

A Review on Heavy Metals Removal using Zerovalent Iron Nanoparticles: Synthesis, Mechanism, Applications, and Challenges

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Abstract

The application of zerovalent iron nanoparticles in diverse organic transformations has garnered significant attention over the past decade, primarily due to the high natural availability, low toxicity, and cost-effectiveness of iron metal. The core of zerovalent iron nanoparticles, composed of zerovalent iron, acts as a reducing agent for contaminants, while its outer iron oxide shell offers active sites for chemisorption and facilitates electrostatic interactions with heavy metals. Advances in synthetic methodologies for producing Fe nanoparticles and their stabilization using various support materials have played a pivotal role in enhancing their utility in catalysis. This review consolidates understanding of the nanoscale zerovalent iron structure, its synthesis techniques, removal mechanisms, practical applications for heavy metals such as cadmium (Cd), copper (Cu), and lead (Pb), as well as the challenges associated with its use. This review explores the catalytic properties of zerovalent iron (nZVI) nanoparticles and their critical role in environmental remediation and catalysis. It highlights the factors influencing their performance, including chemical composition, size, surface properties, and the presence of stabilizing agents. The document emphasizes the importance of advanced characterization techniques such as TEM, SEM, and SAXS for understanding particle morphology and structural properties. Challenges such as agglomeration, rapid oxidation, and environmental concerns are addressed, alongside strategies to enhance their efficiency. This comprehensive discussion underscores the significance of nZVI in academic research and industrial applications, providing insights into both their potential and limitations. Additionally, it provides insights into potential future directions for advancing iron nanoparticle-mediated reduction reactions.

Keywords: Adsorption, Challenges, Heavy metals, Mechanism, Oxidation, Reduction, Synthesis, Zerovalent iron nanoparticles

Introduction

Developing nations face increasing challenges in wastewater treatment and water purification due to the growing demand for clean water. Industrialization has led to the depletion of pure water sources, especially affecting the developing world. Water contaminants, including chemicals, microorganisms, and non-biodegradable heavy metals, pose significant risks to human health [1]. Heavy metals in water pose significant environmental and health challenges due to their toxicity, persistence, and bioaccumulative nature. Heavy

metals are a group of metallic elements that have relatively high densities, atomic weights, and are typically toxic or harmful to living organisms even at low concentrations. The term "heavy metals" is commonly used to refer to metals and metalloids with atomic numbers greater than 20 that have a high density (usually greater than 5 g/cm³). Heavy metals like lead (Pb), cadmium (Cd), arsenic (As), and mercury (Hg) can cause severe health issues, including kidney damage, neurological disorders, developmental issues in children,

and cancer [2]. These metals tend to accumulate in the human body over time, leading to long-term health problems even at low exposure levels. Heavy metals are absorbed by aquatic organisms and magnify as they move up the food chain, affecting predators and eventually humans. Metals like chromium (Cr), nickel (Ni), and copper (Cu) can be toxic to fish and other aquatic species, disrupting ecosystems and reducing biodiversity. Heavy metals do not break down in the environment, leading to their continuous presence in water bodies. Metals settle in sediments, acting as long-term sources of pollution that can re-enter the water column under changing environmental conditions [3]. Presence of metals like arsenic or lead in drinking water sources exceeds safe limits, rendering water unsafe for human consumption. Treating water contaminated with heavy metals is often expensive, burdening water treatment facilities and communities. Heavy metals in irrigation water can accumulate in soil and crops, leading to reduced agricultural productivity and contamination of the food supply. Long-term irrigation with contaminated water results in the build-up of toxic metals in soil, affecting soil health and fertility [4]. Conventional water treatment processes often struggle to effectively remove heavy metals due to their high solubility and complexation with organic and inorganic matter in water. The increasing need for water, driven by industrialization, population growth, and environmental degradation, highlights the urgent need for effective water purification solutions [5].

Various methods, including adsorption, electrochemical treatment, ion exchange, and membrane filtration, are used for the removal of heavy metals from aqueous solutions [6]. The choice of method to be adopted depends on factors like the type of heavy metal, concentration, environmental conditions, and the intended application. Among these, adsorption is considered the most effective due to its affordability and ease of use. Several adsorbents, such as activated carbon [7], biochar, chitosan- Al_2O_3 @ SiO_2 composite [8], and graphene oxide, have been explored for heavy metal removal. Iron nanoparticles (nFe), known for their strong adsorption properties, have gained significant attention in recent years for heavy metal remediation [9]. These nanoparticles are inexpensive, non-toxic, and biocompatible, making them ideal for treating heavy metals in aquatic environments [10].

Although materials like iron nanoparticles (nFe) are highly effective at removing heavy metals from aqueous solutions, challenges such as complex synthesis procedures and the need for expensive reagents have hindered their widespread use [11]. To overcome these limitations, there has been growing interest in biosynthesizing nFe using natural plant extracts as reducing agents, making the process more affordable and environmentally friendly. Zerovalent iron nanoparticles (nZVI) has been extensively studied for treating wastewater contaminated with heavy metals, offering a low-toxicity and abundant natural resource. In recent decades, zerovalent iron nanoparticles (nZVI) have emerged as a cutting-edge material for environmental remediation, particularly for heavy metal removal [11,12]. A study demonstrated that nZVI reduced Cr^{6+} to less toxic Cr^{3+} , which subsequently precipitated as $\text{Cr}(\text{OH})_3$ or adsorbed onto iron hydroxides formed during nZVI oxidation. Optimal removal efficiency (> 95 %) was achieved at pH 5 - 7, with the process following pseudo-2nd-order kinetics. While nZVI efficiently removed Cr^{6+} from synthetic and industrial wastewater, challenges such as particle aggregation, surface passivation, and pH sensitivity limit its scalability. Despite these limitations, nZVI is a cost-effective and environmentally friendly option for heavy metal remediation, with potential improvements achievable through surface modifications and composite materials [13]. nZVI has garnered attention due to its unique physicochemical properties, including high specific surface area which enhances reactivity and interaction with contaminants, high redox potential that facilitates reduction and immobilization of heavy metals. Iron is abundant, non-toxic, and sustainable compared to other nanomaterials. It can combine reduction, adsorption, and co-precipitation mechanisms for efficient contaminant removal [14]. This review begins by highlighting the growing research interest in the various types of heavy metals. Following this, various methods for synthesizing zerovalent iron nanoparticles are discussed. An overview of the heavy metal's removal mechanism and application of different characterization techniques that are essential for examining the structural and morphological characteristics of iron nanoparticles has been described here. The review also outlines the challenges encountered in current research and offers predictions for future directions in the field.

Types of different heavy metals

Heavy metals are dense metallic elements that exhibit toxicity even at low concentrations. Their persistence in the environment and tendency to bioaccumulate pose serious risks to both ecosystems and public health. This review explores the key heavy metals, their toxicological impacts, and the various methods employed for their removal.

Chromium (Cr)

Chromium is mainly produced in tanning industry, electroplating, pigment production, and improper industrial waste disposal. Chromium exists primarily in 2 oxidation states in water: Hexavalent chromium (Cr^{6+}) and trivalent chromium (Cr^{3+}). Cr^{6+} is highly toxic, carcinogenic, and soluble, whereas Cr^{3+} is less toxic and less mobile. It pollutes soil and groundwater near industrial areas and also disrupts aquatic ecosystems by altering pH and toxicity levels. Cr^{6+} is reduced to Cr^{3+} via electron transfer and then Cr^{3+} is immobilized on the surface of nZVI or iron oxides. The process is pH-dependent, with optimal removal in neutral to slightly acidic conditions. Studies by Zou *et al.* [15] have shown > 90 % Cr^{6+} removal using nZVI in batch experiments.

Lead (Pb)

Lead is a non-redox-active metal and is primarily found as Pb^{2+} in water, which is highly toxic and bioaccumulative. Leaded gasoline, battery manufacturing, paint, plumbing materials, mining, and smelting are the main sources of lead production. It affects the central nervous system (CNS), especially in children, leading to cognitive impairments and behavioural issues. Chronic exposure can cause anaemia, kidney damage, hypertension, and reproductive issues. Pb^{2+} binds to nZVI surface through complexation or electrostatic interactions. Pb^{2+} can be reduced to metallic Pb^0 , which deposits on nZVI surfaces. Pb^{2+} is incorporated into oxides or iron hydroxides formed during nZVI oxidation. Li *et al.* [16] demonstrated that nZVI achieved a removal efficiency of 96 % for Pb^{2+} in a contaminated water sample.

Arsenic (As)

Mining, pesticide application, industrial discharge, natural leaching from arsenic-rich rocks are the sources of arsenic. Arsenic exists as arsenite (As^{3+}) and arsenate

(As^{5+}), both of which are highly toxic. Acute effects of arsenic are gastrointestinal distress, vomiting, diarrhoea and the chronic effects include skin lesions, hyperpigmentation, cardiovascular issues, cancer (lung, bladder, and skin). Arsenic species adsorb onto iron oxides and hydroxides formed by nZVI. Ferric hydroxides incorporate arsenic ions into their structure by co-precipitation mechanism. nZVI can also convert As^{3+} to As^{5+} , which is less toxic and more easily adsorbed. Removal efficiency increases in the presence of dissolved oxygen (DO) or hydrogen peroxide (H_2O_2). Research by Sankhla *et al.* [17] reported > 99 % removal of As^{3+} using modified nZVI.

Cadmium (Cd)

Cadmium is a non-redox-active metal and exists predominantly as Cd^{2+} in water. Industrial processes (e.g., electroplating, battery production), phosphate fertilizers, and waste incineration, produce cadmium. It is the cause of kidney damage (Itai-Itai disease in Japan), bone demineralization, and respiratory issues and linked to cancer (lungs and prostate). If cadmium persists in soil, it affects crop quality, contaminates water, making it unsafe for drinking and irrigation. Cd^{2+} binds to surface hydroxyl groups (Fe-OH) of nZVI. Cd^{2+} is trapped in iron hydroxide matrices. Removal is highly influenced by pH, with better adsorption at neutral to alkaline conditions. Studies by Chen *et al.* [18] have shown that surface-modified nZVI enhances Cd^{2+} adsorption capacity by 30 %.

Zinc (Zn)

Mining, smelting, galvanization processes, and industrial discharge are sources of zinc production. Zinc primarily exists as Zn^{2+} , which is toxic at high concentrations and can disrupt aquatic ecosystems. It is vital in trace amounts but becomes toxic at elevated concentrations. Acute effects of zinc include nausea, vomiting, and diarrhoea. Chronic exposure can lead to organ damage. Zn^{2+} adsorbs onto nZVI through electrostatic attraction and ion exchange. Zn^{2+} integrates into ferric hydroxides formed during nZVI oxidation. A comparative study by Gupta *et al.* [19] reported nZVI achieved 85 % Zn^{2+} removal under optimal conditions.

Mercury (Hg)

Mercury exists in elemental, inorganic, and organic forms, with methylmercury being the most toxic. Coal combustion, artisanal gold mining, industrial effluents, and improper disposal of electronic waste produces mercury in high amounts. Mercury acts as a neurotoxin affecting the brain and nervous system [20]. Methylmercury (organic form) bioaccumulates in fish, leading to exposure through consumption. It also causes Minamata disease, characterized by sensory impairment and developmental delays. Hg^{2+} is reduced to elemental mercury (Hg^0) by nZVI. Hg^{2+} binds strongly to nZVI due to its high affinity for iron oxides. Removal efficiency increases in the presence of chloride ions, forming stable Hg-Fe complexes. Research by Fisher and World Health Organization [21] highlighted that nZVI achieved 95 % Hg removal in a contaminated sediment study.

Copper (Cu)

Copper is commonly found as Cu^{2+} , which is toxic at elevated concentrations. Mining, electroplating, and agricultural fungicides are its sources. It is essential for humans and plants, but excessive exposure causes liver and kidney damage. Chronic toxicity leads to Wilson's disease, neurological issues, and gastrointestinal distress. Cr^{2+} is reduced to Cu^0 , depositing on the nZVI surface. Cu^{2+} binds to surface hydroxyl groups. Experimental results from Sharma *et al.* [22] show a 90 % removal efficiency for Cu^{2+} using nZVI at neutral pH.

Different techniques for heavy metal removal

Adsorption

Adsorption is an effective method for removing heavy metal ions, such as hexavalent chromium (Cr^{6+}), from aqueous solutions. Various adsorbents, including biosorbents, carbon-based materials, nanoparticles, and polymers, have been studied for their high adsorption capacity and selectivity [23,24]. Four main mechanisms are involved in the adsorption process [25]:

- 1) Electrostatic interaction between positively charged functional groups (e.g., COOH^+ , NH_4^+) and anionic heavy metal species.
- 2) Complete reduction of heavy metals after adsorption onto the adsorbent.
- 3) A combination of adsorption and reduction of heavy metals, followed by further adsorption.
- 4) Adsorption and transformation of heavy metals, after which some may return to the solution.

The presence of electron-donating sites like O, S, and N can reduce Cr^{6+} to Cr^{3+} , especially when cations like Fe^{2+} are present, enhancing the reduction process. Recent reviews highlight various adsorbents, such as activated carbon, carbon nanotubes, graphene, polymers, magnetic iron oxides, nanomaterials, and biosorbents, that have shown promise in removing heavy metals from water [26,27].

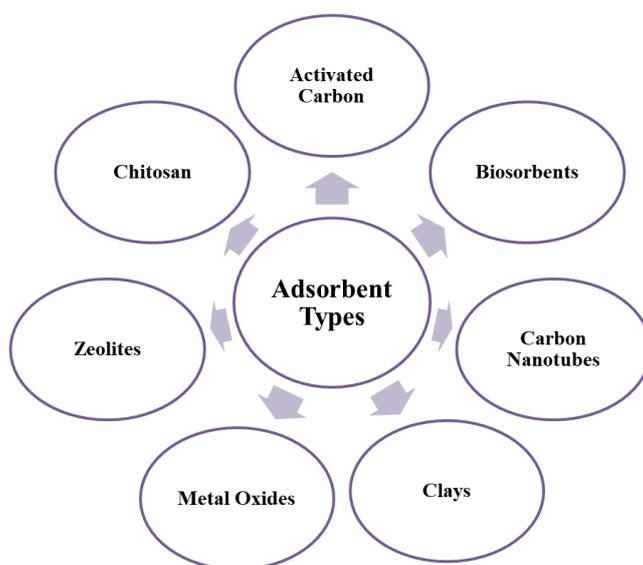


Figure 1 Different types of adsorbents.

Figure 1 categorizes various types of adsorbents, which are materials used to remove substances from liquids or gases by adsorption. The central term, “Adsorbent Types” is surrounded by key categories of adsorbents, including:

- **Activated Carbon:** Widely used due to its high surface area and porosity, effective for removing organic pollutants and impurities.
- **Biosorbents:** Naturally occurring materials like algae, fungi, or agricultural waste that can adsorb heavy metals and dyes.
- **Carbon Nanotubes:** Advanced nanomaterials with excellent adsorption capabilities due to their large surface area and chemical properties.
- **Clays:** Naturally occurring materials with layered structures, used to adsorb heavy metals and organic compounds.
- **Metal Oxides:** Inorganic materials effective in adsorbing pollutants like arsenic and fluoride.
- **Zeolites:** Crystalline aluminosilicates with high ion-exchange capacities, useful for water purification and gas separation.
- **Chitosan:** A biopolymer derived from chitin, effective for adsorbing heavy metals and dyes.

Membrane filtration

Membrane filtration has garnered a lot of interest for wastewater treatment and has been widely used to remove heavy metal ions [28]. To this end, a range of membrane types, including reverse osmosis, ultrafiltration, nanofiltration, and microfiltration, were used, each classified based on the size of the pore [29]. Membrane filtration is a process that uses hydraulic pressure to separate materials using membranes. Membrane filtration is a sophisticated form of water treatment that offers the benefits of ease of use, a compact floor area, having strong selective permeability, no phase shift during the separation process, and the ability to operate at room temperature [30,31]. To treat 240 and 170 mL of copper ions and lead ions, respectively, [32] created a new nanocomposite film. Although the membrane separation method has the advantages of high efficiency, energy conservation, and lack of secondary pollution, it will gradually lose capacity and become polluted if used for an extended period of time. Membrane fouling significantly restricts the widespread use of membrane filtration [31].

Table 1 provides a comparative analysis of various techniques for heavy metal removal from aqueous environments. It categorizes the methods based on their advantages and disadvantages, offering a clear perspective on their efficiency, practicality, and limitations.

Table 1 Comparative analysis of various techniques for heavy metal removal.

Technique	Advantages	Disadvantages
Adsorption	<ul style="list-style-type: none"> - High efficiency and selectivity for heavy metals. - Utilizes a variety of adsorbents like activated carbon, biosorbents, and nanoparticles. - Can be combined with other processes (e.g., reduction). 	<ul style="list-style-type: none"> - Regeneration and disposal of spent adsorbents may be costly and challenging. - Adsorption capacity depends on pH, temperature, and concentration. - Possible desorption of contaminants under certain conditions.
Membrane filtration	<ul style="list-style-type: none"> - High efficiency in removing heavy metals and other pollutants. - Compact design and ease of use. - No secondary pollution during operation. 	<ul style="list-style-type: none"> - Membrane fouling and clogging over extended use. - High operational and maintenance costs. - Limited lifespan of membranes.
Photocatalytic treatment	<ul style="list-style-type: none"> - Environmentally friendly and produces no hazardous by-products. - Effective under UV and visible light with appropriate catalysts. 	<ul style="list-style-type: none"> - Low reduction efficiency and slow reaction rates for certain heavy metals. - High cost of certain photocatalysts like Ag₂S and CdS.

Technique	Advantages	Disadvantages
Electrochemical treatment	<ul style="list-style-type: none"> - Energy-efficient and environmentally compatible. - Can be applied to a variety of contaminants. 	<ul style="list-style-type: none"> - Efficiency highly dependent on electrode material and operating conditions. - High initial setup cost and maintenance requirements.
Microbiological treatment	<ul style="list-style-type: none"> - Utilizes natural processes, reducing chemical usage. - Capable of reducing hazardous metals to less toxic states. 	<ul style="list-style-type: none"> - Slow process and highly sensitive to environmental conditions like pH and temperature. - Requires careful monitoring and optimization for specific bacterial strains.
Floatation	<ul style="list-style-type: none"> - High recovery rates and selective separation of heavy metals. - Simple and fast process. 	<ul style="list-style-type: none"> - Requires chemical additives like precipitants, which may have secondary impacts. - Efficiency may be influenced by water chemistry and contaminant type.
Ion exchange	<ul style="list-style-type: none"> - High removal efficiency with selective ion-exchange resins. - Suitable for large-scale operations. 	<ul style="list-style-type: none"> - Resins are costly and may require frequent replacement. - Sensitive to fouling and clogging by organic and particulate matter.

Photocatalytic treatment

Another very efficient and affordable method that produces no dangerous compounds is the reduction of heavy metals by catalysis and photocatalysis [33]. Much emphasis has been paid to the quest for highly active photocatalysts for the reduction of heavy metals under UV, solar, and especially visible light irradiation [34]. For this purpose, Ag₂S, CdS, CuS, SnS₂, and WO₃, frameworks of metal-organic, and numerous other different photocatalysts have been used; nevertheless, their slow rate of reduction and low reduction efficiency are the primary disadvantages [35].

Electrochemical treatment

The advantages of electrochemical processes, such as their energy efficiency, environmental compatibility, cost, safety, speed, and versatility have led to a notable surge in interest in them as an alternative wastewater treatment method in recent years [36]. The material of electrode and cell parameters, such as current, density, water composition, and mass transfer, affect how efficient these processes are [37].

Microbiological treatment

Different contaminants can be reduced by microorganisms and eliminated from wastewater or the aquatic environment. Higher oxidation states of metallic and metalloid chemicals, which are more hazardous than lower oxidation states, can be reduced by the

microorganisms [38]. Numerous studies have been conducted on the microbial reduction of heavy metals utilising a range of bacteria in both aerobic and anaerobic methods. Unlike anaerobic bioremediation, the aerobic method requires oxygen for microbial activity to occur [39]. The bacteria use oxygen as an electron acceptor and a carbon substrate as an electron giver, respectively. Oxygen can be substituted as an electron acceptor in anaerobic metabolism by organic molecules, oxidised materials, CO₂, nitrate, or sulphate. In order to remove heavy metals from microorganisms, 3 stages are usually required: (i) Attachment to the cell surface, (ii) Translocation of heavy metal within the cell, and (iii) Reduction of heavy metals to lower oxidation states [40].

Floatation

Because of its high recovery, high separation yields, simplicity, speed, and selective separation, floatation is a widely utilised gravity-based separation method in cost-effective wastewater treatment (i.e., selective separation of ions and metal ions recovery) [41]. It comes from mineral processing and can be used for metal ion separation by bubble attachment from liquid phase [42]. Dissolved air floatation, ion floatation, and precipitation-flotation are the 3 primary floatation techniques for the removal of metal ions [43]. It has also been suggested as a helpful method for removing Cr (VI) from aquatic systems, and a number of studies have been documented in the literature. In order to accomplish this,

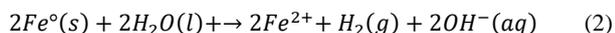
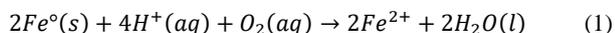
a precipitant, such as ferrous salts, is used to convert Cr (VI) to Cr (III), which may then be extracted by precipitate flotation [44].

Ion exchange

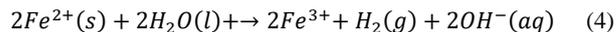
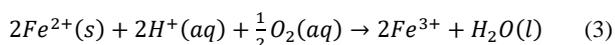
In order to remove heavy metals, 1 well-known physicochemical method that has garnered a lot of interest is the ion exchange procedure, which involves a reversible exchange of ions between solid and liquid phases. Several ion exchange resins were investigated in this regard [45]. For instance, Dowex 2-X4 ion exchange resin is used to remove 100 % of the Cr (VI) ions from genuine plating wastewater [46]. The strongly basic anionic resin was employed as anionic exchangers in columns in its oxide form. Under ideal circumstances, For IRN77 and SKN1 resins, the adsorption capacities were determined to be 35.38 and 46.34 mg/g, respectively [47].

Aqueous chemistry of nZVI (Fe⁰)

Metallic iron (Fe⁰), commonly referred to as zerovalent iron, is highly prone to oxidation in aqueous environments. This oxidation primarily proceeds through an electrochemical mechanism comprising anodic and cathodic processes. At the anode, iron dissolves, forming either soluble ionic species or insoluble oxides and hydroxides, while reduction reactions occur at the cathode. In natural water systems, dissolved oxygen (DO) and water serve as the principal oxidizing agents, with oxygen being the thermodynamically preferred reactant, as shown in Eqs. (1) and (2):



The primary product of these reactions is the ferrous ion (Fe²⁺), which can subsequently undergo further oxidation, as demonstrated in Eqs. (3) and (4):



As indicated by these reactions, an increase in solution pH either consumes protons or generates hydroxide ions. Due to its extremely high reactive surface area (up to 100 m²/g), nZVI rapidly establishes chemically reducing conditions when introduced into aqueous systems, as highlighted in reactions (2) and (4). This property makes nZVI an effective agent in altering the chemical dynamics of aqueous environments [48].

Role of phytonanotechnology

Phytonanotechnology, as described in the paper, is a novel and evolving field that leverages plant-based resources for synthesizing nanoparticles, particularly for environmental and medical applications. Plant extracts contain polyphenols, flavonoids, tannins, and antioxidants that play a dual role: Reducing agents to convert metal ions into their nanoparticle form. Stabilizing agents to prevent aggregation of nanoparticles, ensuring they retain their desired size and surface properties. Examples include extracts from green tea, eucalyptus leaves, mango peels, and peanut skins [49]. Different plants result in nanoparticles with varied properties (e.g., size, shape, and reactivity), which can be tailored to specific applications. Nanoparticles synthesized via phytonanotechnology are effective in removing heavy metals like chromium (Cr), cadmium (Cd), lead (Pb), and copper (Cu) from wastewater. Their high reactivity and surface area enhance adsorption and reduction processes. Nanoparticles synthesized from plants often exhibit greater efficiency in removing metals under acidic conditions, making them suitable for industrial wastewater treatment [50]. Some plant-based nanoparticles (like ZVI NPs) also exhibit antimicrobial activity, making them useful in combating pathogens. Nanoparticles synthesized from plant extracts may have applications in enhancing soil quality and plant health due to their bioactive components [51]. **Table 2** provides a view of how phytonanotechnology works and its advantages for addressing environmental challenges [50].

Table 2 Role of phytonanotechnology.

Aspect	Details
Transformation of metals	<ul style="list-style-type: none"> Converts metal salts (e.g., iron salts) into nanoparticles using plant extracts without harmful chemicals, ensuring an eco-friendly synthesis process.
Use of plant extracts	<ul style="list-style-type: none"> Plant extracts act as both reducing and stabilizing agents Active components: Polyphenols, flavonoids, tannins, antioxidants stabilize nanoparticles and prevent aggregation.
Applications in heavy Metal removal	<ul style="list-style-type: none"> Effective in removing heavy metals like Cr, Cd, Pb, Cu from wastewater Works well at low pH, ideal for treating industrial wastewater.
Cost-effectiveness	<ul style="list-style-type: none"> Uses low-cost, renewable plant materials Energy-efficient process requiring minimal resources and equipment.
Environmental applications	<ul style="list-style-type: none"> Used in water purification via adsorption and reduction of heavy metals Exhibits antimicrobial properties, tackling pathogens in wastewater.
Scalability	<ul style="list-style-type: none"> The simplicity of the process makes it adaptable for large-scale industrial applications.
Advantages	<ul style="list-style-type: none"> Eco-friendly: Biodegradable and non-toxic Produces minimal hazardous byproducts compared to chemical synthesis Suitable for sustainable nanotechnology.

Zerovalent iron nanoparticles (nZVI): Traditional and environmentally friendly methods of synthesis

Zerovalent iron nanoparticles (nZVI) are a prominent nanomaterial utilized for environmental remediation due to their exceptional reactivity and ability to remove contaminants. Their synthesis methods are broadly categorized into traditional methods, which prioritize efficiency but involve chemical and energy-intensive processes, and environmentally friendly (green) methods, which focus on sustainability, reduced toxicity, and the use of renewable materials [52]. A detailed discussion of these methods is presented below:

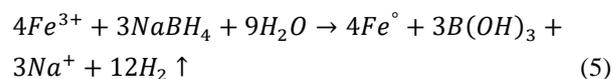
Traditional methods of synthesis

Traditional methods of synthesizing nZVI rely heavily on chemical and physical processes designed for precision and control. These methods are widely studied and applied due to their ability to produce uniform, highly reactive nanoparticles, but they come with significant environmental and economic challenges [53].

Chemical reduction

In this method, iron salts, such as ferric chloride (FeCl₃) or ferrous sulfate (FeSO₄), are dissolved in a solution and reduced by a strong reducing agent like sodium borohydride (NaBH₄) under inert or oxygen-free

conditions. The reaction typically yields nZVI as a black precipitate:



This process produces nanoparticles with high reactivity and uniform size distribution. Also, reaction parameters such as temperature, concentration, and pH can be controlled to fine-tune nanoparticle properties. The drawbacks of using this chemical reduction method is that it requires expensive and hazardous reducing agents, generates toxic by-products like borates, and operates under inert conditions to prevent rapid oxidation, increasing costs.

Physical methods

Ball milling

Ball milling is a mechanical technique used to synthesize zerovalent iron nanoparticles (nZVI) by grinding bulk materials into nanoscale dimensions. This top-down approach has been extensively used for the preparation of various nanomaterials, including nZVI, due to its simplicity, scalability, and ability to produce particles with controlled size and morphology. Iron particles are subjected to mechanical grinding under high

energy to achieve nanoscale dimensions. [54] used high-energy ball milling to synthesize nZVI particles with sizes ranging from 10 to 50 nm. They found that milling time significantly influenced particle size, with prolonged milling leading to finer nanoparticles. Study by Wang *et al.* [55] observed the formation of a core-shell structure in nZVI produced by ball milling. The metallic core was surrounded by an oxide shell, enhancing stability while maintaining reactivity. It is a simple and straightforward process, but consumes high energy. Also, Particles tend to aggregate, requiring additional stabilization steps. Ball milling remains a robust and versatile method for synthesizing zerovalent iron nanoparticles. Its combination of mechanical simplicity and effectiveness in producing reactive nanoparticles ensures its continued relevance in both research and industrial applications.

Thermal decomposition

Thermal decomposition is a chemical method widely used for synthesizing zerovalent iron nanoparticles (nZVI) by decomposing iron precursors at elevated temperatures. This method provides precise control over particle size, morphology, and surface properties, making it a preferred technique for producing high-quality nZVI for advanced applications [56]. The thermal decomposition process involves the breakdown of iron precursors, such as iron pentacarbonyl ($\text{Fe}(\text{CO})_5$), iron acetylacetonate ($\text{Fe}(\text{acac})_3$), or iron oleate, under controlled conditions. Heating these precursors induces chemical reactions that release volatile by-products, leaving behind zerovalent iron nanoparticles. Serda [57] synthesized nZVI using $\text{Fe}(\text{CO})_5$ under argon at 300 °C. They observed uniform spherical particles with a size of ~10 nm. They also reported high reactivity and stability due to the core-shell structure (metallic core with an oxide shell). Kim *et al.* [58] compared nZVI synthesized via thermal decomposition with those produced by chemical reduction. Thermal decomposition-derived nanoparticles showed higher catalytic efficiency in degrading chlorinated hydrocarbons due to their uniform size and higher surface area. This method produces particles with controlled morphology and narrow size distributions. It requires high energy, toxic and volatile precursors.

Microemulsion techniques

Microemulsion techniques are an advanced method for synthesizing zerovalent iron nanoparticles (nZVI) using stabilized emulsions as reaction media. This technique leverages the nanoscale dispersion of reactants within microemulsions, allowing precise control over particle size, morphology, and distribution. It is particularly useful for producing uniform and monodisperse nanoparticles. A microemulsion is a thermodynamically stable mixture of water, oil, and surfactant, often forming distinct domains such as water-in-oil (W/O) or oil-in-water (O/W) phases. In the context of nZVI synthesis, the water phase contains the iron precursor, and the oil phase provides a confined nanoscale environment for controlled particle formation. A study by [59], synthesized iron nanoparticles using a W/O microemulsion with FeCl_3 as the precursor and NaBH_4 as the reducing agent. They reported uniform particle sizes (~10 - 20 nm) with excellent dispersion due to surfactant stabilization. Mukherjee [60] demonstrated that nZVI produced via microemulsions exhibited higher reactivity in removing trichloroethylene compared to those synthesized via conventional methods. Lu *et al.* synthesized core-shell nZVI particles using a microemulsion technique. They reported improved oxidation resistance due to the surfactant-induced stabilization.

Environmentally friendly (green) methods of synthesis

Green synthesis methods are designed to overcome the limitations of traditional techniques by using renewable resources, reducing toxicity, and minimizing the environmental impact. These methods focus on natural reducing agents, biological processes, and eco-friendly conditions, aligning with the principles of green chemistry. Below is an in-depth elaboration of the green synthesis methods with supporting scientific evidence.

Biological methods

Microbial synthesis

Microbial synthesis utilizes the natural metabolic processes of microorganisms such as *Shewanella spp.*, *Geobacter spp.*, and certain fungi to reduce iron ions (Fe^{3+} or Fe^{2+}) to zerovalent iron (Fe^0). Microbial cells produce reducing agents like hydrogen or extracellular metabolites (e.g., flavins, organic acids) during their

metabolism. These agents mediate the reduction of Fe^{3+} to Fe^0 :



It is a sustainable and renewable method. It eliminates the need for hazardous chemicals and produces nanoparticles in aqueous environments, reducing solvent use. The disadvantage of this method is that it requires optimal growth conditions (temperature, pH, and nutrients), and is time-consuming compared to chemical methods. *Geobacter metallireducens* was shown to enzymatically reduce Fe^{3+} to Fe^0 , forming nZVI in situ. TEM analysis revealed nanoparticle sizes ranging from 10 - 50 nm [11]. *Shewanella oneidensis* facilitated the reduction of Fe^{3+} to Fe^0 under anaerobic conditions, confirming the role of microbial metabolism in nZVI synthesis [61].

Enzymatic reduction

This method isolates specific enzymes (e.g., reductases) from microorganisms to catalyse the reduction of iron ions to Fe^0 . Enzymes such as nitrate reductase and hydrogenase catalyse the electron transfer process, reducing Fe^{3+} to Fe^0 . Nitrate reductase extracted from *Fusarium oxysporum* successfully reduced Fe^{3+} to Fe^0 , yielding nanoparticles of 5 - 15 nm. FTIR analysis confirmed the interaction of enzymes with the nanoparticles [62]. The Advantage of this method is targeted reduction with high specificity and is environmentally benign and avoids bulk chemical use. High cost and complexity of enzyme isolation and purification and requirement of a controlled reaction environment are some of its limitations [56].

Plant-based synthesis (Phyto-synthesis)

Phyto-synthesis uses plant extracts containing bioactive compounds such as polyphenols, flavonoids, and tannins to reduce iron salts to nZVI. These biomolecules serve dual roles as reducing agents and stabilizers, preventing nanoparticle aggregation. This method of synthesizing iron nanoparticles is cost-effective and environmentally friendly, as it uses biodegradable, water-soluble plant extracts to reduce iron to the nanoscale. When combined with heated water, these extracts, rich in polyphenols, reduce iron ions to nZVI and act as capping agents. This process produces

spherical nZVI particles with sizes between 5 and 15 nm. Various plant species, such as zinger [63], vine leaves, green tea [64], *Crataegus pentagyna* [65], oak, eucalyptus [64], mint [66], pomegranate leaves, and hippophae [67], have been used for green nanoparticle production. The resulting nanoparticles are covered with proteins and polyphenols, preventing oxidation and ensuring uniform dispersion without aggregation. Studies have shown that green-synthesized nanoparticles have unique morphology and structure, along with high efficiency compared to chemically produced ones [68]. Li *et al.* [69] used green tea extract to synthesize nZVI with particle sizes ranging from 10 - 30 nm. XRD confirmed the crystalline structure of Fe^0 . Neem leaf extract was used to produce stable nZVI, which effectively removed arsenic from contaminated water. SEM images demonstrated the formation of spherical nanoparticles [70]. It is an eco-friendly, renewable, and cost-effective method. It produces nanoparticles with reduced aggregation due to capping by biomolecules and avoids the use of hazardous chemicals.

Green magnetic-assisted synthesis

This technique combines green reducing agents with controlled magnetic fields to enhance the uniformity and reactivity of nZVI. The magnetic field directs the alignment and growth of nanoparticles during synthesis. [71] combined glucose as a reducing agent with a magnetic field to produce nZVI with enhanced reactivity for degrading chlorinated solvents. Magnetic characterization using VSM (vibrating sample magnetometry) confirmed improved magnetic properties. This method produces highly reactive nanoparticles with controlled size and shape and improves uniformity and prevents aggregation.

Environmentally friendly synthesis methods for nZVI, including microbial, enzymatic, plant-based, and green reducing agents, provide sustainable and eco-friendly alternatives to traditional techniques. These approaches leverage renewable resources and natural processes, reducing the environmental footprint of nZVI production [72]. **Table 3** provides a comparative analysis of traditional methods and green methods for synthesizing zerovalent iron nanoparticles (nZVI) based on 5 key criteria: toxicity, scalability, reproducibility, energy requirements, and environmental impact. Scientific studies validate the effectiveness of these

methods, demonstrating their potential in water treatment, environmental remediation, and industrial applications. However, challenges like variability in

natural materials and scaling up production need to be addressed for broader adoption [50].

Table 3 Comparison of methods.

Criteria	Traditional methods	Green methods
Toxicity	High due to chemicals used	Low to negligible
Scalability	Industrially scalable	Potentially scalable with research
Reproducibility	High	Moderate
Energy Requirements	High	Low
Environmental Impact	Significant	Minimal

Enhancing the stability of nZVI

Zerovalent iron nanoparticles (nZVIs) are widely used in environmental remediation, but their practical applications face challenges due to instability, aggregation, and oxidation. Various strategies have been developed to enhance their stability, reactivity, and longevity. Below, the methods are elaborated as:

Integration of a 2nd metal into nZVI

Incorporating a 2nd metal (e.g., Pd, Ni, Cu, or Ag) forms bimetallic nanoparticles, enhancing stability and reactivity. The 2nd metal acts as a catalyst or sacrificial anode, protecting Fe⁰ from oxidation. The secondary metal increases electron transfer rates, promoting efficient contaminant reduction. It forms a galvanic couple with Fe⁰, where the noble metal prevents oxidation of the iron core. Zhang *et al.* [73] synthesized Pd-Fe bimetallic nanoparticles for chlorinated hydrocarbon degradation. Pd enhanced stability by catalysing hydrogen generation and preventing Fe⁰ oxidation. Also, a study by He *et al.* [74] reported increased stability and reactivity of Ni-Fe nanoparticles in removing TCE due to reduced aggregation and passivation.

Surface coating of nZVI

Coating nZVIs with polymers, surfactants, or biomolecules forms a protective layer that prevents aggregation and oxidation. The common coating materials used are polymers like polyethylene glycol (PEG), polyvinyl alcohol (PVA), surfactants like cetyltrimethylammonium bromide (CTAB), sodium

dodecyl sulphate (SDS), and biomolecules such as chitosan, and alginate. The coating provides steric or electrostatic stabilization, reducing particle collisions and aggregation. It forms a barrier against oxygen and water, slowing down oxidation. He *et al.* [74] stabilized nZVI with PVP (polyvinylpyrrolidone), showing improved dispersion and reactivity in TCE degradation. Kharisov *et al.* [75] demonstrated enhanced stability of SDS-coated nZVI in aqueous systems, with slower oxidation and better mobility.

Emulsified zerovalent iron nanoparticles (nZVIs)

Encapsulating nZVIs in water-in-oil emulsions ensures stability and targeted delivery in contaminated environments. The emulsion droplets act as microreactors, confining nZVI and protecting it from aggregation and oxidation. The hydrophobic oil phase reduces direct exposure to water and oxygen. It is particularly effective in treating dense non-aqueous phase liquids (DNAPLs) in groundwater. Quinn *et al.* [76] synthesized emulsified nZVIs with soybean oil for DNAPL remediation. They achieved sustained reactivity and enhanced distribution in the subsurface. Bennett *et al.* [77] demonstrated higher stability of nZVIs in oil emulsions, with improved transport in porous media.

Fixed support

Immobilizing nZVIs on fixed supports (e.g., activated carbon, silica, zeolites) enhances stability and reduces mobility issues. The support provides a physical

matrix that prevents aggregation and facilitates uniform dispersion. Reduces the direct exposure of nZVI to oxygen and water. Li *et al.* [78] immobilized nZVI on activated carbon, achieving improved stability and reactivity for nitrate reduction. Gao *et al.* [79] demonstrated that silica-supported nZVI showed reduced aggregation and prolonged reactivity in heavy metal remediation.

Encapsulation of nZVI

Encapsulation involves enclosing nZVIs in protective matrices such as polymers, hydrogels, or silica shells. The encapsulating material forms a barrier, preventing exposure to oxygen and moisture. It allows controlled release of Fe⁰ for sustained reactivity. Kim *et al.* [58] encapsulated nZVI in polyacrylamide hydrogels for arsenic removal. It improved stability and extended reactivity due to reduced oxidation. Dong *et al.* [80] encapsulated nZVI in mesoporous silica shells, achieving high stability and reusability for contaminant degradation.

Electrostatic stabilization

Electrostatic stabilization involves creating a surface charge on nZVI particles to prevent aggregation. Adding charged stabilizers (e.g., SDS, citrate ions) induces electrostatic repulsion between particles, maintaining dispersion. Phenrat *et al.* [81] stabilized nZVI with carboxymethyl cellulose (CMC), achieving high dispersion and improved stability in water. Dong *et al.* [82] demonstrated that citrate-coated nZVI exhibited reduced aggregation and enhanced mobility in soil systems.

Steric stabilization

Steric stabilization involves using polymeric or surfactant coatings that create physical barriers, preventing particle aggregation. Long-chain polymers

adsorb onto the particle surface, creating steric hindrance that keeps particles separated. He *et al.* [74] applied PEG to nZVI, showing significant stability improvement in aqueous systems. Xu *et al.* [50] demonstrated that PVA-coated nZVI maintained high reactivity for TCE degradation over extended periods.

Stabilizing zerovalent iron nanoparticles is essential for enhancing their practical applications in environmental remediation and catalysis. Strategies such as integrating secondary metals, surface coatings, encapsulation, and electrostatic or steric stabilization have been scientifically validated to improve particle stability, reduce aggregation, and prolong reactivity. Continued research into these methods, particularly using green and scalable approaches, holds great promise for advancing nZVI technology.

Understanding the core-shell structure of nZVI

nZVI nanoparticles typically exhibit a core-shell structure, which plays a crucial role in their reactivity and stability. nZVI nanoparticles are generally spherical or quasi-spherical with diameters ranging from 1 to 100 nm. The inner core is composed of pure metallic iron (Fe⁰) in its zerovalent state. This core is responsible for the redox properties of nZVI, allowing it to act as a reducing agent for contaminants. The outer layer is an oxide or hydroxide shell, usually composed of iron oxides (e.g., FeO, Fe₂O₃, Fe₃O₄) or iron hydroxides (e.g., Fe(OH)₃) [83]. This shell forms due to the rapid oxidation of the iron core when exposed to air or water. It provides some level of protection but can also influence the reactivity of nZVI by acting as a barrier to electron transfer. Their high surface area to volume ratio enhances their reactivity but also makes them prone to aggregation [84]. **Figure 1** emphasizes the dual-layer structure and highlights the importance of the shell in protecting the core while participating in additional environmental processes.

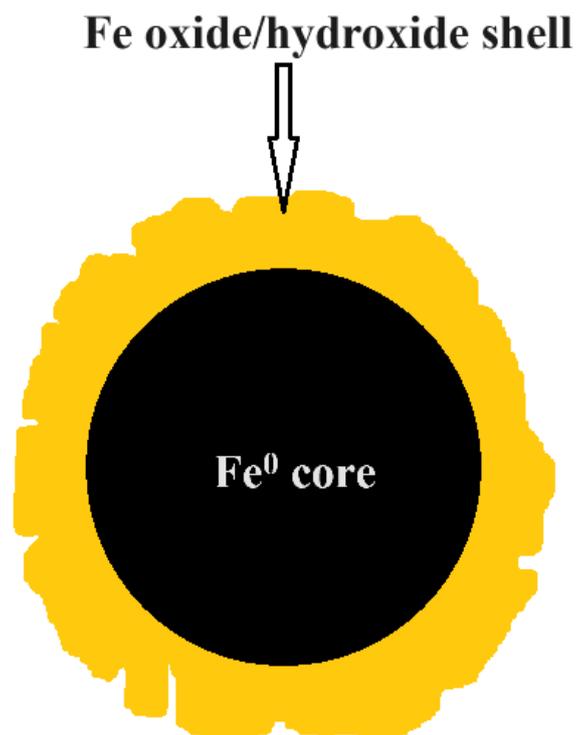


Figure 1 Core-shell model of zerovalent iron nanoparticle.

The surface of nZVI nanoparticles often contains functional groups such as hydroxyl (–OH) and oxide groups. These groups influence the interaction between nZVI and pollutants, as well as the nanoparticles' stability in aqueous environments. Surface modifications, such as coatings with polymers, surfactants, or biochar, are often applied to enhance stability, reduce toxicity, and prevent agglomeration. nZVI nanoparticles tend to aggregate due to their high surface energy and magnetic properties. Aggregation reduces their effective surface area and reactivity. Surface modifications or doping with other metals are common strategies to mitigate this issue [53].

Characterization of zero valent iron nanoparticles

The catalytic efficiency of metallic nanoparticles is heavily impacted by various factors, including their chemical composition, dimensions, size distribution, geometry, surface characteristics, stabilizing agents, or organic coatings present on their surfaces, as well as the metal concentration in the catalytic system within the reaction medium. Consequently, comprehensive characterization of nanoscale Fe-based catalysts through diverse physical techniques is critical. Numerous

analytical methods have been utilized to investigate the properties of Fe nanoparticles, particularly aspects related to their catalytic functionality [85]. Although the mathematical foundations and theoretical details of these techniques fall outside the scope of this discussion, they are extensively detailed in a recent review by [86]. The emphasis here is confined to summarizing the purposes these characterization tools serve.

The size, distribution, and surface topology of Fe nanoparticles are commonly examined using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Advanced approaches like High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM) and High-Resolution Transmission Electron Microscopy (HRTEM) offer enhanced insights into the morphology of Fe nanoparticles and their supporting materials [87]. Dynamic Light Scattering (DLS) is frequently applied to measure the size and size distribution of Fe nanoparticles in liquid dispersions. Additionally, techniques such as UV-Visible (UV-Vis) spectrophotometry, guided by Mie theory, are utilized to estimate the size, size distribution, and shape of Fe-Plasmonic bimetallic or core-shell nanoparticles. Another method, Small-Angle X-ray

Scattering (SAXS), is employed to determine the dimensions of Fe nanoparticles [88].

The structural features of iron nanoparticles, such as atomic arrangement and distribution, are critical for catalytic applications and are analyzed using Wide-Angle X-ray Scattering (WAXS) and X-ray Absorption Near-Edge Spectroscopy (XANES). The nanoscale Fe content within a catalytic system, usually quantified as the molar ratio of the catalyst to the substrate, holds significant relevance for both academic research and industrial applications [89]. This is commonly measured through Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma (ICP) analysis, or Elemental Analysis (EA). Furthermore, these methods are crucial for studying the leaching of Fe nanoparticles from solid supports during catalytic reactions [90]. To evaluate leaching, the Fe nanocatalyst is separated magnetically, and the filtrate from the reaction mixture is analysed using one of the aforementioned methods to quantify the amount of Fe released from the support. These analytical techniques are widely acknowledged and extensively utilized by experts in the field of catalysis for characterizing metal-based catalysts [88].

ZVI-NPs' mechanism of removing heavy metals

Zerovalent iron nanoparticles (nZVI) have emerged as a promising material for removing heavy metals from water and soil due to their high reactivity, large surface area, and redox potential. The removal of heavy metals by nZVI is governed by a combination of redox reactions, adsorption, co-precipitation, and oxidation processes [40]. Each mechanism contributes uniquely, depending on the type of heavy metal, environmental conditions (e.g., pH, presence of oxygen), and the physicochemical properties of nZVI [91]. **Figure 3** represents the schematic diagram for pollutant removal in ZVI systems. Below is an in-depth description of these mechanisms:

Reduction

Reduction is the most critical mechanism for removing heavy metals, particularly those that are redox-sensitive. nZVI acts as an electron donor, reducing the

oxidation state of heavy metal ions to less toxic or less soluble forms [92].

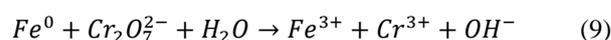
Electron Transfer: nZVI undergoes oxidation, donating electrons to the heavy metal ion:



The released electrons reduce the metal ion:



Example: Hexavalent Chromium (Cr⁶⁺): Cr⁶⁺ (highly toxic) is reduced to Cr³⁺ (less toxic), which precipitates as Cr(OH)₃ under neutral to basic conditions:



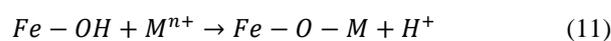
Lead (Pb²⁺): Pb²⁺ is reduced to metallic Pb⁰, which deposits onto the nZVI surface:



Adsorption

Adsorption is a surface phenomenon where heavy metal ions bind to the surface of nZVI through electrostatic interactions, complexation, or ion exchange [93].

Surface Interactions: The surface of nZVI has hydroxyl groups (Fe–OH) and other reactive sites that interact with metal ions:



This mechanism is particularly effective for non-redox-active metals (e.g., Cd²⁺, Zn²⁺) that cannot undergo reduction.

pH Dependence: At lower pH, the surface charge of nZVI becomes positive, reducing adsorption due to electrostatic repulsion with cations. At neutral to alkaline pH, deprotonation of surface hydroxyl groups enhances adsorption.

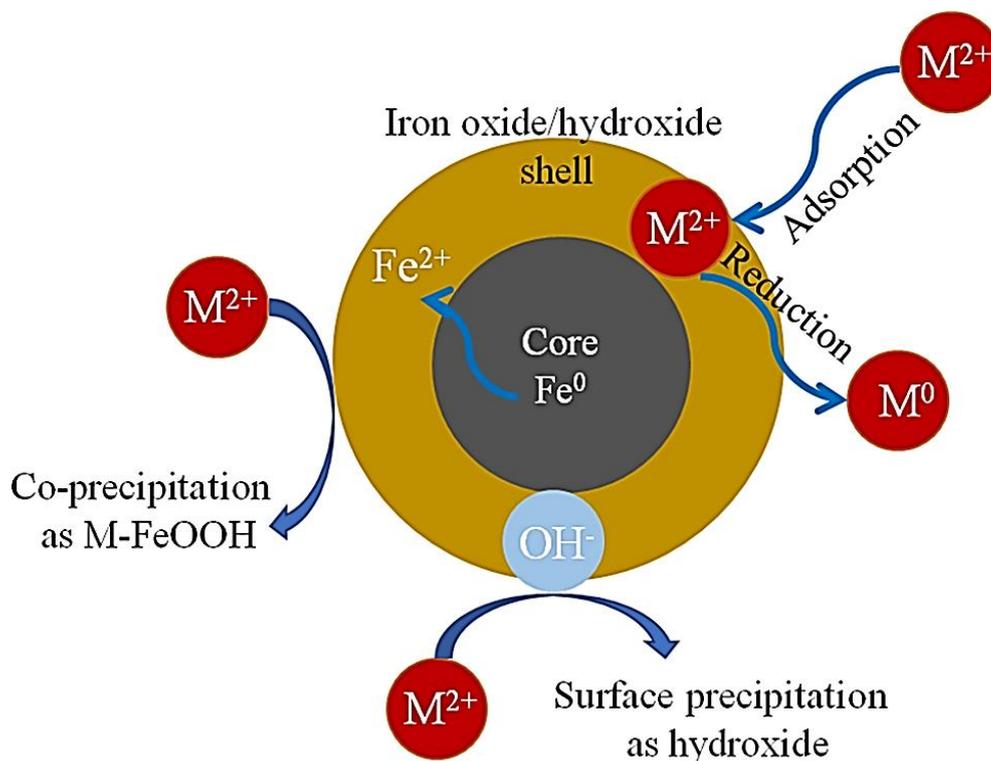
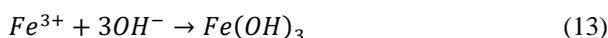
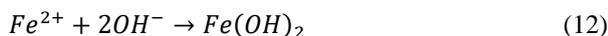


Figure 3 Schematic diagram for pollutant removal in ZVI systems [94].

Co-precipitation

Co-precipitation occurs when iron released during nZVI oxidation forms insoluble compounds (e.g., ferric hydroxides), which trap heavy metals in their structure [95].

Iron Oxide/Hydroxide Formation: As nZVI oxidizes, Fe^{2+} or Fe^{3+} reacts with water or hydroxide ions to form iron oxides or hydroxides:



Heavy Metal Immobilization: Heavy metals either precipitate directly or are incorporated into the iron hydroxide matrix:



Example: Arsenic (As^{3+}/As^{5+}): Arsenic ions are adsorbed onto or co-precipitated with ferric hydroxides, forming stable complexes that immobilize arsenic.

Oxidation (indirect pathway)

nZVI generates reactive oxygen species (ROS) such as hydroxyl radicals ($\bullet OH$) and superoxide (O_2^-) during its reaction with dissolved oxygen or water. These ROS can oxidize heavy metals or degrade organic-bound metals [96].

Fenton-Like Reactions: In the presence of dissolved oxygen or hydrogen peroxide, Fe^{2+} catalyzes the formation of hydroxyl radicals:



Oxidative Transformation: Organic-bound heavy metals are oxidized, releasing free metal ions that can then undergo reduction, adsorption, or co-precipitation.

Heavy metal adsorption process kinetics of nZVI

The kinetics of heavy metal adsorption using nZVI are essential to understanding the rate and mechanism of the process. Kinetic models help describe how adsorption occurs over time and identify rate-limiting steps such as external mass transfer, chemical interactions, or intraparticle diffusion.

Pseudo-first-order kinetics

In pseudo-first order, we assume the adsorption rate is directly proportional to the difference between the amount of metal adsorbed at equilibrium (q_e) and the amount adsorbed at time (q_t). It is typically applied to physisorption or cases where surface adsorption dominates. The differential form of the pseudo-first-order equation is [97]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

where:

q_t : Amount of adsorbate adsorbed at time t (mg/g)

q_e : Amount of adsorbate adsorbed at equilibrium (mg/g)

k_1 : Pseudo-first-order rate constant (1/min)

The integrated form of pseudo-first-order equation is:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t$$

By plotting $\log(q_e - q_t)$ vs. t , a straight line is obtained with slope $k_1/2.303$, and intercept $\log q_e$.

This kinetics is useful when the adsorption process involves physical interactions or weak van der Waals forces, and is often observed during the initial phase of adsorption, where external mass transfer dominates. Limitations: Cannot accurately predict equilibrium adsorption capacity (q_e) in some cases, and does not

account for chemisorption or multi-step adsorption mechanisms.

Pseudo-2nd-order kinetics

Pseudo-2nd order kinetics assumes the adsorption rate is proportional to the square of the difference between q_e and q_t indicating chemisorption as the dominant mechanism. Chemisorption involves the sharing or exchange of electrons between the adsorbate and the adsorbent [97]. The differential form of the pseudo-2nd-order equation is:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

where:

q_t : Amount of adsorbate adsorbed at time t (mg/g)

q_e : Amount of adsorbate adsorbed at equilibrium (mg/g)

k_2 : Pseudo-2nd-order rate constant (g/mg·min)

The integrated form of pseudo-2nd-order equation is:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e}$$

By plotting $\frac{t}{Q_t}$ vs. t , a straight line is obtained with slope $\frac{1}{Q_e}$ and intercept $\frac{1}{K_2 Q_e^2}$.

Pseudo-2nd-order kinetics is typically observed in cases where chemical interactions dominate, such as: Surface complexation between heavy metals and iron oxides, and reduction reactions (e.g., Cr^{6+} to Cr^{3+} by nZVI).

Table 2 Adsorption capacity of different heavy metals by nZVI.

Heavy metal	Initial Concentration (mg/L)	nZVI Dosage (g/L)	pH	Adsorption capacity (mg/g)	Removal efficiency (%)	References
Lead (Pb^{2+})	50	0.5	5.5	190	95	[98]
Chromium (Cr^{6+})	20	0.8	3	120	98	[99]
Cadmium (Cd^{2+})	10	0.4	6	45	85	[100]
Arsenic (As^{3+})	5	0.3	7	12	96	[17]
Nickel (Ni^{2+})	25	0.6	6.5	55	90	[101]
Copper (Cu^{2+})	30	1.0	5	75	92	[22]

Heavy metal	Initial Concentration (mg/L)	nZVI Dosage (g/L)	pH	Adsorption capacity (mg/g)	Removal efficiency (%)	References
Zinc (Zn ²⁺)	15	0.7	6.5	30	88	[102]
Mercury (Hg ²⁺)	10	0.5	4.5	110	99	[21]
Cobalt (Co ²⁺)	20	0.8	5.5	35	87	[103]

Applications of nZVI

ZVI NPs are widely studied and utilized for their effectiveness in removing toxic heavy metals from wastewater. Their applications are based on their unique properties, such as a high surface area, strong reducing capabilities, and ability to adsorb metal ions. Zerovalent iron nanoparticles (nZVI) exhibit remarkable properties such as high reactivity, catalytic efficiency, and magnetic behavior, making them useful in several innovative applications. Below is an account of their application for specific heavy metals:

Environmental remediation

ZVI is frequently utilized for in situ treatment of contaminated groundwater in groundwater remediation projects. By converting them to less hazardous forms, it aids in the removal of contaminants such as heavy metals (such as chromium, lead, and arsenic), organic compounds, and chlorinated solvents (such as trichloroethylene and perchloroethylene). By decomposing hazardous organic molecules and immobilising heavy metals, it can also treat soil pollution, particularly in situations where pesticides or industrial waste have leaked. By eliminating impurities from drinking water and wastewater, such as phosphates, arsenic, and nitrates, ZVI can improve water treatment procedures [11,54]. It has demonstrated efficacy in combating dyes, medications, and other organic pollutants. By lowering metal ion toxicity and encouraging the breakdown of organic contaminants, sediment remediation has been utilised to treat contaminated sediments.

Control of air pollution

nZVI can catalyze the breakdown of toxic gases, including trichloromethane (CHCl₃) and carbon tetrachloride (CCl₄), both of which are common industrial pollutants. It facilitates redox reactions that

degrade these harmful volatile organic compounds (VOCs) into non-toxic by-products. The surface of nZVI provides active sites for catalytic decomposition. nZVI promotes reductive dehalogenation, breaking down halogenated compounds like CHCl₃ and CCl₄ into less toxic substances, such as methane or simple hydrocarbons. Kim *et al.* [58] demonstrated that nZVI effectively degraded CCl₄ in gas-phase reactions, achieving up to 90 % reduction under controlled conditions. Sun *et al.* [104] reported significant removal of VOCs in air using nZVI catalysts coated onto porous media, improving air quality in industrial environments.

Antimicrobial application

ZVI has potent antibacterial qualities and can be used to kill germs and pathogens by disinfecting surfaces or water. Systems for water supply, sanitation, and healthcare could benefit from this. By preventing microbial development, ZVI can be added to food packaging to form antimicrobial coatings that improve food preservation. It generates reactive oxygen species (ROS) and releases iron ions, disrupting microbial membranes and metabolic pathways [105]. Direct mechanism involves physical interaction between nZVI and bacterial cell membranes causes structural damage. Indirect mechanism involves generation of ROS like hydroxyl radicals (\bullet OH) during the oxidation of nZVI. The release of Fe²⁺ ions, catalyse Fenton-like reactions to produce ROS, enhancing antimicrobial effects. nZVI are effective in killing waterborne pathogens such as *E. coli* and *Salmonella*. They are ideal for water treatment systems in remote areas or emergency situations. They can be used in coatings for surgical instruments, medical devices, and hospital surfaces to prevent infections. They can be incorporated into antimicrobial coatings for food packaging to inhibit microbial growth, extending shelf life [69].

Chemical reaction catalysis

ZVI has the ability to catalyze a number of chemical reactions, including the oxidation of organic contaminants, the breakdown of dyes, and the synthesis of hydrogen. It speeds up oxidation processes by promoting Fenton-like reactions ($\text{Fe}^{3+} \text{H}_2\text{O}_2$), which convert organic contaminants into less dangerous forms. Li *et al.* [69] demonstrated efficient degradation of methylene blue using nZVI, with a 95 % reduction achieved in 60 min. Shi *et al.* [106] showed enhanced hydrogen production from water splitting using Pd-doped nZVI, with increased catalytic efficiency.

Magnetic separation and sensing

By using magnetic separation techniques, pollutants can be separated from liquid wastes using magnetic nZVI. To identify pollutants, biological agents, and heavy metals in environmental samples, nZVI can be included into biosensors. nZVI is integrated into biosensors to detect pollutants, biological agents, or heavy metals. Changes in magnetic or electronic properties upon interaction with target molecules are measured to provide detection signals. Phenrat *et al.* [81] demonstrated the efficient removal of arsenic from water using magnetic nZVI, achieving 98 % removal in less than an hour.

Techno-economic challenges and opportunities

Zerovalent iron nanoparticles (nZVI) are widely used for environmental remediation due to their high reactivity and surface area. However, their application comes with several challenges. Nanoparticles tend to aggregate due to strong magnetic and van der Waals forces, reducing their effective surface area and reactivity. nZVI oxidizes quickly in the presence of water and oxygen, forming iron oxides/hydroxides that reduce its reactivity and lifespan. Poor mobility in soils and sediments makes it difficult to evenly distribute nZVI in contaminated sites, limiting its remediation efficiency [107]. Potential toxicity to aquatic organisms, plants, and humans due to the release of iron ions or nanoparticles themselves. Concerns about long-term environmental persistence and unknown ecological impacts. Synthesis and stabilization of nZVI can be expensive, especially for large-scale applications. The formation of passivating layers of iron oxides/hydroxides reduces the active sites available for

contaminant degradation. nZVI reacts with a wide range of compounds, including non-target species, which can lead to inefficient use and secondary reactions. Due to rapid oxidation and reactivity, nZVI has a limited functional duration in remediation processes [108]. Effectiveness varies depending on the type of contaminant (e.g., chlorinated hydrocarbons, heavy metals), and not all contaminants can be effectively treated. Challenges in monitoring nanoparticle distribution, concentration, and reactivity in the field make it difficult to optimize performance. Efforts to overcome these challenges include surface modification, stabilization using polymers or surfactants, and combining nZVI with other materials to enhance its performance and reduce risks [52].

To address the challenges associated with the use of zerovalent iron nanoparticles (nZVI) for environmental remediation, several strategies have been developed. These aim to improve nZVI performance, stability, and safety while optimizing its environmental and economic viability. Coating nZVI particles with stabilizing agents like polymers (e.g., polyethylene glycol, polyvinyl alcohol) or surfactants (e.g., sodium dodecyl sulfate) can reduce aggregation, increase dispersion in water, and enhance mobility in soils [109]. These coatings also help protect nZVI from rapid oxidation and increase its longevity. Creating a controlled passivation layer on nZVI (e.g., a thin iron oxide or organic layer) reduces excessive reactivity while maintaining sufficient activity for contaminant degradation. Encapsulating nZVI in micro- or nanocapsules (e.g., silica shells or polymeric capsules) ensures controlled release, targeted delivery to contaminated zones, and reduced exposure to non-target species. Formulating nZVI in oil-in-water emulsions enhances mobility in soils and groundwater, improving distribution in the subsurface. Adding reducing agents or scavengers (e.g., ascorbic acid, sulfite) during synthesis or deployment can delay oxidation and extend nZVI's active lifespan. Doping nZVI with secondary metals (e.g., palladium, nickel, or copper) enhances its reactivity and selectivity for specific contaminants while reducing undesired secondary reactions [89].

Conclusion and future perspectives

The removal of heavy metals by nZVI is a complex, multi-step process involving reduction,

adsorption, co-precipitation, and oxidation. This review paper provides an overview of recent advancements in the synthesis and characterization of iron (Fe) nanoparticles, along with their applications as catalysts in reduction reactions. Additionally, a concise summary of the characterization techniques for Fe nanoparticles is presented. The interplay of nZVI mechanisms ensures high efficiency in diverse environmental conditions. Understanding the specifics of these mechanisms allows for optimizing nZVI synthesis and application strategies for targeted heavy metal remediation. Optimizing the functional effectiveness of nanomaterials, particularly zerovalent iron nanoparticles (nZVI), depends on controlling synthesis conditions. These particles exhibit a core-shell structure, with the core being zerovalent iron and the shell consisting of iron oxide (FeOOH). While nZVI is effective for environmental restoration, its main challenge is aggregation, which impacts its transport through soil. Research has focused on modifying nZVI to improve its mobility and functionality. Some specific and innovative research avenues for advancing heavy metal removal using nZVI are nanoengineering for controlled release, which aims to prolong nZVI reactivity and enable controlled release in contaminated environments. This can be achieved by developing encapsulated or core-shell nanoparticles for gradual release, preventing rapid passivation, and using stimuli-responsive materials (e.g., pH-sensitive coatings) to activate nZVI at specific sites. The Life-Cycle Analysis (LCA) and safety assessments for nZVI applications to evaluate their long-term environmental impacts and safety. This involves conducting LCAs to assess the environmental footprint of nZVI synthesis, deployment, and disposal, as well as investigating its potential toxicity to aquatic ecosystems to develop guidelines for safe use. The hybrid nZVI composites to enhance performance by leveraging synergies between nZVI and other materials. This includes combining nZVI with porous materials like activated carbon, graphene oxide, or biochar to improve adsorption and structural stability, incorporating magnetic materials for easy recovery and reuse, and developing multi-functional composites capable of addressing multiple contaminants, such as heavy metals and organic pollutants. Despite its advantages over traditional zerovalent iron, further studies are needed to mitigate potential environmental risks and optimize its use for remediation. Understanding

the interplay of these mechanisms and optimizing conditions can enhance the efficiency and applicability of nZVI for environmental remediation. Continued advancements in nZVI synthesis, surface modification, and deployment strategies are essential to overcoming existing challenges and realizing its full potential. Future research could explore the relationship between nanoparticle morphology and catalytic activity. For optimal catalytic efficiency, Fe nanoparticles should be synthesized with uniform size distribution, small particle size, and robust stabilization.

References

- [1] J Sardans, F Montes and J Peñuelas. Electrothermal atomic absorption spectrometry to determine As, Cd, Cr, Cu, Hg, and Pb in soils and sediments: A review and perspectives. *Soil and Sediment Contamination* 2011; **20(4)**, 447-491.
- [2] X Wang, A Wang, J Ma and M Fu. Facile green synthesis of functional nanoscale zero-valent iron and studies of its activity toward ultrasound-enhanced decolorization of cationic dyes. *Chemosphere* 2017; **166**, 80-88.
- [3] A Verma, A Roy and N Bharadvaja. *Remediation of heavy metals using nanophytoremediation*. In: MP Shah (Ed.). *Advanced oxidation processes for effluent treatment plants*. Elsevier, Amsterdam, Netherlands, 2021, p. 273-296.
- [4] M Hashim, S Mukhopadhyay, JN Sahu and B Sengupta. Remediation technologies for heavy metal contaminated groundwater. *Journal of Environmental Management* 2011; **92(10)**, 2355-2388.
- [5] H Karimi-Maleh, A Ayati, S Ghanbari, Y Orooji, B Tanhaei, F Karimi, M Alizadeh, J Rouhi, L Fu and M Sillanpää. Recent advances in removal techniques of Cr(VI) toxic ion from aqueous solution: A comprehensive review. *Journal of Molecular Liquids* 2021; **329(15)**, 115062.
- [6] G Dognani, P Hadi, H Ma, F Cabrera, AE Job, DL Agostini and BS Hsiao. Effective chromium removal from water by polyaniline-coated electrospun adsorbent membrane. *Chemical Engineering Journal* 2019; **372(3)**, 341-351.
- [7] A Kumar and A Jha. *Drug development strategies*. In: A Kumar and A Jha (Eds.). *Anticandidal agents*. Academic Press, London, 2017, p. 63-71.

- [8] Z Pan, X Zhu, A Satpathy, W Li, JD Fortner and DE Giammar. Cr(VI) adsorption on engineered iron oxide nanoparticles: Exploring complexation processes and water chemistry. *Environmental Science & Technology* 2019; **53(20)**, 11913-11921.
- [9] V Nishad, C Mandal and M Sahu. Study of bioaerosol disinfection kinetics and application of nonlinear regression modeling for optimization of TiO₂-based photocatalytic disinfection process. *Nanotechnology for Environmental Engineering* 2023; **8(4)**, 911-922.
- [10] P Zan, C Yang, H Sun, L Zhao, Z Lv and Y He. One-pot fabricating Fe₃O₄/graphene nanocomposite with excellent biocompatibility and non-toxicity as a negative MR contrast agent. *Colloids Surf B Biointerfaces* 2016; **145**, 208-216.
- [11] M Stefaniuk, P Oleszczuk and YS Ok. Review on nano zerovalent iron (nZVI): From synthesis to environmental applications. *Chemical Engineering Journal* 2015; **287(3)**, 618-632.
- [12] HK Boparai, M Joseph and DM O'Carroll. Cadmium (Cd²⁺) removal by nano zerovalent iron: Surface analysis, effects of solution chemistry and surface complexation modeling. *Environmental Science and Pollution Research* 2013; **20(9)**, 6210-6221.
- [13] M Mahmood-UI-Hassan, M Yasin, M Youstra, R Ahmad and S Sarwar. Kinetics, isotherms, and thermodynamic studies of lead, chromium, and cadmium bio-adsorption from aqueous solution onto *Picea smithiana* sawdust. *Environmental Science and Pollution Research* 2018; **25(13)**, 12570-12578.
- [14] V Madhavi, TNVKV Prasad, AVB Reddy, BR Reddy and G Madhavi. Application of phyto-genic zerovalent iron nanoparticles in the adsorption of hexavalent chromium. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 2014; **116(C)**, 17-25.
- [15] Y Zou, X Wang, A Khan, P Wang, Y Liu, A Alsaedi, T Hayat and X Wang. Environmental remediation and application of nanoscale zero-valent iron and its composites for the removal of heavy metal ions: A review. *Environmental Science & Technology* 2016; **50(14)**, 7290-7304.
- [16] Y Li, HY Bi, XM Mao, YQ Liang and H Li. Adsorption behavior and mechanism of core-shell magnetic rhamnolipid-layered double hydroxide nanohybrid for phenolic compounds from heavy metal-phenolic. *Applied Clay Science* 2018; **162**, 230-238.
- [17] MS Sankhla and R Kumar. Arsenic-induced neurotoxic & carcinogenic effects on humans. *Open Access Journal of Toxicology* 2018; **3(4)**, 555617.
- [18] D Chen, Y Cheng, N Zhou, P Chen, Y Wang, K Li, S Huo, P Cheng, P Peng, R Zhang, L Wang, H Liu, Y Liu and R Ruan. Photocatalytic degradation of organic pollutants using TiO₂-based photocatalysts: A review. *Journal of Cleaner Production* 2020; **268(3)**, 121725.
- [19] VK Gupta, A Nayak and S Agarwal. Bioadsorbents for remediation of heavy metals: Current status and their future prospects. *Environmental Engineering Research* 2015; **20(1)**, 1-18.
- [20] C Mandal, V Nishad and M Sahu. Impact of spatial distribution of light intensity on disinfection kinetics of *Mycobacterium smegmatis* and *E. coli* using TiO₂-based photocatalyst. *Nanotechnology for Environmental Engineering* 2023; **8(2)**, 567-579.
- [21] J Fisher and World Health Organization. Elemental mercury and inorganic mercury compounds: Human health aspects, Available at: <https://apps.who.int/iris/bitstream/handle/10665/42607/9241530502.pdf>, accessed July 2003.
- [22] F Akbal and S Camcıotless. Copper, chromium and nickel removal from metal plating wastewater by electrocoagulation. *Desalination* 2011; **269(1-3)**, 214-222.
- [23] B Doshi, A Ayati, B Tanhaei, E Repo and M Sillanpää. Partially carboxymethylated and partially cross-linked surface of chitosan versus the adsorptive removal of dyes and divalent metal ions. *Carbohydrate Polymers* 2018; **197**, 586-597.
- [24] A Zeraatkar Moghaddam, E Ghiamati, A Ayati and MR Ganjali. Application of the response surface methodology for optimizing the adsorptive removal of chromate using a magnetic crosslinked chitosan nanocomposite. *Journal of Applied Polymer Science* 2019; **136(8)**, 47077.

- [25] VE Pakade, NT Tavengwa and LM Madikizela. Recent advances in hexavalent chromium removal from aqueous solutions by adsorptive methods. *RSC Advances* 2019; **9(45)**, 26142-26164.
- [26] Z Farooqi, M Akram, R Begum, W Wu and A Irfan. Inorganic nanoparticles for reduction of hexavalent chromium: Physicochemical aspects. *Journal of Hazardous Materials* 2021; **402**, 123535.
- [27] BH Hintermeyer and EL Tavani. Adsorption, biosorption and bioaccumulation used to remove chromium (III) from tanning wastewaters: A critical review. *Journal of the Society of Leather Technologists and Chemists* 2013; **97(6)**, 231-237.
- [28] B Tanhaei, MP Chenar, N Saghatoleslami, M Hesampour, M Kallioinen, M Sillanpää and M Mänttari. Removal of nickel ions from aqueous solution by micellar-enhanced ultrafiltration, using mixed anionic-non-ionic surfactants. *Separation and Purification Technology* 2014; **138**, 169-176.
- [29] U Misra, V Nishad and SP Singh. *Introduction to membrane distillation and its application in emerging contaminants removal. Energy, Environment, and Sustainability. In: SP Singh, AK Agarwal, T Gupta and SM Maliyekkal (Eds.). New trends in emerging environmental contaminants.* Springer, Singapore, 2022, p. 427-462.
- [30] X Pei, L Gan, Z Tong, H Gao, S Meng, W Zhang, P Wang and Y Chen. Robust cellulose-based composite adsorption membrane for heavy metal removal. *Journal of Hazardous Materials* 2021; **406**, 124746.
- [31] JE Efome, D Rana, T Matsuura and CQ Lan. Experiment and modeling for flux and permeate concentration of heavy metal ion in adsorptive membrane filtration using a metal-organic framework incorporated. *Chemical Engineering Journal* 2018; **352**, 737-744.
- [32] S Deng, X Liu, J Liao, H Lin and Fang Liu. PEI modified multiwalled carbon nanotube as a novel additive in PAN nanofiber membrane for enhanced removal of heavy metal ions. *Chemical Engineering Journal* 2019; **375**, 122086.
- [33] Z Zhao, H An, J Lin, M Feng, V Murugadoss, T Ding, H Liu, Q Shao, X Mai, N Wang, H Gu, S Angaiah and Z Guo. Progress on the photocatalytic reduction removal of chromium contamination. *The Chemical Record* 2019; **19(5)**, 873-882.
- [34] Y Liu, D Yang, T Xu, Y Shi, L Song and ZZ Yu. Continuous photocatalytic removal of chromium (VI) with structurally stable and porous Ag/Ag₃PO₄/reduced graphene oxide microspheres. *Chemical Engineering Journal* 2020; **379**, 122200.
- [35] G Niu, C Si, J Jiao, Q Han, M Guo and M Li. An electron-rich metal-organic framework for highly efficient photocatalytic reduction of Cr (VI). *Journal of Alloys and Compounds* 2020; **830(224)**, 154696.
- [36] TK Tran, KF Chiu, CY Lin and HJ Leu. Electrochemical treatment of wastewater: Selectivity of the heavy metals removal process. *International Journal of Hydrogen Energy* 2017; **42(45)**, 27741-27748.
- [37] C Carolin, P Kumar, A Saravanan, GJ Joshiba and M Naushad. Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. *Journal of Environmental Chemical Engineering* 2017; **5(3)**, 2782-2799.
- [38] LY Kit and JS Chang. Bioremediation of heavy metals using microalgae: Recent advances and mechanisms. *Bioresource Technology* 2020; **303(2)**, 122886.
- [39] V Kumar and SK Dwivedi. Hexavalent chromium reduction ability and bioremediation potential of *Aspergillus flavus* CR500 isolated from electroplating wastewater. *Chemosphere* 2019; **237**, 124567.
- [40] S Singh, D Kapoor, S Khasnabis, J Singh and PC Ramamurthy. Mechanism and kinetics of adsorption and removal of heavy metals from wastewater using nanomaterials. *Environmental Chemistry Letters* 2021; **19(3)**, 2351-2381.
- [41] O Lobacheva, N Dzhevaga and A Danilov. The method of removal yttrium (III) and ytterbium (III) from dilute aqueous solutions. *Journal of Ecological Engineering* 2016; **17(2)**, 38-42.
- [42] FS Hoseinian, B Rezai and E Kowsari. The main factors effecting the efficiency of Zn (II) flotation: Optimum conditions and separation mechanism. *Journal of Environmental Management* 2018; **207**, 169-179.

- [43] E Deliyanni, GZ Kyzas and KA Matis. Various flotation techniques for metal ions removal. *Journal of Molecular Liquids* 2016; **225**, 260-264.
- [44] AS Abyaneh and MH Fazaelpoor. Evaluation of rhamnolipid (RL) as a biosurfactant for the removal of chromium from aqueous solutions by precipitate flotation. *Journal of Environmental Management* 2016; **165**, 184-187.
- [45] S Aoudj, A Khelifa, N Drouiche, R Belkada and D Miroud. Simultaneous removal of chromium (VI) and fluoride by electrocoagulation-electroflotation: Application of a hybrid Fe-Al anode. *Chemical Engineering Journal* 2015; **267**, 153-162.
- [46] J Korak, R Huggins and M Arias-Paic. Regeneration of pilot-scale ion exchange columns for hexavalent chromium removal. *Water Research* 2017; **118**, 141-151.
- [47] R Soltani, A Marjani, M Hosseini and S Shirazian. Synthesis and characterization of novel N-methylimidazolium-functionalized KCC-1: A highly efficient anion exchanger of hexavalent chromium. *Chemosphere* 2020; **239**, 124735.
- [48] SVAR Sastry, BS Rao and DV Padma. Studies on selective batch adsorption of Cu(II) and Cr(VI) from aqueous solution. *TEST Engineering and Management* 2020; **83**, 6794-6797.
- [49] S Bhattacharjee, F Habib, N Darwish and A Shanableh. Iron sulfide nanoparticles prepared using date seed extract: Green synthesis, characterization and potential application for removal of ciprofloxacin and chromium. *Powder Technology* 2021; **380(3)**, 219-228.
- [50] W Xu, T Yang, S Liu, L Du, Q Chen, X Li, J Dong, Z Zhang, S Lu, Y Gong, L Zhou, Y Liu and X Tan. Insights into the synthesis, types and application of iron nanoparticles: The overlooked significance of environmental effects. *Environment International* 2022; **158(2)**, 106980.
- [51] D Karabelli, Ç Üzümlü, T Shahwan, AE Eroğlu, TB Scott, KR Hallam and I Lieberwirth. Batch removal of aqueous Cu²⁺ ions using nanoparticles of zero-valent iron: A study of the capacity and mechanism of uptake. *Industrial & Engineering Chemistry Research* 2008; **47(14)**, 4758-4764.
- [52] RA Crane and TB Scott. Nanoscale zero-valent iron: Future prospects for an emerging water treatment technology. *Journal of Hazardous Materials* 2012; **211-212**, 112-125.
- [53] SVAR Sastry. Green synthesis and characterization of silver nano particles. *Journal of Water and Environmental Nanotechnology* 2020; **5**, 81-91.
- [54] MAV Ramos, W Yan, X Li, BE Koel and W Zhang. Simultaneous oxidation and reduction of arsenic by zero-valent iron nanoparticles: Understanding the significance of the core-shell structure. *Journal of Physical Chemistry* 2009; **113(33)**, 14591-14594.
- [55] P Wang, J Hu, T Liu, G Han, W Ma and J Li. New insights into ball-milled zero-valent iron composites for pollution remediation: An overview. *Journal of Cleaner Production* 2023; **385**, 135513.
- [56] MM Tarekegn, AM Hiruy and AH Dekebo. Nano zero valent iron (nZVI) particles for the removal of heavy metals (Cd²⁺, Cu²⁺ and Pb²⁺) from aqueous solutions. *RSC Advances* 2021; **11(30)**, 18539-18551.
- [57] MM Serda. 2013, Synteza i aktywność biologiczna nowych analogów tiosemikarbazonowych chelatorów żelaza. Ph. D. Dissertation. Uniwersytet śląski, Katowice, Poland.
- [58] C Kim, JY Ahn, TY Kim, WS Shin and I Hwang. Activation of persulfate by nanosized zero-valent iron (NZVI): mechanisms and transformation products of NZVI. *Environmental Science & Technology* 2018; **52(6)**, 3625-3633.
- [59] N Nassar and M Husein. Preparation of iron oxide nanoparticles from FeCl₃ solid powder using microemulsions. *Physica Status Solidi (A) Applications and Materials* 2006; **203(6)**, 1324-1328.
- [60] R Mukherjee, R Kumar, A Sinha, Y Lama and AK Saha. A review on synthesis, characterization, and applications of nano zero valent iron (nZVI) for environmental remediation. *Critical Reviews in Environmental Science and Technology* 2016; **46(5)**, 443-466.
- [61] TK Teal, DP Lies, BJ Wold and DK Newman. Spatiometabolic stratification of *Shewanella oneidensis* biofilms. *Applied and Environmental Microbiology* 2006; **72(11)**, 7324-7330.

- [62] DV Padma and SVAR Sastry. Biosorption of hexavalent chromium using mallet flower leaves powder as adsorbent. *TEST Engineering and Management* 2020; **83**, 15714-15729.
- [63] KP Kumar, W Paul and CP Sharma. Green synthesis of gold nanoparticles with Zingiber officinale extract: Characterization and blood compatibility. *Process Biochemistry* 2011; **46(10)**, 2007-2013.
- [64] T Wang, J Lin, Z Chen, M Megharaj and R Naidu. Green synthesized iron nanoparticles by green tea and eucalyptus leaves extracts used for removal of nitrate in aqueous solution. *Journal of Cleaner Production* 2014; **83**, 413-419.
- [65] MA Ebrahimzadeh, S Mortazavi-Derazkola and MA Zazouli. Eco-friendly green synthesis and characterization of novel Fe₃O₄/SiO₂/Cu₂O-Ag nanocomposites using Crataegus pentagyna fruit extract for photocatalytic degradation of organic contaminants. *Journal of Materials Science: Materials in Electronics* 2019; **30(12)**, 10994-11004.
- [66] KS Prasad, P Gandhi and K Selvaraj. Synthesis of green nano iron particles (GnIP) and their application in adsorptive removal of As(III) and As(V) from aqueous solution. *Applied Surface Science* 2014; **317**, 1052-1059.
- [67] M. Nasrollahzadeh, S. M. Sajadi, and M. Maham. Green synthesis of palladium nanoparticles using *Hippophae rhamnoides* Linn leaf extract and their catalytic activity for the Suzuki-Miyaura coupling in water. *Journal of Molecular Catalysis A: Chemical* 2015; **396**, 297-303.
- [68] X Weng, L Huang, Z Chen, M Megharaj and R Naidu. Synthesis of iron-based nanoparticles by green tea extract and their degradation of malachite. *Industrial Crops and Products* 2013; **51**, 342-347.
- [69] S Li, W Wang, W Yan and WX Zhang. Nanoscale zero-valent iron (nZVI) for the treatment of concentrated Cu (II) wastewater: A field demonstration. *Environmental Science: Processes & Impacts* 2014; **16(3)**, 524-533.
- [70] M Nasrollahzadeh, S Mohammad Sajadi, A Rostami-Vartooni and M Khalaj. Green synthesis of Pd/Fe₃O₄ nanoparticles using *Euphorbia condylocarpa* M. bieb root extract and their catalytic applications as magnetically recoverable and stable recyclable catalysts for the phosphine-free Sonogashira and Suzuki coupling reactions. *Journal of Molecular Catalysis A: Chemical* 2015; **396**, 31-39.
- [71] M Zhang, F He, D Zhao and X Hao. Degradation of soil-sorbed trichloroethylene by stabilized zero valent iron nanoparticles: Effects of sorption, surfactants, and natural organic matter. *Water Research* 2011; **45(7)**, 2401-2414.
- [72] WX Zhang and DW Elliott. Applications of iron nanoparticles for groundwater remediation. *Remediation Journal* 2006; **16(2)**, 7-21.
- [73] Y Zhang, J Huang, Z Dong, Y Zhan, J Xi, J Xiao, S Huang and F Tian. Pd-Fe bimetallic nanoparticles anchored on N-doped carbon-modified graphene for efficient catalytic organic reactions. *Carbon Letters* 2023; **33(1)**, 77-87.
- [74] F He and D Zhao. Hydrodechlorination of trichloroethene using stabilized Fe-Pd nanoparticles: Reaction mechanism and effects of stabilizers, catalysts and reaction conditions. *Applied Catalysis B: Environmental* 2008; **84(3-4)**, 533-540.
- [75] BI Kharisov, OV Kharissova and HVR Dias. *Nanomaterials for environmental protection*. Wiley, New Jersey, U.S, 2015, p. 592.
- [76] J Quinn, C Geiger, C Clausen, K Brooks, C Coon, S O'Hara, T Krug, D Major, WS Yoon, A Gavaskar and T Holdsworth. Field demonstration of DNAPL dehalogenation using emulsified zero-valent iron. *Environmental Science & Technology* 2005; **39(5)**, 1309-1318.
- [77] P Bennett, F He, D Zhao, B Aiken and L Feldman. In situ testing of metallic iron nanoparticle mobility and reactivity in a shallow granular aquifer. *Journal of Contaminant Hydrology* 2010; **116(1-4)**, 35-46.
- [78] X Li, DW Elliott and WX Zhang. Zero-valent iron nanoparticles for abatement of environmental pollutants: Materials and engineering aspects. *Critical Reviews in Solid State and Material Sciences* 2006; **31(4)**, 111-122.
- [79] C Gao, W Yu, Y Zhu, M Wang, Z Tang, L Du, M Hu, L Fang and X Xiao. Preparation of porous silicate supported micro-nano zero-valent iron from copper slag and used as persulfate activator

- for removing organic contaminants. *Science of The Total Environment* 2021; **754**, 142131.
- [80] H Dong, L Li, Y Wang, Q Ning, B Wang and G Zeng. Aging of zero-valent iron-based nanoparticles in aqueous environment and the consequent effects on their reactivity and toxicity. *Water Environment Research* 2020; **92**, 646-661.
- [81] T Phenrat, T Thongboot and GV Lowry. Electromagnetic induction of zerovalent iron (ZVI) powder and nanoscale zerovalent iron (NZVI) particles enhances dechlorination of trichloroethylene in contaminated groundwater and soil: Proof of concept. *Environmental Science & Technology* 2016; **50(2)**, 872-880.
- [82] X Dong, LQ Ma and Y Li. Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing. *Journal of Hazardous Materials* 2011; **190(1-3)**, 909-915.
- [83] C Wang, DR Baer, JE Amonette, MH Engelhard, J Antony and Y Qiang. Morphology and electronic structure of the oxide shell on the surface of iron nanoparticles. *Journal of the American Chemical Society* 2009; **131(25)**, 8824-8832.
- [84] W Stumm and JJ Morgan. *Aquatic chemistry: Chemical equilibria and rates in natural waters*. 3 Ed. Wiley-Interscience, New Jersey, U.S., 2012, p. 1827.
- [85] RBN Baig, S Verma, RS Varma and MN Nadagouda. Magnetic Fe@g-C₃N₄: A photoactive catalyst for the hydrogenation of alkenes and alkynes. *ACS Sustainable Chemistry & Engineering* 2016; **4(3)**, 1661-1664.
- [86] S Mourdikoudis, RM Pallares and NTK Thanh. Characterization techniques for nanoparticles: Comparison and complementarity upon studying nanoparticle properties. *Nanoscale* 2018; **27(10)**, 12871-12934.
- [87] Z Ban, YA Barnakov, F Li, VO Golub and CJ O'Connor. The synthesis of core-shell iron@gold nanoparticles and their characterization. *Journal of Materials Chemistry* 2005; **15(43)**, 4660-4662.
- [88] AL Kustov, AM Frey, KE Larsen, T Johannessen, JK Nørskov and CH Christensen. CO methanation over supported bimetallic Ni-Fe catalysts: From computational studies towards catalyst optimization. *Applied Catalysis A: General* 2007; **320(2)**, 98-104.
- [89] N Koi, T Oku and M Nishijima. Fe nanowire encapsulated in boron nitride nanotubes. *Solid State Commun* 2005; **136(6)**, 342-345.
- [90] R Hudson, V Chazelle, M Bateman, R Roy, CJ Li and A Moores. Sustainable synthesis of magnetic ruthenium-coated iron nanoparticles and application in the catalytic transfer hydrogenation of ketones. *ACS Sustainable Chemistry & Engineering* 2015; **3(5)**, 814-820.
- [91] Z Pan, Y Lin, B Sarkar, G Owens and Z Chen. Green synthesis of iron nanoparticles using red peanut skin extract: Synthesis mechanism, characterization and effect of conditions on chromium removal. *Journal of Colloid and Interface Science* 2019; **558**, 106-114.
- [92] Y Wei, Z Fang, L Zheng and EP Tsang. Biosynthesized iron nanoparticles in aqueous extracts of Eichhornia crassipes and its mechanism in the hexavalent chromium removal. *Applied Surface Science* 2017; **399**, 322-329.
- [93] MS Abesekara, KNR Kosvinna and BMWPK Amarasinghe. Adsorption and desorption studies of Ni²⁺ ions on to coconut shell char. *IOP Conference Series: Earth and Environmental Science* 2020; **427**, 012005.
- [94] R Garg, M Mittal, S Tripathi and NO Eddy. Core to concept: Synthesis, structure, and reactivity of nanoscale zero-valent iron (NZVI) for wastewater remediation. *Environmental Science and Pollution Research* 2024; **31(60)**, 67496-67520.
- [95] Q Chen, Y Yao, X Li, J Lu, J Zhou and Z Huang. Comparison of heavy metal removals from aqueous solutions by chemical precipitation and characteristics of precipitates. *Journal of Water Process Engineering* 2018; **26**, 289-300.
- [96] R Anjali and S Shanthakumar. Insights on the current status of occurrence and removal of antibiotics in wastewater by advanced oxidation processes. *Journal of Environmental Management* 2019; **246**, 51-62.
- [97] RV Mathai, JC Mitra, SK Sar and MK Jindal. Adsorption of chromium (VI) from aqueous phase using Aegle marmelos leaves: Kinetics, isotherm and thermodynamic studies. *Chemical Data Collections* 2022; **39**, 100871.
- [98] X Zhao, W Liu, Z Cai, B Han, T Qian and D Zhao. An overview of preparation and applications of

- stabilized zero-valent iron nanoparticles for soil and groundwater remediation. *Water Research* 2016; **100(1)**, 245-266.
- [99] NF Fahim, BN Barsoum, AE Eid and MS Khalil. Removal of chromium(III) from tannery wastewater using activated carbon from sugar industrial waste. *Journal of Hazardous Materials* 2006; **136(2)**, 303-309.
- [100] PS Kumar, S Ramalingam, V Sathyaselvabala, SD Kirupha, A Murugesan and S Sivanesan. Removal of cadmium(II) from aqueous solution by agricultural waste cashew nut shell. *Korean Journal of Chemical Engineering* 2012; **29(6)**, 756-768.
- [101] G Basaran, D Kavak, N Dizge, Y Asci, M Solener and B Ozbey. Comparative study of the removal of nickel(II) and chromium(VI) heavy metals from metal plating wastewater by two nanofiltration membranes. *Desalination Water Treat* 2016; **57(46)**, 21870-21880.
- [102] JJ Moreno-Barbosa, C López-Velandia, ADP Maldonado, L Giraldo and JC Moreno-Piraján. Removal of lead(II) and zinc(II) ions from aqueous solutions by adsorption onto activated carbon synthesized from watermelon shell and walnut shell. *Adsorption* 2013; **19(2-4)**, 675-685.
- [103] R Wang, L Deng, X Fan, K Li, H Lu and W Li. Removal of heavy metal ion cobalt (II) from wastewater via adsorption method using microcrystalline cellulose-magnesium hydroxide. *International Journal of Biological Macromolecules* 2021; **189(1)**, 607-617.
- [104] Y Sun, X Li, W Zhang and HP Wang. A method for the preparation of stable dispersion of zero-valent iron nanoparticles. *Colloids and Surfaces A Physicochemical and Engineering Aspects* 2007; **308(1-3)**, 60-66.
- [105] F Mujeeb, P Bajpai and N Pathak. Phytochemical evaluation, antimicrobial activity, and determination of bioactive components from leaves of *Aegle marmelos*. *BioMed Research International* 2014; **2014(1)**, 497606.
- [106] L Shi, T Wang, H Zhang, K Chang, X Meng, H Liu and J Ye. An amine-functionalized iron (III) metal-organic framework as efficient visible-light photocatalyst for Cr (VI) reduction. *Advanced Science* 2015; **2(3)**, 1500006.
- [107] NA Rashidi and S Yusup. A review on recent technological advancement in the activated carbon production from oil palm wastes. *Chemical Engineering Journal* 2017; **314**, 277-290.
- [108] Y Wu, CYu Guan, N Griswold, L Hou, F Xin, A Hu, Z Hu and CP Yu. Zero-valent iron-based technologies for removal of heavy metal(loid)s and organic pollutants from the aquatic environment: Recent advances and perspectives. *Journal of Cleaner Production* 2020; **277(7)**, 123478
- [109] BR Albuquerque, SA Heleno, M Oliveira, L Barros and ICFR Ferreira. Phenolic compounds: Current industrial applications, limitations and future challenges. *Food & Function* 2021; **12(1)**, 14-29.