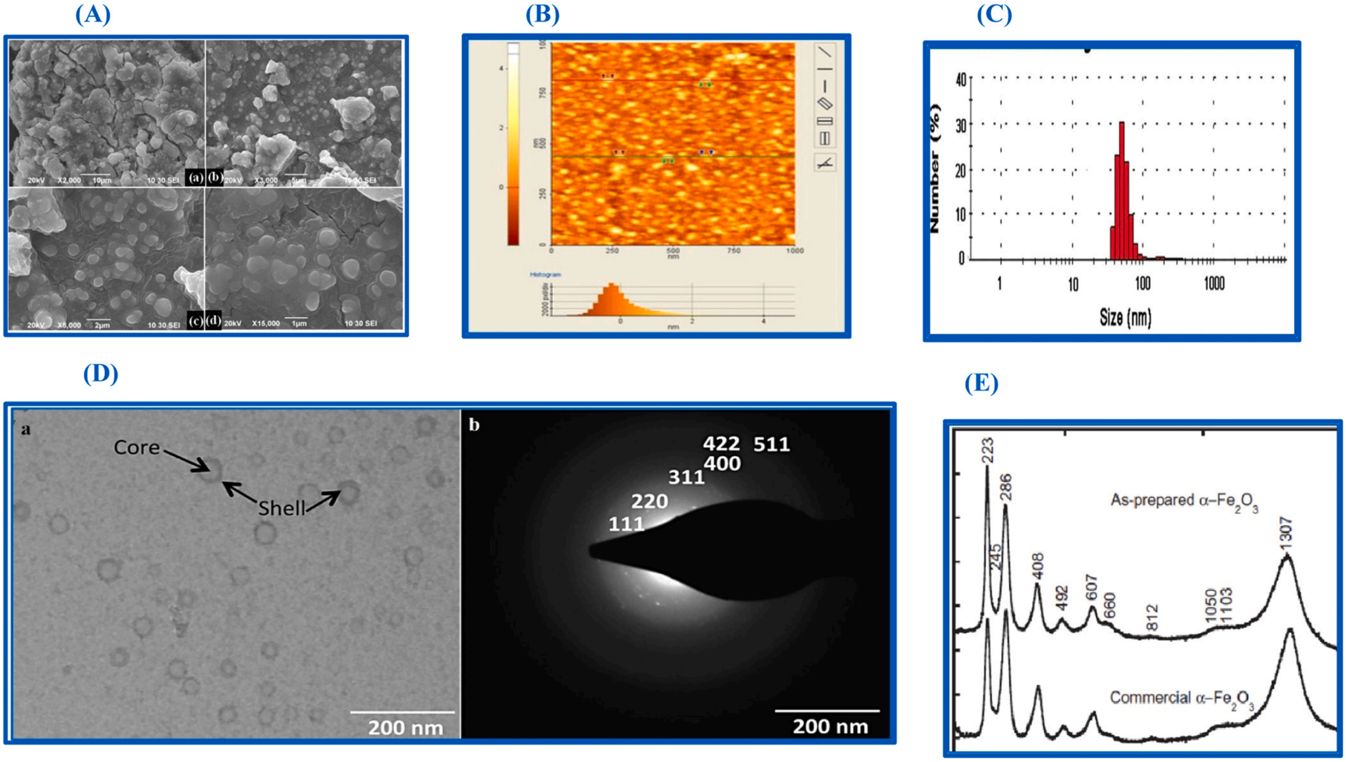

Fig. 2. Characterization of green-synthesized iron-nanoparticles (Fe-NPs) by using plant-based material. (A) Scanning-electron-microscopy (SEM) representations of iron-oxide (Fe_3O_4-NPs) produced via tridax daisy (*Tridax procumbens* L.) leaves solution/extract at (a) 10 μm, (b) 5 μm, (c) 2 μm, and (d) 1 μm magnification levels (Senthil and Ramesh, 2012). (B) Atomic-force-microscopy (AFM) representation of the green-synthesized Fe-NPs produced via purple hopbush (*Dodonaea viscosa* L.) leaves solution/extract (Daniel et al., 2013). (C) Dimension dispersal of iron oxide-NPs synthesized via barley (*Hordeum vulgare* L.) solution/extract (Makarov et al., 2014a, 2014b). (D) (a) Transmission-electron-microscope (TEM) representation, and (b) Selected-area-electron-diffraction (SAED) visualization of Fe-NPs synthesized via spearmint (*Mentha spicata* L.) leaves solution/extract (Prasad et al., 2014). (E) Raman-spectra image of natural-synthesized (as-prepared/plant-extract) and commercialized α-Fe_2O_3 NPs (Ahmmad et al., 2013).

tridax-daisy (*Tridax procumbens* L.) leaf extract were obtained. Fe_3O_4-NPs possessed an asymmetrical sphere-shaped and varied in dimension from 80 to 100 nm, as illustrated in Fig. 2A, (Senthil and Ramesh, 2012). AFM was used in another experiment to differentiate the morphology. AFM is crucial in nanoscience for its high-resolution imaging and precise analysis of surface morphology at atomic scales. Its versatility in different environments aids in studying biological samples, polymers, and NMs, providing quantitative data for advancing nanoscale research and applications. The figure in Fig. 2B reveals that green produced Fe-NPs had a consistent shape and were between 30 and 40 nm in size (Daniel et al., 2013). The characterization of FeO-NPs generated via barley (*Hordeum vulgare* L.) extract in 30 min through DLS is shown in Fig. 2C (Makarov et al., 2014a, 2014b). A selected area electron diffraction (SAED) pattern was mostly used in conjunction with TEM, in which the dispersion ring/spot reflected the transparent phase, whereas the diffused ring came after its shapeless form. SAED and TEM examination in the creation of Fe-NPs via peppermint (*Mentha piperita* L.) leaves extract revealed that transparent Fe-NPs having a core-shell structural formation and were polydisperse sphere along with diameters ranging from 20 to 45 nm, as shown in Fig. 2D (Prasad et al., 2014).

5.2. *Structural composition of the iron nanoparticles*

In general, XPS and EDS are used to determine the surface structural composition of Fe-NPs, as well as the fraction of each component or element. Likewise, EDS assessment of Fe-NPs made from extract derived from oolong-tea found that C (49.51 percent), O (20.34 percent), Fe (11.63 percent), and S (5.05 percent) were the most abundant component, (Benković et al., 2023). The S signal was derived from the biosynthesis precursor, but the O and C signals were attributed to polyphenols group and other C-containing compounds in the oolong-tea extract. C 1 s, O 1 s, N 1 s, and Fe 2p signals were detected in XPS data for Fe_3O_4-NPs made from the sprouts of soybean (*Glycine max* L.), (Cai et al., 2010). Fe compounds were linked to binding energies of 710.5 and 723.8 eV, respectively, corresponding to Fe $2p_{3/2}$ and Fe $2p_{1/2}$. The presence of polysaccharides or proteins on the surface of Fe_3O_4-NPs was validated by further deconvolution of C 1 s, O 1 s, and N 1 s XPS spectra. Chemical composition can be determined using X-ray absorption near-edge structure spectroscopy (XANES), electron energy loss spectroscopy (EELS), and FTIR to some extent. Herrera-Becerra et al. (2007) used EELS to demonstrate the existence of Fe and O in green produced Fe_3O_4-NPs, while Senthil and Ramesh, (2012) used FTIR to confirm the existence of Fe_3O_4-NPs resulting from the vibration of Fe-O at 587 cm^{-1}. Wang used XANES to assess the mean Fe valence state in Fe-NPs using extract synthesized from leaves of eucalyptus (*Eucalyptus globulus* L.), and the findings revealed that ferric valence was the most prevalent (Wang, 2013).

5.3. *Structure of the iron nanoparticles*

The most extensively utilized techniques for analysing the structure/architecture of Fe-NPs are SAED and X-Ray Diffraction (XRD). The expressions of (220), (311), (511), and (440) in the XRD investigation on Fe_3O_4-NPs synthesized by Aloe vera (*Aloe barbadensis miller* L.) extract revealed the crystalline structure of Fe_3O_4-NPs (Phumying et al., 2013). This was subsequently supported by SAED, which revealed patchy ring patterns of crystalline inverted cubic spinel nanostructures. A diffuse ring in SAED arrangements and no diversion peak at 44° in XRD revealed Fe-NPs produced by the extract of sorghum (*Sorghum bicolor* L.) bran were structurally amorphous in another investigation (Njagi et al., 2010). However, that XRD alone might identify the structural arrangement of coated Fe-NPs comparable Au-coated Fe-NPs, presumably because their diffraction peaks overlap (Genuino et al., 2013). FTIR, TEM, XANES, XPS, and raman spectroscopy can provide focus on providing structure information in specific cases. XRD was used by Ahmmad et al. (2013) to analyse green generated α-Fe_2O_3.NPs, and their findings revealed that the established α-Fe_2O_3-NPs were crystalline and very natural. To additional confirm the crystalline structure, they later associated the Raman spectra of green-synthesized α-Fe_2O_3 and commercial/artificial α-Fe_2O_3. Seven phonon lines, specifically two $A_{1\,g}$ modes (225 and 498 cm^{-1}) and five Eg modes (247, 293, 299, 412, and 613 cm^{-1}) were estimated in the Raman spectrum of α-Fe_2O_3-NPs, crystallized as a corundum-type structural arrangement. All spectra of as-prepared α-Fe_2O_3-NPs were comparable with those of commercial/artificial α-Fe_2O_3, nevertheless certain alterations happened due to changes in particle shape and size, as illustrated in Fig. 2E (Ahmmad et al., 2013). XPS was then used to analysed the shell-structure of α-Fe_2O_3. Apart from for the two distinctive peaks of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ at 711 and 725 eV, an isolated satellite peak at 719 eV, which was entirely attributable to the Fe^{3+} ions of α-Fe_2O_3 indicated that the organized nanomaterials were pure α-Fe_2O_3-NPs. According to Manquián-Cerda et al. (2017), Fe-NPs produced with grape (*Vitis vinifera* L.) leaf extract have a core-shell structure, with certain biomolecules and pretty much inevitable iron oxides forming during the synthesis process and covering the surface of Fe-NPs. XPS and TEM were used to detect the probable components on the surface of Fe-NPs to prove this idea. A single Fe-NPs was bounded by a membrane layer of biomolecules, as seen by TEM. Fe $2p_{3/2}$ peak at 712 eV in XPS spectra, simultaneously associated with the OH group (~531 eV) affirmed the presence of FeOOH. Some biomolecules encapsulated on the surface of Fe NPs, based on the existence of O 1 s and C 1 s. These findings confirmed with the theory that the shell on the surface was mostly made up of FeOOH and biomolecules (Manquián-Cerda et al., 2017). FTIR was employed by Gupta et al. (2023), to discover potential biomolecules on the surface of Fe-NPs produced with eucalyptus leaf extract. Carbonyl carboxyl, amines, and phenols and were detected as peaks at 1361, 1048, 1611, 1720, and 3379 cm^{-1}.

5.4. *Additional surface characterizations*

Additional surface parameters, such as charges on particle surface, permeability/porosity, and potential surface area, and have a substantial impact on Fe-NPs reactivity, particularly catalytic activity. The standard BET method (Brunauer–Emmett–Teller isotherm) can be used to calculate the pore volume and surface area of NPs. Ahmmad et al. (2013) used green-tea extract to generate α-Fe_2O_3-NPs with pore volume and BET surface area and of and 0.078 cm^2/g and 47.2 m^2/g, respectively. Photocatalytic activity was shown to be higher in α-Fe_2O_3-NPs with a larger surface area. The zeta (ζ) potential, that is a significant factor regulating particle dispersion and assessing colloidal system stability, is typically used to describe the surface charge of Fe-NPs. Zeta (ζ) stable condition is defined mostly as a potential greater than 30 mV. Fe-NPs synthesized using sorghum (*Sorghum bicolor* L.) bran extract collected at 80, 50, and 25 °C, respectively, had potentials of 11.4, 13.3, and 14.6 mV signifying unstable colloidal systems (Njagi et al., 2010). After a week, however, no significant sedimentation was seen, indicating that some biomolecules present in the sorghum (*Sorghum bicolor* L.) bran extract may be able to stabilize Fe-NPs.

In the content of NPs synthesis and application, the variability in shape and size presents a spectrum of advantages and limitations, which are contingent upon the particular requirements of their intended application. Specifically, within catalytic environments, the pursuit of uniformity in NP size and shape is common practice to ensure predictable reactivity and optimal efficiency (Kumar et al., 2023). Conversely, in certain environmental remediation contexts, a spectrum of shapes and sizes can improve adsorption capacity and surface interactions with contaminants, thereby enhancing remediation efficacy. Consequently, the variability in NPs attributes should not be seen as a flaw but rather as a customizable feature to optimize performance across diverse applications. Moreover, a range of plant extracts such as *Medicago sativa* (alfalfa), *Camellia sinensis* (green tea), *Eucalyptus globulus* (eucalyptus), *Azadirachta indica* (neem), and others are used in synthesizing green-synthesized Fe-NPs (Kumar et al., 2023; Gupta et al., 2023). The variations in phenolic compounds, terpenoids, and other constituents in these extracts contribute to the diversity in the shape and size of Fe-NPs. Additionally, Fe-NPs synthesized from microorganisms, algae, and their derivatives also exhibit variations in shape and size. Therefore, these variations are not considered drawbacks, as all these Fe-NPs have been extensively utilized for remediating both organic and inorganic contaminants.

6. Stability, accumulation, mobility, and fate of green synthesized Fe-NPs

The stability of green synthesized NPs is a crucial factor that determines their long-term performance and effectiveness in environmental applications (Siji et al., 2017); Rónavári et al., (2017). The stability of Fe-NPs can be influenced by various factors, such as the composition of the plant extracts used for synthesis, the synthesis conditions, and the environmental conditions in which they are deployed (Gupta et al., 2023). Several studies have reported that the presence of capping agents and stabilizing biomolecules in plant extracts can enhance the stability of green synthesized Fe-NPs. For example, Rajput et al. (2016) found that Fe-NPs synthesized using *Azadirachta indica* (neem) leaf extract exhibited excellent stability in aqueous solutions due to the presence of polyphenols and other biomolecules that acted as capping and stabilizing agents. Similarly, Makarov et al., (2014a), (2014b) demonstrated that Fe-NPs synthesized using *Diospyros kaki* (persimmon) leaf extract were highly stable in a wide range of pH and ionic strength conditions, owing to the stabilizing effect of the plant-derived biomolecules.

The accumulation and mobility of green synthesized Fe-NPs in the environment are important considerations, as they can impact their distribution, bioavailability, and potential environmental impacts (Silveira et al., 2017). Studies have shown that the accumulation and mobility of Fe-NPs can be influenced by factors such as their size, surface properties, and interactions with environmental matrices. Smaller Fe-NPs tend to have higher mobility and can potentially travel longer distances in the environment, while larger Fe-NPs may be more prone to aggregation and sedimentation (Keller et al., 2010).

The surface properties of green synthesized Fe-NPs, such as the presence of capping agents or stabilizing biomolecules, can also affect their accumulation and mobility. For instance, Saif et al. (2016) found that Fe-NPs synthesized using *Camellia sinensis* (green tea) extract exhibited lower accumulation and higher mobility in soil compared to chemically synthesized Fe-NPs, due to the stabilizing effect of the plant-derived biomolecules. The fate of green synthesized Fe-NPs in the environment is an important consideration, as it can determine their long-term impact and potential for environmental remediation. Several studies have investigated the fate of green synthesized Fe-NPs in different environmental compartments, such as soil, water, and sediments. Keller et al. (2010) reported that Fe-NPs can undergo various transformation processes, such as oxidation, dissolution, and aggregation, which can affect their fate and behavior in the environment. The fate of green synthesized Fe-NPs can also be influenced by their interactions with other environmental components, such as organic matter, minerals, and microorganisms. For example, Bolade et al. (2019) found that the presence of organic matter in soil can enhance the stability and longevity of green synthesized Fe-NPs, thereby improving their effectiveness for environmental remediation. In conclusion, the stability, accumulation, mobility, and fate of green synthesized Fe-NPs are crucial factors that need to be considered when evaluating their potential for environmental applications. Ongoing research in this area can help to optimize the synthesis and deployment of these nanoparticles for effective and sustainable environmental remediation.

7. Applications of green synthesized Fe-NPs for environmental remediation

7.1. *Remediation of wastewater, organic compounds, pesticides, and dyes*

Water is the most crucial natural resource on the planet for all living organisms to survive (Chandanshive et al., 2018; Ahmed et al., 2023). Inorganic and organic compounds, industrial effluents, microbes, and antibiotics are all known to contaminate water (Ali et al., 2021; Akash et al., 2024). Regrettably, farmers in underdeveloped nations use such contaminated water extensively for irrigation of their agricultural fields, resulting in considerable and severe effects on soil fertility and plant growth (El-Sayed, 2020). Furthermore, contaminants in polluted water and soil are translocated into plants, which may have an impact on human health through the oral intake (Xiong et al., 2020; Haider et al., 2022). Wastewater from various industries, i.e., ink, paper, plastic industries, and textile, contains significant levels of hazardous and synthetic dyes (Ali et al., 2020; Gopalakrishnan et al., 2023). Raw dyes that didn’t attach to colored items make their way to water bodies in the range of 15–50 % (Ali et al., 2021). However, some industries treat their hazardous waste before dumping them into sewage systems; however, these treatments are either ineffective or result in more harmful metabolites, which have a substantial influence on the environment and ecosystem (Al-Tohamy et al., 2020). Researchers are striving to develop mechanical, physical, and chemical solutions to these issues, believing that non-toxic and safer food and feed resources require healthier and cleaner water.

Green synthesized Fe-NPs offer a clever method for treating industrial effluents and wastewater which are both cost-effective and efficient (Mondal et al., 2020; Ali et al., 2021). Using green synthesized Fe-NPs, there have been several studies on contaminates removal from wastewater, as shown in Table 2. In an experiment, transportation of Fe-NPs generated from green-tea extract using media i.e., aluminum-hydroxide coated sand and refined silica-sand was observed (Chrysochoou et al., 2012). Studies reported that, when green generated Fe-NPs were injected, the pH of the effluent dropped rapidly from 8.5 to 2. The existence of Fe^{3+} as residuary discharge in the solution, as well as hydrolysis processes, resulted in this occurrence. Instead of the presence of Fe^0 in the produced NPs, the redox potential increased from 150 to 550 mV (Chrysochoou et al., 2012). This action was seen as a result of polyphenol oxidation in green tea, which indicates that green synthesized Fe-NPs are transported through the medium. Patil and Chandrasekaran, (2020) used *Eucalyptus* leaves extract to biosynthesize Fe-NPs for the treatment of poultry breeding wastewater. The mean particle size of Fe-NPs generated from eucalyptus leaves extract was found to be lower than that of chemically synthesized Fe-NPs. After 21 days, the removal of chemical oxygen demand (COD), total phosphorus, and total nitrogen were determined to be 84.5, 30.4, and 71.7 %, respectively. Similarly, green synthesized Fe-NPs from Katong Laut (*Cynometra ramiflora* L.) leaves extract were significantly utilized for remediation of dye (Rhodamine B), with the help of Fenton-like catalytic process (Groiss et al., 2017). In addition, this procedure was shown to create the least amount of sludge, making it superior to other Fenton-catalyzed processes.

Recent studies highlighted that green synthesized Fe-NPs have significant potential for degradation of polycyclic-aromatic hydrocarbons i.e., phenanthrene and anthracene to 90 % at optimum pH (7) within 48 hours (Shanker et al., 2017; Mondal et al., 2020). Similarly, green synthesized Fe-NPs prepared from mango (*Mangifera indica* L.) leaves degraded the crude oil by 50 % (Al-Ruqeishi et al., 2016). Application of green synthesized Fe-NPs prepared from white oak (*Quercus alba* L.) leaves significantly degraded the amoxicillin (antibiotic) by 100 % in wastewater (Machado et al., 2017). Extracts of green-tea leaves synthesized Fe-NPs were used to remediate rifampicin (antibiotic) from an aqueous solution (Kumar et al., 2023). Similarly, extract of loose-leaf green-tea leaves synthesized Fe-NPs was used to remediate rifampicin

Table 2
Application of green synthesized Fe-nanoparticles for remediation of dyes, drug residues, and organic compounds from wastewater.

Contaminates	Initial conc.	NP source	NP type	Reaction time	Remediation efficiency %	References
Dyes						
Bromothymol blue	500 mg L^{-1}	*Camellia sinensis*	nZVI	20 min	83.3 %	Hoag et al. (2009)
Aqueous cationic and anionic dyes	50 mg L^{-1}	Green tea	Fe_3O_4 NPs	6 h	100 %	Shahwan et al. (2011)
Bromomethyl blue	500 mg L^{-1}	*Sorghum bicolor* bran	Fe NPs	30 min	90 %	Njagi et al. (2011)
Azo dyes	100 mg L^{-1}	*Eucalyptus tereticornis*	Fe-Polyphenol NPs		1.6 g dye/g NPs	Wang (2013)
Acid orange (Azo dues)	10.0 mg L^{-1}	*Vitis vinifera*	Fe_3O_4 NPs	180 min	80 %	Luo et al. (2014)
Bromothymol blue	100 mg L^{-1}	Tie Guanyin tea extract	nZVI	60 min	90 %	Xin et al. (2016)
Congo red	100 mg L^{-1}	*Punica granatum* leaves	FeO magnetic NPs	60 min	93 %	Prasad et al., (2017a), (2017b), (2017c), (2017d)
Methyl orange	100 mg L^{-1}	*Pisum sativum* peels	FeO magnetic NPs	60 min	96.2 %	Prasad et al., (2017a), (2017b), (2017c), (2017d)
Methyl orange	25 mg L^{-1}	*Cupressus sempervirens* leaves	nZVI	6 h	95.8 %	Ebrahiminezhad et al. (2017)
Malachite green	20 mg L^{-1}	*Moringa oleifera* leaves	Nickel-supported FeO-NPs	25 min	91.6 %	Prasad et al., (2017a), (2017b), (2017c), (2017d)
Methylene blue	3.5 mg L^{-1}	Green tea leaves	Fe_3O_4-NPs	16 min	95 %	Singh et al. (2017)
Acid black Acid brown	20 ppm	*Capsicum annuum* leaves	FeO/palladium nanocomposite	120 min	97 %	Khaghani and Ghanbari, (2017)
Methylene blue	20 ppm	*Cynometra ramiflora* fruit	FeO-NPs	110 min	100 %	Bishnoi et al. (2017)
Rhodamine B	0.28 mM	*Cynometra ramiflora* leaves	FeO-NPs	15 min	100 %	Groiss et al. (2017)
Blue 235 dye	10 mg L^{-1}	*Syzygium cumini* leaves		240 min	98.75 %	Natarajan and Ponnaiah, (2017)
Methylene blue	50.0 mg L^{-1}	Green tea extract	Fe-NPs	50 min	98.7 %,	Fierascu et al. (2018)
Malachite green	50 mg L^{-1}	*Oolong tea* leaves	Fe-NPs	60 min	75.5 %	Ying et al. (2022)
Methyl orange	10 mg L^{-1}	*Eucalyptus globulus* leaves	Fe-NPs	180 min	99.6 %	Ahmad et al. (2023)
Malachite green	50 mg L^{-1}	Green tea	Fe-NPs	60 min	82.47 %	Benković et al. (2023)
Azo dyes	100 mg L^{-1}	*Eucalyptus tereticornis, Melaleuca nesophila,* and *Rosemarinus officinalis*	Fe-Polyphenol NPs	200 min	100 %	Gupta et al. (2023)
Drug residues						
Ibuprofen	10 mg L^{-1}	*Vitis vinifera* marc, black tea leaves, *Vitis vinifera* leaves	nZVI	193 hours	50 %	Machado et al. (2013)
Ibuprofen	10 mg L^{-1}	*Vitis vinifera* marc, black tea leaves, *Vitis vinifera* leaves	nZVI	216 hours	55 %	Machado et al. (2013)
Ibuprofen	2.8 mg ibuprofen kg−1	*Vitis vinifera* marc, black tea leaves, *Vitis vinifera* leaves	nZVI	168 hours	65 %	Machado et al. (2013)
Ametryn	4.54 ppm	*Eucalyptus globulus* leaves	FeO-NPs	135 min	100 %	Sangami and Manu, (2017)
Propranolol	10 μg L^{-1}	Black tea	FeO-NPs	40 min	90 %	Ali et al. (2017)
Amoxicillin	10 mg L^{-1}	*Quercus alba* leaves	nZVI	95 min	100 %	Machado et al. (2017)
Rifampicin	50 mg L^{-1}	Loose-leaf green tea	Fe/Ni-NPs	40 min	94.3 %	Cheng and Wen, (2022)
Rifampicin	50 mg L^{-1}	Green tea leaves	Fe-NPs	120 min	91.6 %	Kumar et al. (2023)
Organic residues						
Heavy oil	0.2–0.8 g L^{-1} nanorods added to 1 L of oil	*Mangifera indica* leaves extract	Fe-NPs	60 min	50 %	Al-Ruqeishi et al. (2016)
4-nitrophenol	50 mg L^{-1}	*Withania coagulans* leaves	Fe_3O_4	1 min	100 %	Atarod et al. (2016)
Nitrobenzene	(v/v=1:2, 3 mL)	*Silybum marianum* L.	Fe-NPs	90 min	95 %	Sajadi et al. (2016)
PAHs	250 mg L^{-1}	*Sapindus mukorossi*	$[Fe(CN)_6]^{3-}$	48 hours.	80 %	Shanker et al. (2017)
Nitrate and phosphate from wastewater	Nitrate: 14.77 mg L^{-1} Phosphate: 23.50 mg L^{-1}	*Eichhornia crassipes, Lantana camara,* and *Mimosa pudica* leaves	Fe-NPs	24 hr	74.52 % of nitrate and 55.39 % of phosphate	Prabhakar et al. (2017)
Cyanation of Aldehydes	50 mg L^{-1}	*Euphorbia bungeiboiss* leaves	Fe_3O_4	120 min	93 %	Nasrollahzadeh et al. (2017)
Ipso-hydroxylation of boronic acid	50 mg L^{-1}	*Zanthoxylum rhetsa* fruit	Fe2O3@SiO2	120 min	98 %	Saikia et al. (2017)
COD, Total Nitrogen, and Phosphorus	COD = 677.25 mg L^{-1}, total N = 25.57 mg L^{-1}, and P = 10.55 mg L^{-1}	*Eucalyptus globulus* leaves	Fe-NPs	21 days	84.5 % for COD, 71.7 % for total N, 30.4 % and for total P	Patil and Chandrasekaran, (2020)
2,4-dichlorophenol	50 mg L^{-1}	*Euphorbia cochinchensis* leaves	FeO-NPs	120 min	64 %	Talha et al. (2022)
Phosphate	20 mg·L^{-1}	*Eucalyptus globulus* leaves	Fe-NPs	100 min	95 %	Kassem et al. (2022)

from an aqueous solution (Cheng and Wen, 2022). Hoag et al. (2009) and Njagi et al. (2011) used green tea extract and sorghum (*Sorghum bicolor* L.) bran extract respectively, to synthesize Fe-NPs, which they then used to catalyze H_2O_2 for bromomethyl blue dyes degradation in an aqueous solution. Extract of Java plum (*Syzygium cumini* L.) leaves synthesized Fe-NPs was used to remediate blue-235 dye from an aqueous solution (Natarajan and Ponnaiah, 2017). Shahwan et al. (2011) used green tea extract to synthesize Fe-NPs, which they then used to catalyze H_2O_2 for methylene orange and methylene blue dyes degradation in an aqueous solution. Similarly, Ahmad et al. (2023)

significantly degrade the methylene orange in an aqueous solution upto 99.6 % in 3 hours by utilizing Fe-NPs synthesized from eucalyptus (*Eucalyptus globulus* L.) leaves extract. Reductive degradation is typically used to remove organic pollutants like chlorinated chemicals. Hazardous chlorinated chemical i.e., 2,4-dichlorophenol was significantly degraded upto 64 % by the application of Fe-NPs synthesized from Chinese Croton (*Euphorbia cochinchensis* L.) leaves extract (Talha et al., 2022).

In another study, Rónavári et al. (2023), delved into the innovative realm of upgrading green NPs syntheses using plant waste extracts, aiming at economic and environmental benefits. Moreover, the feasibility of utilizing green tea, coffee arabica, and Virginia creeper waste residues was explored for Fe-NPs, assessing their recyclability and NPs generation efficiency. The findings of study revealed that through multiple extraction rounds, green tea and Virginia creeper residues proved reutilizable, unlike coffee arabica, which showed suitability only in the first extract. Furthermore, the synthesized Fe-NPs revealed their potential in degrading chlorinated volatile organic compounds, with impressive efficiency rates across green tea and Virginia creeper extracts. Fe-NPs can produce a thin coating of iron hydroxides on their surface when exposed to oxygen and water, forming a core-shell structural composition. The inner Fe^0 surface could operate like a powerful reduction agent, whereas the outside surface can adsorb pollutants in some cases (Fig. 3).

In short application of green synthesized Fe-NPs and its remarkable solutions have the potential to clean contaminates i.e., p-chlorophenol, nitro-aromatic compounds i.e., (nitroamines), 4-nitrophenol nitrobenzene, chlorinated natural residues i.e., chlorinated (atrazine and carbaryl pesticides, pentachlorophenol, polybrominated diphenylethers, deisopropylatrazine, polychlorinated biphenyls etc), nitrate, azo dyes, and nitroaromatics from wastewater before they are used in agricultural irrigation, degrading fertility of the soil, and reducing crop growth. The only issue is the potential toxicity of NPs to soil microbiota, plants, and farmers who are regularly touching and applying agricultural NPs products. Unfortunately, most researchers who researched green synthesized Fe-NPs did not include any *in vivo* or *in vitro* toxicity assessment in their research. So, more attention to the negative impacts of green synthesized Fe-NPs should be paid, ideally during the research stages, so that safer green synthesized nano-based solutions for the ecosystem and environment may be developed.

7.2. Remediation of heavy metals and metalloids

Owing to their permanence and toxicity in the ecosystem, the poisoning of soil and waters by heavy metals and metalloids is a serious environmental issue (Yong et al., 2010; Haider et al., 2021; Zulfiqar et al., 2023a). Heavy metals in the environment and agricultural soils because of fast industrialization, sewage sludge, large-scale chemical fertilizers application, farmyard manure, and air deposition (Tow et al., 2018; Song et al., 2019; Mehr et al., 2021; Zulfiqar et al., 2023b; Shaghaleh et al., 2024). Heavy metals and metalloids: antimony (Sb), chromium (Cr), copper (Cu), lead (Pb), zinc (Zn), nickel (Ni), mercury (Hg), molybdenum (Mo), arsenic (As), and cadmium (Cd) have contaminated more than 20 million hectares of land worldwide (Tow et al., 2018; Ahmed et al., 2021). Heavy metals and metalloids are able to infiltrate plant systems, leading to contamination of the food supply, which in turn poses a significant risk to both food quality and human health (Zheng et al., 2021; Shaghaleh et al., 2024). Green-synthesized Fe-NPs offer an eco-friendly and cost-effective approach that has proven highly effective in detoxifying soil and ecosystems contaminated by heavy metals, removing a wide range of toxic heavy metals (Fig. 3; Table 3). The Fe-NPs employ a multifaceted approach for heavy metal remediation (Komal et al., 2024). Firstly, they efficiently absorb and trap heavy metal species, effectively cleansing the environment. Secondly, they catalyze the transformation of hazardous ionic forms of heavy metals into stable, metallic states, immobilizing the contaminants and reducing their toxicity. Lastly, they act as catalysts, aiding chemical reactions that aid in detoxifying and stabilizing heavy metal pollutants (Mondal et al., 2020).

The preparation of colloidal nZVI through the utilization of green tea extract resulted in nanoparticles with an average particle size ranging from 5 to 10 nm, accompanied by a polyphenol coating that functioned as both a capping and reducing agent. This innovative approach proved highly efficient in the remediation of Cr(VI) from groundwater as it passed through porous soil beds (Mystrioti et al., 2014). Heavy metals are eliminated by surface adsorption and redox reaction process using green synthesized Fe-NPs (Ponder et al., 2000). The various oxidation states of iron are the key factor that controls the reactively Fe-NPs. Extract of Chinese croton (*Excoecaria cochinchinensis* L.) leaves synthesized Fe-NPs was used to remediate Cd from an aqueous solution (Muthukumaran et al., 2022). The chemical features of any metals, as

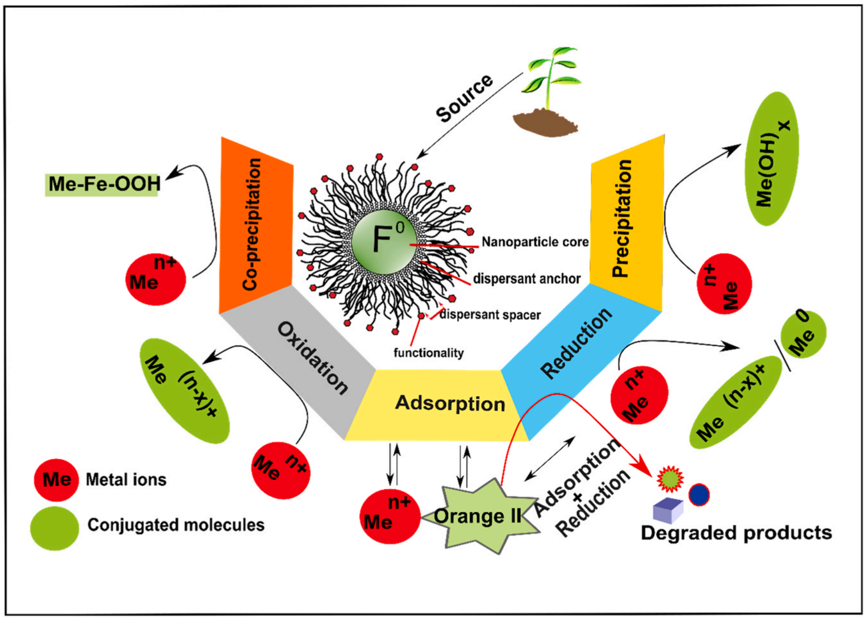

Fig. 3. Mechanistic representations for the decontamination of organic dyes, chlorinated complexes, and toxic trace-metals by iron-nanoparticles (Fe-NPs) with a core-shell structure. (Modified from Li and Zhang, 2007; Yang et al., 2019).

Table 3

Application of green synthesized Fe-nanoparticles for remediation of heavy metals contaminants.

Contaminates	Initial conc.	NP source	NP type	Reaction time	Remediation efficiency %	References
Lead (II)	16 mg L^{-1}	*Punica granatum*	Fe-NPs	30 min	99.9 %	Hajdu et al. (2012)
Chromium (VI)	100 mg L^{-1}	*Eucalyptus globulus*	nZVI	30 min	98.1 %	Madhavi et al. (2013)
Arsenic (III)	10 mg L^{-1}	Black tea	Fe-NPs	30 min	99 %	Tandon et al. (2013)
Arsenic (III), (V)	200 mg L^{-1}	*Mentha spicata*	Fe-NPs	30 min	100 %	Prasad et al. (2014)
Cadmium	5 mg L^{-1}	*Citrus reticulate* peel	FeO-NPs	90 mins	90 %	Ehrampoush et al., (2015)
Chromium	100 mg L^{-1}	*Citrus maxima*	Fe-NPs	90 mins	99.29 %	Wei et al. (2016)
Nickel	5 mg L^{-1}	Fatty acids in Olive oil	FeO-NPs	20 mins	72 %	Es'haghi et al. (2016)
Arsenic (V)	25 mg L^{-1}	*Eucalyptus globulus*	Fe-NPs	24 hrs	147 μg/g maximum adsorption capacity	Martínez-Cabanas et al. (2016)
Chromium (VI)	50 mg L^{-1}	*Syzygium jambos*, Oolong tea, *Aleurites moluccana*	Fe NPs	60 min	100 %	Xiao et al. (2016)
Chromium	300 mg L^{-1}	*Rosa damascene*, *Thymus vulgaris*, and *Urtica dioica*	Fe-NPs	25 mins	100 %	Fazlzadeh et al. (2017)
Chromium	50 mg L^{-1}	*Syzygium jambos* leaves	nZVI	90 mins	99.45 %	Xiao et al. (2017)
Lead	30 mg L^{-1}	*Murraya koenigii* leaves	FeO-NPs	80 mins	96 %	Prasad et al., (2017a), (2017b), (2017c), (2017d)
Chromium	100 mg L^{-1}	*Eichhornia crassipes* leaves	Fe-NPs	80 mins	89.9 %	Wei et al. (2017)
Chromium	100 mg L^{-1}	*Eichhornia crassipes* leaves	nZVI	90 mins	89.9 %	Wei et al. (2017)
Fluoride	6 mg L^{-1}	*Moringa oleifera* leaves	FeO-NPs	40 mins	1.40 mg g^{-1}	Silveira et al. (2017)
Nickel	50 mg L^{-1}	*Lantana camara* fruit	FeO-NPs	100 mins	99 %	Nithya et al. (2017)
Arsenate	57.1 mg g^{-1}	*Vaccinium corymbosum* leaves and shoots extract	Fe-NPs	2 hrs	76 %	Manquián-Cerda et al. (2017)
Nitrate	10–20 mg L^{-1}	*Moringa oleifera* seed and leaves	Fe-NPs	1 day	85 %	Katata-Seru et al. (2017)
Calcium and Cadmium	50 mg L^{-1}	*Cocos nucifera* husk extract	Fe-NPs	2 hrs	55 % Ca, and 40 % Cd	Sebastian et al. (2018)
Lead	50 mg L^{-1}	Green tea leaves	Fe-NPs	120 min	100 %	Lin et al. (2019)
Lead (II)	60 mg L^{-1}	*Punica granatum* rind	Fe_3O_4-NPs	120 min	~46.18 mg/g max adsorption capacity	Venkateswarlu et al. (2014)
Cadmium	10 mg L^{-1}	*Excoecaria cochinchinensis*	Fe-NPs	240 min	98.50	Muthukumaran et al., (2022)
Lead	50 mg L^{-1}	Loose-leaf green tea	Fe/Ni-NPs	90 min	87.5 %	Cheng and Wen, (2022)
Arsenic	100 mg L^{-1}	*Eucalyptus globulus*	Fe-NPs	24 hrs	27.7 %	Litter, (2022)
Chromium and copper	15 mg L^{-1}	*Eucalyptus globulus* leaves	nZVI	60 mins	58.9 % Cr and 33.0 % Cu	Dejen et al. (2023)
Chromium (VI)	40 g L^{-1}	*Eucalyptus globulus*	Fe-NPs	12 hrs	98.6 %.	Ifthikar et al. (2023)
Copper	10 mg L^{-1}	*Eucalyptus globulus*	Fe/Ni-NPs	10 min	60 %	Kumar et al. (2023)

well as the mechanisms of the reaction between metal and impurities, will vary depending on its oxidation state (Tang and Lo, 2013). The production of Fe-NPs through the use of extracts from rose apple, candlenut tree, and oolong-tea leaves demonstrated a remarkable capacity to remediate Cr(VI) in aqueous solutions, achieving up to 90 % removal within the first 5 minutes, primarily due to the high antioxidant properties of the Fe-NPs. However, complete removal required approximately 60 minutes, as indicated in a study by Xiao et al. (2016). The efficiency of Cr(VI) removal was notably influenced by several factors, such as the initial concentration of Cr(VI), the dosage of Fe-NPs, solution pH, and temperature. Keeping the concentration of Cr(VI) constant, an increase in Fe-NPs dosage led to an enhancement in removal rates, attributed to the greater availability of active sites (Xiao et al., 2017). Coconut palm (*Cocos nucifera* L.) husk extract to make Fe-NPs, which they used to adsorb Cd and calcium (Ca) in low concentrations. After 120 minutes, the elimination of Cd and Ca was confirmed to be greater than 40 and 50 %, respectively (Sebastian et al., 2018). The Fe-NPs derived from foliar extracts of highbush blueberry (*Vaccinium corymbosum* L.) were used to remediate arsenate from an aqueous solution (Manquián-Cerda et al., 2017). Mandarin orange (*Citrus reticulata* L.) peel extract Fe-NPs significantly reduced Cd contamination by 90 % at 4 pH (Ehrampoush et al., 2015) and Pb contamination by 96 % at 5 pH (Prasad et al., 2017a, 2017b, 2017c, 2017d). Fruit extract of lantana (*Lantana camara* L.) synthesized Fe-NPs was used to remediate Ni from an aqueous solution (Nithya et al., 2017). Extract of loose-leaf green-tea leaves synthesized Fe-NPs was used to remediate Pb from an aqueous solution (Cheng and Wen, 2022)

Various potential mechanisms for the efficient decontamination of inorganic pollutants using environmentally friendly synthesized Fe-NPs have been postulated in the literature, including processes such as precipitation, adsorption, complexation, and reduction (Ahmed et al., 2021). The most widely recognized method for removing HMs involves reduction, followed by adsorption. According to Li and Zhang (2007), in cases where trace-metal ions exhibit a more negative standard-redox potential (E^0) than or are similar to that of Fe^0 (-0.41 V), the decontamination process involving green-synthesized Fe-NPs is primarily governed by surface complexation and adsorption. However, when trace-metal ions possess significantly more positive E^0 values compared to Fe^0, precipitation and reduction of metal ions become the dominant mechanisms (Kumar et al., 2023). When metal cations have E^0 values somewhat more positive than Fe^0, both reduction and adsorption processes occur (Nithya et al., 2017; Ahmed et al., 2021). Other potential mechanisms include co-precipitation and Fe-hydroxide oxidation, as described by Sebastian et al. in 2018. In addition, bimetallic Fe-NPs and Fe-oxides are utilized to remove pollutants through catalytic degradation and adsorption (Nithya et al., 2017).

Nonetheless, significant constraints and areas of uncertainty need to be resolved in order to gain widespread acceptance of environmentally friendly synthesized Fe-NPs for the secure remediation of hazardous HMs. Therefore, it is imperative to conduct additional field studies to assess the safety, dependability, efficacy, environmental fate, inherent toxicity of Fe-NPs, and the long-term consequences of Fe-NPs on the presence and absorption of trace metals in contaminated soils. In order to fully exploit the potential benefits of this technology in the environmental domain, forthcoming research should prioritize optimizing the dosage and ensuring the safe and targeted deployment of Fe-NPs.

8. Adverse impacts of Fe-NPs on the environment

Despite their numerous environmental benefits, Fe-NPs pose a significant threat to the environment. Industrial wastes and wastewater may be improperly managed, posing distinct environmental risks in soil and groundwater (Mehr et al., 2021). Synthesized Fe-NPs, on the other hand, can be moved from one medium to another for specialized remedial goals. Fe-NPs efficiency and dose evaluation are crucial for human health and environmental protection (Tripathi et al., 2017). NPs toxicity is mostly determined by their kind, bind efficacy, and solubility (Kalwani et al., 2022). The electrostatic interaction between Fe-NPs and cytoplasmic content has been reported to help NPs infiltrate the cell wall through sensitive regions (Aziz et al., 2016). Fe-NPs can interact with a diverse range of soil-dwelling organisms, including essential macrofauna such as earthworms, mites, springtails, nematodes, and ants. These soil organisms extensively interact with the microflora and play a vital role in regulating soil health and ecosystem functioning (Kalwani et al., 2022). The potential impacts of Fe-NPs on these soil biotas are an important consideration that requires further investigation. Among other Fe-NPs, zero-valent Fe-NPs (nZVI) is thought to be the most reactive (Mondal et al., 2020). It was discovered that when nZVI were used to address groundwater contamination, they were transported porous soil and transformed when they interacted with contaminates and the exposed environment (Ali et al., 2021). The harmful effects of Fe-NPs on microbes and soil fauna have an impact on the ecosystem, either indirectly or directly. The induced stress of nano-sized Fe-NPs is harmful to soil microbes and results in a variation in microbial density and diversity (Sacca et al., 2014). Due to their unique surface energy, production process, morphological traits, self-assembly, and particle size, Fe-NPs interact significantly with enzymes of livings organisms and metals in the environment. In some studies utilization of hazardous compounds i.e., hydrazine as capping agents in biosynthesized Fe-NPs makes it a mildly toxic agent for the environment (Mondal et al., 2020). Antisari et al. (2013) and Fajardo et al. (2013) reported the harmful effects of synthesized Fe-NPs on microbial biomass. Similarly, the cytotoxic effects of various Fe-oxides, i.e., nZVI, maghemite, and magnetite were investigated against gram-negative *Escherichia coli* and observed that nZVI showed a stronger cytotoxic impact comparison to other Fe-oxide NPs (Auffan et al., 2008). The development of oxidative stress by reactive-oxygen species causes the cytotoxic impact on microbes i.e., green algae (*Chlorella vulgaris* L.) (Barhoumi and Dewez, 2013). Various properties of Fe-NPs, including agglomeration, sedimentation rate, and 'redox' activity have been discovered to cause morphological alterations in rodent microglia and neuron cells. Due to the restricted exposure of the Fe-NPs to the cells, encapsulating surface-modified nZVI with poly-aspartate resulted in decreased toxicity (Phenrat et al., 2009).

The term nano-phytotoxicity is frequently used to describe the interaction between NPs and plants, as well as their potential negative impacts on physiology, genetics, and biochemical properties of plants (Ali et al., 2021). Uptake, transportation, and accumulation of Fe-NPs are three factors that are critically important in nano-particles-associated phytotoxicity (Javed et al., 2021). The introduction of nanoparticles into the plant-soil system is accounted for by two exposure routes (Li et al., 2014). The usage of sewage sludge in agriculture activities, which contain primarily nanoparticles i.e., silveroxide (AgO), siliconoxide (SiO_2), titanium oxide (TiO_2), zinc oxide (ZnO), iron oxide (FeO) is the principal entry route (Javed et al., 2021). The alternative method involves nano-based agrochemical treatments, such as nano-pesticides and nanofertilizers, which exposed plants to NPs directly (Dev et al., 2017). As a result, NPs interact with and target plants incessantly, limiting their growth and modifying their biochemical, genetic, and physiological characteristics (Javed et al., 2021). Certain parameters, i.e., exposure period, NPs shape and size, and plant type, significantly influence the translocation of NPs to the aerial portions of plants (Mondal et al., 2020; Kalwani et al., 2022). Through the apoplastic pathway, NPs in the rhizosphere can easily penetrate the epidermis and cortex section of plant cells. The formation of ROS in plants has been explained properly by nano-phytotoxicity, as shown in Fig. 4. Organelles with the highest oxidizing metabolic processes and rate of electron flow, i.e., peroxisomes, mitochondria, and chloroplast are found in plants and are hence the primary generators of cellular ROS (Saxena et al., 2021). Various biotic and abiotic stimuli increase ROS generation, whereas failure of the ROS-metabolizing pathway causes oxidative stress, which causes cellular homeostasis, organelle disruption, and leads to cell death (Dev et al., 2017). Various studies have been conducted to develop and change the synthesis of green Fe-NPs, which have been determined to be less hazardous and environmentally benign for engineered-Fe-NPs (Shakibaie et al., 2013). Experiments have revealed that capping or stabilizing compounds i.e., polyvinylpyrrolidone coated Fe-NPs (Baumann et al., 2014) don't diminish the toxicity of Fe-oxide NPs (Mondal et al., 2020). Siji et al. (2017) observed that application of green-synthesized iron nanoparticles at 50 mg L^{-1} in pearl millet (*Pennisetum glaucum* L.) significantly improved the plant height, plant root length, plant biomass, soluble sugar contents, and chlorophyll a of the plant by 23.08, 65.52, 40.54, 60.00, and 60.75 % respectively higher as compared to control. Likewise, in another experiment, it was reported that application of green-synthesized iron nanoparticles as nano-fertilizers at 20 mg L^{-1} in pumpkin (*Cucurbita pepo* L.) field significantly improved the photosynthesis pigments contents, plant fresh and dry biomass, leaf area, and overall yield of pumpkin by 39.52, 41.22, 21.68, 37.36, and 22.26 % respectively greater as compared with control (Shebl et al., 2019). Despite the potential advantages of green-synthesized Fe-NPs, there is limited information available regarding their environmental toxicity. Although some studies indicate that these nanoparticles can be compatible with living organisms and ecosystems, more research is necessary to comprehensively grasp and minimize any adverse effects. This entails refining the synthesis of green Fe-NPs to make them safer and environmentally friendly.

9. Prospective and Conclusion

The current review collated pertinent literature and examined recent advancements in the green synthesis of Fe-NPs, derived from plant-based resources. The burgeoning interest in plant-based materials within the realm of green nanotechnology is evident from recent literature and ongoing research. Synthesizing Fe-NPs through plant-based resources offers a non-toxic, clean, long-term, environmentally benign, and cost-effective approach. This promising avenue not only simplifies scalability but also addresses potentially hazardous environmental and economic concerns. We have examined various key processes: characterization of Fe-NPs using various techniques, highlighting their application in the remediation of wastewater, organic residues, dyes, and inorganic contaminants. Despite the promising progress, there remains much work to be done to further advance this field. Researchers should explore the utilization of more affordable and discarded plant-based materials beyond those commonly consumed by humans, such as agricultural waste or invasive plant species, as precursors for Fe-NPs synthesis. Optimizing the experimental parameters, including extraction temperature, reaction time, and plant biomass to solvent ratios, can enhance the effectiveness and efficiency of the green synthesis process. Additionally, gaining better control over the molecular architecture, morphology, and density of the naturally synthesized Fe-NPs is crucial, which can be achieved by employing specialized analytical techniques to identify the specific biomolecules and compounds produced during the plant-mediated synthesis.

Furthermore, it is essential to investigate the pollutant removal mechanisms of the green-synthesized Fe-NPs in depth and address the paucity of studies on their potential adverse effects in water and soil environments. Focusing on understanding the subsurface mechanistic pathways, transport, and fate of these nanoparticles will be crucial in

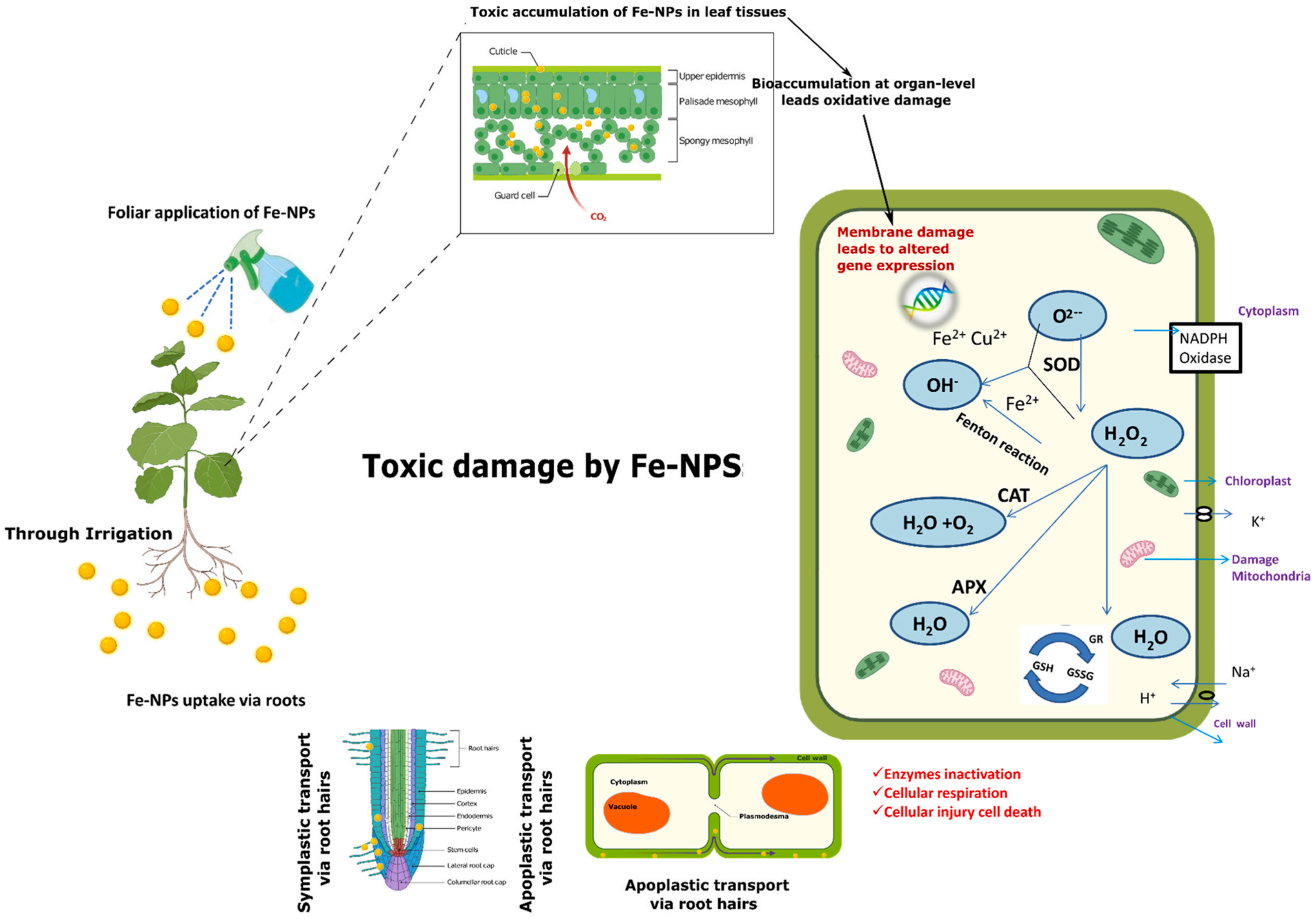

Fig. 4. Iron-nanoparticles (Fe-NPs) induced oxidative stress in plant species. Under normal circumstances, cellular respiration generates $O_2.^-$, which is subsequently converted into hydrogen peroxide (H_2O_2) through the enzymatic action of superoxide dismutase (SOD). The H_2O_2 molecule is then transformed into O_2 and H_2O through a coordinated series of enzymatic reactions involving ascorbate peroxidase (APX), catalase (CAT), glutathione reductase (GR), and glutathione peroxidase (GPX). The toxicity of Fe-NPs has been observed to disrupt this process, leading to an increased accumulation of $O_2.^-$ and H_2O_2 within the cellular environment. The excessive presence of these reactive oxygen species (ROS) remains incompletely neutralized by the cellular antioxidants, resulting in the generation of highly toxic hydroxyl radicals (HO.) through Fenton reactions. These HO. radicals are recognized as the most damaging ROS, capable of causing lipid peroxidation, enzyme inactivation, and cell death.

mitigating any environmental toxicological consequences. By addressing these key priorities through a multidisciplinary approach, researchers can pave the way for more effective and sustainable environmental remediation strategies utilizing the green-synthesized Fe-NPs. Future research should also focus on developing predictive models to simulate the behaviour and performance of green-synthesized Fe-NPs in various environmental scenarios. Computational modelling techniques, such as molecular dynamics simulations and finite element analysis, can provide valuable insights into the interactions between Fe-NPs and environmental matrices, the transport and fate of these nanoparticles, and their efficacy in contaminant removal. By integrating experimental data with computational modeling, researchers can optimize the design and application of green-synthesized Fe-NPs, leading to more effective and sustainable environmental remediation strategies.

In conclusion, synthesizing Fe-NPs using plant extracts offers a promising and eco-friendly approach with a wide range of applications in environmental remediation. Using biomolecules from plants for Fe-NPs synthesis offers advantages such as simplicity, rapidity, energy efficiency, sustainability, and cost-effectiveness. These factors collectively suggest the feasibility of large-scale production of green-synthesized Fe-NPs. However, it is essential to consider the feasibility of using NPs in mass production. While the green synthesis route holds the potential for scalability, challenges related to standardization, cost-effectiveness on a larger scale, and environmental impacts must be carefully evaluated. Future research directions could focus on optimizing production processes, addressing scalability challenges, and conducting comprehensive life cycle assessments to ensure the sustainable and responsible use of Fe-NPs in mass production scenarios. This review serves as a comprehensive resource for readers interested in exploring the green synthesis of Fe-NPs and their role in addressing environmental challenges.

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CRediT authorship contribution statement

Usman Zulfiqar: Methodology, Writing – original draft. **Fasih Ullah Haider:** Conceptualization, Data curation, Visualization, Writing – original draft. **Jean Wan Hong Yong:** Resources, Writing – review & editing. **Yuelin Li:** Project administration, Resources, Supervision, Writing – review & editing. **Saddam Hussain:** Writing – review & editing. **Noor ul Ain:** Data curation, Formal analysis, Methodology, Software. **Mukkaram Ejaz:** Methodology, Validation, Writing – review

& editing. **Muhammad Faisal Maqsood:** Data curation, Formal analysis, Methodology.

Declaration of Competing Interest

The authors declare that there is no conflict of interest either financially or otherwise. We further declare that all the authors have read this manuscript and agreed to its submission in current form

Data Availability

Data will be made available on request.

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