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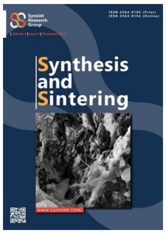

Review article

Recent advances in synthesis, properties, and applications of nano-zero valent iron: A promising material for environmental remediation

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ABSTRACT

Nano-zero valent iron (nZVI) is increasingly recognized as a promising material for environmental remediation because of its high reactivity and efficient removal of various contaminants. This comprehensive review delves into the unique structure, synthesis techniques, and characterization methods of nZVI. It explores real-world applications of nZVI in remediating contaminated water, showcasing its efficacy in eliminating pollutants like heavy metals, organic compounds, and radionuclides. Studies suggest that nZVI composites demonstrate superior adsorption properties for heavy metals and pollutants with their distinctive core-shell structures and surface functional groups. Unlike conventional materials, nZVI composites exhibit heightened adsorption capabilities and easier retrieval from solutions, making them more effective in heavy metal removal. Moreover, the environmental ramifications of nZVI synthesis methods are critically analyzed, considering factors such as energy consumption and potential secondary pollution. The review underscores the significance of ongoing research and development to optimize nZVI's performance and reduce its environmental impact, thereby bolstering its role in promoting a sustainable environment.

KEYWORDS

Nano-zero valent iron (nZVI)
Environmental remediation
Contaminant removal
Organic compounds
Heavy metals
Sustainable environment

1. Introduction

To progress human society, a significant quantity of resources is essential. To ensure a continuous provision of the materials needed for sustenance, we must operate certain substances that can have detrimental effects on the environment. These substances encompass dyes, organic acids, metals, nutrients, and insecticides, as well as halogenated and phenolic substances, which can be harmful when discharged into the environment. Numerous methods have been developed to address such pollutants or contaminants, each with advantages and disadvantages. One strategy that has gained significant favor among scientists is the combination of redox degradation and adsorption using nanomaterials, which is favored for its sustainability, eco-friendliness, and cost-effectiveness [1–4]. In recent times, nanotechnology has been increasingly employed across various sectors, including material production, wastewater management,

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pharmaceuticals, and the creation of bio-nanomaterials and biosensors [5]. Research has demonstrated that nanomaterials tend to change their catalytic, electronic, mechanical, chemical, physical, optical, and magnetic characteristics owing to their small size [6]. Reducing the size of particles has the effect of increasing the likelihood of molecules, atoms, and complexes, leading to improved adsorption and reactivity for stabilizing charges. Most recently, a range of nanomaterials has been applied to eliminate pollutants from water, originating from industries and agriculture. These include carbon carriers, iron nanoparticles such as nano zero-valent iron (nZVI), hematite, and magnetite, as well as clays, nanofiltration membranes, nanofibers, nanobiocides, polymeric nanoparticles, nanoenzymes, ferritin, natural and human-made adsorbents, and various microorganisms, offering higher efficiency compared to standard adsorbents [7, 8].

In the past few years, there has been significant advancement in the utilization of nZVI (Fe^0 or nZVI) technology, focusing on its efficiency in reacting with contaminants in the environment, improving mobility through surface modifications, and carrying out field trials at both pilot and complete scales [9]. In addition, there has been a transition from using micro-iron particles to operating non-iron particles which have demonstrated efficacy as a catalyst and reductant when dealing with various metal ions and chlorinated organic compounds [10, 11]. Adsorption, chemical reactions involving redox processes (primarily reduction), and precipitation are notable methods that nZVI can operate to reduce water contaminants. Nanoparticles composed of zerovalent iron have been effectively applied for treating various pollutants, including pharmaceuticals, metalloids, organic dyes, inorganic anions, phenols, halogenated organic compounds, heavy metals, and radioactive elements in water and soil environments. Furthermore, nZVI also demonstrates bactericidal effects and toxicity towards Gram-negative (including Pseudomonas fluorescens and Escherichia coli) and Gram-positive (specifically Bacillus subtilis) microorganisms. The bactericidal properties of nZVI effectively eliminate hazards produced by microorganisms in water, such as fungi, bacteria, and viruses [12, 13]. Despite their powerful magnetic pull, nano zerovalent iron serves not only as a sorbent for remediation of the targeted compound at the polluted location but also exhibits regenerative properties post-application [14, 15]. The eradication of groundwater pollution in the subsurface realm was predominantly achieved through permeable reactive barriers (PRBs). Nevertheless, the efficacy of these barriers is hindered by their cost and effectiveness. Subsequent advancements addressed these restrictions by implementing the direct introduction of nZVI particles into the underground environment [16–18].

Because of their minimal size, large surface area, internal magnetic properties, and strong reducing capabilities, nZVI particles are highly prone to coalescing and rapid oxidation, making it challenging to regenerate and separate them from depleted systems. As a result of these challenges, the use of nZVI in environmental remediation could be significantly restricted. Nevertheless, various adjustments and modifications to its surface have been carried out or are currently ongoing to address these challenges [12]. Modifying the surface properties of nanoparticles is a crucial process focused on improving the spread of nZVI in water and its mobility in a porous substance. The enhancement of nanoparticle (nZVI) surface alters their capacity for either adsorption or degradation of contaminants, or both processes simultaneously. Uncoated nZVI and its integration with different substances have demonstrated enhanced effectiveness in addressing pollution in both water and soil environments [19, 20]. In water-based solutions, nanoscale zero-valent iron (nZVI) is highly vulnerable to oxidation, leading to the formation of a layer of iron hydroxides ($Fe(OH)_x$) on its surface. This accumulation on the outer layer of nZVI hinders its ability to catalyze the removal of contaminants effectively. This issue has been addressed by amalgamating a less responsive metal or metals such as nickel, platinum, silver, palladium, and copper with nZVI to form bimetallic nanoparticles (B-NPs) as described in various studies [21–23]. nZVI is an electron donor due to its significant negative redox potential, while the other metal in bimetallic particles functions as an electron acceptor with lower reactivity. Conversely, the second metal acts as a catalyst to boost the reactivity of nZVI because of its beneficial redox potential. Nevertheless, these dual-metal iron nanoparticles exhibit superior reducing capacity compared to pure nZVI [24, 25].

A significant issue of interest is the potential environmental advantages of nZVI, alongside concerns about its toxicity, which has been a focus of past studies indicating uncertainty. Regarding the toxicity of iron, it is important to highlight that iron is an essential nutrient for growth in nearly all living beings, and a deficiency can result in various conditions, such as low levels of red blood cells. In all instances, excess iron can be toxic and lead to liver injury in the human body. There are two recognized forms of iron toxicity in the surroundings: (1) natural iron toxicity and (2) toxicity arising from its nanoscale size (< 30 nm), known as nZVI. In any circumstance, nZVI has demonstrated bactericidal effects on bacterial cells in a laboratory setting, with increased efficacy observed under limited oxygen availability. Research findings revealed that the harmful effects of ionic forms of nanoscale iron (Fe^{2+} and Fe^{3+}) were more pronounced in both Gram-negative and Gram-positive strains of microorganisms compared to nZVI. This suggests that the toxicity associated with nZVI could be attributed to ionic iron on the surface of the non-iron particles [26]. Increased levels of nZVI concentration and quicker oxidation harm the reactivity and toxicity of nZVI. Researchers suggested that the oxidized form of a specific type of nZVI is less harmful than the pristine nZVI containing Fe^0 in its core. Moreover, studies indicate that as the materials become increasingly oxidized, the toxicity of the Fe-based substances decreases. In studies conducted on the impact of nZVI exposure on humans, it has been observed through in vitro experiments that both nZVI and iron oxide nanoparticles can pose dangers to human and other animal cell cultures, possibly because of the production of reactive oxygen species (ROS). The significance of these remains uncertain when considering the toxic properties of nZVI in its natural applications. It has been discovered that the end products of nanoparticle oxides, such as those derived from nanoparticles like nZVI, exhibit long-lasting properties in biological systems due to their limited solubility. The ongoing persistence continually disrupts the biological system and ultimately leads to mutagenesis. Nanoparticles assimilated or clustered together are inherently stationary compared to their initial state. Due to their limited movement, they can be accessed by certain sediment-dwelling organisms and filter feeders, ultimately impacting the ecosystem adversely. In addition, the toxicity of nZVI can be influenced by the introduction of metals such as palladium and the application of coating materials for surface alteration, as these substances may possess inherent toxicity. Furthermore, these additives can impact the reactivity of nZVI. Certain environmental factors such as altered pH levels or changes in the redox environment, along with the production of harmful byproducts during treatment, contribute to the secondary harmful effects of nZVI [27].

This review explores the potential of nZVI as a powerful tool for environmental remediation. It delves into the unique structure of nZVI particles and analyzes various synthesis techniques used to create them. The review then examines methods for characterizing nZVI and investigates its practical implementation in real-world remediation applications. Finally, it critically assesses the environmental impact of nZVI synthesis methods. Through this comprehensive review, the goal is to provide a clear understanding of nZVI's capabilities and limitations, paving the way for its effective and environmentally sound use in addressing environmental challenges.

2. Structure of nZVI particles

The nZVI created through a bottom-up method displays a core-shell configuration that comprises metallic iron at the core and a mixed-valence oxide shell containing both Fe(II) and Fe(III) resulting from the core's oxidation process. This zero-valent iron (ZVI) is a synthetic substance and is not naturally occurring like Fe(II) and Fe(III). nZVI shows significant reactivity in aqueous environments and has strong electron-donating characteristics, rendering it a flexible option for environmental remediation [7, 28]. The core functions as the source of electrons, supplying reducing power for reactions, while the shell serves as the location for electrostatic interactions and complex chemical reactions (chemisorptions). The arrangement of the core-shell significantly affects the chemical characteristics of nZVI. The disordered and flawed state of the oxide shell could make it more reactive than a basic unreactive oxide layer found on a large iron surface [29]. The outer layer shows a minimal difference from the thick inner core. When the nanoparticles cluster together, they feature a constant oxide coating while the metal centers are divided by a slender interfacial oxide stratum, approximately 1 nm thick. The amorphous and chaotic oxide layer results from the nanoparticles' exceptionally tiny radii, which obstructs the development of a crystalline structure. Including boron in the initial material also plays a role in creating imperfections within the structure and forming the oxide coating [7, 30]. The semiconductor characteristics of the oxide layer facilitate rapid charge transfer, making it easier for the reduction of contaminants to take place thanks to its thinness and the existence of faulty sites [29]. Besides reducing various inorganic pollutants and halogenated organic compounds, nZVI has the potential for utilization in a broader range of contaminants that can undergo reduction, adsorption onto precipitation, surfaces, or a combination of these processes [31]. As per the core-shell concept, the oxide shell with mixed valence is mainly insoluble at neutral pH, providing a protective barrier against quick oxidation for the core. Forming the oxide shell is influenced by the production method and surrounding environmental factors [32].

nZVI has been the subject of thorough research due to its capacity to treat wastewater effluents contaminated with heavy metals from various sectors. nZVI's low toxicity and widespread presence in nature have contributed to its extensive use in addressing environmental pollution issues. nZVI comprises a core made of Fe^0 and an outer shell consisting of Fe oxide. The core possesses reducing capabilities, while the outer shell is a site for electrostatic and chemisorption interactions. Mechanisms like decreasing; assimilation, settling, and transformation have significantly eliminated heavy metals from liquid phases with the aid of nZVI. Upon being mixed with water, nZVI demonstrates characteristics similar to ligands. Under conditions of low acidity, the iron oxide coating carries a positive charge, drawing in anions such as sulphates and phosphates; conversely, at high acidity levels, it acquires a negative charge, leading to the attraction of cations like metal ions. Subsequently, heavy metal contaminants are immobilized on the solid nZVI surface post-reaction [33–36].

3. The nZVI synthesis techniques

Nine techniques for producing nZVI were recognized: thermal reduction, liquid chemicals like sodium borohydride and hydrogen gas, electrochemical methods, micro-emulsion, ultrasonic methods, eco-friendly synthesis, and milling. These approaches encompass a range of physical and chemical techniques, as well as bottom-up and top-down technologies.

Among the techniques that have been recognized, only the milling technique involves a physical approach that starts from the top. The remaining approaches consist of chemical processes and bottom-up strategies. One way we acquired information was from data released by nZVI manufacturers and scientific literature on three methods for industrial nZVI production: milling, chemical vapor deposition, and chemical reduction using hydrogen gas [37–39].

3.1. Chemical reduction in liquid phase using sodium borohydride

The primary method for producing nZVI is chemical reduction, involving the reduction of iron salts using reducing agents through chemical processes. Sodium borohydride ($NaBH_4$) is commonly employed as a reducing agent in liquid reduction processes, especially in small-scale research settings, owing to its straightforward nature.

The production of nano zero-valent iron involves combining equivalent amounts of aqueous solutions of $NaBH_4$ and iron chloride ($FeCl_3$). The former substance is combined with the latter gradually, under constant stirring, for approximately 20 minutes at room temperature, as recommended by various studies. The nZVI nanoparticles become visible as soon as the initial drops of the reducing agent solution are added [40, 41]. To be suitable for environmental cleanup, the produced nZVI needs to undergo filtration, washing, and drying processes. The process of separation typically involves utilizing vacuum filtration, rinsing is carried out using deionized water, acetone, or ethanol, and drying takes place in an environment devoid of reactive gases. Using ethanol and acetone for rinsing prevents rapid oxidation of the nZVI during the cleaning process, forming a high-quality black powder substance [41–43]. Ferric iron is converted to a zero valence through the reaction outlined in Eq. 1 [43].

$$4Fe^{3+}(aq) + 3BH_4^- + 9H_2O \rightarrow$$
$$12Fe^0(s) + 3H_3BO_3(aq) + 12H^+(aq) + 9H_2(aq) \quad (1)$$

3.2. Thermal reduction

An approach examined for creating cost-effective and practical nZVI is thermal reduction, commonly referred to as carbothermal reduction. This technique involves the reduction of gaseous Fe^{2+} oxide particles or salts at elevated temperatures using thermal energy while in the company of gaseous reducing agents like CO, CO_2, or H_2 generated through the thermal decomposition of carbon-based materials (e.g., nano carbon particles, biochar, black carbon) [37, 44]. Fe^0 is produced through a high temperature endothermic reaction (> 500 °C) as stated in Eqs. 2 & 3 [45]. At first, a mixture of the carbon source and deionized water is blended through stirring, creating a solid substance that is then isolated from the liquid above it using vacuum filtration, according to Hoch et al. [45]. The solid is removed from the filter during a gentle solidification phase and then moved to a vacuum oven for drying without any additional heating, typically for around 12 hours [45]. Upon completion of the drying process, the samples undergo charring within a tube furnace that is heated under a nitrogen flow for approximately three hours. The heating temperature typically falls within the range of 500 to 1,000 degrees Celsius. Subsequently, the samples undergo a gradual cooling process until they reach the ambient room temperature, resulting in the production of nZVI supported by carbon (C-Fe^0) as evidenced by various studies [45–47]. Through this approach, carbon-encapsulated nZVI demonstrates reduced particle aggregation and enhanced degradation capabilities when compared to its non-encapsulated counterpart. Studies by Hoch et al. [45] and Dai et al. [46] have evaluated this improved efficacy in hexavalent chromium reduction.

$$Fe_3O_4(aq) + 2C(s) \rightarrow 3Fe^0(s) + 2CO_2(aq) \qquad (2)$$

$$Fe(C_2H_3O_2)_2(aq) + C(s) \rightarrow Fe^0(s) + 2CH_2CO(g) + CO(g) + H_2O(g) \quad (3)$$

As stated by Orlandi et al. [47], carbo-thermal reduction has the flexibility to utilize various forms of carbon sources, with carbon black frequently employed but alternatives such as graphite, carbon nanotubes, and even sugar have been successfully used in this process. Nonetheless, disparities persist in synthesis effectiveness when utilizing various carbon sources [47].

3.3. Hydrogen gas-based chemical reduction

The primary approach to reducing gas involves employing hydrogen gas as a reducing agent. In this process, the production of nZVI is achieved through the reduction of hematite and goethite particles under elevated temperatures using hydrogen gas, as outlined in the reaction described in Eq. 4 [48, 49].

$$Fe_3O_4(s) + 4H_2(g) \rightarrow 3Fe^0(s) + 4H_2O(g) \qquad (4)$$

In the initial phase of nZVI preparation, hematite (α-Fe_2O_3) and goethite (α-FeO/OH) particles are generated. The latter can be achieved by conventional means with the passage of an oxygen-rich gas through a mixture containing a deposit of ferrous material (iron hydroxides or carbonates) resulting from the interaction with a liquid solution containing ferrous compounds, and substances like alkaline carbonates, alkaline hydroxides, and so forth. Purifying the water-based solution is crucial in restricting the presence of contaminants within goethite particles. Hematite particles are produced by subjecting goethite particles to a controlled heating process known as dehydration. This process is conducted within a temperature range of 250 to 350 degrees Celsius [50].

Following this procedure, particles of goethite and hematite are subjected to a decrease in temperature through heating in a hydrogen gas environment. The nZVI particles collected are then cooled down, extracted, and moved into water to prevent the development of an oxidation layer on their surface while in the gas phase. Following oxidation, the particles undergo a drying process inside greenhouses maintained at a temperature below 100 degrees Celsius, resulting in the production of nZVI. Through the reduction of goethite and hematite particles through heat treatment, iron particles are formed, consisting entirely of the α-Fe^0 phase. As mentioned by Uegami et al. [50], the catalytic function of α-Fe^0 results in the decomposition of water into oxygen and hydrogen when iron particles are introduced into the water. The nZVI particles produced contain two parts composed of α-Fe^0, and Fe_3O_4 formed through a reaction with water [50].

The method uses a thermogravimetric analysis instrument on a small scale in the lab. The magnetite minerals are positioned within a container and inserted into the thermogravimetric analysis apparatus, where the temperature is raised slowly in an argon environment. Upon achieving the desired reaction temperature, the hydrogen gas is introduced into the device. After the reduction process is entirely carried out, the hydrogen supply is halted, and the argon flow is reinstated. The powder that has been decreased in size is cooled within an argon environment and taken out of the apparatus when the temperature reaches approximately 300 to 400 degrees Celsius [49].

3.4. Green synthesis

In recent times, there has been an increasing adoption of green synthesis approaches. These techniques have surfaced as a substitute for the conventional chemical and physical means of generating nZVI, primarily driven by the elevated costs associated with production. Consequently, green synthesis offers not only reduced expenses but also proves to be a sustainable approach as opposed to conventional techniques, which typically entail significant energy and resource usage, as well as the production of sewage, waste, and emissions necessitating proper disposal and treatment methods [51–53].

The process of green synthesis involves the utilization of plant extracts and microorganisms like bacteria and fungi in a method that starts from the bottom. Plant phytochemicals and microbial enzymes often have antioxidant or reducing properties. These properties are crucial for changing metallic compounds through reduction and oxidation processes. The substances found in these solutions interact with ferric iron in the mixture leading to the creation of nZVI [51, 54, 55].

The process of green synthesis using botanical extracts primarily involves those with substantial total polyphenol content and strong antioxidant properties, including ingredients like grape, bran, black tea, balm, lemon, green tea, sorghum, coffee plants, and more [44, 56]. As indicated by Machado et al. [56], there is promising potential in using leaves from fruit trees to produce nZVI. Using microorganisms for green synthesis is not currently widely adopted among the scientific community. Moreover, employing microorganisms in the production of nZVI necessitates strict adherence to aseptic conditions, leading to higher production costs as skilled personnel are required. One additional element to consider is the speed of response, which is noted to be higher in the interaction with plant extracts compared to microorganisms in the synthesis process. Consequently, opting for plant-based methods in green synthesis is often favored over utilizing microorganisms [44].

The process of green synthesis using plant extracts is straightforward. It involves creating a polyphenolic solution through heating plant extracts in water until it is close to boiling. These passages could be pulverized or found in their original state according to previous studies. The plant residue extract is separated and blended with a solution containing Fe^{2+}. Iron ions are converted to Fe^0 in the presence of polyphenols. The byproducts produced using this technique consist of paper sheets and filters, which need to be appropriately discarded in designated areas such as landfills or incinerators as they could potentially harbor iron compounds similar to the wastewater produced in this process [40, 44, 56].

Green manufacturing techniques can readily be implemented on a large scale in industry, as they do not necessitate high temperatures, pressure, or extra energy inputs, in addition to being cost-effective. Nevertheless, numerous writers assert that additional research is required to comprehend the manufacturing and utilization procedures, the physical and chemical characteristics, and the reactivity and aggregation of the nanoparticles generated. Moreover, there is a possibility of incomplete conversion of iron to nZVI in the synthesis phase, leading to the production of various iron oxides and iron forms [44, 56, 57]. In Fig. 1, the schematic of the green synthesis of nZVI using Ricinus communis seed extract is shown.

3.5. Micro-emulsion

Numerous writers have explored micro-emulsions as a technique for enhancing the properties of nZVI. Nevertheless, this approach was employed by different researchers for the synthesis of nZVI nanoparticles [59–61].

The micro-emulsion technique involves incorporating an inorganic phase into tiny water emulsions dispersed in oil to produce consistently sized metallic particles. It constitutes a solitary stage consisting of a minimum of three elements: a pair of which are immiscible, like water and oil, while the third element is a surfactant positioned at the water/oil boundary [62]. Micro-emulsions may form through two mechanisms: (1) through the dispersion of oil micelles in the water phase (oil-in-water micro-emulsion - O/W), or (2) through the dispersion of water micelles in the oil phase (water-in-oil micro-emulsion - W/O, also known as reverse micro-emulsion). The production of nZVI takes place within reverse micelles, known as micro reactors, where multiple tiny water droplets are dispersed in an organic phase utilizing a surfactant. In this approach, the method parameters, like the dimensions of water droplet molecules, regulate the morphology and size of produced particles [59, 60, 62]. To implement the technique, it is essential to identify the formula of surfactants and micro-emulsions according to the intended end product. The combination of these micro-emulsions takes place by mixing one with the metallic precursor (such as ferric chloride) and the other with the precipitating agent (such as sodium borohydride). It leads to the reagents interacting through droplet and coalescence collisions, forming nanometric-sized precipitates. The quick interchange of reagents can occur rapidly, typically happening solely while mixing. Syntheses transpire within droplets, exerting control over the ultimate particle dimension [60, 63].

In the reduction process, a solution produces a black-colored solid along with a gas. The gas produced is released into gathering setups. Subsequently, there is another round of stirring, followed by centrifugation to isolate the nZVI material [64]. The particles undergo a cleaning process using ethanol or acetone before being eliminated. There are several techniques available for removing nZVI, including the RESS (rapid expansion of supercritical fluid solution) method [65], in situ deposition [66], and the use of magnets [60, 64]. The complete manufacturing process needs to be conducted within a nitrogen environment. The size of nanoparticles produced using the microemulsion technique varies based on the size of the microemulsion droplet employed, the concentration of substances (particularly the surfactant), and the pliability of the surfactant layer surrounding the nanoparticles [60].

3.6. Milling

The creation of nZVI is achieved using machinery that facilitates the abrasion of particles, including planetary ball mill systems, and high-speed rotating chambers, among other options. The milling setup primarily comprises two main components: (1) the milling apparatus, which includes steel balls, an agitator, a grinding chamber, and an engine and (2) a system for particle cooling and circulation, which

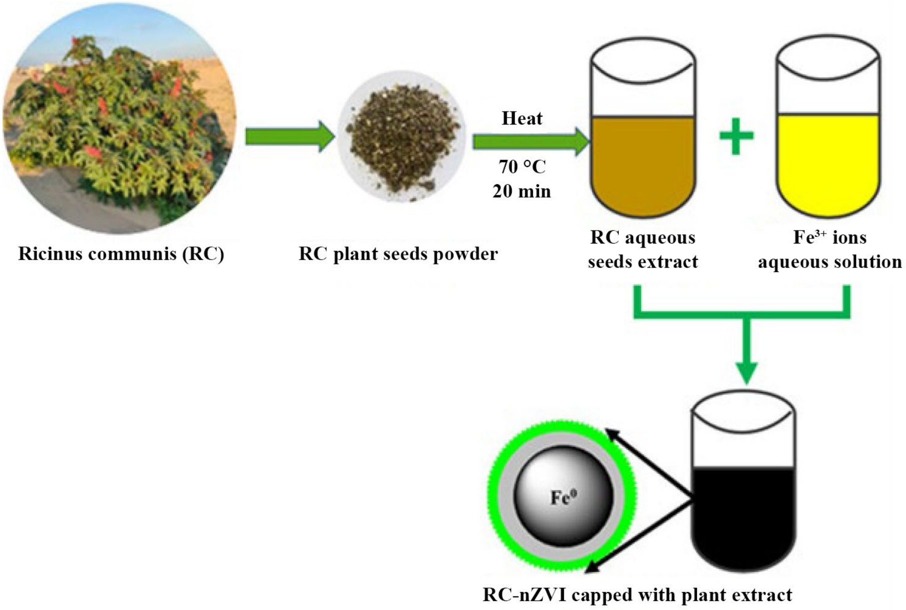

Fig. 1. Schematic of green synthesis of nZVI using Ricinus communis seed extract [58]. Used under Creative Commons Attribution 3.0 License. For more information, visit https://creativecommons.org/licenses/by/3.0/.

involves a pump and a retention tank used to regulate the temperature of the iron suspension both within the tank and in the mill. Steel balls (250 µm in diameter) and iron microparticles are placed in the grinding chamber. These materials make up the medium for forming nZVI. The ratio in mass between steel spheres and particles varies from 20:1 to 40:1 based on the technique and tools employed for the study [67, 68].

While milling, the agitator is powered by the motor to rotate at a specific speed, stirring the milling medium composed of balls and iron particles ranging from 1 to 50 µm in size. The metal particles are smashed by the steel balls, causing the material to break into tinier fragments due to the energy of the collision. The chamber that spins has a cylinder serving as a filter to keep the steel balls in while letting the processed iron material flow through to the holding tank. Within the tank, the iron particles are recirculated back into the milling system through a circulation pump until they reach the desired diameter. The nZVI is gathered at the end of the milling procedure. Throughout the operation, iron particles undergo mechanical abrasion until they achieve a nanoscale dimension [69].

The process of milling can be carried out in conditions that are either dry or wet. In the dry milling process, milling balls and iron particles are utilized exclusively, whereas wet milling involves the incorporation of reagents into the procedure. Within the initial procedure, the common factors influencing the physicochemical characteristics of the particles include the type of milling equipment, particle rigidity, duration, energy input, the ratio of balls to powder, and feed particle size. During the final stage, factors related to the suspension, such as concentration of solids, thickness, and acidity level, need to be taken into account alongside the characteristics of the powder [70].

3.7. Electrochemical method

The process of electrochemical technique involves utilizing electrolysis to create nZVI by applying solutions that contain iron compounds (such as Fe^{2+} and Fe^{3+}), along with electric currents and electrodes (cathodes and anodes) [44]. The approach suggested by Chen et al. [71] integrates both ultrasonic and electrochemical methodologies.

The nZVI is created through the reduction of ferric chloride as described by the reactions shown in Eqs. 5 & 6 [71]. The atoms of nZVI that are created are slowly accumulated on the negative electrode. Nonetheless, they exhibit a pronounced inclination towards clustering. To swiftly eliminate nZVI from the cathode, cationic surfactants are employed as stabilizing agents along with the essential energy supply provided by ultrasonic waves [44, 71, 72].

$$Fe^{3+} + 3e^{-} + \text{stabilizer} \rightarrow nFe^{0} \tag{5}$$

$$Cl^{-} \rightarrow \frac{1}{2} Cl_2 + e^{-} \tag{6}$$

The process of generating nZVI begins with creating the ferric chloride solution. This solution is then utilized in an electroplating setup where precautions are taken by ensuring the electrodes are coated with non-reactive substances to prevent undesired interactions with the newly formed nZVI. The electroplating chamber is positioned within an ultrasonic generator containing water, which assists in delaminating the cathode from the nZVI before amalgamation and is also utilized concurrently in the process to supply kinetic energy for the delamination [71]. The solution of ferric chloride (III) is moved into the reactor and combined with the stabilizing agents (for instance, cetylpyridin chloride (CPC)) and polyvinylpyrrolidone (PVP) to prevent the agglomeration of the nanoparticles. The nZVI that is generated needs to be gathered in water devoid of oxygen, which is why argon is utilized. In Fig. 2, the schematic of the electrochemical method for nZVI synthesis is shown.

3.8. Ultrasonic method

The technique involving ultrasonic waves enhances the production of nZVI by employing physical and chemical synthesis methods [44, 74]. The process of producing nZVI begins by combining solutions of ammonium hydroxide, $NaBH_4$, and Fe^{3+} with deionized water. Subsequently, the resulting mixtures are moved to a balloon reactor equipped with three open necks. Ultrasonic frequencies are used by

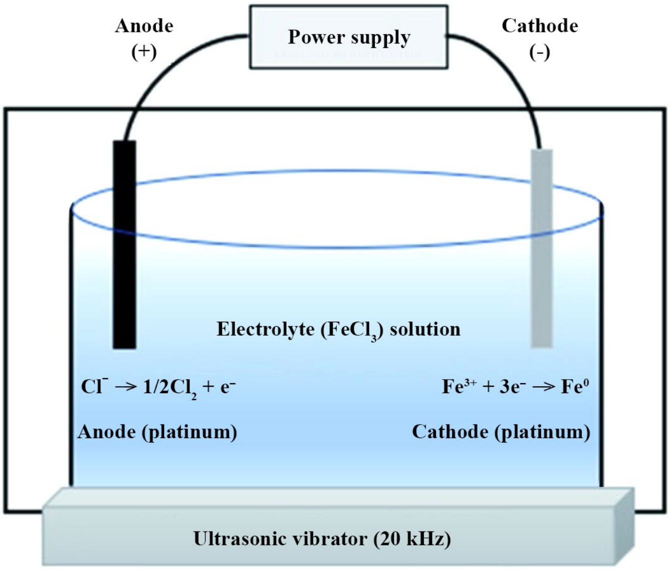

Fig. 2. Schematic of the electrochemical method for nZVI synthesis [73]. Used under Creative Commons Attribution 3.0 License. For more information, visit https://creativecommons.org/licenses/by/3.0/.

immersing a titanium device into the solution, operating at a fixed frequency such as 20 kHz, and delivering power levels between 0 to 1,000 watts. Nitrogen gas and argon are injected into the necks of another bottle to eliminate oxygen and avoid oxidation during the procedure. The response balloon must be positioned underwater to regulate the solution's temperature, as it tends to rise when ultrasonic waves are present during the reaction [74]. The produced nZVI undergoes filtration using a membrane filter followed by rinsing with pure ethanol; subsequently, it is subjected to centrifugation to eliminate any moisture content present. The solid residues obtained are dehydrated in a vacuum oven for a minimum of 24 hours and then preserved in a refrigerator to prevent oxidation [74].

This technique involves incorporating ammonium hydroxide into the solution to prevent nZVI oxidation triggered by hydrogen emission during the production reaction, thereby enhancing the quantity of generated nZVI. The chemical reduction combined with sodium borohydride reacts with the ultrasonic wave method as indicated by the equation presented in Eq. 7 [74].

$$4Fe^{2+}(aq) + BH_4^-(aq) + 7NH_4OH(aq) \rightarrow$$
$$4Fe^0(s)\downarrow + H_3BO_3(aq) + 7NH_4^+(aq) + H_2O(g) \quad (7)$$

4. nZVI characterization

Iron nanoparticles were generated through ferric iron reduction using sodium borohydride. These nanoparticles were characterized using transmission electron microscopy (TEM) and scanning electron microscopy (SEM) [75, 76] (Fig. 3). To prepare the samples for analysis a dilute ethanol solution of the nanoparticles was applied to a carbon film-coated 300-mesh copper grid. It involves carefully dispensing 2–3 drops of the solution onto the grid's surface, ensuring adequate coverage of the carbon film. Subsequently, the specimen was positioned within a vacuum enclosure until all the ethanol had dissipated entirely [75]. The findings from the analysis using TEM indicate that the nanoparticles aggregate together in a linear arrangement due to interactions involving both magnetism and electrostatic forces. The image suggests that there is a concentrated center within a particle, enveloped by a slender layer that is notably less distinct in comparison to the central core [31].

The dimensions and distribution of nZVI are determined using an Acoustic Spectrometer, which employs sound waves passing through a suspended particle solution to assess the characteristics of the particles. The device is linked to a conical flask with four necks that holds a mixture of iron nanoparticles in purified water. One benefit of using this device is its adaptability, allowing for examining non-transparent substances without constraints [7]. The classic BET method, known as the Brunauer–Emmett–Teller isotherm, is utilized to ascertain the precise surface area of nanoparticles by analyzing the extent of nitrogen adsorption on the surface. To prepare the samples, they are dried at room temperature (22 ± 1 °C) within a vacuum desiccator. Following this step, they are degassed under vacuum at 90 °C for one hour and then at 200 °C for four hours [75, 78]. The analysis of the structural composition of nanoparticles is conducted through X-ray diffraction techniques. The diffraction pattern indicates that the particles primarily existed in a state of zero valence, and all iron atoms were in a cubic structure at a closed phase [79]. X-ray photoelectron spectroscopy (XPS) can be utilized to analyze the surface construction of iron nanoparticles at depths of less than 10 nanometers. The iron nanoparticles are readied by desiccating them in a compact nitrogen-purged enclosure at ambient temperature and then inserting them into the sample chamber immediately to avoid sample oxidation. X-ray absorption near edge structure ([80]) method utilizes synchrotron light to excite the inner electrons of iron atoms, offering valuable insights into the iron's oxidation state. The zeta potential, a key parameter for iron nanoparticles, refers to the electric potential at the particle's surface compared to that in the surrounding medium, playing a crucial role in the particles' movement in an electric field [75, 81]. BET and XRD analyses of nZVI can be seen in Fig. 4.

5. Practical implementation of nZVI remediation technology

The unique core-shell structure of nZVI and its composites resulted in distinct adsorption properties, leading to different behaviors in the remediation of heavy metals and other pollutants. It was due to the presence of surface functional groups. Table 1 summarizes the application of some nZVI composites in removing various pollutants. Further examination was conducted on the efficacy of nZVI materials in addressing heavy metal contamination. The findings suggest that the adsorption capabilities of nanoparticles offer a significant edge

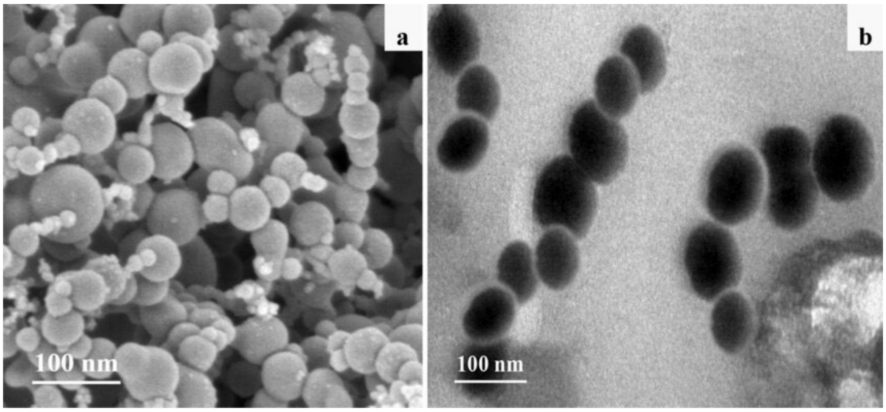

Fig. 3. a) SEM and b) TEM image of NZVI [77]. Used under Creative Commons Attribution 3.0 License. For more information, visit https://creativecommons.org/licenses/by/3.0/.

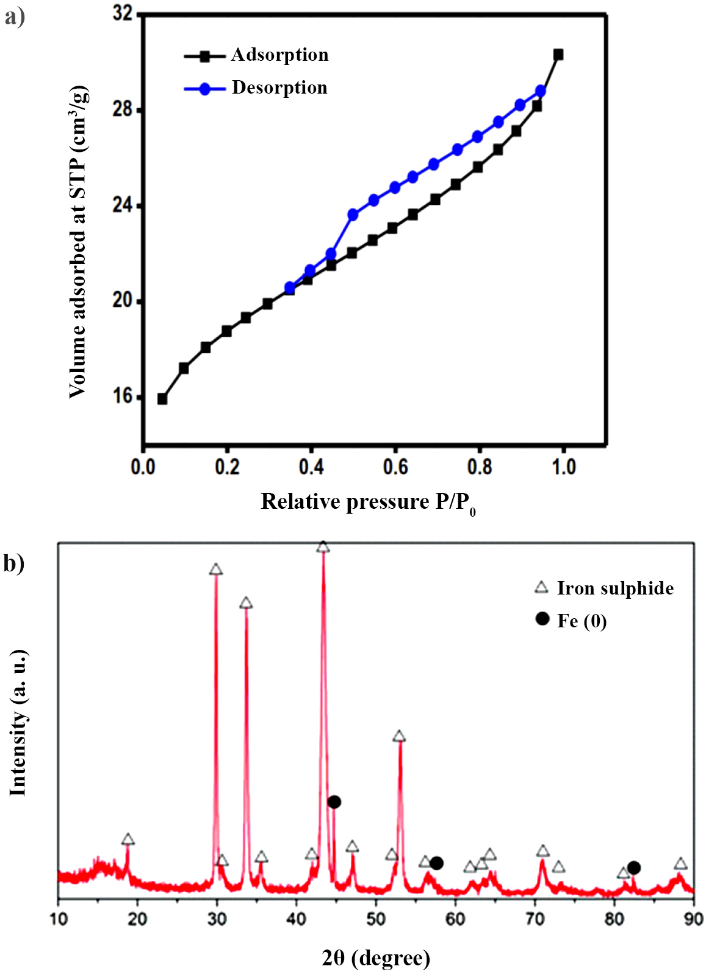

Fig. 4. a) BET surface area for nZVI [82] and b) XRD pattern of nZVI [83]. Used under Creative Commons Attribution 3.0 License. For more information, visit https://creativecommons.org/licenses/by/3.0/.

compared to traditional materials. In contrast to alternative substances, nZVI compounds are more accessible to isolate and retrieve from a solution because of their granular composition and robust mechanical properties. Vilardi employed oxalic acid, sodium hydroxide, and deionized water to restore and reclaim chromium from the adsorbent surface, demonstrating that a significant majority of the adsorbed Cr (>98%) could be retrieved. Furthermore, traditional materials and certain silica-based substances exhibit heightened sensitivity to variations in pH levels, resulting in a gradual reduction in adsorption effectiveness as pH shifts occur. On the other hand, nZVI composites have a wider pH tolerance and are less influenced by pH changes because of the inclusion of modified materials. As a result, nZVI and its composites show promise for use in in situ environmental remediation [8, 84, 85].

Currently, the primary emphasis in articles is on the characteristics of altered substances, with little attention given to the potential financial and environmental issues. For instance, while chitosan and cellulose-based materials have gained significant research attention, their production and operational expenses may elevate during practical applications. Nevertheless, composites containing nZVI have demonstrated exceptional consistency, durability, and reusability, leading to additional cost savings. Li et al. [103] successfully overcame challenges related to the large-scale production of zero-valent iron and the limitations of its surface passivation layer by utilizing surface stabilization techniques, cost-effective macro preparation methods, and secure storage and transportation technologies. Additionally, the in-place immobilization foundation of zero-valent iron was adjusted by employing oxygen-containing acidic derivatives to eliminate antimony metal ions from mine wastewater using a multi-stage alley filling technique, preserving a removal efficiency of over 90% for an extended period and meeting the standard treatment requirement for a water volume of 500 m^3 per day [103].

A popular technique for cleaning up polluted underground water sources involves using a permeable reactive barrier (PRB) made of zero-valent iron. This method typically entails digging a trench downstream of the contaminated area and filling it with a reactive material primarily composed of nZVI composite materials, effectively creating a barrier that prevents further contamination [104]. As contaminated groundwater moves through the specially designed barrier, the pollutants come into contact with the reactive materials.

Table 1. Application of some nZVI composites in removing various pollutants.

Composite	Pollutants	Adsorption isotherm	Adsorption kinetic	Adsorption capacity (mg/g)	Removal efficiency (%)	Ref.
PEG (polyethylene glycol)-zeolite- nZVI	Norfloxacin	Temkin	Pseudo-second-order	56.67	90	[86]
	Ofloxacin			48.88		
Activated low rank coals/nZVI	Cr (VI)	Freundlich		196.50	95	[87]
Chitosan-stabilized biochar supported S-nZVI	Cr (VI)	Langmuir		244.07	80.09	[88]
nZVI	As (III)			14.29	70.9	[89]
	As (V)			36.90	99.9	
Cellulose nanocrystals-nZVI	Ni (II)	-		-	98.5	[90]
Amorphous zero valent iron-nZVI	Sb (III)	Langmuir		558.20	99	[91]
nZVI@MBenes (2D transition metal borides)	U (VI)			107.80	88.5	[92]
	Cr (VI)			68.60	84.6	
nZVI/MoS$_2$	U (VI)			71.80	95	[93]
nZVI/copper	Cefixime			4.31	98.71	[94]
nZVI@Fe$_2$O$_3$/PC (porous carbon)	Sulfamethoxazole (SMX)	Temkin		329	99	[95]
Calcium alginate-nZVI-biochar	Pb (II)	Langmuir		247.99	-	[96]
	Zn (II)			71.77	-	
	Cd (II)			47.27	-	
Pyrogallic acid-nZVI	Cr (VI)	-		-	81.7	[97]
Ethylenediamine-nZVI				-	77.1	
Sodium persulfate-nZVI				-	55.1	
nZVI/reduced graphene oxide	Se (IV)	Langmuir	First-order	173.53	99	[98]
Carbon@nZVI	Pb (II)		Pseudo-second-order	98.37	98.7	[99]
	Zn (II)			26.38	99.4	
nZVI/clay	U (VI)			88.90	96.6	[100]
nZVI-biochar	Cr (VI)		Second-order	105	96.1	[101]
Chitosan-nZVI@biochar	Cr (VI)	Freundlich	Pseudo-second-order	246	83	[102]

This interaction results in the pollutants being immobilized or broken down into harmless substances. Consequently, the groundwater that emerges from this barrier is cleaner than when it entered. nZVI materials have been used successfully to clean up contaminated groundwater in over one hundred instances across North America, Europe, and Taiwan, China. In contrast to small-scale laboratory tests, the real-world implementation of PRBs encounters more intricate operational circumstances, including fluctuating flow velocities, levels of oxygen in solution, pH, temperature, and the impact of additional ions [105]. In a recent study, researchers led by Tasharrofi et al. [106] explored the real-world applications of a novel material, a NaZ-nZVI composite, within a specific type of environmental remediation technology known as a PRB. It was noted that detectable levels of cadmium at the PRB outlet were only evident when the quantity of the adsorbent was inadequate relative to the degree of contamination ($V > V_b$). The findings indicated that the discharge of cadmium would occur at a very gradual pace and become less concentrated. Although this approach is less expensive, the regeneration process is more complicated. The utilization of zero-valent iron in PRB represents cutting-edge technology. However, the restricted reactivity due to passivation and clogging has prompted some scientists to implement it in a fluidized bed reactor (FBR) to circumvent these issues [106–108]. Fluidization through water flow prevents clogging by generating fresh iron surfaces through particle collisions. Simultaneously, the corrosion byproducts are removed from the solution during transport, and the filter cake enables additional metal retrieval. Just like FBRs, Bilardi et al. [109] studied practical methods for leachate pretreatment. They placed the reactive material in a tank with three consecutive slots, each containing a mixture of pumice and ZVI, a mixture of ZVI and zeolites, and granular activated carbon (GAC). While the GAC fraction of the material shows very little ability to remove contaminants, it effectively removes copper, zinc, and nickel with an efficiency exceeding 94%. It makes GAC a valuable component as it can be easily replaced or separated when its capacity is reached. This unique characteristic makes it an efficient alternative for use in PRB [109].

The most extensive testing of permeable reactive barriers, including smaller pilot projects and full-scale implementations, has taken place in North America [44]. The US Environmental Protection Agency (EPA) has documented a significant number of cases–25 in total–where nZVI was used or tested extensively in the United States for cleaning up contaminated soil. Data analysis revealed that in over half of the instances (56%), a significant decrease in contaminant levels was observed, indicating a successful reduction in the contaminant load. This reduction was characterized by a consistent downward trend in contaminant concentration, averaging approximately 70% [110]. In the United States, the effectiveness of nZVI in cleaning up contaminated soil was demonstrated at several US Navy facilities, including the Naval Air Engineering Station near Lakehurst, New Jersey, and the Naval Air Station in Jacksonville, Florida. These locations were affected by the presence of various contaminants, namely 1,1,1-trichloroethane (1,1,1-TCA), dichloroethylene (DCE), trichloroethylene (TCE), and perchloroethylene (PCE). Research has revealed that when chlorine compounds undergo a specific chemical reaction known as beta-elimination, the removal of chlorine atoms occurs faster, resulting in a lower production of unwanted byproducts. The researchers emphasized the importance of maintaining a precise ratio of iron to soil when applying nZVI for remediation. They recommend using a weight ratio of 0.004, meaning that for every 1000 grams of soil, 4 grams of iron should be used. Furthermore, they highlighted the need to minimize the amount of water used for injection, as water containing high levels of oxidants can quickly deactivate the iron, hindering its effectiveness in cleaning up the soil [44].

6. Environmental features of nZVI synthesis methods

The synthesis of nZVI through chemical methods often involves hazardous reagents, leading to environmental impacts because of their construction and potential presence in waste, emissions, and wastewater. While most methods use minimal water, the ultrasonic wave method is particularly water-intensive. This results in wastewater generation containing harmful compounds like boron, chlorine, and surfactants, requiring proper treatment before disposal or reuse. The industrial sector, being a significant contributor to water demand and wastewater pollution, must prioritize water efficiency and explore water reuse options to mitigate these environmental challenges. The environmental impact of nZVI production methods is influenced by energy consumption, atmospheric emissions, and solid waste generation. Methods like gas reduction with hydrogen gas and ultrasonic wave methods exhibit high energy consumption, contributing to greenhouse gas emissions and resource depletion. Solid waste generation, mainly from filtration processes, necessitates proper treatment to prevent chemical contamination. Atmospheric emissions, mainly from electrochemical, thermal reduction, and chemical vapor deposition methods, require control measures to mitigate environmental and human health risks. Notably, the environmental impact of energy consumption is significantly influenced by the arrangement of the energy matrix in the country of production, with more significant impacts associated with a reliance on non-renewable energy sources [111–114].

The milling method emerges as the most environmentally friendly option, with minimal water consumption, waste generation, wastewater, and emissions, despite using corrosive materials. The green synthesis methods rank second, with the former utilizing ecological processes but requiring more inputs and resulting in wastewater generation, while the latter generates significant atmospheric emissions. The hydrogen gas reduction, micro-emulsion, and thermal reduction methods share third place, with the first two relying heavily on energy consumption and the third producing substantial wastewater and waste. The electrochemical method, ultrasonic wave, and reduction with sodium borohydride methods exhibit the lowest environmental rankings. They share a significant number of red-rated aspects, indicating high environmental risks. The electrochemical method has concerns regarding inputs and atmospheric emissions, while the sodium borohydride reduction method has issues with inputs, wastewater, and solid waste. The ultrasonic wave method faces the most significant challenges with red ratings for inputs, energy consumption, water consumption, and wastewater generation. This analysis highlights the need for targeted improvements in these methods to minimize their environmental footprint [111, 115–117]. Table 2 summarizes the advantages and disadvantages of nZVI synthesis methods.

Table 2. Advantages and disadvantages of nZVI synthesis methods.

Method	Advantages	Disadvantages
Milling	Minimum water consumption, waste generation, wastewater, and emissions	Uses corrosive materials
Green synthesis (using bio-reductants)	Ecological processes	Requires more inputs and results in wastewater generation
Green synthesis (using plant extracts)	Ecological processes	Generates significant atmospheric emissions
Hydrogen gas reduction	High purity, controllable particle size, scalable	High energy consumption, contributing to greenhouse gas emissions and resource depletion
Micro-emulsion	Controlled particle size and morphology, high surface area	High energy consumption, contributing to greenhouse gas emissions and resource depletion
Thermal reduction	Simple and cost-effective, versatile	Produces substantial wastewater and waste
Electrochemical	Environmentally friendly, controlled synthesis	Concerns regarding inputs and atmospheric emissions
Ultrasonic wave	Fast and efficient, potential for continuous production	High environmental risks: red ratings for inputs, energy consumption, water consumption, and wastewater generation
Sodium borohydride reduction	Fast and efficient, high yield	Issues with inputs, wastewater, and solid waste

7. Conclusions and perspective

nZVI presents a promising solution for environmental remediation, offering a high reactivity and efficacy in removing a wide range of contaminants. Its unique structure, diverse synthesis methods, and effective characterization techniques have been thoroughly investigated, revealing its potential for both in-situ and ex-situ applications. The successful implementation of nZVI in various remediation scenarios demonstrates its practical value in addressing environmental challenges

However, continued research and development are crucial to optimize nZVI's performance and minimize its environmental footprint. Key areas for future investigation include:

- Improving the stability and reactivity of nZVI: Strategies for enhancing the long-term stability and reactivity of nZVI in various environmental conditions are essential for maximizing its effectiveness.
- Developing more environmentally friendly synthesis methods: Exploring alternative synthesis methods that minimize energy consumption and reduce the potential for secondary pollution is crucial for ensuring the sustainability of nZVI applications.
- Expanding the application range of nZVI: Investigating the potential of nZVI for remediating a wider range of contaminants, including emerging pollutants and microplastics, is necessary to address evolving environmental concerns.
- Optimizing nZVI delivery and recovery methods: Developing efficient methods for delivering nZVI to contaminated sites and recovering it after remediation is critical for ensuring cost-effectiveness and minimizing potential risks.

By addressing these challenges, nZVI's potential as a powerful tool for environmental remediation can be fully realized, contributing to a cleaner and healthier environment for future generations.

CRediT authorship contribution statement

Mohammad Ghaffarzadeh: Conceptualization, Writing – original draft.
Reza Rasouli Khorjestan: Formal Analysis, Methodology, Writing – review & editing.
Alireza Afradi: Validation, Writing – review & editing.
Aria Bandehpey: Methodology, Data curation, Writing – review & editing.
Gity Behbudi: Investigation, Supervision, Writing – review & editing.

Data availability

The data underlying this article will be shared on reasonable request to the corresponding author.

Declaration of competing interest

The authors declare no competing interests.

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