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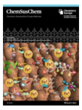

Sustainable Synthesis of Nanoscale Zerovalent Iron Particles for Environmental Remediation

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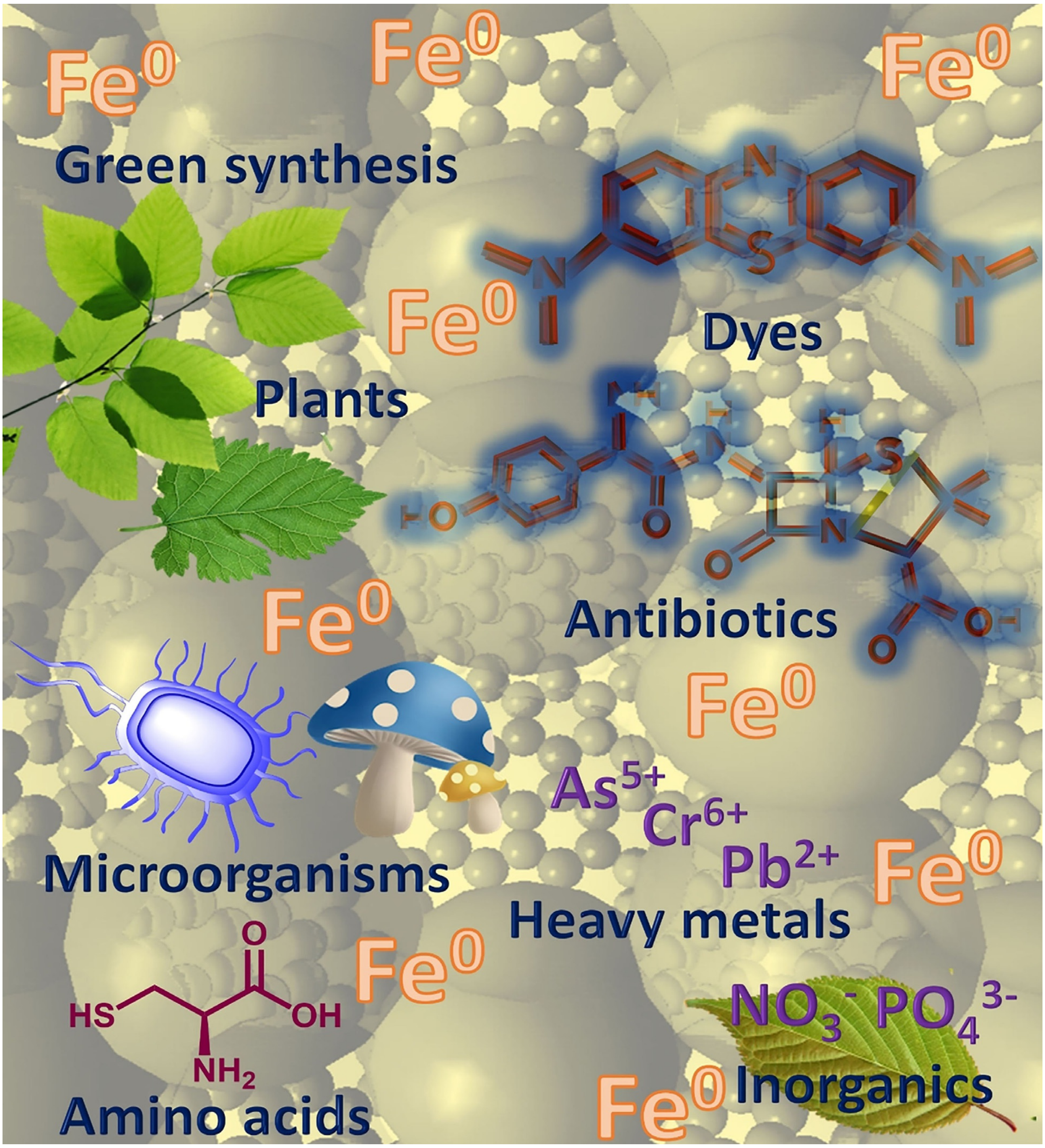

Nanoscale zerovalent iron (nZVI) particles represent an important material for diverse environmental applications because of their exceptional electron-donating properties, which can be exploited for applications such as reduction, catalysis, adsorption, and degradation of a broad range of pollutants. The synthesis and assembly of nZVI by using biological and natural sustainable resources is an attractive option for alleviating environmental contamination worldwide. In this Review, various green synthesis pathways for generating nZVI particles are summarized and compared with conventional chemical and physical methods. In addition to describing the latest environmentally benign methods for the synthesis of nZVI, their properties and interactions with diverse biomolecules are discussed, especially in the context of environmental remediation and catalysis. Future prospects in the field are also considered.

1. Introduction

Sustainable development is a route to minimizing the risk that human beings will transgress ecological boundaries. It is necessary to meet the demands of modern society, the relevance and significance of which will only continue to grow. The benefits of sustainable protocols are manifold and can help to solve major global concerns related to social, environmental, and economic issues.[1] Owing to recent advances in chemical technology, the emphasis has markedly shifted to nanoscale materials. The unique physicochemical properties of nanomaterials and their broad applicability in different fields, such as catalysis, photocatalysis, imaging, photonics, nanoelectronics, sensors, biomaterials and biomedicine, encompass many scientific disciplines.[2] Although the area of nanomaterials is rapidly progressing and developing, their emergence at breakneck speed has been associated with adverse environmental effects. In particular, the effects of reagents used for their preparation are still largely unknown.[3] Therefore, development of eco-friendly methods employing biocompatible reagents for their preparation could decrease the toxicological burden of nanocomposites on humans and the environment.[4]

The chemistry of iron, the most abundant transition metal and fourth most abundant element in the Earth's crust, can play a vital role in decreasing environmental contaminants and enabling greener syntheses, biomedical applications, and sustainable technologies, because of its relatively nontoxic nature, biocompatibility, and high catalytic efficiency among the transition elements.[2d,5] In nature, iron mainly exists in the form of oxides such as magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and hematite (α-Fe_2O_3), hydroxides such as goethite and lepidocrocite (α- and γ-FeOOH, respectively), carbonates, and silicates. Owing to their ease of synthesis, surface modification and magnetic recyclability, ability for magnetic manipulation and specific optical, magnetic and chemical properties. Iron oxide nanoparticles have been widely explored for a wide variety of applications, such as catalysis, dye adsorption, drug delivery, and photonics, as well as environmental applications.[2d,5f,6,7] Elemental iron in the zerovalent state mostly exists in a bcc crystal structure as α-Fe and is highly prized for environmental applications,[8] mainly in its very reactive nanoscale form.[9] Nanoscale zerovalent iron (nZVI) particles are a well-known reducing agent and have gained worldwide popularity as a material for remediation, groundwater treatment, biomedical applications, catalysis, and electrochemistry.[8b,9,10] The small particle size and large surface-to-volume ratio of nZVI, a typical trait of nanomaterials, renders the nanoparticles highly active, versatile and functional for several applications. Thus, they have a higher tendency to interact, adsorb and react with other atoms or molecules to attain stabilization compared to bulk materials of the same composition.[11]

Numerous methods have been reported for the preparation of nZVI particles and many research groups worldwide have explored the synthesis of nZVI particles, as well as the mechanisms of their interaction with various pollutants and versatile applications.[10g,12] Recently, advanced technologies for large-scale syntheses of nZVI particles and their pilot/full-scale application in field trials for groundwater remediation have been developed.[8a,10f,j,15] Various field studies have been carried out on the geofixation/removal of heavy metals or chemical degradation of organic contaminants.[13–15] For example, zerovalent iron nanoparticles have been used for the treatment of acid mine water containing a miscellaneous mixture of pollutants from in situ chemical leaching of uranium (Stráž pod Ralskem, Czech Republic) with the aim of verifying the validity of the technology for the removal of contaminants.[10f] In another study, nZVI modified with a stable dispersion of Tween 80, an environmentally benign surfactant, was applied for the onsite degradation of chlorinated hydrocarbons.[15b]

However, sustainable synthesis of nZVI by using plants and microorganisms or by biochemical approaches could provide an interesting and ecologically friendly alternative to chemically manufactured nanoparticles.[16] Plants (extracts or parts such as root, stem, leaves, and latex) and microorganisms (bacteria, virus, fungus, and algae) have been used for the formation of

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a wide variety of stable metal nanoparticles. Such synthetic efforts open new doors for the development of greener processes (Figure 1) with numerous benefits, including (a) the avoidance of toxic chemicals, (b) the use of active element-like enzymes that can act as a reducing as well as a capping agent, (c) easy implementation on a large scale, (d) avoidance of the need for high pressure and temperature conditions, thus saving energy, and (f) simple methodologies that use renewable materials.[10a,18]

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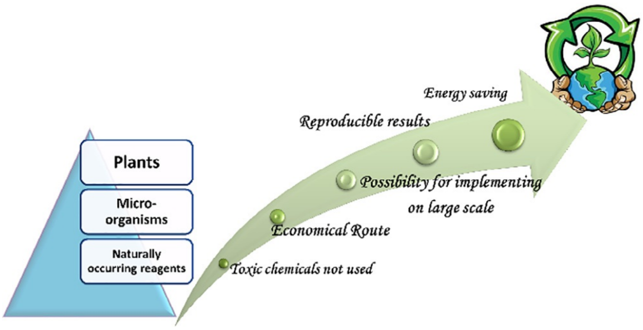

Figure 1. Advantages of bio-based methods.

2. Focus

This Review provides an updated summary of reported studies on the preparation of nZVI particles involving plant extracts, microorganisms, and other naturally occurring substances, and together with their environmental/catalytic applications.

A sustainable approach to synthesis is undoubtedly imperative for our continued existence on the planet. Herein, we focus on the sustainable synthesis of nZVI particles and their applications for environmental remediation. We discuss the pros and cons compared with conventional chemical and physical synthetic approaches and outline biotic and abiotic methods involving plant extracts and microorganisms, for example. This information will aid biologists and chemists to take a multidisciplinary approach that may open up new avenues in this field of research. We also broadly discuss applications for environmental remediation, encompassing the degradation of harmful halogens, dyes, drugs, and other chemicals.

3. Properties, Mechanism and Essential Chemistry of nZVI

Macroscale zerovalent iron particles have been recognized as excellent electron donors. Since the 1990s, they have been used for remediation of polluted sites, mainly by creating permeable reactive barriers.[19] With advancements in nanoscale chemical technology, nZVI particles are gradually replacing macroscale zerovalent iron particles in these applications, as they can achieve higher efficiency in the same remedial work.[20] Indeed, nZVI particles are endowed with remarkable properties, such as (1) high activity for contaminant removal, (2) abundance, (3) low toxicity of reaction products, and (4) good mobility in porous media, rendering them suitable for in situ remediation as replacements for expensive permeable reactive barrier techniques.[15b] nZVI particles possess excellent electron-donating properties, which are responsible for their high reactivity in aqueous media, the reactivity being determined by the corrosion reactions of Fe^0 and unselective reaction with dissolved oxygen.[12f]

These chemical reactions can be accelerated or inhibited depending on the solution chemistry. In general, application of nZVI creates low redox and anoxic conditions, evolving H_2 and increasing the pH of the solution medium.[21] The released electrons reduce other compounds with the formation of various Fe^{II} and Fe^{III} species (Figure 2).

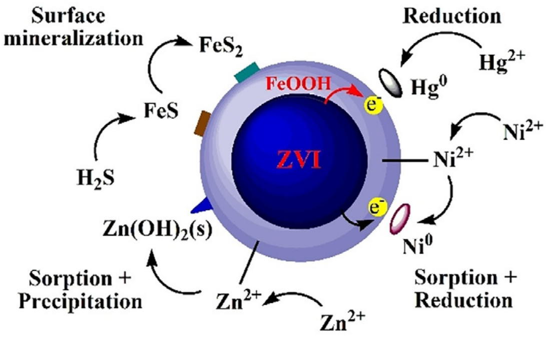

Figure 2. Core-shell model of nZVI and possible reaction mechanisms. Adapted with permission from references [18] and [22].

Particles of nZVI synthesized in the laboratory or on an industrial scale by one of the aforementioned methods exhibit a typical core–shell structure, where the core consists of metallic iron and the shell of mixed oxide Fe^{II} and Fe^{III}[14,23] (Figure 2). This has significant implications for the chemical properties of nZVI. The metallic core provides the reducing power (electron source) for reactions, whereas the oxide shell provides sites for chemical reactions by chemisorption and/or electrostatic interaction.[18] According to Li et al., the mixed valence oxide shell is largely insoluble at neutral pH, and thereby protects the core from rapid oxidation.[18] However, the defective and disordered nature of the oxide shell has been reported to make it very reactive, in contrast to the simple passive oxide layer that forms on bulk iron.[14,24]

4. Synthetic Approaches

4.1. Physical and chemical methods

The synthesis of nZVI is largely achieved by two types of approach: top-down or bottom-up (Table 1 and Figure 3). Compared with physical methods, biological approaches may be a viable alternative for the synthesis of nZVI as they are reported to proceed under ambient pressure and temperature conditions, potentially offering vast energy savings (Figure 3).

4.2. Green synthesis of nZVI particles

Various approaches, including the use of biodegradable chemicals, environmentally benign solvents, inexpensive biomaterials, microwaves, and ultrasound, have been investigated extensively for the green synthesis of nZVI particles.[2e,25]

4.2.1. Green synthesis of nZVI nanoparticles using plants

In recent years, biosynthetic strategies using plant extracts have gained popularity as suitable alternatives for the assembly of metal nanoparticles,[26] particularly the plant-mediated synthesis of nZVI.[10a,27] Biochemical molecules, such as enzymes, proteins, amino acids, vitamins, organic acids (citrates), and polysaccharides, which are abundant in biomass extracts, may serve as efficient reducing as well as capping agents for the reduction of metal salts or can be produced themselves in nanoform.[17b,28]

*4.2.1.1. **Mechanism of metal ion reduction to zerovalent nanoparticles by plant extracts***

Phytochemicals are secondary metabolites of plants that are generally involved in defense mechanisms against pathogens and harmful ultraviolet radiation. Some phytochemicals and other food polyphenolics are of increasing scientific interest because of their beneficial effects on human health. Many phytochemical compounds, such as polyphenols, glutathione, met-

Table 1. Top-down and bottom-up approaches for synthesizing nZVI.

Entry	Top-down			Bottom-up			Ref.
	Methods	Procedure	Cost/disadvantages	Methods	Procedure	Cost/disadvantages	
1	Mechanical	Breakdown of massive granules by ball-milling, thermal reduction, vacuum sputtering or other large machine.	High cost required for large instruments	Chemical synthesis	Synthesis in liquid medium containing reactants (i.e., iron salts) and a variety of reducing agents (e.g., sodium borohydride, sodium dithionite, potassium bitartarate, or methoxypolyethylene glycol, hydrazine). A stabilizing agent (e.g., sodium dodecylbenzyl sulfate or polyvinyl pyrrolidone) is often added to the mixture.	Use of hazardous chemicals, production of toxic waste and hazardous byproducts. Cost of using harmful chemicals	[14,15]
2	Chemical	Breakdown by chemical etching or pyrolysis at high temperature.	Requires harmful chemicals and equipment to attain high temperature.				[16]
3	Thermal reduction	Breakdown of goethite or hematite particles at elevated temperature (200–600 °C) under H_2 environment.	Explosive hydrogen gas is used. Requires equipment to attain high temperature.				[9]

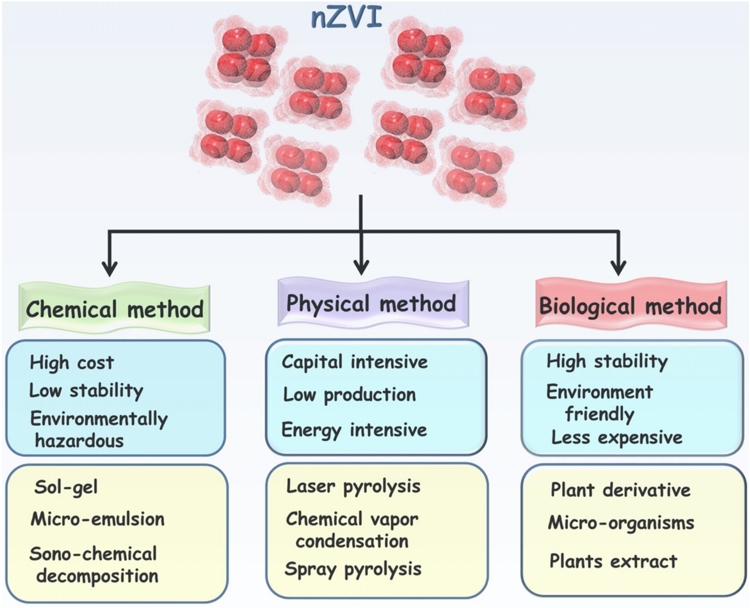

Figure 3. Comparison of different methods for the synthesis of iron nanoparticles and their advantages/disadvantages.

allothioneins and ascorbates, possess active functional groups that may activate metal ions by chelation and by suppressing superoxide driven reactions, assist in the synthesis of stable nanoparticles. In a typical synthesis, metal ions in solution (e.g., iron in aq. $FeCl_3$ or $FeCl_2$ solution) and a plant extract are mixed together to form reduced nZVI particles. The Fe^{2+} or Fe^{3+} ions are complexed with phenolic -OH groups present in various biomolecules of the extract and are subsequently reduced to Fe^0. These biochemical molecules also act as stabilizing agents helping the metal to remain in nanosized form and preventing aggregation of the nanoparticles. Generally, nanoparticles form spontaneously within a time ranging from a few minutes to a day depending on the specific combination of metal-extract used, with the extract controlling the reactivity and size distribution of the resulting nanoparticles.

4.2.1.2. *Recent trends in the synthesis of nZVI by plant extracts or plant derivatives*

Various plants extracts have been explored for the bio-mediated synthesis and stabilization of nZVI and the ensuing nanoparticles or nanocomposites have been evaluated for potential applications, such as catalysis or the immobilization and degradation of pollutants.[12h,29] The reduction efficiency of plant extracts depends on the chemical nature of the biomolecules present, such as polyphenols and reducing agents. Some plants, such as tea and coffee, are rich in polyphenols. Thus, they have been found to be suitable candidates for the bio-mediated synthesis of nZVI.[30] Recent studies on nZVI, including its synthesis by using plant extracts, and its applications are summarized in Table 2.[31]

Chrysochoou et al. studied the synthesis of nZVI particles from green tea and pure epigallocatechin gallate (EGCG) solution and used them for the reduction of Cr^{IV}. The nZVI prepared from green tea (GT-nZVI) was able to reduce twice the amount of Cr^{VI} than direct reduction of Cr^{VI} with green tea.[32,33] Kozma et al. compared the reductive dehalogenation efficiency of nZVI particles in removing volatile chlorinated organic compounds from untreated groundwater.[10a] Wang et al. synthesized polydispersed iron particles from green tea and eucalyptus leaf extracts.[34] The resulting nZVI formed quasi-spherical particles with diameters of 20–80 nm.

Machado et al. used natural extracts from several tree leaves (Table 2) to reduce iron(III) in aqueous solution to generate nZVI.[35] The quality of the extracts was evaluated with respect to their antioxidant capacity.[36] The same group produced green nZVI by using wastes from citrine juice (orange, lime, lemon and mandarin), which could be exploited for several applications, including environmental remediation. Pattanayak and Nayak confirmed the formation of nZVI from Neem extract under atmospheric conditions.[37] Although many studies have been undertaken on the green synthesis of iron nanoparticles from plant extracts, the active ingredients involved in these processes are still largely unknown.[38]

To elucidate the active biomolecules involved in the reduction, Luo et al. analyzed grape leaf extract in methanolic solution by GC-MS and concluded that phytols, terpenoids (α- and β-amyrins, β- and δ-sitosterols), and antioxidants (δ-stan-3,5-diene, vitamin E) served the dual role of reducing and capping agents.[39,40] In another study, Madhavi et al. reported Fe/Pd bimetallic nanoparticles synthesized using grape leaf extract. SEM, TEM, XPS and EDS analysis revealed the synthesis generated 2–20 nm quasi-spherical particles in the Fe^0 state. Furthermore, FT-IR and GC-MS analysis of the extract showed the presence of various active biomolecules, such as methoxyphenyl-oxime, *N*-benzoyl-2-cyano-histamine, 2-ethyl-phenol, 1,2-benzenediol, β-hydroxyquebracamine, hydroquinone, 2-methoxy-4-vinylphenol, 5-methyl-2-furancarboxaldehyde, 4-(3-hydroxybutyl)-3,5,5-trimethyl-2-cyclohexen and some polyphenolic compounds, which were suggested to be responsible for the reduction and capping of the iron salts (Figure 4).[41]

Oenothein B present in *Eucalyptus globulus* leaf extract was found to form complexes with iron and act as both a reducing and stabilizing agent.[41] The obtained nZVI particles were found to be stable for at least one month.

Xiao and co-workers compared 15 plant extracts for the plant mediated synthesis of nZVI particles from $FeCl_3$.[42] The nZVI synthesized by three of the plant extracts i.e., Willd (*Aleurites moluccana* L.), Oolong tea, and Alston (*Syzygium jambos* L.), were tested for Cr^{VI} removal. *S. jambos* was found to be most active for Cr^{IV} removal (91.9% in 5 min and 100% in 60 min), with a maximum removal capacity of 698.6 mg Cr^{VI} g^{-1} Fe, consistent with its higher reducing capability.

Use of nZVI immobilized on various porous supports may be a promising strategy for achieving better adsorption/reduction performance together with enhanced stabilization. The supported nZVI particles can be synthesized using synthetic chem-

Table 2. Summary of studies on the synthesis of nZVI using plant extracts.

Entry	Authors	Approach	Application/findings	Reference
1	Hoag et al.	Tea (*Camellia sinensis*) extract containing polyphenols was treated with ferric nitrate (as a precursor) at room temperature for the synthesis of nZVI particles. Formation of nZVI was confirmed by a color change from pale yellow to dark greenish/black.	The obtained nanoparticles were utilized to catalyze hydrogen peroxide for the treatment of organic contaminants. The results were compared with those using Fe-EDTA and Fe-EDDS.	[27b]
2	Chrysochoou et al.	Green tea polyphenols and pure epigallocatechin gallate (EGCG) solution were used for the synthesis of nZVI.	NPs were used for the reduction of Cr^{IV}. nZVI prepared from green tea (GT-nZVI) was able to reduce twice the amount of Cr^{VI} than direct reduction of Cr^{VI} with green tea.	[32]
3	Kozma et al.	Green tea and coffee (Virginia creeper) were used as reducing and capping agents. A semi-green method employed industrial chemicals at room temperature and tap water (instead of distilled water).	The reductive dehalogenation efficiency of nZVI particles in removing volatile chlorinated organic compounds from untreated groundwater was assessed.	[10a]
4	Njagi et al.	Aqueous *Sorghum* Sp. bran extract prepared by treating sorghum bran powder in double distilled water at various temperatures for half an hour was used for the synthesis of nZVI.	Enhanced H_2O_2 decomposition with increasing concentrations of nZVI particles was obtained, demonstrating that the synthesized nZVI particles may be potentially useful for the degradation of organic pollutants.	[29]
5	Wang et al.	Diverse polydisperse iron (nZVI, Fe_3O_4, Fe_2O_3) particles were synthesized from green tea and eucalyptus leaf extracts. The nZVI displayed quasi-spherical particles with diameters of 20-80 nm.	Application of these green Fe NPs for treating swine wastewater demonstrated a promising environmental pollution management option for large-scale eutrophic wastewater treatment.	[34]
6	Machado et al.	Natural extracts from several tree leaves (e.g., apple, apricot, avocado, cherry, eucalyptus, kiwi, lemon, mulberry, oak, olive, orange, passion fruit, peach, pear, pine, pomegranate, quince, raspberry, strawberry, black tea, green tea, vine, walnut) were used to reduce iron(III) in aqueous solution. The same group produced green nZVI using wastes from citrine juice (orange, lime, lemon and mandarin), which can be exploited for several applications, including environmental remediation.	The quality of the extracts was evaluated with respect to their antioxidant capacity. The results showed that dried leaves produced extracts with higher antioxidant capacities than non-dried leaves. The most favorable extraction conditions (temperature, contact time, and volume/mass ratio) were identified for each leaf with the aim of developing a greener protocol using water as the solvent. The extracts were classified into three categories according to their antioxidant capacity (expressed as Fe^{II} concentration): i.e., $>40\ mmol\ L^{-1}$, 20–40 $mmol\ L^{-1}$ and 2–10 $mmol\ L^{-1}$; with Oak, pomegranate and green tea leaves produced the richest extracts.	[35,36]
7	Pattanayak et al.	nZVI particles were formed from an *Azadirachta indica* (neem) extract under atmospheric conditions.	The resultant NPs of 50–100 nm size showed good stability in solution under the UV-visible wavelength 200–600 nm. Spectral analysis revealed an absorption peak at 216–268 nm due to excitation of surface plasmon vibrations in the Fe NP solution,	[37]
8	Luo et al.	Analysis of grape leaf extract in methanolic solution by GC-MS showed that phytols, terpenoids (α- and β-amyrins, β- and δ-sitosterols) and antioxidants (δ-stan-3,5-diene, vitamin E) could serve the dual role of reducing and capping agents.		[39]
9	Luo et al.	Fe/Pd bimetallic nanoparticles were synthesized by using grape leaf extract and characterized by SEM, TEM, XPS, and EDS. The results revealed the synthesis of quasi-spherical 2–20 nm particles in the Fe^0 state.	FT-IR and GC-MS analysis of the extract revealed the presence of various active biomolecules (e.g., methoxyphenyl oxime, *N*-benzoyl-2-cyano-histamine, 2-ethyl-phenol, 1,2-benzenediol, β-hydroxyquebracamine, hydroquinone, 2-methoxy-4-vinylphenol, 5-methyl-2-furancarboxaldehyde, 4-(3-hydroxybutyl)-3,5,5-trimethyl 2-cyclohexen and some polyphenolic compounds), which were suggested to be responsible for the reduction and capping of iron salts.	[40]
10	Madhavi et al.	Bio-derived compounds such as oenothein B present in *Eucalyptus globulus* leaf extract were found to form complexes with iron and serve as reducing and stabilizing agents.	The resulting nZVI particles were used for the reduction of hexavalent chromium (Cr^{VI}) monitored by UV/Vis spectrometry.	[41]
11	Xiao and co-workers	Fifteen plant extracts, including Willd. (*A. moluccana* L.), Presl. (*C. camphora* L.), Franco (*P. orientalis* L.), *B. variegata* L., Oolong tea, Black tea, *A. Carambola* L., *E. citriodora*, *S. aromaticum*, Alston (*S. jambos* L.), Lour (*D. longan*), *N. indicum*, *G. robusta*, *D. regia*, and *L. speciosa* Pers., were tested for the plant-mediated synthesis of nZVI particles from $FeCl_3$.	The role of the polyphenol content in affecting the reducibility was shown in the syntheses of nZVI by three plant extracts, i.e., Willd., Oolong tea and Alston, and the resulting NPs were tested for Cr^{VI} removal. nZVI synthesized from *S. jambos* was found to be most active in Cr^{IV} removal (91.9% in 5 min and 100% in 60 min), with a maximum removal capacity of 698.6 $mg\,g^{-1}$.	[42]
12	Tandon et al.	Clay-supported nZVI particles were prepared by mixing ferric nitrate-impregnated montmorillonite K10 with tea liquor.	Upon mixing with As^V contaminated water, the clay-supported nZVI particles achieved 99% removal for arsenic (As^{III}) in 30 min at pH 2.75–11.1.	[43]
13	Soliemanzadeh et al.	Bentonite-supported nZVI particles were synthesized from green tea extract.	FTIR and EDS analysis of the bentonite-nZVI composite revealed the presence of polyphenols and other carbonaceous materials emanating from the green tea extract. The nZVI/bentonite composite acted as both a reducing and capping agent.	[44]

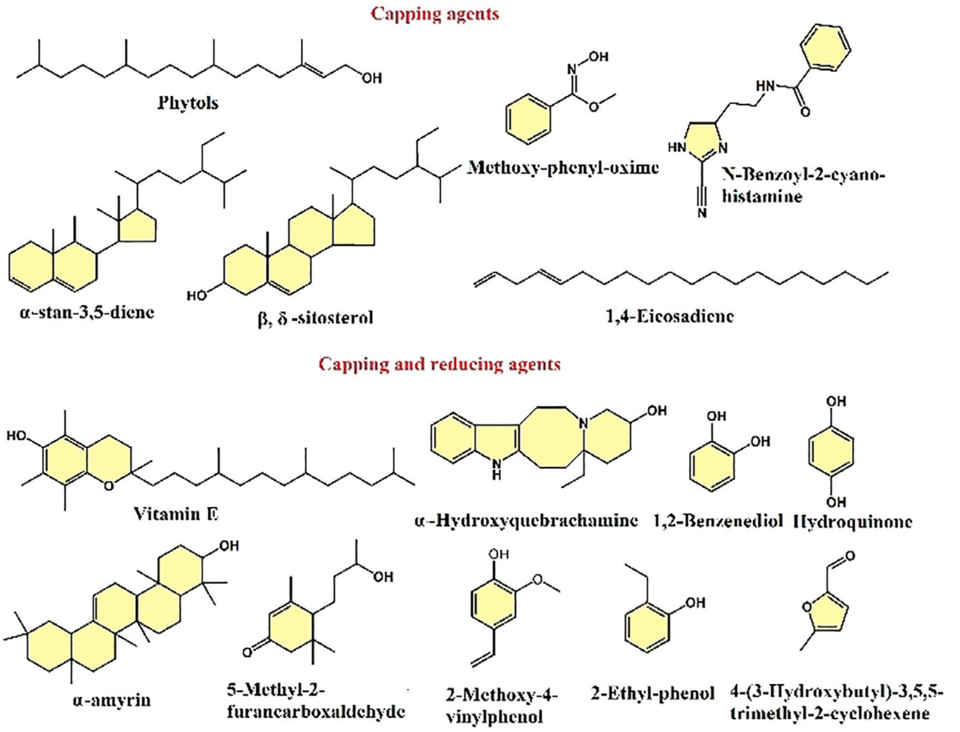

Figure 4. Various capping and reducing agents present in tea and grape extracts identified by GC-MS and IR spectroscopy.[39,40]

icals, plant extracts or by pyrolysis. The synthesis of supported nanoparticles using plant extracts involves the addition of plant extract to metal salt impregnated supports, which reduces the iron salt to nZVI particles. Tondon et al. prepared clay-supported nZVI particles by mixing ferric nitrate impregnated montmorillonite K10 with tea liquor.[43] Following a similar methodology, Soliemanzadeh and Fekri synthesized bentonite-supported nZVI particles from green tea extract.[44] FTIR and EDS analysis of the nZVI/bentonite composite revealed the presence of polyphenols and other carbonaceous material emanating from the extract, which behaved as reducing as well as capping agents.

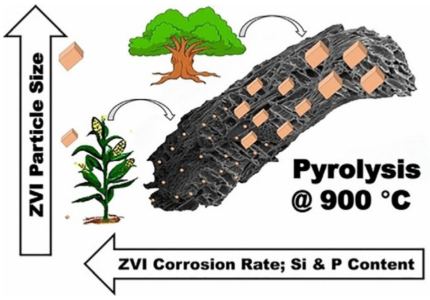

Figure 5. General scheme for synthesizing biochar–zerovalent iron (BC–ZVI) from corn. Reprinted with permission from ref. [46]. Copyright 2017, American Chemical Society.

4.2.3. Biomass approach

Apart from mixing a plant extract and iron salt for the production of nZVI, other methods can be used, such as pyrolysis of biomass with an iron salt to generate carbon/biochar-supported nZVI particles.[45] The main advantages of the pyrolysis method are the ready availability of starch-based biomass and the high surface area and synergistic adsorption mechanism on the surfaces of activated carbon and nZVI. Lawrinenko et al. recently reported the synthesis of biochar–zerovalent iron (BC–ZVI) by pyrolysis of $FeCl_3$-impregnated biomass, such as cellulose, corn stover, dried distillers' grain, red oak, and switchgrass (Figure 5).[46] A nZVI/bamboo charcoal composite was also synthesized by pyrolyzing $FeCl_3$-impregnated bamboo charcoal at varying temperatures.[47] In another study, nZVI particles distributed over the surface of porous carbon (PC) were generated by the pyrolysis of pinewood sawdust and $FeCl_3$ at 800 °C under nitrogen. The resulting nZVI/PC nanocomposite was found to be highly porous with a specific BET (Brunauer–Emmett–Teller) surface area of 423 m^2g^{-1} and pore volume of 0.23 cm^3g^{-1}.[48]

4.2.4. Green synthesis of nZVI particles by microorganisms

Besides chemical synthesis, living organisms have a huge potential for the production of nanoparticles.[49] As reported by Thakkar et al., many unicellular and multicellular microorganisms produce inorganic materials either intracellularly or extracellularly.[17a] Some bacteria accumulate iron in magnetic form in their cell for navigation purposes. During the past decade, it has been shown that many biological systems (including plants and algae, diatoms, bacteria, yeast, fungi, and human cells) can transform inorganic metal ions into metal nanoparticles through the reductive capacities of proteins and metabolites present in these organisms.[50] The rate of intracellular particle formation, and therefore size of the nanoparticles, can be manipulated to some extent by controlling the pH, temperature, substrate concentration, or exposure to the substrate.[50c] Similarly, by changing the key growth parameters, the size and shape can be manipulated extracellularly. To produce highly stable and well-characterized iron nanoparticles, the following aspects should be considered:

- Selection of the best organism for the synthesis: To select the best strain, it is important to focus on intrinsic properties such as enzyme activities and biochemical pathways of the microorganism/organism. Microorganisms that have great capability for detoxification and metal accumulation are ideal contenders for the synthesis.
- Conditions for the best growth and activity: It is important to optimize the environment and conditions, such as temperature, inoculums size, light, pH, or buffer, to enhance the enzyme activity.
- Optimal reaction conditions: To scale methods up to a large scale, sustainable alternatives, such as the use of visible light or microwaves, may be needed.[51]

Hence, microbes may serve as a renewable and eco-friendly resource for the synthesis of nZVI and other nanoparticles with the desired morphological characteristics. The major drawback of microbe-mediated nanoparticle synthesis is the strict requirement for aseptic conditions. The attributes and easy availability of plants in nature probably make them preferable biological resources compared to microbes.

4.2.4.1. *Synthesis of nZVI particles by microorganisms and their synergistic interaction for enhanced activity*

Microorganisms have many useful properties, including fast multiplication rates, production of various secondary metabolites, fast growth rates in a limited and confined space and capabilities for the deactivation of contaminants with synergistic mechanisms. Hence, they are a good vehicle for the synthesis of nZVI particles.

Only a few microbes or specific strains, such as different species of acidophilic prokaryotes, widely distributed within the domains of *Bacteria* and *Archaea,* can reduce iron salts. Bioprocessing of iron by these microbes is generally carried out under extremely acidic environments ($pH < 3$).[52] Different strains of acidophilic microorganisms have been shown to have varied capacities for iron oxido-reduction, which can be further influenced by the presence of electron donors and growth conditions used.[53] Ding et al. reported that *Bacillus subtilis* can enhance the U^{VI} reduction performance of nano-Fe^0.[54] Dehalobacter-containing Fe^0 showed a 14-fold increase in degradation of trichloroethane.[55] *S. cerevisiae* cells modified with nZVI were used as a magnetic biosorbent for Ni^{II} ion removal from aqueous solution.[56] An aerobic strain *Rhodococcus sp.* coupled with zerovalent iron/activated carbon (ZVI/AC) was found to promote the degradation of BDE-209.[57]

Chen et al. investigated the biological responses of Gram-positive and Gram-negative bacteria toward nZVI particles, Fe^{2+} and Fe^{3+} ions.[58] Two Gram-positive bacteria (*Bacillus subtilis var. niger* and *Staphylococcus aureus*) and two Gram-negative bacteria (*Pseudomonas fluorescens* and *Escherichia coli*) were treated with nZVI particles (Figure 6). The results revealed that Fe^{2+} and Fe^{3+} had stronger inactivation effects on all the tested bacteria than nZVI under the same experimental conditions. This effect was especially pronounced for *E. coli.* For nZVI particles ($0.56\ mg\,mL^{-1}$), bacterial growth was promoted when the volume of nZVI was increased, most significantly for *S. aureus*. In general, culturing and viability tests showed that Fe^{2+} had stronger inactivation effects on Gram-negative bacteria, whereas Fe^{3+} largely inactivated Gram-positive ones. The inactivation of the iron combinations was observed to vary greatly with bacterial types. Reactive oxygen species (ROS) data showed that the inactivation of the bacterial cells may

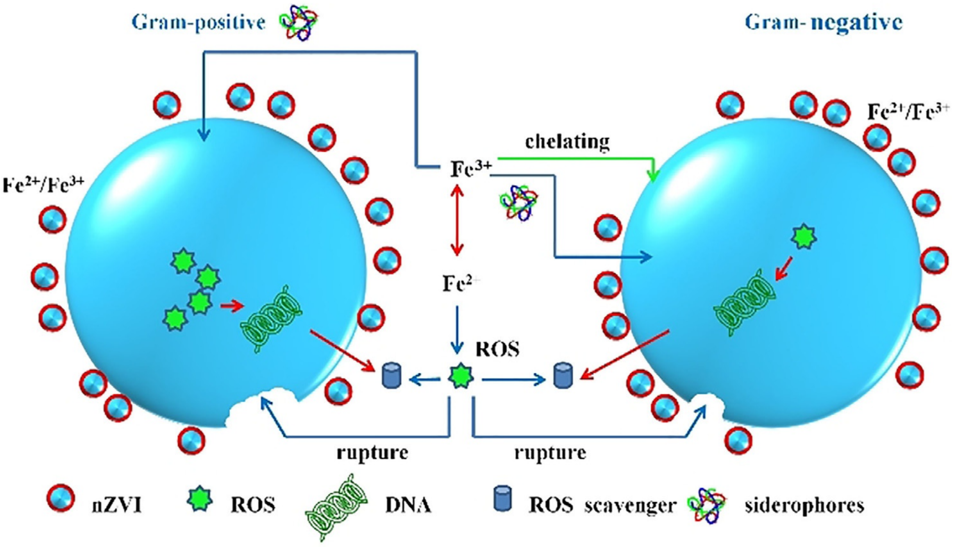

Figure 6. Schematic representation of the interaction of Gram-positive and Gram-negative bacteria with nano zerovalent iron (nZVI), Fe^{2+} and Fe^{3+} ions. Reprinted with permission from ref. [58]. Copyright 2013 Royal Society of Chemistry).

have resulted from in vivo damage caused by increased intracellular ROS levels. Higher magnetic removal efficiencies were observed for the bacteria under the conditions tested, except for Gram-positive bacteria mixed with nZVI particles followed by addition of Fe^{3+}. XPS data showed strikingly different surface chemistry for nZVI particles after interaction with *B. subtilis* and *E. coli*, and a more stable form of iron was produced for *E. coli*. The results from this study suggested that microbial inactivation by nZVI primarily arises from Fe^{2+} and Fe^{3+} on the particle surface. Apart from bacteria, various strains of fungi, such as *C. globosum,* have been reported to produce Fe^0 from Fe_2O_3.[59]

4.2.5. Green in situ synthesis and surface modification of nZVI using plant products

The high reactivity of nZVI particles is often compromised in real applications because of agglomeration and oxidation through interaction with water and soils. However, the in situ synthesis in deep surfaces and stabilization of nZVI particles by biomolecules make them suitable for many different applications. Coating nZVI with various biopolymers reduces or eliminates oxidation as well as enhances their stability. The presence of similar charges (e.g., hydroxy groups in cellulose) on the surfaces of biopolymers prevent them from agglomeration owing to repulsion. Furthermore, the biodegradability of naturally occurring nontoxic biopolymers renders them suitable agents for surface modification, as well as stabilization of various nanoparticles. Several plant-derived components, such as guar gum,[60] chitosan,[61] starch,[62] xanthan gum,[63] riboflavin,[64] cellulose,[65] agar–agar,[66] and Pluronic F-127,[67] have been used for the stabilization of nZVI particles.

He et al. reported the synthesis of nZVI with a range of sizes using carboxymethyl cellulose (CMC) as a stabilizer.[68] Smaller nanoparticles were generated at higher CMC/Fe^{2+} molar ratio. Presumably, CMC stabilizes the nanoparticles by increasing the speed of nucleation of iron atoms and forming a negatively charged layer by sorption of CMC over the iron atoms, thus preventing the nanoparticles from aggregation through electrostatic stabilization.

Grapeseed extract-stabilized nZVI (GS-nZVI) particles have been synthesized and evaluated for the degradation of the azo dye Reactive Brilliant Red K-2G (RBR) and the anthraquinone dye Reactive Brilliant Blue KN-R (RBB).[69] The synthesized nanoparticles had a higher surface area than nZVI synthesized without stabilizer and also exhibited a much higher degradation efficiency. Gum Karaya (*Sterculia urens*)-stabilized nZVI particles were found to be better agents than bare nZVI for the removal of hexavalent chromium.[70] Chitosan, a glucosamine biopolymer derived from crustaceans, is an important surface modifier because of its excellent film-forming ability, cost-effectiveness, hydrophilicity, biocompatibility, and biodegradability. The abundance of $-NH_2$ and -OH functional groups present in chitosan polymer provide binding sites and superior stability (Figure 7).[71] nZVI particles encapsulated in chitosan nanospheres have been used for improved arsenic removal. A $0.5\,g\,L^{-1}$ loading of nanoparticles decreased the concentrations of As^{III} and As^{V} from $2\,mg\,L^{-1}$ to $<5\,\mu g\,L^{-1}$ in less than 180 min.[61b] Moreover, the chitosan-stabilized nZVI particles were found to be stable in air for up to two months. The chromium removal efficiency was 1–3 times higher than that with nanoparticles synthesized in an ethanol–water mixed system.[72]

In addition to plant extracts and biomass, amino acids (e.g., L-cysteine, L-glutamic acid, glutathione, and L-arginine)[73] and organic acids (e.g., citric acid[74]) have been used in either an in situ or post-synthesis approach for surface stabilization of nZVI particles. Owing to the presence of $-NH_2$, -SH, -COOH groups, such nZVI particles can interact with the Fe^0 surface either by ionic interaction or by formation of bonds with -OH groups on an oxidized surface.

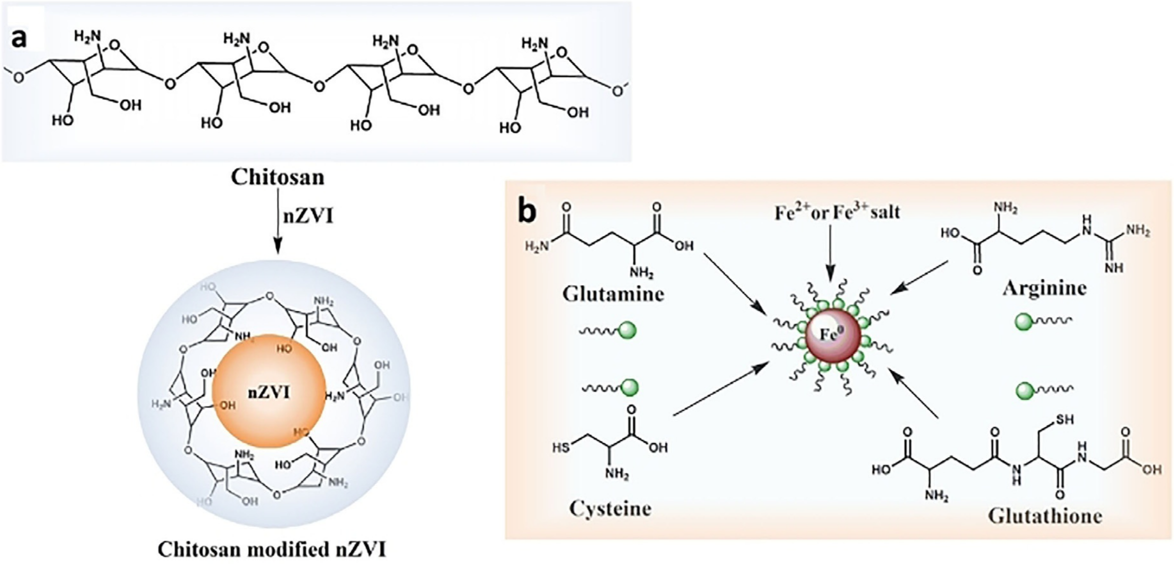

Figure 7. Schematic representations of a) chitosan-modified nanoparticles[71] and b) amino acid-mediated synthesis of surface modified Fe^0 nanoparticles.[73]

Siskova et al. discussed a wet chemical synthesis of nZVI in the presence of selected L-amino acids.[73b,75] Based on characterization of the nZVI particles by Mössbauer spectroscopy, the authors concluded that the choice of L-amino acid is crucial for mediating the generation of Fe^0. Among the four L-amino acids studied, L-glutamic acid was found to be most effective for Fe^0 generation, whereas L-cysteine served as a mediator of iron particle generation-induced ferric oxide/oxyhydroxide formation. The presence of L-glutamine and L-arginine during the generation of iron particles produced Fe^0/Fe^{III} ratios between those for L-glutamic acid and L-cysteine. The results highlighted the importance of the chemical structure of the L-amino acid and its role during dissolution of ferrous sulfate. Instead of an iron salt, biologically bound iron present in hemoglobin and myoglobin has also been considered as a precursor for nZVI particles. Arshad et al. synthesized surface-stabilized nZVI particles by using human hemoglobin or horse myoglobin dispersed in a pyridine–water system.[76] The one-pot synthesis of stable iron nanoparticles was conducted by using a single-phase chemical reduction approach, wherein reduction of iron ions in the bio-precursors was accomplished at room temperature, thus avoiding the use of additional chemical reagents. The size distribution of the crystalline product was in the narrow range 2–5 nm.[76]

5. Applications of Sustainably Synthesized nZVI

Unsurprisingly, reliable, eco-friendly, and simple methods for the production of nanomaterials are in high demand. Any technology designed for environmental applications should be eco-sensitive, cost-effective and easily available. This section discusses applications of nZVI particles synthesized by the aforementioned sustainable methods.

5.1. Catalytic applications of nZVI

Only a few reports have described catalytic applications of green synthesized iron nanoparticles (some are summarized in Table 3). Most of these are for the dehalogenation of aromatic halides and Fenton-type reactions. However, nZVI particles are promising materials for catalytic applications because of their excellent electron-donating capability and high reactivity.

Kuang et al. compared the degradation of monochlorobenzene (MCB) in green tea, oolong tea, and black tea extracts.[77] The MCB removal efficiencies were found to be 69 %, 53 %, and 39 %, respectively, after 180 min. Although, MCB cannot be oxidized by using H_2O_2 alone as an oxidant, Fe^0 nanoparticles and H_2O_2 appeared to catalyze the oxidation of MCB in a Fenton-like process. The nZVI particles synthesized from green tea extract showed the highest degradation activity, most likely because green tea contained the highest concentration of polyphenols. Machado et al. investigated the degradation of ibuprofen in aqueous solutions and contaminated sandy soils.[78] The results were compared with other common chemical oxidants, such as potassium permanganate, hydrogen peroxide, and Fenton's reagent. The degradation efficiency achieved in aqueous solutions (54–66 % of the initial amount) and sandy soils was satisfactory and could be further enhanced up to 95 % by complementing the process with a nZVI-catalyzed

Table 3. Overview of the applications of nZVIs synthesized by using plant extracts.

Entry	Authors	Green reagent	Reaction	Reference
1	Kuang et al.	Green tea, black tea, oolong tea	Degradation of monochlorobenzene	[77]
2	Machado et al.	Extracts of grape marc, black tea, and vine leaves	Remediation of soils contaminated with the common anti-inflammatory drug ibuprofen	[78]
3	Hoag et al.	*Camellia sinensis* tea	Catalysis of hydrogen peroxide for the treatment of organic contamination	[27b]
Degradation of organic contaminates				
4	F. Luo et al.	Grape leaf extract	Degradation of Orange II	[84]
5	Huang et al.	Tea species	Degradation of malachite green	[30a]
6	Shahwan et al.	Green tea leaves extracts	Decolorization of methylene blue (MB) and methyl orange (MO) dyes	[30b]
7	X. Wang et al.	Tea polyphenols	Ultrasound-assisted decolorization of malachite green (MG) and methylene blue.	[85]
8	Njagi et al.	Sorghum bran	Degradation of bromothymol blue	[29]
Miscellaneous applications				
9	Wang et al.	Eucalyptus leaf extract	Treatment of swine wastewater	[113]
10	Machado et al.	Milled oak leaves	Degradation of antibiotic amoxicillin	[114]
11	Nadagouda et al.	Green tea	Human keratinocyte cell (HaCaT) line	[17e]
12	Ebrahiminezhad et al.	Mediterranean cypress (*Cupressus sempervirens*)	Methyl orange removal	[12p]
13	Leili et al.	Nettle and thyme leaf extracts	Cephalexin antibiotic removal	[106]
14	Chen et al	Green tea extract	Ciprofloxacin removal	[107]
15	Pirsaheb et al.	Gum Tragacanth	Amoxicillin and ciprofloxacin removal	[108]
16	Nasiri et al.	*F. persica* extract	Crystal violet degradation	[109]
17	Sravanthi et al.	*Calotropis gigantea* flower extract	Methylene blue removal	[110]
18	Lin et al.	Eucalyptus leaves	Triclosan and copper removal	[111]
19	Perroti et al.	Yerba Mate and black tea extracts	Methyl orange removal	[112]

Fenton-like reaction. This study showed that remediation by ZVI could be a promising alternative to traditional technologies. As discussed earlier, nZVI serves as electron donor [Eq. (1)]:[79]

$$\mathrm{Fe^0} \rightarrow \mathrm{Fe^{2+}} + 2\,\mathrm{e^-} \tag{1}$$

whereas chlorinated compounds accept electrons and undergo reductive dechlorination [Eq. (2)]:

$$\mathrm{RCl} + \mathrm{H^+} + 2\,\mathrm{e^-} \rightarrow \mathrm{RH} + \mathrm{Cl^-} \tag{2}$$

For dechlorination with nZVI, three potential transformation mechanisms have been proposed:[80]

(1) Direct reduction at the metal surface.

(2) Reduction by ferrous iron at the nZVI surface.

(3) Reduction by hydrogen.

Ferrous iron, in association with certain ligands, slowly reduces chlorinated hydrocarbons. In some cases, electron transfer through bare nZVI may be slow. Therefore, to enhance the activity, a catalytic metal can be incorporated into the surface of nZVI particles. The expeditious reactions generated by such bimetallic nanoparticles also help to reduce byproduct formation and accumulation. Both surface-modified and unmodified nZVI has been found to catalyze dehalogenation reactions. For example, nZVI has been explored for the dechlorination of trichloroethylene (TCE) to ethylene.[81] The degradation of lindane or γ-hexachlorocyclohexane (γ-HCH; HCB), a potent carcinogenic and teratogenic chemical used previously as an insecticide, is of concern owing to its long persistence in the environment. nZVI particles donate electrons from their core, enabling dechlorination to benzene via tetrachlorocyclohexene and dichlorocyclohexadiene intermediates.[82] The degradability of HCB on a nZVI surface was also reported by Elliott et al.[83]

Hoag et al. compared results with iron ethylenediaminetetraacetate (Fe-EDTA) and iron ethylenediamine-N,N′-disuccinate (Fe-EDDS). In their approach, the concentration of bromothymol blue was monitored by UV/Vis spectroscopy in the visible range at pH 6 during treatment with iron catalyst and H_2O_2. Various concentrations of nZVI particles were tested to allow the determination of initial rate constants for the different iron sources.[27b]

5.2. Removal and/or degradation of organic contaminants

Use of nZVI for the degradation of a range of organic contaminants has received increasing attention as organic contaminants not only pollute water but also increase the chemical oxygen demand (COD) of water. Furthermore, organic dyes used in some industries, such as the textile and leather industries, exhibit high visible-light absorbance, which can reduce the availability of sunlight to organisms in a body of water. nZVI particles synthesized from grape leaf extract have been employed to elucidate the removal and degradation mechanism of Orange II from adsorption and kinetic studies.[84] The degradation of Orange II on nZVI was well-fitted to a pseudo-first-order kinetic model. Furthermore, the activation energy was calculated as 14.53 kJ mol^{-1} (< 15 kJ mol^{-1}), indicating that diffusion was the predominant phenomenon during the adsorption. LC-MS analysis of the degraded product in solution and extraction from the surface of the nZVI particles showed the presence of 1,2-dihydroxynaphthalene, 4-hydrobenzenesulfonate, 4-sulfophenylhydroperoxide, 1-diazo-2-naphthol, 2-naphthol and benzenesulfonate intermediates, suggesting that Orange II adsorbed to the surface through an interaction with the surface capping agent FeOOH and oxides, followed by cleavage of the azo bond by electrons of Fe^0 present in the core (Figure 8).

Huang et al. reported that nZVI particles synthesized from various tea species were very active for the degradation of malachite green.[30a] Assuming first-order kinetics, the activation energies calculated for nZVI synthesized from green tea, oolong tea, and black tea (GT-Fe, OT-Fe, and BT-Fe) were 23.86, 21.53, and 20.29 kJ mol^{-1}, respectively. Shahwan et al. used green tea leaf extract (GT-Fe NPs) to generate nZVI particles, which were then utilized as a Fenton-like catalyst for the decolorization of aqueous solutions containing methylene blue (MB) and methyl orange (MO) dyes. The rate of removal of MB followed second-order kinetics, whereas it was closer to first order for MO. Only 10–200 mg L^{-1} was needed to almost completely remove both dyes from water. In comparison with the nZVI particles produced by borohydride reduction, the green tea-prepared nZVI particles demonstrated more effective capability as a Fenton-like catalyst, both in terms of kinetics and percentage removal.[30b]

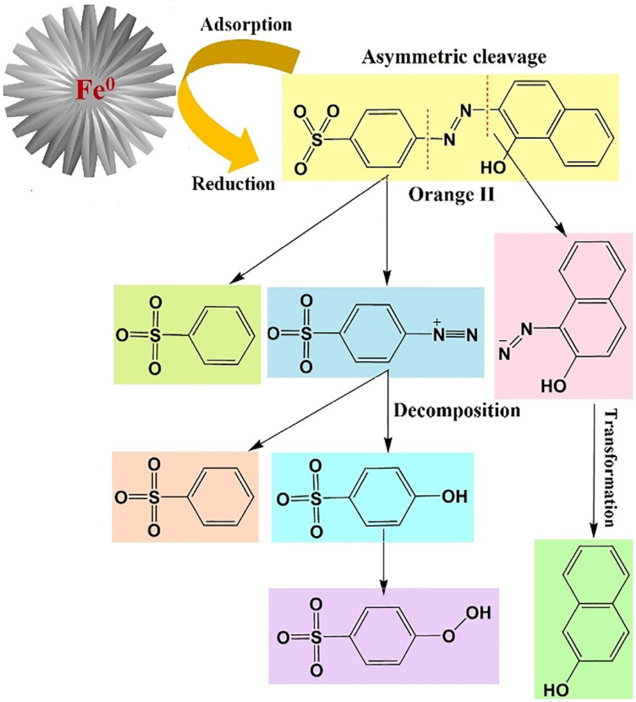

Figure 8. Reductive degradation mechanism for the removal of Orange II by core–shell-structured Fe NPs. Adapted with permission from ref. [84]. Copyright 2015, Elsevier.

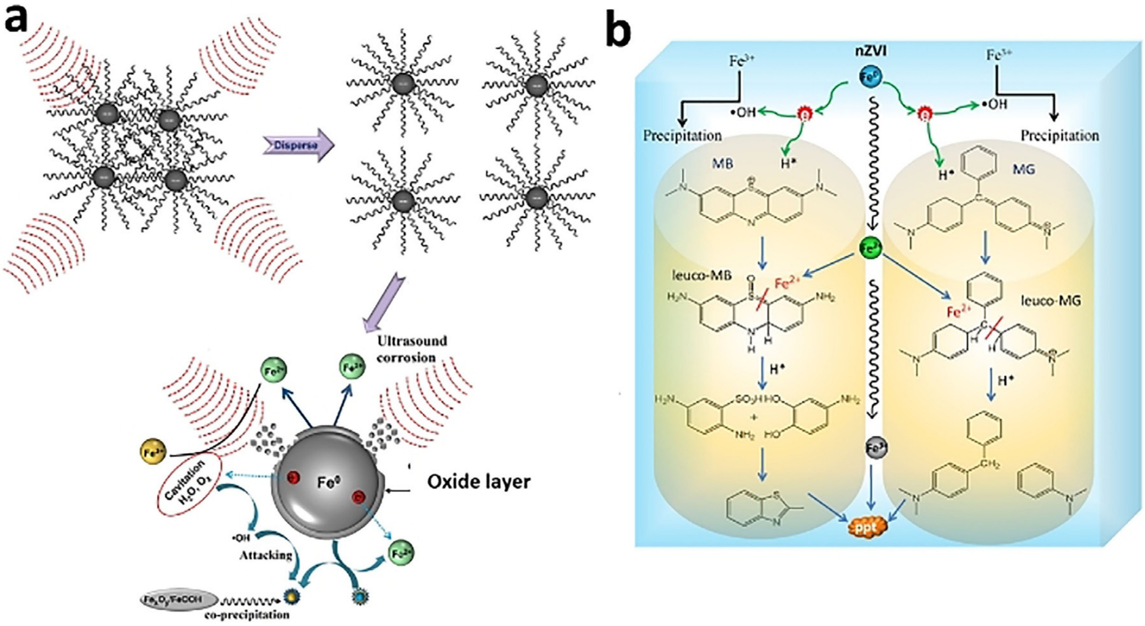

Figure 9. a) Schematic of ultrasound-assisted cavitation and dye degradation mechanism in a nZVI-containing system. Reprinted with permission from ref. [85]. Copyright 2017, Elsevier. b) Degradation pathway for malachite green (MG) and methylene blue (MB) on nZVI. Adapted from ref. [85]. Copyright 2017, Elsevier.

Wang et al. reported the use of nZVI synthesized from tea polyphenols for the ultrasound-assisted decolorization of malachite green (MG) and MB (Figure 9a).[85] A decrease in the major absorption bands at 617 nm and 664 nm attributed to C=C and C=N bonds in the UV/Vis spectra of MB and MG revealed that the removal process involved bond cleavage. When tea polyphenol-derived nZVI was used without sonication, only 10.18% and 8.49% total organic carbon (TOC) removal efficiencies were achieved for MG and MB, respectively, owing to coverage of the nZVI surface by iron hydroxides/oxides. However, when using ultrasound, up to 52% TOC removal efficiency was attained for both MG and MB. Although ultrasound generates some $^{\bullet}OH$ radicals, the amount remains too low to drive the reaction to a significant extent. The decrease in TOC could be attributed to adsorption of the dye molecule by long-chain capping agents, followed by coprecipitation and adsorption. The superior removal performance obtained with ultrasound was explained by a better mass transfer rate of MG and MB on the nZVI surface, followed by absorption on reactive sites of the nZVI particles. The electrons generated by Fe^0 can directly migrate to dyes. Subsequent trapping by H_2O/H^+ yields highly reactive H* species or dissociation of dissolved oxygen, generating strong oxidative species such as $^{\bullet}HO_2$, $^{\bullet}O$, and $^{\bullet}OH$, followed by cleavage of the chromophore groups and conjugated systems. Furthermore, corrosion products deposited on TP-Fe could be expelled by ultrasound and replenish the surface of nZVI (Figure 9b). Coagulation of the corrosion products (i.e., iron hydroxides/oxides) leads to sedimentation and coprecipitation, which might be the mechanisms responsible for the TOC removal process.

The catalytic activity of nZVI synthesized by using sorghum bran has been evaluated for the H_2O_2-catalyzed degradation of bromothymol blue as a model organic contaminant.[29] Enhanced H_2O_2 decomposition with increasing concentrations of nZVI particles was discerned, indicating that nZVI particles synthesized by the aforementioned methods may be potentially useful for the degradation of organic pollutants.

5.3. Remediation of inorganic contaminants

Iron nanoparticles can reduce relatively stable inorganic compounds, such as heavy metals, perchlorate, or nitrate. In water, nZVI behaves like either a metal or a ligand depending on the solution chemistry. At low pH, iron oxides are positively charged and attract negative ligands, such as sulfates and phosphates. When the solution is above the isoelectric point, the surface becomes negatively charged, and then the iron nanoparticles can form complexes with metal cations. As described previously, ZVI has a standard reduction potential (E^o) of -0.44 V, which is much lower than those for many other metals, such as Pb, Zn, As, Pb, Ag, Cd, Ni, and Cr. Hence, these compounds can be easily reduced by nZVI.[86]

Several other plant-based synthesis protocols have been used for the synthesis of nZVI applied for hexavalent chromium Cr^{VI} removal. For example, Madhavi et al. reported the synthesis of nZVI by using Eucalyptus globules. Response surface and contour plots of Cr^{VI} sorption efficiency (%) as a function of the initial Cr^{VI} concentration were constructed with Mini-tab software to explain the reduction of Cr^{VI}. The efficiency of nZVI for Cr^{VI} reduction attained the highest value of 98.1% with a reaction time of about 30 min and 0.8 $g\,L^{-1}$ loading of nZVI, removing 400 $mg\,L^{-1}$ hexavalent chromium.[41] Similarly, Soliemanzadeh et al. showed the presence of FeOOH (goethite) and Fe_2O_3 (hematite) after Cr^{VI} removal by XRD analysis.[44] Iron-based nanoparticles have also been synthesized by a rapid method at room temperature using yerba mate (YM) extracts with $FeCl_3$ in different proportions. Materials prepared from green tea extracts were also synthesized for comparison. The YM-derived nanoparticles were more efficient than other nanoparticles and Fe^{II} in solution, and were able to achieve virtually complete Cr^{VI} reduction, leaving only very low Cr and Fe concentrations in the treated solutions.[87] Chrysochoou et al. studied the synthesis of nZVI from green tea and EGCG solution and used it for the reduction of Cr^{IV}. nZVI prepared from green tea (GT-nZVI) could reduce twice the amount of Cr^{VI} than direct reduction with green tea alone.[32,33] In another study, the comparative Cr^{VI} remediation performance for contaminated soil was investigated by using green tea extract-synthesized nZVI and calcium polysulfide (CPS). The functionality of nZVI and CPS was evaluated by using columns packed with contaminated soil, and the eluents were analyzed by colorimetric and micro-X-ray absorption near edge structure (XANES) analysis. The CPS for Cr^{VI} removal increased the mobilization of Mn and As, and also increased the acidity for a short period.[32,33] Chromium reduction has also been carried out by using green nZVI derived from willow leaves, *Citrus limetta* peel, *Nephrolepis auriculate* extract, green tea extracts, *Eriobotrya japonica*, Eucalyptus leaves, *Rosa damascene*, *Thymus vulgaris* and *Urtica dioica*, *S. jambos* Alston, Oolong tea and *A. moluccana* Willd extract and *S. jambos* Alston leaves.[88–96]

Phosphorus-containing surfactants, such as fertilizers, are the main source of phosphorus pollution in the environment. They can promote eutrophication owing to a significant increase in the phosphorus concentration in bodies of water. Some reports have demonstrated that bio-derived nZVI is an excellent candidate for inorganic phosphate removal.[97] Like phosphates, nitrates can also increase eutrophication and acidity, detrimentally affecting the heath of soil, bodies of water, and aquatic life. nZVI particles facilitate transformation of the nitrates into N_2 and other less assimilable species.[98,34]

Wang et al. reported that in batch experiments, the NO_3^- removal efficiency of nZVI synthesized from green tea and eucalyptus leaf extracts (GT-Fe and EL-Fe NPs) reached up to 59.7% and 41.4%, respectively, whereas Fe_3O_4 nanoparticles attained only 11.7% removal efficiency for nitrate. The long-term applicability for nitrate removal by GT-Fe and EL-Fe NPs was examined for two months. The removal efficiency of nZVI underwent a 2.1-fold decrease (45.4%), whereas GT-Fe and EL-Fe NPs displayed almost identical nitrate removal efficiencies (51.7% and 40.7%, respectively) to those of the freshly prepared particles.[34] Heavy metals, such as arsenic, cadmium, mercury, and lead, are extremely toxic and recalcitrant carcinogens that pose serious hazards to aquatic and marine life. nZVI can transform toxic heavy metals into nontoxic forms by reducing them to a low-valent state, followed by hydroxide and oxide formation. Tandon et al. reported that upon mixing with As^{V} contaminated water, clay-supported nZVI particles can achieve 99% removal of arsenic (As^{III}) in 30 min at pH values ranging from 2.75 to 11.1.[43] Other researchers have reported a similar approach for arsenic removal by using eucalyptus, mango, jamun, and guava leaf extracts and blueberry plant extracts.[99–102] Budi et al.[103] reported Pb^{II} removal by using clove extracts for the nZVI synthesis (Table 4).

Harmful weed plants have also been successfully utilized for the synthesis of nZVI, which serves the dual purpose of saving the environment, as well as precious fodder used by animals.

Table 4. State-of-the-art approaches for the removal of inorganic contaminants by using bio-derived nZVI.

Entry	Authors	Green reagent	Inorganic contaminant removal/degradation	Reference
1	Madhavi et al.	Eucalyptus globules	Cr^{VI} removal	[41]
2	Soliemanzadeh et al.	Green tea extract	Cr^{VI} removal	[44]
3	Garcia et al.	Yerba mate extract	Cr^{VI} removal	[87]
4	Yao et al.	Willow leaves	Cr^{VI} removal	[88]
5	Dalal et al.	*Citrus limetta* peel	Cr^{VI} removal	[89]
6	Yi et al.	*Nephrolepis auriculate* extract	Cr^{VI} removal	[90]
7	Zhu et al.	Green tea extracts	Cr^{VI} removal	[91]
8	Onal et al.	*Eriobotrya japonica*	Cr^{VI} removal	[92]
9	Liu et al.	Green tea extract	Cr^{VI} removal	[93]
10	Jin et al.	Eucalyptus leaves	Cr^{VI} removal	[94]
11	Fazlzadeh et al.	*Rosa damascene*, *Thymus vulgaris* and *Urtica dioica*	Cr^{VI} removal	[95]
12	Xiao et al.	*Syzygium jambos* Alston, Oolong tea *A. moluccana* Willd. extract	Cr^{VI} removal	[42]
13	Xiao et al.	*Syzygium jambos* Alston leaves	Cr^{VI} removal	[96]
14	Chrysochoou et al.	Green tea extract	Cr^{VI} removal	[32]
15	Yin et al.	Synergistic interaction between microbes in the sludge and nZVI–H_2O	Cr^{VI} removal	[105]
16	Devatha et al.	Mango, curry, Neem, champa leaf extracts	Phosphorus removal	[97]
17	Katata-Seru et al.	*Moringa oleifera* extracts	Nitrate removal	[98]
18	Wang et al.	Eucalyptus leaf extracts	Nitrate removal	[34]
19	Wu et al.	Eucalyptus leaves	As^{V} removal	[99]
20	Rana et al.	Eucalyptus, mango, jamun and guava leaves extract	As^{V} removal	[100]
21	Tondon et al.	Tea liquor	As^{V} removal	[43]
22	Prasad et al.	Mint leave extract	As^{III} and As^{V} removal	[101]
23	Manquián-Cerda et al.	Blueberry plant extract	As^{V} removal	[102]
24	Chrysochoou et al.	Green tea extract	Mobilization of Mn and As	[33]
25	Budi et al.	Clove extracts	Pb^{II} removal	[103]
26	Wei et al.	Water hyacinth (*Eichhornia crassipes*)	Cr^{VI} removal	[104]

For example, Wei et al. synthesized nZVI from an aqueous extract of water hyacinth (*Eichhornia crassipes*), an invasive weed that causes serious ecological damage, owing to its very high fertility and growth rate.[104] The synthesized nZVI particles were shown to be excellent agents for the removal and reduction of hexavalent chromium from water, with a removal efficiency of 89.9%. The removal process included adsorption of Cr^{6+} on the surface of the nZVI particles, followed by reduction. After pH adjustment of the solution, Cr^{III} and Fe^{3+} were transformed into $Cr(OH)_3$ or Cr^{III}/Fe^{III} and hydroxides such as $Cr_xFe_{1-x}OOH$ or $(Cr_xFe_{1-x})(OH)_3$, and then coprecipitated (Figure 10).

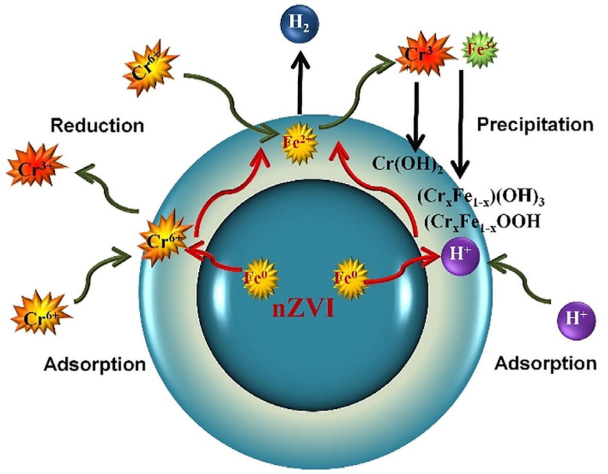

Figure 10. Removal mechanism of Cr^{VI} by nZVI particles. Adapted with permission from ref. [104]. Copyright 2017, Elsevier.

5.4. Miscellaneous applications of sustainably synthesized nZVI

Aside from the degradation of environmental pollutants and catalytic applications, zerovalent iron has also been used for various other applications. Yin et al. studied the synergistic interaction between microbes present in sewage sludge and a nZVI-H_2O system by examining the abiotic and biotic effects of the iron and microorganisms on Cr^{VI} removal efficiency.[105] In brief, a 0.55 mass ratio of volatile suspended solids (VSS) and mixed liquor-suspended solids (MLSS) obtained from secondary sewage plant was studied under anaerobic conditions. Transformation of secondary iron corrosion products by microorganisms into more reactive species, such as green rusts, vivianite, and magnetite, significantly promoted electron transfer from Fe^0 to Cr^{VI}. The bio-iron system showed 4.6 times higher Cr^{VI} removal efficiency than the abiotic system. In four recycling experiments, it was demonstrated that the Cr^{VI} removal capacity of Fe^0 in the biotic iron system was 12.4 times higher, with a lifespan of 64 days, than that for Fe^0 in the abiotic system, with a lifespan of only 30 days. Secondary metabolites originating from microorganisms, such as acidic metabolites (e.g., exopolysaccharidic substances) and biogenic cathodic reactants (e.g., H_2S), promoted iron corrosion and hydrogen production. Furthermore, reduction of Fe^{3+} by the biotic iron system induced positive iron corrosion and was responsible for the Cr^{VI} removal via a complex synergistic abiotic adsorption–reduction–coprecipitation mechanism (Figure 11).

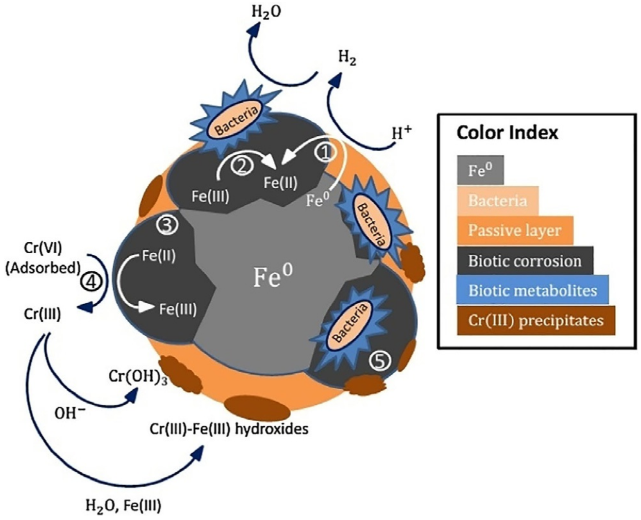

Figure 11. Mechanism for enhanced Cr^{VI} removal by nZVI particles with bio-amended iron corrosion: bio-induced iron corrosion, bio-reduction of Fe^{III}, growth of the positive corrosion, reduction of Cr^{VI} to Cr^{III} and passivation of reactive sites by Cr^{III} precipitates. Reprinted with permission from ref. [105]. Copyright 2016, Elsevier.

As summarized in Table 3, several other research groups have reported work in this area.[12m, 106–112] Wang et al. reported that nZVI particles synthesized by a one-step, room-temperature biosynthetic route using eucalyptus leaf extracts could be a promising material for the treatment of swine wastewater. They found that nitrogen and phosphorus species responsible for water eutrophication were removed with an efficiency of 71.7% for total N and 30.4% for total P, along with 84.5% for the COD.[34, 113]

nZVI particles fabricated from milled oak leaves have been used for the degradation of the common antibiotic amoxicillin (AMX).[114] The degradation mechanism involved transformation into AMX penicilloic acid by β-lactam ring opening, followed by its decarboxylation.[115] Although use of a catalyst under Fenton reaction conditions in the presence of H_2O_2 generated faster degradation (15 min) than nZVI alone, the study demonstrated the viability of nZVI as an alternative catalyst for the degradation of AMX in the Fenton reaction.

Nadagouda et al. observed the in vitro biocompatibility of green synthesized nZVI using the human keratinocyte cell HaCaT line, as assessed by mitochondrial function (MTS) and membrane integrity (LDH). The prepared nZVI particles were found to be nontoxic to the human keratinocytes in comparison with nZVI synthesized via the borohydride route.[17e]

Several reducing and capping agents, including flavonoids, tannins, and saponins, present in a leaf extract of *Dodonaea viscosa* have also been used for synthesis of nZVI particles.[116] Good antimicrobial activity was discerned against human pathogens such as Gram-negative *Escherichia coli*, *Klebsiella pneumonia*, *Pseudomonas fluorescens,* and Gram-positive *Staphylococcus aureus*, and *Bacillus subtilis.* Martins et al. applied life-cycle assessment as an eco-design strategy to evaluate the environmental performance of green syntheses of nZVI and identify the critical stages of the synthetic processes.[117] Benign syntheses appear to have a lower environmental impact than traditional methods. The critical stage in the green synthesis is the extraction process, which in turn is related to electricity production. Use of renewable energy-based electricity production systems will also help to reduce the environmental impact.

Starch has been used for the stabilization and chelation of diethylenetriamine pentaacetic acid (DTPA) to enhance the stability of nZVI particles (18 nm).[118] This easy and inexpensive protocol does not require any special containers/vessels. Removal of radioactive uranium from groundwater using these nZVI particles has been studied and the presence of aqueous Fe^{II}, Fe^{III}, hydrogen, free radicals, and other species, including precipitates of iron-hydroxy complexes, were implicated in the removal. The bulk of U^{VI} remained in contact with the reactive sites of the nZVI particles and facilitated the reduction of U^{VI} to U^{IV}. In particular, UO_2^{2+} species were transformed to $UO_2(s)$ as nZVI was oxidized to the ferrous iron (Fe^{2+}).

6. Concluding Remarks, Future Perspectives, Challenges, and Opinions

6.1. Conclusion and future perspectives

The physical and chemical procedures employed to generate nZVI often entail nonsustainable approaches regarding their intensive energy and resource usage and need for hazardous chemicals. Greener syntheses of nZVI from bio-based materials is an attractive option for producing stabilized and ready-to-use nanoscale zerovalent iron particles with minimum impact on the environment. Various active molecules present in biological systems or their derivatives can act as potent reducing agents for transforming an iron salt into zerovalent iron. Active constituents present in plant and agricultural residues mainly include polyphenols, reducing sugars, and amino acids. Additionally, capping agents play a crucial role by enhancing the adsorption properties and stabilization of nanoparticles. Microbial metabolites can be widely exploited to produce nZVI on a relatively large scale, owing to their exponential growth rate. The biosynthesized nanoparticles display improved performance and better stability than nZVI synthesized by traditional chemical methods, as a result of surface modification with active constituents from plants. The excellent electron-donating ability and absorbance of substrate molecules on the nanoparticle surface render them ideal for the adsorption, degradation and reduction of pollutants, and other types of environmental applications. However, variation of the chemical composition of such extracts and the concentration of reducing agents therein may impact the reproducibility of nZVI particles in terms of their size and capping. Use of biosynthesized nZVI of a range of sizes will only have a slight effect on Fenton type chemistry in the presence of additional oxidants. This review provides reflection on the current state-of-the-art approaches and highlights the prospects for developing newer, cost-effective and sustainable strategies for the assembly of nanoparticles and their greener environmental applications.

6.2. Challenges

Despite encouraging advances, this field still faces many challenges. The following issues must be addressed to obtain a deeper understanding of sustainable zerovalent iron nanoparticles to ultimately enable the development and benign design of sustainable nZVI for advanced applications.

Chemical syntheses of zerovalent metal nanoparticles often include the use of toxic, hazardous, and sometimes carcinogenic material, which carries a risk of bioaccumulation. Biogenesis of reduced nanoparticles by using metal salts and plant/microorganism-based products/extracts offers the advantage of improved stability by incorporation of capping agents. Nature has evolved a series of enzymatic and nonenzymatic processes to degrade bio-based chemicals in an efficient and eco-friendly manner, which renders these nanomaterials more biocompatible and biodegradable. These abundant nanomaterials can be used to treat water contamination at point emission sources in a sustainable way without affecting aquatic biota. However, the long-term biological effects of nZVI on biological cycles and their fate in the environment need to be thoroughly investigated to ensure safe usage. Additionally, surface capping agents prevent faster oxidation of zerovalent iron and slow down the dissolution of particles under "actual" practical conditions due to the protected surface, leading to the slow release of active species to realize optimum performance. Although bio-based syntheses of nZVI may provide a sustainable route, better control is needed over the particle size and morphology. Only a few microorganisms (e.g., magnetotactic bacteria) can accumulate iron in their cell and produce uniform particles. Genetically engineered microorganisms may be envisaged to solve the problem. However, their use for large-scale synthesis is still in its infancy. Furthermore, the risks of infection and contamination cannot be overlooked. As the composition of reducing and capping agents in bio-based phytochemicals varies from species to species and with different environmental conditions, standardizing the synthetic protocols can be problematic. Various constituents, including amino acids, polyphenols, vitamins, saponins, alkaloids, and sugars, have different reducing capacities. Therefore, it may be difficult to ensure the compositional uniformity of nanoparticles. Even though numerous reports are available on the greener synthesis of nZVI, scalable syntheses on an industrial scale have rarely been reported because of the tedious and energy-intensive extraction processes needed for plant extracts. Plant-based materials are abundant in nature, but the separation of active reducing, capping, and stabilizing phytochemicals from bulk filler/structural materials poses another issue that hampers large-scale deployment of the technology. The large-scale production of bio-derived iron from plants will require the harvesting of reducing constituent-rich plants, which may lead to biodiversity loss through the extinction of local flora and fauna. Additionally, the acidic nature of reducing phytochemicals and the relatively long biodegradation timeframe of such crops may have detrimental effects on soil health. The industrial success of any technology is highly dependent on the availability and cost of precursor materials. Additionally, bio-based syntheses may intensify deforestation, which causes serious environmental problems such as soil erosion and increased greenhouse gas concentration. Appropriate measures should be ascertained before commercial-scale production of these nanomaterials from plant-based products.

6.3. Opinions and benefits

Chemistry performed in the conventional way must be adapted to find better and more advanced alternatives that enable sustainable protocols and technologies having a minimal environmental footprint. The use of greener and less toxic chemicals is desirable to maintain the health of the environment and living creatures. Bio-inspired synthesis of nanomaterials is becoming popular, owing to advantages such as low cost, nontoxic green synthesis, absence of secondary pollution, and scalability. Among such nanomaterials, nZVI has been extensively investigated because of its excellent reducing capability and large surface area-to-volume ratio, making it suitable for application in pollutant removal and degradation, disinfection, and catalysis.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: environmental applications · greener synthesis · nanoparticles · plant extracts · zerovalent iron

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