

## ARTICLE TYPE

# Nanoremediation: Tiny objects solving Huge environmental problems

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**Abstract: Background.** The application of zero valent iron nanoparticles (nZVI) to remediate soil and groundwater has gained increased attention within the last decade, primarily due to its high reactivity, cost effectiveness and potential to treat a broad range of contaminants (e.g. chlorinated organic solvents, inorganic anions, or metals).

**Objective.** In this paper, the state of the art of the applicability of nanomaterials especially the most frequently used nZVI in soil and groundwater is presented. The purpose of this article is to give an overview of the current knowledge pertaining to the synthesis, employment, limitations, and risk of iron nanoparticles.

**Methods.** Therefore, the authors have reviewed and discussed the recent developments and approaches made on the synthesis of iron nanoparticles emphasizing the justification of green synthesis methods. The studies related to the effective use of nanoparticles in remediating organic and inorganic contaminants are addressed. The potential limitations, challenges, and risks of this innovative nanoremediation technology are also discussed.

**Results.** Studies suggest that nZVI have successfully been applied in nanoremediation, however little is known about the particles' fate and impacts. Additionally, it has already been proven that synthesis and modification can largely determine the physicochemical and biological properties of the particles.

**Conclusion.** This review corroborates the suitability of nanoparticles in the remediation of contaminated media, simultaneously highlighting the work still needed to optimize the syntheses and careful use of such materials, concluding that comprehensive screenings should be performed prior nZVI applications to assess their behavior and impact on the environment and living systems.

**Keywords:** environmental remediation, groundwater, nanomaterials, nanoremediation, zero valent iron nanoparticles (nZVI), green synthesis.

## 1. INTRODUCTION

Nowadays, environmental pollution is undoubtedly one of the most serious global problems [1]. Contaminants in water and soil environments pose a significant risk to human health, while contaminated areas are serious environmental hazards to terrestrial and aquatic ecosystems that affect their biodiversity. Particularly, many valuable environmental resources, such as groundwater, are constantly threatened by various natural and anthropogenic contaminants [2]. Halogenated organic compounds, heavy metals, pesticides, dyes, herbicides, industrial effluents, and sewage are just a few examples of the many contaminants found in such areas [3].

Therefore, a wide range of techniques and different types of materials have been developed for their application in remediation processes [3].

Considering that the demand for fresh water is increasing dramatically, cleaning the environment from various pollution sources is an imperative need to protect both ecological and public health. Thus, it is still crucial to assess and remediate the pollution caused by largely decommissioned former pollution activities. However, such inherited contaminants cannot be easily detected, are difficult to access, and have long-term toxicity to soil and groundwater, which make them particularly dangerous [4]. In the USA and Europe alone, there are around 300,000 potentially contaminated areas that need to be remediated, which would cost more than \$200 billion [5].

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Environmental remediation procedures involve technical, financial, and administrative activities as well as a series of measures taken for environmental purposes to modify the interactions between pollutants and the environment under controlled conditions and to initiate a controlled decomposition process that would reduce the amount of pollutants or convert them into non-hazardous compounds. Since the early 1990s, various physical (e.g., soil washing and air sparging), chemical (e.g., *in situ* chemical oxidation), biological (e.g., use of enzymes), and integrated (e.g., combination of chemical and biological techniques such as the simultaneous use of zerovalent iron nanoparticles (nZVI) with anaerobic dechlorinating bacteria) remediation technologies have been developed to effectively manage contaminated geological resources and groundwater and to mitigate the damage caused (Table 1) [6]. A number of traditional remediation methods are known depending on the properties of the contaminant, and their applicability in a given situation can be determined by their advantages and disadvantages.

However, these conventional methods cannot achieve the desired remediation goals, as they cannot completely transform the emerging contaminants [7]. Moreover, the existing wastewater treatment techniques require high energy consumption, do not allow the complete removal of contaminants, and may also generate toxic products and/or by-products [8].

More specifically, the application of the widely employed bioremediation technology for wastewater treatment is limited, as it is a slow process restricted by the coexistence of non-biodegradable contaminants, while toxic contaminants can also affect the microorganisms used [9]. Similarly, the air sparging technique cannot be applied to layered soils and to treat closed aquifers. In addition, during thermal treatment, soil excavation is required, making this process particularly expensive. Therefore, there is an urgent need to develop more efficient, innovative, and powerful technologies for the effective cleaning of contaminated sites.

Table 1. Main types of remediation processes [10].

Remediation method	Targeted contaminants	Advantages	Disadvantages
Natural attenuation	Metals and organic contaminants	Non-invasive, eco-friendly	Slow
Thermal soil remediation	Volatile and semi-volatile components, polynuclear aromatic hydrocarbons	Cheap, fast	Decomposition of soil constituents
Soil washing	Organic contaminants, heavy metals, radionucleotides	Wide range of pollutants	Only <i>ex situ</i>
Air sparging	Volatile organic compounds	<i>In situ</i>	Generation of potentially dangerous vapors in the atmosphere
Electrokinetic remediation	Heavy metals	<i>In situ</i>	External fluid required
Phytoremediation	Metals	Eco-friendly, cheap	Slow, limited to the surface
Bioremediation	Benzene, toluene, pesticides, polyaromatic hydrocarbons, polychlorinated biphenyls, chlorinated solvents, ethylbenzene, and xylene	<i>In situ</i> , biocompatible	Slow, sensitive to environmental factors

The application of nanotechnology to the growing pollution problems and environmental aspects has evolved into the so-called nanoremediation processes for wastewater treatment [11,12]. It has been reported that nanomaterials have unique physical, chemical, electronic, catalytic, magnetic, optical, and mechanical properties owing to their small size [13]. Moreover, they offer a unique surface chemistry compared to conventional processes, as they can, for instance, be functionalized or modified with other materials, which can target specific desired molecules for the efficient treatment of contaminated water environments. The modulation of the chemical and physical properties of nanomaterials, such as their size, morphology, and composition, can also confer

additional improved characteristics, which can directly enhance their remediation performance and overcome many of the challenges posed by the conventional methods [14]. In addition, nanomaterials are attractive alternatives to the existing remediation technologies due to their 1) mobility and transportability in aquifers or porous media, 2) high reactivity with the target pollutants to form less toxic and mobile products, 3) long-lasting reactivity, and 4) biocompatibility [15]. Moreover, their cost effectiveness, facile and/or green synthesis, recyclability, and biodegradability are important features to consider when developing a new nanoremediation technology.

To date, a variety of efficient, eco-friendly, and cost-effective nanomaterials have been developed for wastewater treatment applications, thus making nanotechnology-based methods one of the most advanced techniques for remediation processes [16]. The most commonly used nanomaterials are metal nanoparticles, especially nZVI, whose application in wastewater remediation and anaerobic degradation enhancement has gained increased attention in recent years [17]. Due to its small size, nZVI has a higher surface area, greater reactivity toward a broad range of contaminants, including halogenated organic compounds, nitrates, phosphates, polycyclic aromatic hydrocarbons, and heavy metals, and a higher mobility than its bulk form. Hence, as indicated by the significant number of relevant published studies, nZVI is considered a promising remediation strategy suitable for several applications and environments [18].

However, to assess the impact of the nanomaterial application in the remediation process, it is important to explore their behavior, limitations, and possible toxicity. The development of effective nanomaterials capable of addressing environmental problems requires a thorough understanding of the material platforms and their synthesis process as well as optimization of their performance. Thus, this review aims to provide a general overview of the currently available nanomaterials and nanocomposites used for the environmental remediation of various pollutants and to describe the main properties, applicability potential, and risk of the most frequently used nZVI particles while highlighting the current research trends, especially green approaches, for their production.

## 2. NANOMATERIALS IN REMEDIATION PROCESSES

To date, a series of innovative, eco-friendly, low-cost, and effective nanomaterials with unique properties have been developed and applied to wastewater treatment processes for the potential removal of various contaminants [16]. Based on the nature of the employed nanomaterials, these technologies can be divided into four main categories, i.e., nanoadsorbents, nanocatalysts, nanomembranes, and their combination (Table 2).

### 2.1 Nanoadsorbents

Recently, numerous studies investigating the removal of organic and inorganic pollutants, such as heavy metals and micropollutants, from wastewater using nanoadsorbent materials have been published [19].

Nanoadsorbents can overcome the limitations of the conventional adsorbents due to their very high specific surface area, active adsorption sites, and surface chemistry. Moreover, they have a considerably higher adsorption rate for organic compounds than granular activated carbon, and can also adsorb toxic substances through ion exchange, ion precipitation, and adsorption. Particles used as nanoadsorbents for the removal of heavy metals should be non-toxic and very effective even at small concentrations, while they should have high adsorption capacity toward pollutants that can be easily removed from their surface, so that they can be recycled several times [20].

Nanoadsorbents can be divided into four categories, namely carbon-based (e.g., carbon nanotubes), metal-based (e.g., iron, titanium dioxide, and zinc oxide), polymeric (e.g., resin-supported nZVI), and zeolites (e.g., Ag-zeolite nanoadsorbents) [21,22,23]. Currently, among the most widely used particles are the nZVI particles, which can be employed for the remediation of various pollutants, especially of chlorinated hydrocarbons in contaminated groundwater. Specifically, a suspension of nZVI can be injected into the targeted groundwater, allowing its *in situ* treatment. Nevertheless, although nZVI is more reactive than conventional granular iron due to its high specific surface, its high reactivity can significantly reduce its lifetime, thus, stabilization of these nanoparticles is necessary [20].

### 2.2 Nanocatalysts

Nanomaterials, such as metal oxides and semiconductors, have also received great attention in recent years for the development of novel wastewater treatment technologies. Various types of nanocatalysts, including photocatalysts, electrocatalysts, and Fenton-based catalysts, have been applied to improve the chemical oxidation of organic pollutants [24].

Semiconductor nanocatalysts have also been proved to be highly effective for the degradation of halogenated and non-halogenated organic compounds and heavy metals. It was revealed that the photocatalytic mechanism is mainly based on the photoexcitation of electrons in the catalyst, as the irradiation with light generates holes and excited electrons in the conduction band, while in aqueous media, the generated hydroxyl radicals oxidize the organic contaminating compounds. Titanium dioxide and zinc oxide are the most widely applied nanocatalysts in photocatalysis due to their chemical stability and high reactivity under ultraviolet light [25]. However, it should be noted that the photocatalytic efficiency of various synthesized catalysts depends on the particle characteristics, they are most effective under ultraviolet radiations. Thus, further modifications are required to enhance their activity for the effective removal of pollutants under visible light sources.

### 2.3 Nanomembranes

Membranes serve as a physical barrier for substances depending on their pore and molecule size, and this technology has been well developed as a wide and reliable automated process for the treatment of water and wastewater areas. Nanomembranes are one of the most effective water treatment strategies due to their small pore size, low-cost, and effective disinfection and can be developed from nanomaterials such as nanometal particles (nZVI), non-metal particles, and carbon nanotubes [26]. Especially in wastewater treatment, the nanomembrane separation technology has been used for the effective removal of dyes, heavy metals, and other contaminants. A membrane fabricated using carbonaceous nanofibers has also been disclosed with outstanding selective removal efficiency under high pressure, while zeolite-based nanomembranes (MFI-type) were proven to be effective for aqueous osmosis separations [27].

Table 2. Categories of nanomaterials used in remediation processes [20].

Remediation method	Nanomaterial	Applications	Advantages	Disadvantages
Nanoadsorbents	Carbon nanotubes	Heavily degradable contaminants (pharmaceuticals, antibiotics), some heavy metals	Reusable, bactericidal	Expensive, possible health risk
	Polymeric	Organics and heavy metals	Bifunctional (organics and heavy metals), reusable	Complex production process
	Zeolites	Heavy metals	Bactericidal, controlled release of nanoparticles	Inefficient large-scale production
	Metals and metal oxides	Chlorinated hydrocarbons, heavy metals	Cheap production, low environmental toxicity, biocompatible	Limited durability, stabilization required
Nanocatalysts	Metal oxides	Dyes and other organic pollutants, micropollutants, microbial pathogens	Antimicrobial	Ultraviolet radiation required
	Semiconductors	Organic pollutants (dyes, detergents, pesticides), heavy metals	Very effective even at small concentration	Unknown toxicity
Nanomembranes	Metal nanoparticles and nanofibers	Dairy effluents	High efficiency	Low biocompatibility
	Non-metal nanoparticles and nanofibers	Heavy metals	Biodegradable	Possibly release of nanofibers
	Carbon nanotubes	Oil, microbial pathogens	Extremely high strength, high flexibility, large aspect ratio	Expensive, non-biodegradable

## 2.4 Combined technologies

The most frequently used combined methods involve the integration of the aforementioned nanotechnologies with biological methods [28]. Earlier studies have shown that the

integration of a biological wastewater treatment process with advanced nanotechnology results in an efficient water purification system. Moreover, it has been found that the integration of nanoparticles can significantly improve the

efficiency of several biological processes such as the activated sludge process [29].

One of the most promising integrated methods is the combination of a biological aerobic degradation process with the nZVI-based treatment. This method can degrade organic contaminants and has been successfully used for the remediation of chlorinated organic compounds in groundwater. However, although the application of these combined technologies allows the efficient and environmental friendly recovery of water, their introduction is limited mainly due to the high-level technical approach and the lack of knowledge regarding the impact of nZVI on the biochemical processes and the indigenous microbial communities. In addition, the cultivation of microbes requires a lot of time, making these processes particularly time-consuming [12].

### 3. ZEROVALENT IRON NANOPARTICLES (nZVI)

As already mentioned, nZVI is one of the most widely used nanomaterials for environmental remediation. Due to its structure, which consists of a metallic iron core encapsulated by a thin amorphous oxide shell, and its reduced size, nZVI has a high reactivity toward a broad range of contaminants including dyes, heavy metals, and various other chemical pollutants [30]. Moreover, in terms of cost-effectiveness, the use of nZVI is generally considered less expensive compared to traditional remediation techniques, while the nZVI particles may also reach areas that are difficult or impossible to access by other techniques for *in situ* use [31]. Furthermore, the use of nZVI in remediation processes is considered a sustainable application of nanomaterials research and is usually mentioned among the “green” nanotechnology related approaches that can benefit environmental health. To better assess the potential of these particles, their synthesis and application possibilities were further reviewed in this section.

#### 3.1 Synthesis of nZVI particles

In general, nZVI can be synthesized using chemical or physical methods, either by reducing the size of bulk iron to nanoscale (top-down approach) or by generating nanoiron structures from atoms produced by ions or entire molecules (bottom-up approach) [11]. Representative examples of the top-down approach include the ball-milling method and the sputtering deposition of nanoparticles. However, these methods are limited due to the high production cost, the need for special equipment, and their inability to be used on a large scale. Instead, the microemulsion, ultrasound-assisted, electrodeposition, chemical vapor condensation, thermal decomposition, and chemical reduction-based methods are based on the bottom-up approach.

Among the available synthesis methods for the preparation of nZVI, the most widely used is the reduction-based approach, where  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  salts are mainly used as precursors and the iron ions are reduced to zero valent iron (ZVI) upon treatment in solution with sodium borohydride as the reducing agent [11,12,32]. The properties of the obtained nZVI, such as reactivity and mobility, strongly depend on its size, surface, modifying capping material, oxide layer, and support material, and therefore on its production process. In addition, differences have been identified in the structure of the oxide coating. Therefore, depending on the application, the appropriate synthesis conditions must be selected [33].

Nevertheless, the conventional physical or chemical methods are particularly expensive and energy- and time-consuming while the chemicals used represent a significant environmental burden.

Thus, green synthesis strategies of metal nanoparticles have recently attracted more attention, providing safer and economical alternatives to conventional chemical methods and a low environmental footprint. Such approaches use mild experimental conditions (ambient temperature and pressure) but require careful selection of non-toxic, environmentally friendly solvents, reducing agents, and capping materials. Therefore, they frequently involve living organisms such as bacteria and fungi. Given that microbes play a direct or indirect role in many geochemical biological processes, metals in the soil have developed a kind of natural relationship with biological components from the beginning of life. Taking into account this interesting fact, several studies have reported the preparation of nanoparticles using microorganisms or their active components. For instance, nZVI has been successfully synthesized using *Aspergillus fumigatus* or *Chaetomium globosum* species [34]. However, the syntheses using microorganisms are often slow, the availability and maintenance of the various species used in the process is difficult, and the particles produced are often polydisperse.

In contrast, the use of extracts from different plant parts (leaf, stem, seed, root, and fruit) is a simple, cost- and energy-efficient, well reproducible, and fast approach that can also be applied on an industrial scale [35]. The mechanism of nanoparticle formation using plant extracts has also been extensively studied, indicating that more than one biomolecules is responsible for the reduction of metal ions. Specifically, several plant components rich in secondary metabolites are involved, such as various enzymes, proteins, amino acids, vitamins, polysaccharides, alkaloids, polyphenols, flavonoids, and organic acids, which are biodegradable substances (and non-toxic in the majority of cases) that can act both as reducing and capping agents, thus promoting the formation of nanoparticles and inhibiting their agglomeration [35]. Typically, such a synthesis is very simple, as the metal salt solution only needs to be mixed with the natural product extract and the desired nanoparticles are formed spontaneously within a few minutes to one day [33]. Moreover, the reducing and stabilizing content of the extract used can determine the size of the particles formed and, thus, their reactivity in subsequent reactions. Ashokkumar *et al.* observed that the particle size decreased with increasing concentration of the plant extract, while another study described that the number of the particles formed correlates with the amount of plant extract used [36]. Moreover, the shape selectivity was observed by varying the dosing rate of the bioreducing agent [34,35].

To date, several examples of nZVI produced using plant extracts have been reported in the literature [34-36]. In 2009, Hoag *et al.* successfully generated nZVI through a one-step environmentally friendly biosynthesis method using tea [37]. More specifically, the green tea extract reacted with an aqueous solution of  $\text{FeCl}_3$  for a few minutes at room temperature affording stable nanoparticles. It was found that during the reaction, the polyphenols in tea not only acted as reducing agents but also as stabilizers. Huang *et al.* also prepared nZVI using three types of tea extracts (green, oolong, and black), which were then tested for the decomposition of

malachite green [38]. Due to its high polyphenol/caffeine content, green tea exhibited the best performance. Moreover, Machado *et al.* studied the applicability of leaves of 26 different plants as potential bioreducers [39]. Based on their results, oak, pomegranate, and green tea had the highest antioxidant capacity, and the nZVI particles were successfully produced using these tea extracts. Similarly, nZVI particles were prepared by an environmental friendly, one-step synthesis process using leaf extracts from coffee, grapes, eucalyptus, roses, henna, gardenia, and various fruit trees, such as passionflower, cherry, peach, avocado, and orange [40]. These and further relevant studies have highlighted that the careful selection of the bioreducing agent is very important, because the reduction of  $\text{Fe}^{3+}$  ions is not always complete and the degradation capacity of the green synthesized nanoparticles is often lower than that of the conventionally produced particles [41].

It is thus clear that green syntheses offer a good alternative to conventional methods, but there is still a need for further development using plants that are widely and readily available and that can be synthesized on an industrial scale. Moreover, it should be noted that since the green material or entity used can largely define the physical, chemical, and biological characteristics of the obtained nanomaterials, a comprehensive screen of the products should be performed prior to their application, similar to the conventionally generated particles, to delineate their behavior and fate in the presence of living systems.

### 3.2 Application of nZVI particles for remediation

In recent years, the use of nZVI particles in remediation has attracted increased attention due to their high reactivity and variety of application options. Since nZVI can be used *in situ* through direct push injections, recirculation using injection wells, or pneumatic fracturing, this technology allows access to pollutants in hard-to-reach areas such as zones under existing infrastructures that are not easily accessible by other treatment methods. Moreover, as described in the following paragraphs, to date, nZVI has been successfully used for the remediation of a wide variety of organic and inorganic water and soil contaminants, including heavy metals at high oxidation states, halogenated organic compounds, polycyclic aromatic hydrocarbons, and pesticides [42].

#### 3.2.1 Removal of inorganic contaminants by nZVI

It has been well established that heavy metals are not biodegradable and can accumulate in living organisms causing health concerns. Thus, numerous studies have focused on the removal of Cr(VI) by nZVI, as Cr(VI) is a common toxic pollutant originated from industrial waste sites and mainly from metallurgy. These studies suggested that the degradation mechanism involved in the treatment of heavy metal pollutants comprises the instantaneous adsorption of Cr(VI) on the iron surface, followed by an electron transfer and the reduction of Cr(VI) to Cr(III) along with the oxidation of iron to Fe(III), leading to the subsequent precipitation of mixed Cr and Fe hydroxides. However, the formation of these hydroxides on the surface of oxidized iron can self-inhibit the reduction reaction, which can be overcome using bimetallic nanoparticles (e.g., copper, and palladium) [43].

The prevailing geochemical conditions may also affect the removal of inorganic contaminants. Liu *et al.* have investigated the effect of various geochemical constituents,

such as humic acid, bicarbonate, and calcium ions, and found that the calcium ions or humic acid did not have a remarkable impact on the removal, whereas bicarbonate considerably enhanced the removal efficiency of nZVI. In contrast, the coexistence of calcium ions and bicarbonate significantly reduced the Cr(VI) removal by nZVI [44]. Moreover, Cissoko *et al.* found that nZVI exerted a greater Cr(VI) removal efficiency than ZVI powder and that the Cr(VI) removal efficiency increased with decreasing initial pH [45].

The nZVI particles have also been successfully used to remove both arsenite and arsenate, which are among the most toxic pollutants often found in wastewater, and to achieve the regulated arsenic level in drinking water. The mechanism of arsenic removal by nZVI involved a series of different processes, i.e., adsorption, reduction, surface precipitation, and co-precipitation with various iron corrosion products such as ferrous/ferric (hydr)oxides. The removal rate of arsenite under different pH values and in the presence of various ions was also examined, indicating that most of these parameters negatively affected the arsenite removal [46]. In addition, Liu *et al.* investigated the interactions of Cr(VI) and As(V) and the effect of humic acid and bicarbonate in the removal process of Cr(VI) and As(V) by ZVI [47]. Their study showed that the Cr(VI) removal was not affected by the presence of humic acid and As(V), but the As(V) removal was inhibited by the co-presence of Cr(VI).

The removal of other heavy metal ions by nZVI has also been investigated. Efcan *et al.* reported a great adsorption potential of Ni(II) ions by the nZVI particles through complexation and surface precipitation [48]. A complete Ni(II) removal was observed and it was also assumed that the nZVI particles acted as both sorbent and reductant agents. Studies on additional heavy metal cations, such as copper, cadmium, cobalt, zinc, selenium, and uranium, revealed high uptake capacities and slight desorption of nZVI [49]. Furthermore, the comparison between fresh and 2-month aged nZVI revealed that both were effective for the removal of cobalt ions. Li *et al.* also found that the removal mechanism using nZVI depends on the standard redox potential ( $E^0$ ) of the metal contaminant. In particular, adsorption is the preferred removal mechanism if  $E^0$  is more negative than the  $E^0$  of  $\text{Fe}^0$  (e.g., zinc, cadmium), whereas at  $E^0$  values more positive than those of  $\text{Fe}^0$  (e.g., chromium, arsenic), the metals are preferably removed by reduction and precipitation [50].

In further studies, nZVI has been used to remove nitrates and phosphates from contaminated areas, indicating that it can efficiently degrade nitrates, thus allowing fast and effective denitrification [51]. Moreover, low pH values and high ionic strength in the solution enhanced the nitrate removal. The use of nZVI also resulted in 90% removal of phosphates within the first 10 min, while 100% removal was achieved after 30 min. It was also determined that the phosphate removal mechanism involved simultaneous adsorption and chemical precipitation.

Green synthesized nZVI particles have also been successfully applied in the remediation of inorganic compounds. In particular, Mystrioti *et al.* investigated the applicability of five raw materials, namely green tea, clove, spearmint, pomegranate, and red wine, for the synthesis of nZVI particles and found that only the nZVI suspensions synthesized by tea, pomegranate, and red wine could effectively reduce Cr(VI) [52]. In addition, Wu *et al.* reported

the efficient removal of arsenic by green synthesized nZVI nanoparticles using eucalyptus leaves [53].

### 3.2.2 Removal of organic contaminants by nZVI

Apart from heavy metals, organic pollutants, such as chlorinated organic and nitroaromatic compounds, also pose a serious threat to environmental safety and ecosystem health [54]. These contaminants are persistent, highly toxic, and widespread in the environment due to the extensive manufacture and utilization of various relevant products such as dyes, pesticides, and pharmaceuticals. Gillham and O'Hannesin first demonstrated the promising effectiveness of nZVI in the dehalogenation of 1,4-chlorinated ethene, ethane, and methane [54]. The dehalogenation of trichloroethylene (TCE) and carbon tetrachloride using ZVI has been reported as well. In particular, the nZVI particles have been successfully applied in contaminated sites to degrade chlorinated compounds, including TCE, tetrachloroethylene, polychlorinated biphenyls, vinyl chloride, and organochlorine pesticides. In these remediation applications, nZVI served mainly as a potent and cost-effective electron donor for the reductive dehalogenation of the chlorinated compounds. Moreover, iron, as a strong reductant with a reduction potential of 0.440 V, reduced the chlorinated compounds while being oxidized. It has also been found that the decomposition of chlorinated hydrocarbons takes place through several reduction pathways such as hydrogenolysis or  $\beta$ -elimination. Their main difference is that  $\beta$ -elimination does not generate vinyl chloride, which is more toxic than the parent compounds. Nevertheless, it should be noted that although earlier studies have reported that the degradation of TCE by nZVI can proceed through both reaction pathways, more recent data suggest that  $\beta$ -elimination is the major route [55].

Furthermore, a series of studies have reported that nZVI can degrade contaminants at higher rates than the larger bulk iron particles. Thus, in order to preserve the stability and reactivity of the nZVI particles, their synthesis was optimized and their surface was modified, thus enhancing the particle dispersion and effectively maintaining their reactivity. The addition of a second noble metal (e.g., Ag, Cu, and Pd) also significantly enhanced the performance of the nZVI particles.

It is also known that pesticides and drugs can be detected in water. Thus, the degradation of tetracycline was analyzed in batch experiments, revealing that the transformation was highly dependent on the temperature and pH values, while Ghauch *et al.* explored specifically the degradation pathways of amoxicillin and ampicillin by nZVI [56].

Additional studies revealed that the nZVI particles can also generate strong oxidants under oxic conditions and degrade dyes. Combined with air process, ZVI can decolorize dyes more rapidly and achieve significantly higher chemical oxygen demand removals for both investigated dyes than those obtained by the Fenton oxidation [57]. In addition, it has been reported that dye decolorization could be enhanced by combining nZVI particles with anaerobic microbes, as the addition of nZVI may provide an efficient and long-term effective strategy to promote the anaerobic environment, which in turn might improve the outcome of an anaerobic treatment.

As in the case of inorganic contaminants, green synthesized nZVI particles were obtained from green, oolong,

and black tea extracts and applied in the degradation of malachite green. The corresponding removal rates were 81.2%, 75.6%, and 67.1%, respectively, suggesting that the degradation rate depended on the applied extract during the particle synthesis. Furthermore, Smuleac *et al.* presented a membrane-based approach using tea mediated nZVI particles for the reductive degradation of toxic TCE from water [58]. In another study pertaining to hydrocarbon remediation, berry extract synthesized iron nanoparticles successfully decomposed petroleum hydrocarbons after 32 hours of treatment [59].

Therefore, it is clear from the above literature data that for the effective and safe application of nanoparticles, a thorough investigation of their behavior and aggregation tendency, as well as the relevant adsorption and reduction mechanisms should be carried out before their use. It is also expected that the results of such additional studies may enhance the performance of nZVI.

## 4. LIMITATIONS AND CHALLENGES OF USING NZVI

Notable potential has been presented for the utilization of nanomaterials especially nZVI for the remediation of a wide range of contaminants. In spite of their effectiveness which arises from their *in situ* application and great reactivity, nZVI have limitations including a lack of stability, passivation, and limited mobility due to the formation of agglomerates and retention within aquifers, difficult separation from the purified medium [15]. To help counteract these problems and, thus, enhance the potential of nZVI in remediation, a number of modifications to the nanoparticles have been developed to stabilize the particles such as coating, doping, emulsification, embedding the particles to a supporting matrix and forming bimetallic nanoparticles [11,12,15,60]. However, there remains significant challenges to their effective and sustainable use. Any innovation at the nanoscale for subsurface remediation must consider barriers to nanomaterials transport and distribution in porous media. On the other hand, these new structures may pose risks and have ecotoxicity concerns thus they need to be handled with the right precaution.

Moreover, regarding the life cycle and the possible toxicity of particles, not much is known yet. Evaluating their routes from entrance points to untargeted environments and understanding the reaction mechanisms of nZVI with contaminants is a major problem, because the detection of nanoparticles in complex environmental media has proven challenging, as more and more studies are indicating that the occurring reactions are rather complex since oxidation, adsorption, reduction, surface complexation and co-precipitation may be involved [2,52].

As mentioned above, these nanoparticles are being released into the environment and interact with contaminants and living organisms alike. There is little literature regarding the risk that these particles may pose on human health and environment [5,33]. The available data are also confusing. While nZVI have been reported to be highly toxic, most field studies have demonstrated limited adverse effects on microorganisms [11]. To ensure the ecological impacts of particles can be predicted accurately, we need a reliable understanding of the interactions between nZVI and

indigenous microbial species in contaminated sites. Before use, the nanoparticles require verification of their efficacy and safety in the field as they have been successfully demonstrated in the laboratory scale [61].

The reaction time of nZVI is also important for evaluating the potential long-term stimulation of biological processes. The toxic effects of nZVI change with their transformation in the environment, hence the long-term impacts of particles on the environment cannot be adequately predicted from acute toxicity studies. Currently, long term field studies for the environmental impact of nZVI are very scarce, therefore more field studies should be conducted to understand reaction mechanisms and long term (biological) effects [11,62].

Additional concerns are the difficulties and the cost of scale-up from laboratory experiments to field work. In addition, the cost-effectiveness is likely to be specific to site circumstances and features [7,59].

These limitations might probably be the reason why nanotechnology-based applications for environmental cleanup have not been widely commercialized for now. These limiting challenges must be overcome to estimate the comprehensive potential and safe utilization of nanomaterials for remediation process (Figure 1).

However, the nanoremediation-based methods have not been widely used commercially, as nanoparticles may enter the environment during their preparation and application, where they can accumulate and pose a risk of environmental pollution. Based on the present literature review, even the different synthesis method may significantly affect the properties of the produced nanomaterials. Thus, further field studies are required to evaluate their behavior and life cycle and to assess their benefits and risks. Additional research is also needed to better understand the ecological impacts related to the use of nZVI, which is clearly an effective and versatile tool for the purification of water and soils, and to elucidate the behavior and fate of these nanomaterials in remediation processes. Another concern is the high cost of the synthesis of nanometals for field application, which is addressed by constantly looking for new suppliers, alternative materials, and synthesis methods. In this regard, innovative “green” approaches as alternatives to the conventional methods could also help overcome some of the nanoremediation drawbacks. Therefore, considering that nanotechnology offers numerous strategies for tackling pollution, facing these problems would enhance the assessment of nanoremediation technologies and contribute to their safe application.

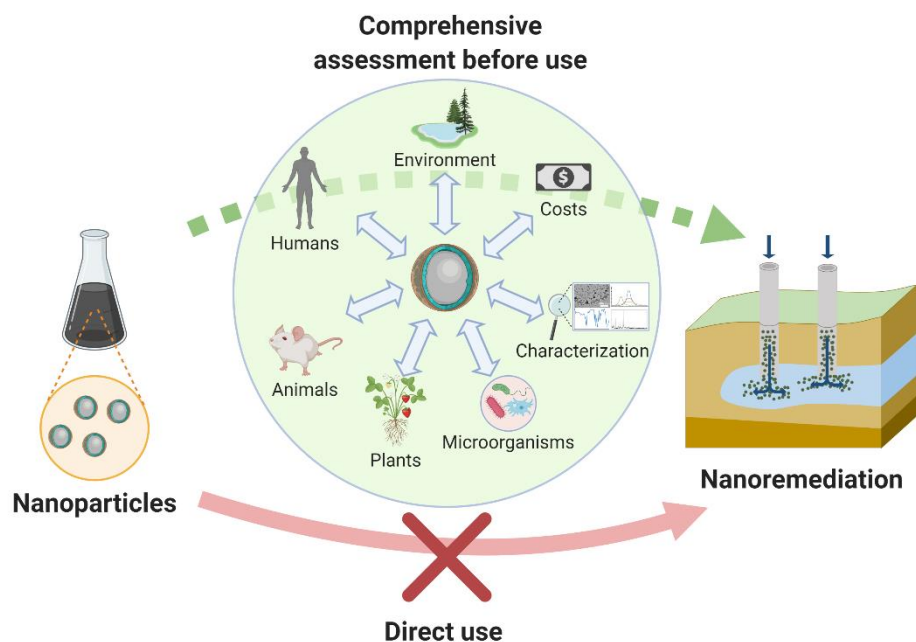


Figure 1. Sustainable and ecosafe nanoremediation. A way forward to overcome current challenges.

## 5. CONCLUSIONS AND FUTURE PERSPECTIVES

Nowadays, there is a significant need for advances in water treatment to protect and ensure high water quality and removal of contaminations. In this regard, nanotechnology is considered an attractive potential candidate to improve the existing water treatment processes. In recent years, the remediation of contaminated media by nanomaterials has gained considerable attention, and various nanomaterials have been successfully developed and applied as nanoadsorbents, nanocatalysts, or nanomembranes in remediation techniques.

## CONFLICT OF INTEREST

The authors report no conflict of interest in this work.



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