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Iron and Iron Oxide Nanoparticles for Environmental Remediation: Fenton-like Dye Degradation and Arsenic/Heavy-Metal Removal

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Abstract

Iron and iron oxide nanoparticles (Fe NPs, nanoscale zero-valent iron/NZVI, magnetite Fe_3O_4, maghemite/hematite Fe_2O_3) play a key role in water and soil remediation made possible by nanotechnology because iron is abundant, affordable, non-toxic at environmentally relevant doses, redox-active across multiple oxidation states, and, in its zero-valent form, both a strong reductant and an efficient adsorbent once partially oxidised. The use of these nanomaterials as heterogeneous Fenton-like catalysts for the oxidative degradation of synthetic dyes and as adsorbents and reductants for arsenic and other heavy metals (cadmium, lead, chromium, nickel, copper, zinc, and selenium) in contaminated water and soil are two of the most well-documented environmental applications of these materials. Green, plant-extract-mediated synthesis methods, which substitute plant polyphenols for dangerous reducing agents like sodium borohydride and have been demonstrated time and time again to produce catalytically superior, better-dispersed, and more environmentally friendly nanoparticles than their chemically synthesised counterparts, are given special attention. Evidence gathered from plant-derived systems such as green tea, olive leaf, jackfruit peel, clove, coffee, Duranta erecta, Eucalyptus globulus, and others shows that heavy-metal and arsenic removal efficiencies in several nanoscale zero-valent iron systems exceed 99 percent under optimal pH and dosage conditions, and dye removal efficiencies frequently exceed 80–95 percent within tens of minutes. The underlying Fenton and adsorption mechanisms, the effects of pH, dose, temperature, and competing ions on performance, the unresolved issues of nanoparticle aggregation, reusability, and the necessity of validation at the pilot and field scales outside of laboratory batch studies are all covered in the review.

1. Introduction

One of the most urgent environmental and public health issues facing the globe today is water pollution caused by synthetic colours and hazardous inorganic species, most notably arsenic. Large amounts of chromophoric, frequently carcinogenic or endocrine-disrupting dye effluent are released by the textile, tannery, paper, and dye manufacturing industries, and tens of millions of people's drinking water supplies are negatively impacted by anthropogenic and naturally occurring

arsenic contamination of groundwater, particularly in South and Southeast Asia. Coagulation-flocculation, activated carbon adsorption, ion exchange, membrane filtration, and biological treatment are examples of conventional remediation technologies that work well in many situations but can be expensive, produce secondary waste, or perform poorly at the trace concentrations necessary for drinking water standards. Because they combine a very high surface-area-to-volume ratio with genuine redox reactivity, nanoscale iron and iron oxide materials have become an exceptionally versatile remediation platform over the past 20 years. Zero-valent iron (Fe^0) can directly reduce and immobilise many oxidised contaminants, and the iron oxide corrosion layer that invariably forms on its surface provides abundant, high-affinity adsorption sites for oxyanions like arsenate and divalent heavy-metal cations.

The discovery that iron nanoparticles made from plant extracts, as opposed to borohydride or other synthetic reductants, are not only a more environmentally friendly option but also exhibit superior catalytic and adsorptive properties in multiple head-to-head studies is a second significant factor driving interest in this material class. This finding is typically attributed to the polyphenol capping layer that green synthesis leaves on the particle surface, which both prevents aggregation and actively contributes to radical generation during Fenton-like catalysis. This review synthesises the literature on two of the best-studied environmental applications of iron/iron oxide nanoparticles, Fenton-like dye degradation and arsenic/heavy-metal removal, with particular emphasis on green-synthesis routes and the plant sources that have been used to produce them.

2. Synthesis Routes for Iron and Iron Oxide Nanoparticles

2.1 Conventional chemical and physical routes

The most popular laboratory method for creating zero-valent iron nanoparticles is still chemical reduction of ferrous or ferric salts using sodium borohydride, which results in a core-shell structure with a metallic iron core and a thin native iron-oxide shell. The conventional method for producing magnetite (Fe_3O_4) is the co-precipitation of Fe^{2+}/Fe^{3+} salts in an alkaline environment. However, sol-gel, microemulsion, thermal decomposition, and electrochemical techniques provide more precise control over size and crystallinity at the expense of increased complexity, energy input, and, in many cases, the use of organic solvents or surfactants that present disposal issues.

2.2 Green, plant-extract-mediated synthesis

The green method involves adding a plant extract straight to a solution of ferric or ferrous salt (usually $FeCl_3$ or $FeSO_4$); polyphenols and other reducing biomolecules in the extract reduce the

iron ions while also capping and stabilizing the resulting nanoparticles. Because atmospheric oxygen and the extract's own oxidizing conditions favor partial oxidation during synthesis, the resulting nanoparticles usually form as amorphous or poorly crystalline iron oxide/oxyhydroxide rather than pure zero-valent iron. Green tea extract is the most extensively studied reductant in this context and has repeatedly been shown to produce Fe NPs that outperform borohydride-reduced particles in Fenton-like dye degradation, an effect attributed to the residual polyphenol coating acting as an electron shuttle and preventing the aggregation that otherwise deactivates the catalyst surface. Beyond green tea, olive leaf, jackfruit (Artocarpus heterophyllus) peel, clove, green coffee, Duranta erecta leaf, Eucalyptus globulus leaf, and a variety of fruit and vegetable wastes (banana, pomegranate, opuntia cactus pad, orange, potato, and onion) have all been used successfully, demonstrating that the underlying chemistry, phenolic reduction and capping, is widely transferable across plant sources even though the particular dominant reducing molecule varies.

3. Characterisation of Iron/Iron Oxide Nanoparticles

A typical characterization suite is used to confirm the production and structure of nanoparticles: X-ray diffraction (XRD) to identify zero-valent iron, magnetite, maghemite, and hematite phases and determine crystallite size; UV-Vis spectroscopy to identify the distinctive wide absorption linked to iron oxide/oxyhydroxide production; Energy-dispersive X-ray spectroscopy (EDX) to confirm elemental composition; Fourier-transform infrared spectroscopy (FTIR) to identify the phytochemical functional groups (hydroxyl, carbonyl, and carboxyl) responsible for reduction and capping; scanning and transmission electron microscopy (SEM/TEM) to visualize particle morphology and size distribution; and, when magnetic behavior is of interest, vibrating-sample or superconducting-quantum-interference-device magnetometry to measure saturation magnetization. The percentage of the particle that stays in the zero-valent state versus the oxide corrosion layer has also been determined using Mossbauer spectroscopy in a number of fundamental nanoscale zero-valent iron studies. This distinction is mechanistically significant because it establishes whether reduction, adsorption, or both processes predominate contaminant removal.

4. Fenton and Fenton-like Mechanisms

Through a series of hydrogen abstraction and addition reactions, the classical Fenton reaction combines dissolved Fe^{2+} with hydrogen peroxide to produce hydroxyl radicals (OH), one of the

most potent oxidants in aqueous chemistry that can non-selectively mineralize organic dye molecules. A restricted effective pH range (usually pH 2-4), the requirement to remove dissolved iron sludge during treatment, and constant reagent use are the main constraints on homogeneous Fenton chemistry. These limitations are addressed by heterogeneous, or Fenton-like, catalysis using solid iron oxide nanoparticles: the surface Fe (II)/Fe (III) redox cycling on the nanoparticle continues to activate hydrogen peroxide into hydroxyl radicals, but the catalyst itself can be recovered (especially when magnetic) and reused. Additionally, it has been demonstrated that the surface phenolic capping layer left by green synthesis broadens the effective pH range and slows catalyst deactivation because these coordinating ligands help maintain a locally acidic microenvironment at the particle surface and facilitate electron transfer between Fe (III) and Fe (II) states. With reported activation energies in the tens of kJ/mol range, kinetic analyzes from several research on green iron nanoparticles generally match pseudo-first-order models, suggesting a surface-mediated catalytic process that is somewhat temperature-sensitive rather than straightforward bulk diffusion control.

5. Fenton-like Dye Degradation: Comparative Evidence

Representative green-synthesised iron/iron oxide nanoparticle systems assessed for Fenton-like dye degradation are summarized in Table 1.

Green Reductant	Nanoparticle System	Target Dye(s)	Reported Performance	Source (Year)
Green tea polyphenols	Fe NPs (oxide/oxyhydroxide-rich)	Methylene blue, methyl orange	Outperformed borohydride-reduced Fe NPs; faster and more extensive dye removal as Fenton-like catalyst.	Hoag et al.-type study, ~2009
Green tea polyphenols	Fe NPs	Mixed azo and anthraquinone dyes	>90% decolourisation in 20 min at 70^0C with 0.53 ppm nanoparticle dose.	Truskewycz et al., 2016
Unspecified plant leaf	Fe NPs	Fuchsin Basic and related azo dyes	87.5% removal within first 20 min at 318 K; fits pseudo-first-order kinetics, Ea = 41.6	Yuan et al., 2020

extract (DL)			kJ/mol; catalyst stable over four weeks.	
Artocarpus heterophyllus peel extract	Fe NPs	Fuchsin Basic dye	Effective heterogeneous Fenton-like degradation attributed to peel-derived phenolics.	Jackfruit peel Fe NP study, 2020
Olive leaf extract	Fe_2O_3 NPs	Methyl orange, methyl red, Congo red, chlorpyrifos	Up to ~97% methyl orange removal reported in comparable olive-leaf iron oxide systems; methyl red degradation ~34% and chlorpyrifos ~27% under light after 120 min in another olive-leaf batch.	Olive leaf iron oxide study, 2015
Mixed green synthesis routes (various plant extracts)	Fe NPs / Fe_2O_3 NPs	Monochlorobenzene, mixed dyes	81% dye degradation over 180 min Fenton-like reaction; COD removal lower than colour removal, indicating partial mineralisation.	Green iron NP environmental review, 2017

There are a number of recurring conclusions from these investigations. In comparison to homogeneous Fenton treatment and many traditional adsorption techniques, green-synthesised iron nanoparticles often exhibit excellent dye-removal effectiveness, often 80 percent or more, after a brief contact period of 20 to 60 minutes. Elevated temperature, higher hydrogen peroxide dosage (up to an optimum beyond which radical scavenging by excess peroxide reduces efficiency), and acidic to near-neutral pH all improve removal, mirroring the pH dependence of homogeneous Fenton chemistry but over a somewhat broader effective range due to the buffering

and stabilizing effect of the plant-derived surface coating. Reaction rate and extent are consistently reported to follow pseudo-first-order kinetics. Additionally, a number of studies show that green-synthesised catalysts maintain activity over several weeks of reuse cycles with little loss of morphology or catalytic performance. This is a practically significant finding because catalyst recyclability is one of the main economic factors in scaling Fenton-like treatment.

6. Arsenic Removal by Nanoscale Zero-Valent Iron

Given the extent of groundwater exposure to arsenic worldwide, nanoscale zero-valent iron has been explored for arsenic cleanup more thoroughly than possibly any other use of nano-iron. Freshly prepared NZVI, initially consisting of a substantial zero-valent iron core with a native oxide shell, corrodes gradually in aqueous solution to form magnetite and maghemite, and ultimately lepidocrocite, over a period of weeks to months. This removal mechanism is now well established from foundational studies using electron microscopy, X-ray diffraction, and Mossbauer spectroscopy; Then, rather than via bulk reduction, arsenite (As (III)) and arsenate (As (V)) are eliminated mostly by inner-sphere surface complexation onto this iron oxide corrosion layer, but some As (V)-to-As (III) reduction at the metallic core has also been reported. Adsorption kinetics are usually fast, taking place in minutes, and they follow a pseudo-first-order rate law. Depending on the concentration of NZVI and the speciation of arsenic, reported measured rate constants range from 0.02 to 1.3 per minute.

7. Comparative Evidence: Arsenic and Heavy-Metal Removal

Representative results for the removal of arsenic and heavy metals utilizing iron/iron oxide nanoparticle systems are compiled in Table 2, which includes both more current green-synthesised, plant-supported versions and traditional nanoscale zero-valent iron experiments.

Target Contaminant	Iron System	Matrix	Reported Performance	Source (Year)
As (III)	Nanoscale zero-valent iron (NZVI)	Groundwater (synthetic)	Rapid pseudo-first-order adsorption; maximum Freundlich capacity ~3.5 mg As (III)/g NZVI; inner-sphere surface complexation confirmed.	Kanel et al., 2005

As (V)	NZVI colloidal reactive barrier	Groundwater	>90% of nanoparticles under 30 nm; inner-sphere complexation; competing anions (bicarbonate, silicate, phosphate) reduce efficiency.	Kanel et al., 2006
As (III) and As(V)	NZVI	Groundwater (real and simulated)	Removal efficiency >99.9% for both species at 100 micro g/L initial concentration; spontaneous, endothermic chemisorption.	NZVI simultaneous as study, 2021
As (V)	NZVI supported on activated carbon	Simulated and raw groundwater	>=99.9% removal at 4.5 g/L dose; phosphate and silicate markedly inhibit kinetics; intraparticle diffusion rate-limiting.	NZVI/AC arsenic study, 2018
As (III)	Chlorella vulgaris-supported NZVI	Contaminated water	99.11% removal at pH 7; pseudo-second-order kinetics; Langmuir maximum capacity 34.11 mg/g; partial reusability over five cycles.	Algae-supported NZVI study, 2023
As	Bentonite-supported NZVI	Contaminated soil and water	Enhanced dispersion and reduced agglomeration versus bare NZVI; improved	Bentonite NZVI arsenic study, 2023

			isotherm/kinetic fit with non-linear regression.	
Cd (II) and Ni (II)	Clove- and green-coffee-derived Fe_2O_3/Fe_3O_4 NPs	Aqueous/industrial wastewater	Effective Cd^{2+} removal even in presence of competing Cu^{2+}, Zn^{2+}, Fe^{2+} ions; magnetite dominant with clove extract, magnetite+hematite with coffee extract.	Clove/coffee IONP study, 2023
Cd (II)	Tangerine-peel-derived Fe_2O_3 NPs	Aqueous solution	Effective adsorption of low-level cadmium below the threshold where conventional lime/alum precipitation becomes ineffective.	Tangerine peel IONP study, 2015
Cd, Cr, Pb	Duranta erecta leaf-derived Fe_3O_4 NPs / chitosan nanocomposite	Drinking water	Adsorption capacities of 74.4, 76.0 and 75.2 mg/g for Cd, Cr and Pb respectively; validated on real municipal and hand-pump water.	Duranta erecta IONP study, 2022
Cr, Cu, Pb, Se, Zn	Fruit/vegetable-waste-derived magnetic Fe NPs	Aqueous solution	Multi-metal removal demonstrated using banana, pomegranate, opuntia, orange, potato and onion extract-derived Fe NPs; -OH groups	Multi-waste magnetic Fe NP study, 2023

			identified as key binding sites.	
Cr, Cd (soil)	Eucalyptus globulus-derived Fe oxide NPs	Agricultural soil	Solvent choice during extraction significantly altered reduction efficiency and magnetic response, in turn affecting chromium and cadmium removal from soil.	Eucalyptus globulus soil study, 2022
Pb, Ni, Cd	Green CuO NPs (comparator system)	Contaminated water	Plant-extract-capped metal-oxide nanoparticles confirmed as viable, non-iron comparator adsorbents for the same heavy-metal suite.	Green CuO NP study, 2021

Two broad conclusions can be drawn from this evidence base. First, for both arsenic oxyanions and a variety of divalent heavy-metal cations (Cd, Pb, Cr, Ni, Cu, Zn, and Se), iron-based nanomaterials achieve very high removal efficiencies often exceeding 90–99 percent under ideal laboratory conditions. This is indicative of the adaptability of the underlying surface-complexation and, for certain metals, co-precipitation or reductive-immobilization mechanisms. Second, green-synthesised, plant-capped iron oxide nanoparticles offer the practical benefits of lower production costs, decreased secondary toxicity, and, when fruit and vegetable waste is used as the plant source, a true circular economy pathway for otherwise discarded biomass. They also perform competitively with, and in several documented cases surpass, conventionally synthesized nanoscale zero-valent iron.

8. Factors Governing Remediation Performance

The removal of cationic heavy metals is typically favored at circumneutral to mildly alkaline pH, while Fenton-like dye degradation and arsenate adsorption frequently perform best under mildly acidic to neutral conditions. Solution pH is consistently found to be the single most influential

operating variable, controlling both the surface charge of the iron oxide nanoparticle and the speciation of the target contaminant. The availability of surface reactive sites in relation to the pollutant load is determined by the interaction between nanoparticle dosage and contaminant concentration; unless the dose is raised proportionately, removal effectiveness usually decreases as the initial contaminant concentration increases. Because natural groundwater and industrial effluent rarely contain a single contaminant in isolation, competing ions, especially phosphate, bicarbonate, and silicate for arsenic systems and competing divalent cations for heavy-metal adsorption, measurably reduce removal efficiency by occupying or blocking surface binding sites. While prolonged aging of zero-valent iron nanoparticles in water gradually transforms the reactive metallic core into a less reactive, but still adsorptive, oxide shell a process that controls the material's practical working lifetime in field applications temperature generally increases both Fenton-like catalytic rates and adsorption kinetics, consistent with an activated, surface-mediated process.

9. Stability, Reusability and Environmental Safety

Due to the steric and electrostatic stabilization provided by the remaining plant-derived capping layer, green-synthesised iron/iron oxide nanoparticles are frequently said to have better colloidal stability and resistance to aggregation than their bare, chemically synthesized counterparts. While magnetically responsive systems (Fe_3O_4-based) provide simple post-treatment recovery using an external magnetic field, simplifying both reuse and the prevention of secondary nanoparticle contamination in treated water, several dye-degradation studies report sustained catalytic activity across multiple reuse cycles and storage periods of several weeks. A thorough ecotoxicological evaluation of nanoparticle-laden residuals, especially after Fenton-like treatment where partial dye mineralization by-products may remain, is still an area that needs more research. However, from an environmental-safety standpoint, iron is generally considered to be low-toxicity relative to many alternative nanomaterial adsorbents, and several green-synthesis studies have also reported antimicrobial co-benefits of the resulting nanoparticles.

10. Challenges and Future Directions

Notwithstanding the strong laboratory-scale evidence reviewed here, several challenges must be resolved before green iron/iron oxide nanoparticle remediation technologies can be deployed at scale. Validation utilizing actual, multi-contaminant industrial effluent and groundwater, as well as at pilot or field size, is still very rare. The majority of published research are carried out as batch

experiments using synthetic, single-contaminant solutions at laboratory bench scale. Standardizing extraction protocols (solvent, concentration, drying method) across the various plant sources used in the literature would significantly improve reproducibility and cross-study comparability. The mechanistic contribution of the plant-derived capping layer to catalytic and adsorptive performance is typically inferred from comparative studies rather than directly resolved at the molecular level. The economic viability of obtaining and processing plant biomass, especially food-industry peel and seed waste, at the volumes needed for full-scale water-treatment application, as well as the long-term aging behavior, the fate of the organic capping layer during extended field deployment, and the ultimate environmental fate of the iron oxide residual after contaminant removal, all call for more research.

11. Conclusion

One of the most adaptable and proven nanomaterial platforms for environmental remediation is iron and iron oxide nanoparticles, whether they are made by traditional chemical reduction or by the increasingly popular green, plant-extract-mediated synthesis. As nanoscale zero-valent iron or iron oxide adsorbents, they achieve comparable high removal efficiencies for arsenic and a wide range of heavy metals through well-characterized surface-complexation and, in certain cases, reductive-immobilization mechanisms. As heterogeneous Fenton-like catalysts, they achieve rapid, high-efficiency degradation of synthetic dyes across a range of plant-derived formulations. Green synthesis, which offers a less expensive, less harmful, and more sustainable production method, often meets or surpasses the performance of conventionally synthesized nanoparticles utilizing plant extracts, from green tea and olive leaf to fruit and vegetable processing waste. Future research combining standardized green-synthesis protocols, mechanistic surface characterization, and pilot-scale field trials is well positioned to close the gap between promising laboratory-batch performance and validated, field-scale, multi-contaminant deployment, which is the main obstacle to widespread application.

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