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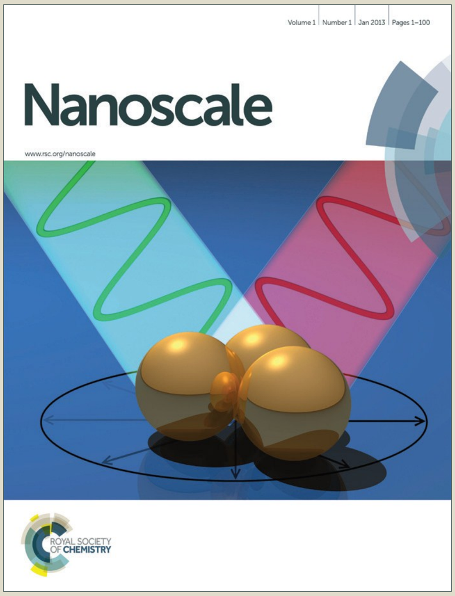

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REVIEW

Mechanism, Synthesis and Modification of Nano Zerovalent Iron in Water Treatment

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Owing to strong reducing ability, high reaction activity, excellent adsorption properties, good mobility and relatively low cost, nano zerovalent iron (nZVI) is an extremely promising nanomaterial for use in water treatment. In this paper, the working mechanisms of nZVI in the degradation of various contaminants in water are outlined and discussed. Synthesis methods and their respective advantages and disadvantages are discussed in detail. Furthermore, a variety of modification methods which have been developed to improve the mobility and stability of nZVI as well as to facilitate the separation of nZVI from degraded systems are also summarized and discussed. Numerous studies indicate that nZVI holds considerable potential to become an efficient, versatile and practical approach for large-scale water treatment.

Introduction

In the past decades, nanotechnology has emerged as a useful and promising approach to water treatment. Due to excellent activity towards recalcitrant contaminants and their flexibility in application, a variety of nanomaterials are the subject of active research and development in this area. Among them, nano zerovalent iron (nZVI) is one of the most prevalent nanomaterials. Due to its nanometer length scale (1-100 nm) and hence large specific surface area, nZVI has higher reducing ability and activity, stronger adsorption properties and better mobility than bulk or microscale iron particles. These characteristics allow nZVI to work as an effective remediating agent for a wide range of contaminants. Furthermore, it has been shown to have a strong bactericidal effect and toxicity towards microorganisms. The high effectiveness and versatility of nZVI has demonstrated that it is a suitable technology for practical applications in water treatment.

As a result of this potential, significant research efforts have been devoted to the preparation of nZVI. Broadly speaking, the synthesis methods can be divided into two principle categories: physical methods and chemical methods. Physical methods are well established, whereas chemical methods are thought to be potentially advantageous for nZVI manufacturing and have been the focus of recent research efforts, resulting in the development of a diverse range of chemical synthesis techniques of nZVI.

In spite of its merits, such as large specific surface area, intrinsic magnetic interaction, high reducing ability and strong adsorption properties, nZVI is prone to aggregation and oxidation, and it has difficulty in separation from degraded systems. These issues can impede the performance of nZVI to a great extent. However, many modification approaches have been proposed and have been found to be effective to overcome these drawbacks.

Mechanism

Due to the extremely small size and hence large specific surface area of nZVI, it has excellent adsorption properties, reducing ability and activity. Under anaerobic conditions, according to eqn (1)-(2), Fe^0 can be oxidized by H_2O or H^+ and yields Fe^{2+} and H_2, both of which are also potential reducing agents for contaminants. Therefore, there are three major reductants (Fe, Fe^{2+} and H_2) in the Fe-H_2O system as a result of corrosion.[1]

$$\mathrm{Fe+2H_2O \rightarrow Fe^{2+}+H_2+2OH^-} \tag{1}$$

$$\mathrm{Fe+2H^+ \rightarrow Fe^{2+}+H_2} \tag{2}$$

nZVI has been extensively studied and employed in the treatment of chlorinated organic compounds since Gillham et al. found that the degradation of halogenated aliphatics could be enhanced by zerovalent iron.[2] In the presence of a proton donor like water, the general dehalogenation reaction can be shown by eqn (3).

$$\mathrm{Fe^0+RX+H^+ \rightarrow Fe^{2+}+RH+X^-} \tag{3}$$

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In addition, corrosion of Fe^0 will result in an increase of pH in weakly buffered systems, and the effect is more pronounced under aerobic conditions because the corrosion is much more rapid. Fe^{3+} appears as the oxidation product of redox reaction between Fe^{2+} and contaminants. The increase of pH associated with corrosion facilitates the formation of $Fe(OH)_3$ which is a good flocculant.[1]

Furthermore, the ability of nZVI to induce precipitation can also play an important role in the removal of contaminants, for example Cr(VI), which is toxic, carcinogenic and harmful to the environment. During the reaction, Cr(VI) is instantaneously adsorbed to the surface of nZVI and reduced via electron transfer, leading to the generation of Cr^{3+} and Fe^{3+} which can form $Cr(OH)_3$ and $Fe(OH)_3$, according to eqn (4)-(5). The flocculation effect of $Fe(OH)_3$ facilitates the precipitation of $Cr(OH)_3$ from water. Compared with Cr(VI), the resultant species $Cr(OH)_3$ or Cr(III)/Fe(III)(oxy)hydroxide are more stable and approximately 10–100 times less toxic.[3]

$$Cr_2O_7^{2-}+2Fe+14H^+ \rightarrow 2Cr^{3+}+2Fe^{3+}+7H_2O \tag{4}$$

$$Cr^{3+}+Fe^{3+}+6OH^- \rightarrow Cr(OH)_3\downarrow+Fe(OH)_3\downarrow \tag{5}$$

Dissolved oxygen (DO) also plays an important part in the degradation of contaminants by nZVI. As per eqn (6)-(8), the presence of DO can lead to the formation of hydroxyl radicals, whose oxidability is strong enough to degrade a wide range of organic compounds. For example, dyes and phenols can be oxidized into carbon dioxide and water by hydroxyl radicals.[1]

$$Fe^0+O_2+2H^+ \rightarrow Fe^{2+}+H_2O_2 \tag{6}$$

$$Fe^0+H_2O_2+2H^+ \rightarrow Fe^{2+}+2H_2O \tag{7}$$

$$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+\bullet OH+OH^- \tag{8}$$

To summarize, nZVI can degrade water contaminates through a variety of mechanisms: adsorption, reduction, precipitation and oxidation (in the presence of DO). It has been applied in the removal of a large variety of contaminants, including halogenated organic compounds[4-7], nitroaromatic compounds[8-10], organic dyes[11-14], phenols[15-16], heavy metals[17-18], inorganic anions[19-20], metalloids[21-22] and radio elements[23]. Though the reaction mechanism varies with contaminants, it's generally a combination of the effects mentioned above, as shown in Fig. 1.

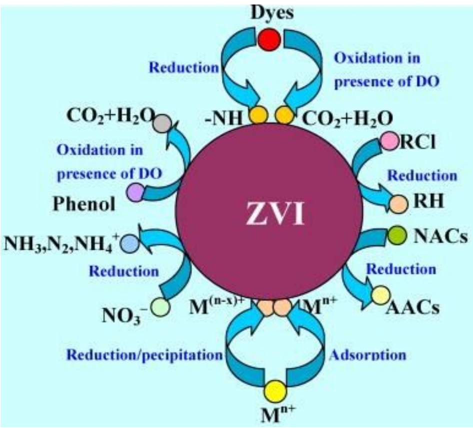


Fig. 1 Schematic representation of reaction mechanism of nZVI with different contaminants. Reprinted from ref. 24 with permission. Copyright © 2014 Elsevier B.V.

Moreover, nZVI has been discovered to have a strong bactericidal effect and toxicity against both Gram-positive (Bacillus subtilis)[25] and Gram-negative (Escherichia coli and Pseudomonas fluorescens) bacteria[26], showing promise to remove the threat of water-borne bacteria, fungi, and viruses posed on human health.

The effectiveness of nZVI in degrading a wide range of aqueous contaminants and microorganisms makes it an attractive technology for large-scale applications in water treatment.

Synthesis

The promise of nano zerovalent iron in water treatment has driven the development of a wide variety of synthesis/ manufacturing techniques. Generally speaking, they can be divided into two principle categories: physical methods and chemical methods.

Physical Methods

In general, physical methods possess the superiority of simple operation and easy separation of products over chemical methods. Specific physical methods, such as gas condensation processing and ball milling, have been well-documented.[27-28]

Gas Condensation Processing In gas condensation processing (GPC), nano iron particles are obtained by condensing the vapour of iron atoms in an inert gas atmosphere via cooling with liquid nitrogen, as shown in Fig. 2.[27] The GPC method enables good control of particle size and a lognormal size distribution. However, highly restricted preparing conditions are required (high temperature, high pressure and substantial coolant) with intensive energy consumption. The yield of GPC method is also extremely low, thus limiting its application for industrial manufacturing.

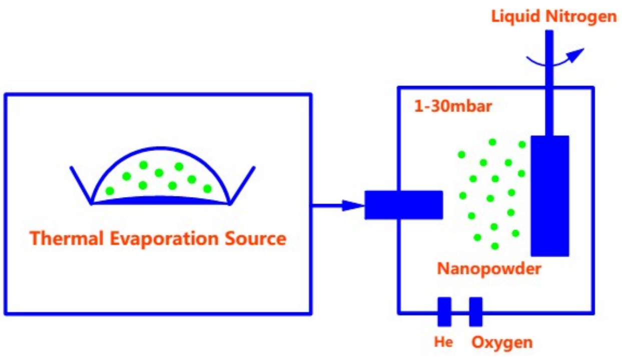


Fig. 2 Schematic representation of gas condensation processing.

Ball Milling As a common mechanical method, ball milling is often applied to decrease the size of materials with the use of heavy milling media, generally metallic balls or beads.[28] In 2009, Li et al. demonstrated that precision ball milling, using micro iron particles as raw materials, could effectively produce zerovalent iron nanoparticles (NPs) of uniform size and high specific surface area.[29] The method is nontoxic, free of secondary pollution and suitable for industrial scale supply. But this method is also energy-intensive and requires specialized equipment to achieve size reduction down to the nanometre scale. In addition, the product homogeneity of this method is not satisfisfactory.

Chemical Methods

In recent years, chemical routes for nZVI preparation have drawn wider attention and been more extensively studied due to potential advantages in delivering improved nZVI product attributes and suitability for industrial supply.

Borohydride Reduction Method After being first reported by Wang et al. in 1997, the borohydride reduction method has been the most widely adopted approach for nZVI preparation both in laboratories and in large scale applications. Typically, the process involves the reduction of Fe^{3+} or Fe^{2+} by $NaBH_4$ according to eqn (9)-(10) in aqueous solutions under ambient temperature and pressure.[30] Despite its extremely wide application, the borohydride reduction method uses expensive and toxic reagents, and generates by-product($B(OH)_3$) which will result in secondary pollution.

$$Fe^{2+}+3BH_4^-+9H_2O \rightarrow Fe^0\downarrow+3B(OH)_3+10.5H_2\uparrow \qquad (9)$$

$$Fe^{2+}+2BH_4^-+6H_2O \rightarrow Fe^0\downarrow+2B(OH)_3+7H_2\uparrow \qquad (10)$$

Many attempts have been made to combine this method with some supplementary means to further improve the quality of nZVI. For example, nZVI with high reductive activity has been prepared by the borohydride reduction method in an aqueous solution of ionic liquids (ILs), which can control the formation and stabilization of NPs.[31] The product obtained by this method is smaller, more uniform and easier to separate.

Ultrasound Assisted Method Ultrasound has been used to synthesize zerovalent iron NPs and was found to impact the growth and coalescence of iron NPs.[32] With increasing ultrasonic power, the morphology of nZVI changes from spherical to platelike and then to needlelike. The nZVI synthesized in this manner has a smaller particle size, a larger specicfic surface area and higher crystallinity than that of the conventional borohydride reduction method. Despite this, the crystallinity of nZVI prepared under ultrasonic conditions is still sub optimal and the size of the aggregates increases under high ultrasonic power.

Carbothermal Synthesis Generally, in carbothermal synthesis, C or CO is used to reduce iron oxide (natural iron ore, such as goethite), ferrous or ferric ions at elevated temperatures (eqn (11)-(14)).[33-34] Raw materials are inexpensive and widely available, providing low production cost. However, the generation of carbon monoxide (CO), a flammable and toxic gas, is an unavoidable drawback of this method.

$$2C+Fe_3O_4 \rightarrow 3Fe+2CO_2\uparrow \qquad (11)$$

$$4CO+Fe_3O_4 \rightarrow 3Fe+4CO_2 \qquad (12)$$

$$C+2Fe(C_6H_5O_7)\cdot 3H_2O \rightarrow 2Fe+2C_3H_6O+6CO_2+CO+5H_2O \qquad (13)$$

$$C+Fe(C_2H_3O_2)_2 \rightarrow Fe+2CH_2CO+CO+H_2O \qquad (14)$$

Thermal Decomposition Method Organometallic molecules containing iron, especially $Fe(CO)_5$, can be used as a starting material for thermal decomposition. Spherical nano iron particles can be generated by adding $Fe(CO)_5$ into trioctylphosphine oxide (TOPO) at 320 °C in an argon atmosphere (eqn (15)).[34] The product from this method has an extremely small size (2 nm) and good homogeneity. Nevertheless, this method also has some drawbacks: (1) $Fe(CO)_5$ is highly toxic and unstable; (2) the process is energy-intensive; (3) a considerable amount of carbon monoxide is generated as a by-product.

$$Fe(CO)_5 \xrightarrow[\text{TOPO}]{320^{\circ}C} Fe^0\downarrow+5CO\uparrow \qquad (15)$$

Recently, nZVI has been produced by combining the thermal decomposition of $Fe(CO)_5$ with both ionic liquids and microwave irradiation.[35] As mentioned above, ionic liquids can control the formation and stabilization of metal NPs. Meanwhile, microwave irradiation is conducive to promoting chemical reactions and precisely controlling the size and size distribution of metal NPs. Owing to the combination, the lifespan of nZVI obtained by this method was significantly prolonged.

Chemical Vapor Condensation As shown in Fig. 3, nZVI can also be produced by chemical vapor condensation (CVC), which combines chemical thermal decomposition and physical condensation. First, iron atoms emerge as the decomposition product of $Fe(CO)_5$ at temperatures in the range of 400 – 1100 °C (eqn (16)). Then, they are transferred by a carrier gas into an atmosphere of inert gas cooled by liquid nitrogen and then condensed into nano iron particles.[27,36] Although the CVC method could generate nZVI with good physical and chemical homogeneity, it suffers from the drawbacks of the thermal decomposition method and the limited operating conditions of the GPC method.

$$Fe(CO)_5 \xrightarrow{400\text{-}1100^{\circ}C} Fe^0 + 5CO \qquad (16)$$

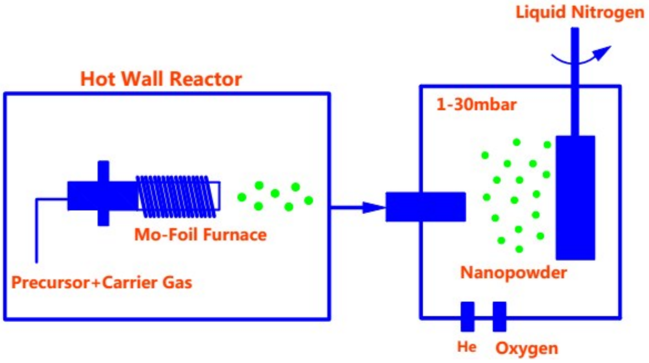


Fig. 3 Schematic representation of chemical vapor condensation.

Hydrothermal Method The hydrothermal method provides another alternative for the synthesis of nZVI. Using glucose and ferric nitrate as precursors, Wang et al. successfully obtained nZVI (ca.10 nm) encapsulated in microscale carbon spheres (6−8 μm) via an one-pot hydrothermal method followed by self-reduction in a N_2 atmosphere, as shown in Fig. 4.[37] The as-prepared nZVI showed an enhancement of transportation, suspension, stability and good reusability. However, the preparation and separation processes of this method are relatively complex.

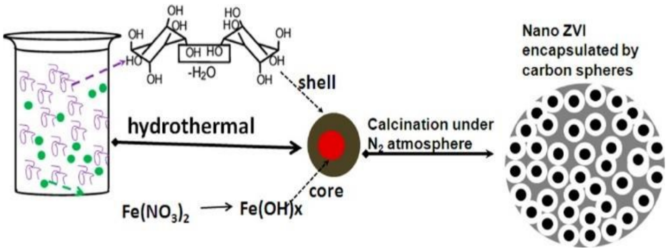


Fig. 4 Schematic representation of one-pot hydrothermal method followed by self-reduction. Reprinted from ref. 37 with permission. Copyright © 2012, American Chemical Society.

Polyol Process The polyol process is a common route for the synthesis of metallic and alloy NPs. However, as polyol was once considered unable to reduce iron, the formation of iron NPs in polyol was not reported until 2007. In 2007, Joseyphus et al. first reported the synthesis of sub-micron size iron particles in liquid polyols, such as trimethylene glycol, propylene glycol and ethylene glycol.[38] Taking ethylene glycol as an example, the reactions are shown in eqn (17)-(18).

$$HOCH_2CH_2OH \rightarrow CH_3CHO + H_2O \qquad (17)$$

$$2CH_3CHO + FeCl_2 \xrightarrow[-2NaCl]{\text{Excess NaOH} \;\; >373K} CH_3COCOCH_3 + 2H_2O + Fe^0 \qquad (18)$$

In 2010, Joseyphus et al. further prepared size controlled iron NPs ranging between 10 and 90 nm by the polyol process through heterogeneous nucleation using H_2PtCl_6 to aid in nucleation.[39] Nanoparticle size could be reduced by increasing the concentration of H_2PtCl_6. When the mean nanoparticle size was larger than 25nm, the as-prepared nZVI showed a cubic morphology. However, it became spherical and agglomerated with further size reduction. Since the polyol medium could prevent nZVI from coming into contact with the oxidizing atmosphere, the as-prepared nZVI was highly stable in the air. The polyol process has the drawback of using caustic chemical reagents (NaOH and H_2PtCl_6).

Reverse Micelle Method The reverse micelle method (microemulsion synthetic method) is also used to generate iron NPs. In a classic process, Fe^{2+} is incorporated into water pools of a reverse micellar solution formed by using cetyltrimethyl ammonium bromide(CTAB) as the surfactant, butanol as cosurfactant and octane as the oil phase. Then, Fe^{2+} is reduced to Fe^0 by hydrazine injected into the system. By controlling the amount of surfactant and water, the fabrication of nZVI in reverse micelles affords good control over the size and shape of iron NPs. As the diameters of microemulsion droplets are nearly the same, the size of nZVI can be precisely controlled. However, the as-prepared nZVI tended to aggregate and was not stable.[40]

Electrochemical Method In 2005, an electrochemical method assisted by ultrasound was demonstrated. As shown in Fig. 5, Fe^{3+} or Fe^{2+} is reduced to Fe^0 on the cathode and Fe^0 is removed into the solution on time before clustering can occur by physical energy provided by ultrasound. The diameters of iron particles obtained by this method are within the range of 1–20 nm and the specific surface area was found to be as large as 25.4 m^2/g.[19] This method has the advantages of simplicity and low cost, though the as-prepared product has shown a tendency to aggregate.

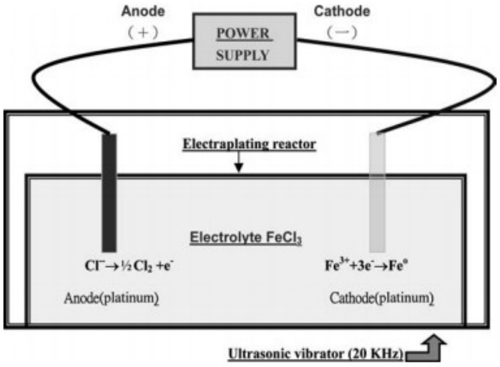


Fig. 5 Schematic representation of electrochemical method assisted by ultrasound. Reprinted from ref. 19 with permission. Copyright © 2005, Springer.

Green Synthesis In recent years, with the enhancement of consciousness of environmental protection and energy efficiency, some researchers have turned their focus to green and sustainable synthesis methods. In 2009, Hoag et al. demonstrated an environmentally friendly single-step preparation of iron NPs using a natural reducing agent (tea polyphenol) to react with ferric nitrate within a few minutes at room temperature.[11] The success inspired a number of followers to obtain nZVI using plant extracts in which the active substances are highly reductive compounds, such as polyphenol and caffeine[41-42]. For instance, Huang et al. synthesized nZVI using extracts from green tea, oolong tea and black tea. They found that due to the high polyphenols/caffeine content in green tea extracts, nZVI synthesized by this method had a high degradation rate of malachite green.[41] Machado et al. also produced nZVI (10-20 nm) with oak, pomegranate and green tea leaves.[42] Apparently, green synthesis is eco-friendly, energy-saving and low-cost. However, the reduction of iron ions is often incomplete and thus will generate several kinds of by-products, such as iron oxides.

The respective pros and cons of each synthesis method are enumerated in Table 1. In order to seek out the most appropriate synthesis method in a specific situation, the final decision should be made after taking into consideration of various factors, such as availability of raw materials, energy consumption, total expense, the quality of product and security.

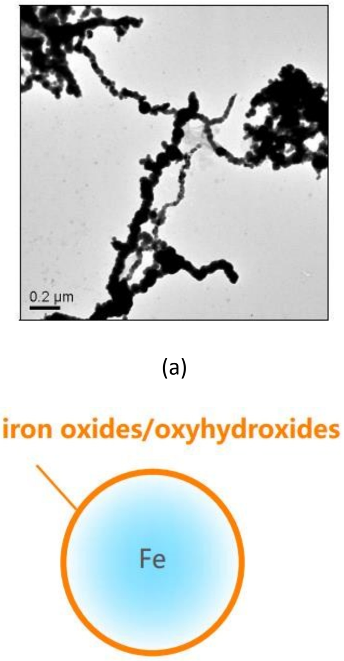
Table 1. Summary of synthesis methods of nZVI

Methods	Pros	cons
gas condensation processing	1, good control of particle size 2, lognormal size distribution	1, highly restricted conditions 2, energy-intensive 3, low yield
ball milling	1, nontoxic 2, no secondary pollution 3, scalable	1, energy-intensive 2, device limitation 3, poor homogeneity
borohydride reduction method	1, mild operating conditions 2, good homogeneity	1, expensive 2, toxic 3, by-product($B(OH)_3$) 4, secondary pollution
carbothermal synthesis	1, low cost 2, easy availability of raw materials	1, energy-intensive 2, flammable and toxic gas (CO)
ultrasound assisted method	1, small particle size 2, large specicfic surface area	1, poor crystallinity 2, agglomeration
thermal decomposition method	1, small size 2, good homogeneity	1, $Fe(CO)_5$ is highly toxic and unstable 2, energy-intensive 3, flammable and toxic gas(CO)
hydrothermal method	1, an enhancement of transportation, suspension, and stability 2, relatively good reusability	complex preparation and separation processes
polyol process	1, controllable size 2, high stability in air	1, agglomeration (when size <25 nm) 2, the use of caustic reagents (NaOH and H_2PtCl_6)
reverse micelle method (microemulsion synthetic method)	good homogeneity	1, agglomeration 2, unstable
electrochemical method	1, simplicity 2, low cost	agglomeration

green synthesis	1, high reactivity 2. eco-friendly 3, energy-saving 4, low cost	1, incomplete reduction of iron ions 2, agglomeration

Modification

As mentioned previously, despite many desirable traits for use in water treatment, nZVI has some significant drawbacks. As a consequence of high surface energy and intrinsic magnetic interaction, nZVI is prone to form chain-like or even larger (micrometer-scale) aggregates[43], as shown in Fig. 6a, leading to a decrease of mobility and reactivity. Due to strong reduction ability, the surface of nZVI is always covered by a thin film composed of iron oxides/oxyhydroxides as the result of oxidation, as shown in Fig. 6b, resulting in decline of reactivity. Futhermore, the separation difficulty caused by its ultrafine size affects its real applications to a great extent. To surmount these problems, many modification approaches, including surface modification, bimetallic nanoparticles, conjugation with supports, magnetization modification and integrated methods, have been applied to improve the properties of nZVI. It's worth mentioning that emulsification has also been proposed to improve the performance of nZVI in the remediation of dense nonaqueous phase liquid (DNAPL). Notably, significant laboratory and field research has demonstrated that a proper combination of these modification methods could produce better nZVI product than any single method.



(a)

(b)

Fig. 6 (a) TEM Image of nZVI. Aggregation into chains is evident in this image. Reprinted from ref. 44 with permission. Copyright © 2009, American Chemical Society. (b) Schematic representation of nZVI covered by an iron oxide/hydroxide thin film.

Surface Modification

To prevent aggregation and enhance the mobility of nZVI, great efforts have been made on surface modification. Generally speaking, surface modification can be achieved by coating modifiers on the surface of the iron nanoparticles. Ideal modifiers should possess the following features: (1) ability to adhere to the surface of nZVI particles;(2) stable to changes in surrounding environment; (3) no secondary pollution; (4) cheap and abundant. In essence, modifiers that can prevent the formation of aggregates by electrostatic repulsion with surface charges, steric repulsion with steric hindrance, or both are sought as shown in Fig. 7.[45] To this end, numerous types of surfactants, polymers and biopolymers have been investigated.

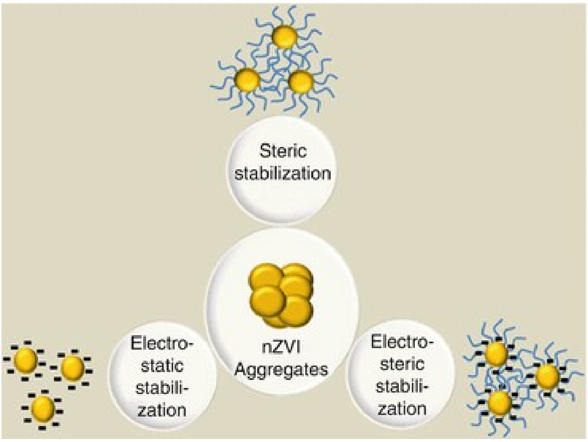


Fig. 7 Schematic representation of the mechanisms of surface modification. Reprinted from ref. 45 with permission. Copyright © 2015, Springer.

Surfactants Normally, surfactants are amphiphilic organic compounds which contain both hydrophobic groups (tails) and hydrophilic groups (heads).The hydrophobic tails adsorb on the surface of the nano-iron particles, and the hydrophilic heads impede aggregation with steric repulsion (non-ionic surfactants) or both electrostatic and steric repulsion (ionic surfactants). Classified by polar head groups, the following surfactants are often used to modify nZVI: (1) non-ionic surfactants, such as polysorbate (Tween)[46], polyoxyethylene alcohol ether (Brij)[47], polyethylene glycol octylphenol ether (Triton X-100)[5]; (2) anionic surfactants, such as sodium dodecyl sulfate (SDS)[46] and sodium dodecyl benzene sulfonate (SDBS)[46]; (3)cationic surfactants, such as cetylpyridinium chloride (CPC)[5], hexadecyltrimethylammonium (HDTMA) bromide[46] and cetyltrimethyl ammonium bromide (CTAB)[15]. Apart from these synthetic surfactants, rhamnolipid biosurfactant has also been verified to be a good surface modifier for significantly minimizing aggregation and improving transportation of nZVI.[48]

Polymers Since aquifer materials at neutral pH are normally negatively charged, the mobility of positively charged polymer-modified NPs is limited due to the electrostatic attraction between NPs and aquifer materials. In this regard, polymers with negative surface charges can serve as a good choice for modification and thus have gained considerable interest.[49]

Many common homopolymers have been put into test, such as polyacrylic acid (PAA)[50],polyvinyl pyrrolidone (PVP)[51], poly(styrene) sulfonate (PSS)[52] and polyethylene glycol (PEG)[53]. In 2015, Wang et al. proposed a facile method to adapt nZVI in water treatment facilities by using polyacrylamide (PAM).[52] The effluent quality of nZVI was improved and its hydrodynamic size was increased by sixty times. The results suggested that PAM could serve as an effective nZVI-aid to improve its performance in water treatment.

With different functional groups in corresponding blocks, block copolymers are multifunctional and exhibit advantages over homopolymers. Olefin-maleic acid copolymer[55], polyvinyl alcohol-covinyl acetate-co-itaconic acid(P3VA)[56] and amphiphilic polysiloxane graft copolymers(APGCs)[57] have been purposely designed to exhibit desirable properties for water treatment (in conjunction with nZVI). Owing to their distinctive structures, polymethacrylic acid–co-polymethyl methacrylate-co-poly(styrene) sulfonate (PMAA-PMMA-PSS) triblock copolymers stand out as an excellent representation of the potential of multi-component nZVI modification. By the chelation of carboxyl groups, the PMAA block anchors to the surface of iron NPs. The hydrophilic PSS block serves to impart good affinity to water and colloidal stability with strong electrosteric interparticle repulsions. The hydrophobic PMMA block also provides a strong affinity to dense nonaqueous phase liquid (DNAPL) and creates a low polarity region which impedes water access to nZVI, minimizing the oxidation before nZVI reaches DNAPL. As shown in Fig. 8, the amphiphilicity makes the modified nZVI stable at the interface between water and DNAPL.[58]

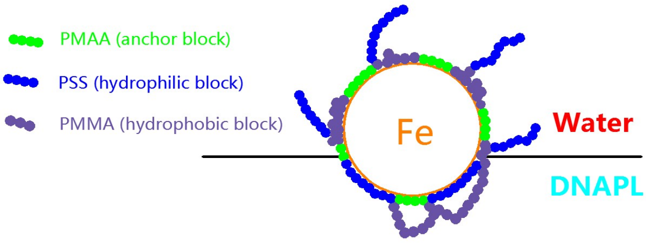


Fig. 8 Schematic representation of PMAA-PMMA-PSS-stabled nZVI at the interface between water and DNAPL.

Biopolymers On account of easy availability, low cost and environmental friendliness, biopolymers, such as alginate[59], soy proteins[48], guar gum[60] and xanthan gum[61], have drawn the attention of researchers and practitioners. Among numerous biopolymers, natural polysaccharides, especially cellulose and its derivatives, stand out as excellent modifiers of nZVI for water treatment applications.

Nowadays, carboxymethyl cellulose (CMC) is the most extensively applied polysaccharide derivative in the modification of nZVI. The complexation between carboxylate groups with iron ions and the intermolecular hydrogen bond between CMC and the iron particle's surface are identified to be the major mechanisms for stabilization.[62] Zhou et al.[63] and Dong et al.[64] pointed out that nZVI coated with CMC not only exhibited better dispersity and stability, but also showed less toxicity to cells, which contributed to easing long-standing concerns about the application of nZVI. Wang et al. innovatively modified nZVI by using hydroxyethyl cellulose (HEC) and hydroxypropylmethyl cellulose (HPMC) as dispersants. In comparison with bare nZVI, the particle sizes of HEC-nZVI and HPMC-nZVI became smaller, while the dispersity, antioxidizability, discoloration efficiency and reaction rates of them were increased, showing promise in water treatment. [12]

In 2015, Velimirovic et al. used agar agar to modify milled zero-valent iron. The stability in suspensions and mobility in heterogeneous sands were improved. However, the reactivity of the obtained product dropped by an order of magnitude compared to that of bare non-stabilized nZVI.[65]

In addition to preventing aggregation and improving the mobility of nZVI, surface modification has also been shown to reduce the toxicity of nZVI by limiting direct contact of nZVI with cells. In 2009, Phenrat et al. found that polyaspartate surface-modified nZVI showed lower toxicity to cells.[66] Later, coating poly(styrene sulfonate)(PSS), poly(aspartate) (PAP), or natural organic matter (NOM) on the surface of nZVI was reported to decrease its toxicity significantly.[67] As mentioned above, nZVI coated with CMC also exhibited similar tendencies.[63-64]

Although surface modification has been applied in field tests, its main drawback is that the coating often affects the ability of nZVI to react with contaminants, resulting in a loss of efficiency.[68]

Bimetallic Particles

Since aggregation and oxidation of nZVI will lead to the decline of its reactivity, a common and efficient scheme to counteract the problem is to incorporate a less active metal (e.g. Pd, Pt, Ni, Ag, Cu) to nZVI to form bimetallic nanoparticles (B-NPs). A large amount of experimental results have proven that this method can dramatically accelerate the degradation of contaminants.

However, although B-NPs have been frequently used, the intrinsic mechanism of enhanced reactivity is still disputed. One theory is that the bimetallic system forms a galvanic cell wherein iron and the second metal serve as the anode and cathode, respectively. Hence, iron is vulnerable to oxidization and the second metal remains unchanged.[69] Meanwhile, many researchers hold the belief that the enhanced reactivity most likely comes from the electrochemical effects, catalytic hydrogenation or intercalation of H_2.[70] Bransfield et al. revealed the following reactivity trend towards 1,1,1–TCA: Ni/Fe≈Pd/Fe>Cu/Fe>Co/Fe>Au/Fe≈Fe>Pt/Fe. This trend was correlated with thermodynamic descriptors for the solubility of hydrogen in different transition metal additives.[71] Therefore, their studies provided support for the second hypothesis to some extent.

In most cases, B-NPs are obtained by chemical solution deposition (CSD).[72] First, nZVI is synthesized by the borohydride reduction method. Then, the second metal is deposited and forms a discontinuous layer on the iron surface, as shown in Fig. 9. However, CSD method has many drawbacks: (1) intensive use of chemicals and secondary pollution; (2) hard to control the uniformity; (3) the second metal is prone to fall off; (4) unstable under ambient conditions; (5) difficulties in storage. In 2012, Xu et al. successfully prepared Fe/Ni B-NPs by ball milling process. This method was free of chemicals and secondary pollution.[73]

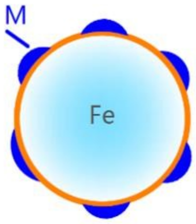


Fig. 9 Schematic representation of bimetallic nanoparticles obtained by chemical solution deposition.

In spite of unparalleled performance in enhancing the reactivity of nZVI, the large-scale application of Pd is greatly restricted by expense. Meanwhile, Ni possesses the advantages of better corrosion stability and lower cost over Pd, making it more suitable for real applications.[74] In addition, among the surface modifier metals for nZVI, Cu has shown superiority and is known as a mild hydrogenation catalyst.[75] The reactivity of three bimetallic NPs Fe/Pd, Fe/Pt and Fe/Cu to nitrate has been evaluated and ranked as Cu>Pd>Pt.[76] What' more, nano silver is a well-known antimicrobial, capable of disturbing key functions in microorganisms that cause antimicrobial resistance.[77] Bimetallic Fe/Ag NPs can combine the antibacterial and antifungal properties of both silver NPs and nZVI. They have been reported to exhibit better activities against a lot of harmful microorganisms than nZVI alone and improve the efficiency of phosphorus removal as well.[20]

Pt/Pd/Fe trimetallic nanoparticles (T-NPs) have been prepared via the reverse micelle technique. Compared to nano Pd/Fe particles which are the best performing B-NPs, the novel T-NPs can show enhanced overall activity and reusability of hydrodechlorination reactions. [78]

Although the reactivity of nZVI can be remarkably enhanced by incorporating a second catalytic metal, B-NPs are still prone to aggregate and form chain-like structures, leading to the decrease of specific surface area and reactivity to some extent.

Conjugation with Supports

In addition to its propensity to aggregate and deactivate (due to surface iron oxides/oxyhydroxides), the ultrafine particle size of nZVI presents challenges in isolation following synthesis/ preparation. Conjugation with a support has proven to be an effective approach to reduce aggregation and to realize convenient isolation of nZVI. As shown in Fig. 10, supported nZVI is better dispersed than bare nZVI. Moreover, the composites exhibit certain ability to control the growth of iron NPs and adsorb contaminants before degradation.[45] In recent years, nZVI has been conjugated with a number of materials: clays, carbon carriers, membranes, membranes, resins, silica, boron nitride nanosheets, chitosan, and $Mg(OH)_2$.

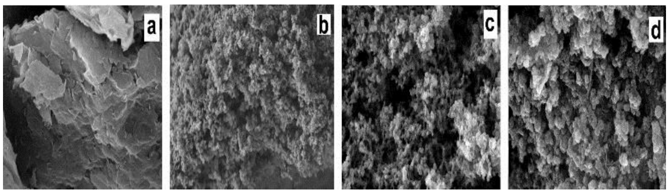


Fig. 10 SEM images of various materials (10,000×): (a) support; (b) bare nZVI; (c) supported nZVI; (d) supported nZVI after degradation. Reprinted from ref. 24 with permission. Copyright © 2011 Elsevier Inc.

Clays Clays are probably the most common adsorbents due to the high porosity, easy availability and low cost. Based on ion exchange and adsorption mechanisms, clays have the ability to remove heavy metal ions.[18] Many experimental results have demonstrated that clays can serve as ideal supporting materials for nZVI. For instance, the Pb(II) adsorption intensity of both zeolite–nZVI composite and montmorillonite–nZVI composite was increased 300 times than the constituent raw materials.[17] Conjugation with bentonite or kaolinite has been found to be able to impede the aggregation and enhance the mobility of nZVI in soil media. [18] In addition, diatomite[79] and attapulgite[80] have been shown to be suitable supporting materials as well.

Carbon Carriers Owing to their favorable mechanical strength and porous structures, carbon carriers are also good supporting materials for nZVI. For instance, graphene nanosheets supported nZVI (nZVI/GNS) have been reported to be able to remove Cr(VI) in water effectively.[81] nZVI/GNS exhibits remarkably higher activity towards Cr(VI) removal than that of unsupported nZVI. The conjugation with graphene also improves the stability of nZVI. Furthermore, graphene coupling facilitates the electron transfer in nZVI and suppresses the surface passivation of nZVI, thus improving the performance of nZVI towards Cr(VI) removal. Activated carbon(AC)[21] and reduced graphite oxide(RGO)[82] have also been selected to support nZVI and to improve its performance in the removal of arsenic on account of their intrinsic adsorption ability. Batch adsorption studies show that the synthesized adsorbents nZVI/AC and nZVI/RGO have much higher adsorption capacity for As(III) and As(V) than common arsenic adsorbents. Furthermore, graphene[83], carbon nanotubes[84] and biochar[85] have been used as supports of nZVI for the removal of phosphorus, nitrate and trichloroethylene, respectively. Notably, in the carbothermal synthesis method mentioned above, the use of excess compressed carbon black[33] or ordered mesoporous carbon[86] has been found to be a successful conjugation method for formation of nZVI composites with these species.

Membranes With the development and maturation of membrane technologies, they have also been used to immobilize nZVI by conjugation in order to increase the effectiveness of contaminant degradation. The relatively large pore size of membranes allows nZVI to reach and destroy aqueous contaminants.[87] For example, polyacrylic acid (PAA) /polyvinyl alcohol (PVA) polymer nanofibers have been used as nanoreactors to immobilize nZVI. The composite nanofibrous mats show large specific surface area, high porosity and excellent reusability.[88]

Resins Polymeric exchange resins are excellent carriers for metal NPs because of their good chemical stability and robust mechanical strength.[89] In 2007, Li et al. presented a novel method for immobilizing nZVI on a microscale strong acid polystyrene cation-exchange resin and successfully demonstrated its use for effective debromination of brominated diphenyl ether. SEM images showed good dispersion of nZVI particles on the resin, reducing the aggregation and environmental leaking risks.[90] In addition, a hybrid anion-exchange resin D201 was used to immobilize nZVI in the dechlorination of monochlorobenzene.[91] However, due to the Donnan co-ion exclusion effect[92], cation and anion exchange resins were only applicable for the removal of cations and anions, respectively. To overcome this limitation, Shi et al. utilized a non-ionic resin DOW 3N to immobilize nZVI and removed inorganic anions and heavy metal ions simultaneously. [93]

Silica Known to bind strongly with iron, low-cost polymeric silica is also frequently used as the supporting material for nZVI. The stability and mobility of nZVI in soil as well as its reactivity towards Cr(VI) can be enhanced by conjugation with silica fume or coating by SiO_2. What's more, silica can inhibit the formation of Fe(III)/Cr(III) precipitation on the surface of nZVI and thus improve the deactivation resistance of iron.[94]

Boron Nitride Nanosheets (BNNSs) Boron nitride nanosheets (BNNSs) are also potential materials for minimizing the aggregation and size effects of nZVI. nZVI supported by ultrathin boron nitride nanosheets has been successfully fabricated via a one-pot synthesis at gram scale. The high specific surface area and density of structural defects allow enrichment of the pollutants, resulting in relatively high conversion by the nearby supported nZVI. The reaction rate of nZVI/BNNSs is almost twice that of unsupported nZVI. Moreover, the nZVI/BNNSs composite is magnetic, so it can be easily separated from water with the aid of magnetic field.[95]

Chitosan As the second most abundant polysaccharide in the world, chitosan(CS) has drawn great attention in nZVI research. Recent studies have reported that chitosan can increase the dispersity and stability of nZVI for the removal of Cr (VI). nZVI is entrapped in chitosan beads for reduction of Cr (VI) from wastewater. Results indicate that entrapment of nZVI in CS beads prevents the particles from aggregation and oxidation without affecting the reaction rate.[96] Apart from reduction, the removal mechanism of Cr (VI) may also include physical adsorption which comes from the excellent adsorption behavior of both CS and nZVI towards heavy metals.[97]

$Mg(OH)_2$ Due to its controlled self-supported flowerlike structure and large specific surface area, nanoscale $Mg(OH)_2$ can also be used as an effective carrier for nZVI. Nano iron particles can be uniformly immobilized on the surface of $Mg(OH)_2$, and thus the aggregation of iron particles is minimized. The composite presents exceptional removal capacity of Pb(II) from aqueous solution in comparison with both $Mg(OH)_2$ and nZVI due to synergistic effects. [98]

However, the application of some supporting materials mentioned above (e.g. reduced graphite oxide, graphene, carbon nanotubes, boron nitride nanosheets) is limited by their shortcomings, such as complexity of preparation, high cost and uneven loading of nZVI. Good carriers need to be cost-efficient, mechanically stable and compatible with nano iron particles for practical implemenation. A strong affinity towards target ions is also desirable for significantly enhancing the performance of nZVI as a whole. [98]

Magnetization Modification

As a feasible alternative modification strategy, magnetization modification is under investigation to facilitate the separation and improve the reusability of nZVI. It involves inducing magnetism in iron NPs and taking advantage of a magnetic field for physical separation. In particular, when nZVI is combined with Fe_3O_4, the magnetism of the nanocomposite is much stronger than each of them when used separately. With the aid of a simple magnet, the nanocomposite can be separated from the solution easily.

Much progress has been made on magnetization modification in recent years. For instance, Lv et al. prepared nZVI–Fe_3O_4 magnetic nanocomposites by an *in situ* reduction method and used it to remove chromium(VI) in an aqueous environment.[99] Later, they optimized the process by assembly of nZVI on magnetic Fe_3O_4/graphene nanocomposites, leading to the formation of micro-nZVI-graphene/nZVI-Fe_3O_4 batteries with strong adsorption capability of broad graphene sheet/Fe_3O_4 surfaces. Fe_3O_4 not only prevented the agglomeration and passivation of nZVI, but also made it easy for separation.[100] Similarly, Yang et al. replaced graphene with reduced graphene oxide and obtained nanocomposites with high catalytic activity, good reusability and superparamagnetism.[101]

As mentioned in discussion of the hydrothermal method, Wang et al. successfully synthesized nZVI encapsulated in carbon spheres, but the catalytic stability was limited by rapid consumption of nZVI under acidic conditions. Subsequently, they came up with a modified approach and fabricated a novel magnetic carbon encapsulated nano Fe^0/Fe_3C composite which showed both high activity and magnetic separation efficiency in catalytic oxidation of phenol solutions.[102]

Emulsification

The emulsification of nZVI is aimed at solving the contamination problems caused by dense nonaqueous phase liquid (DNAPL). As DNAPL presents additional liquid phases to treat, the delivery of nZVI to them and subsequent contaminant transformation can be facilitated by the emulsification of nZVI. Thus, it has been an important innovation to encapsulate nZVI within emulsions to target regions containing DNAPL.[103]

Typically, the nZVI emulsions are water-in oil-in water (W/O/W) type.[103] With food-grade surfactants as stabilizers, emulsified zerovalent iron (EZVI) consists of biodegradable oil, water and nano iron particles. The emulsion droplets containing nZVI in water are surrounded by an oil-liquid membrane, as shown in Fig. 11. As the emulsion is hydrophobic, it's miscible with DNAPL. After the dissolution of the exterior oil membrane, the reactive nZVI is released to diffuse into DNAPL, come into contact with contaminants and degrade them rapidly.

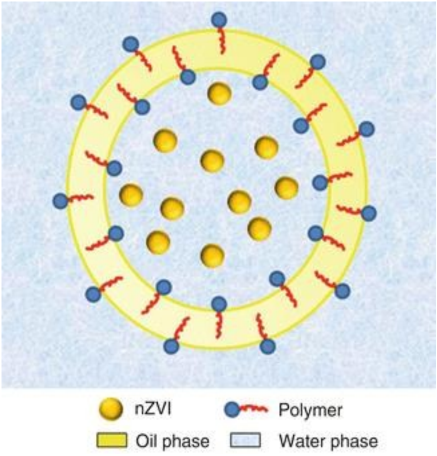


Fig. 11 Schematic representation of W/O/W-type emulsified zerovalent iron. Reprinted from ref. 45 with permission. Copyright © 2015, Springer.

In 2009, Berge et al. proposed a novel approach to deliver nZVI.[104] A different type of nZVI emulsification called oil-in water (O/W) was designed with partially similar materials to W/O/W. The continuous phase was made up of water and water soluble surfactants, and the dispersed phase was comprised of biodegradable oil, oil-soluble surfactants and nZVI. Oil droplets containing nZVI turned out to be readily transported by sandy porous media and had advantages in the remediation of DNAPL.

Integrated Methods

Many studies have demonstrated that a proper combination of several modification methods have complementary advantages and show better performance than any single method.

For example, in recent years, more and more researchers are making attempts to further modify B-NPs by providing supports. Parshetti et al.[105], Weng et al.[106-107], Ni et al.[108] and Liu et al.[80] have successfully immobilized bimetallic Fe/Ni on polyethylene glycol-grafted microfiltration membranes, chitosan, bentonite, cation exchange resin and attapulgite. The immobilization of Fe/Ni NPs on supporting materials not only retains longevity and high reactivity, but also remarkably improves the activity, stability, efficiency and reusability of the obtained product.

However, studies have also shown that the modification of nZVI still has scope for significant improvement. Co-existing organic and inorganic substances will impact each of the modified/immobilized nZVI-composites via different mechanisms, leading to an unavoidable decrease in the activity of a given immobilized-nZVI variant. To address this issue, there is an urgent need to achieve selective adsorption of targeted contaminants for subsequent reduction via the appropriate nZVI species, to ensure sustainable performance of nZVI. To this end, Chang et al. have coated an alginate bead containing nanoscale palladium/nano zero-valent iron (Pd/nZVI) with a highly hydrophobic oleic acid layer (See Fig. 12).[109] This novel material showed similar trichlorophenol removal efficacies regardless of the initial inorganic ion concentrations and showed sustainable performance in the degradation process.

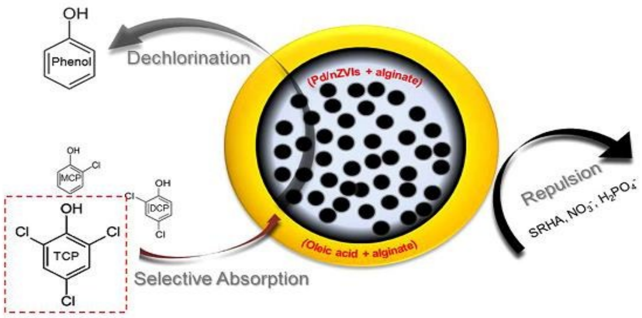


Fig. 12 Schematic representation of Pd/nZVI alginate beads coated with oleic acid layer. Reprinted from ref. 109 with permission. Copyright © 2015 Elsevier B.V.

In summary, with the rapid development of nano zerovalent iron technology, various modification methods have been developed and greatly improved the applicability and effectiveness of nZVI as a water treatment technology. It is important to note that the removal mechanism of a specific contaminant by nZVI should first be considered when choosing a modified nZVI variant. For example, the fact that Cr(VI) is removed by adsorption and reduction mechanisms means surface modification is rarely employed for the elimination of Cr(VI) as it will hinder the contact and reaction between nZVI and Cr(VI), thus reducing the removal efficiency. In order to arrive at an optimal nZVI modification methods, the choice of modified nZVI variant for the elimination of a contaminant should depend on the removal mechanism, modification effect, removal efficiency, the cost and so on.

Future Scope

Due to strong reducing ability, high reaction activity and excellent adsorption properties, nano zerovalent iron is able to degrade a wide variety of contaminants in water. In recent years, various synthesis methods have been put forward and a number of modification approaches have been developed and applied to minimize aggregation issue, improve mobility, increase stability, and to facilitate the separation of nZVI. Considering the current pace of development and application, nZVI looks to be an extremely promising technology for water treatment.

Nevertheless, some problems are still waiting to be solved in the meantime. For example, though nZVI has emerged commercially, it is relatively expensive. Furthermore, with increasingly extensive application of nZVI in water treatment, concerns have also been raised regarding its underlying ecotoxicological effects. Available information in the literature has demonstrated that nZVI harms microorganisms, animal cells, plant cells and human cells. For example, nZVI has been discovered to be toxic to both Gram-positive[25] and Gram-negative bacteria[26] and have a negative effect on reproduction and mortality of soil organisms[110]. nZVI could inhibit the growth of young leaves and decay the older plants[111] and lead to the death of human bronchial epithelium cells[66,112]. However, studies also show that the toxicity of nZVI is below the level observed for other nanoparticles in most cases.[113] Although some work has been done, the environmental risk assessment of nZVI remains a relatively unexplored area at present. Moreover, since the conditions of actual sites are much more complicated than those of laboratories, the feasibility and efficiency of nZVI in practical industrial applications still requires closer examination.

Based on a review of the literature and arguments presented here, the following goals are suggested for future work: (1) improve existing methods or develop new methods to reduce processing and handling costs to enable widespread application of nZVI in water treatment; (2) develop systematic and effective methods or tools for the risk assessment and management of nZVI; (3) establish a thorough evaluation mechanism to reflect the feasibility and efficiency of nZVI in the treatment of actual effluents; (4) combine nZVI with other synergistic technologies, such as membranes, photocatalysis and magnetic separation technologies.

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References

1 L. J. Matheson and P. G. Tratnyek, *Environ. Sci. Technol.*, 1994, **28**, 2045-2053.

2 R. W. Gillham and S. F. O'Hannesin, *Ground Water*, 1994, **32**, 958-967.

3 Y. Wang, Z. Q. Fang, Y. Kang and E. P. Tsang, *J. Hazard. Mater.*, 2014, **275**,230-237.

4 S. Bae and W. Lee, *Appl. Cata. B-Environ.* 2010, **96**, 10-17.

5 D. W. Liang, Y. H. Yang, W. W. Xu,S.K. Peng, S. F. Lu and Y. Xiang, *J. Hazard. Mater.,* 2014, **278**, 592-596.

6 W. X. Zhang, *J. Nanopart. Res.*, 2003, **5**, 323-332.

7 Z. Yuan, A. Sungwoo, A. L. Seyfferth, M. S. Yoko, F. Scott and R. G. Luthy, *Environ. Sci. Technol.*, 2011, **45**, 4896-4903.

8 A. Koutsospyros, J. Pavlov, J. Fawcett, D. Strickland, B. Smolinski and W. Braida, *J. Hazard. Mater.,* 2012, **219-220**, 75–81.

9 Z. K. Xiong, L. Bo, Y. Ping, Y. X. Zhou, J. L. Wang and S. P. Fang, *J. Hazard. Mater.,* 2015, **297**, 261–268.

10 L. Zhou, T. L. Thanh, J. Gong, J. H. Kim, E. J. Kim and Y. S. Chang, *Chemosphere*, 2014, **104**, 155-161.

11 G. E. Hoag, J. B. Collins, J. L. Holcomb, J. R. Hoag, M. N. Nadagouda and R. S. Varma, *J. Mater. Chem*, 2009, **19**, 8671-8677.

12 X. Y. Wang, P. Wang, J. Ma, H. L. Liu and P. Ning, *Appl. Surf. Sci.*, 2015, **345**, 57-66.

13 X. Y. Jin, Z. Zhuang, B. Yu and Z. X. Chen, *Carbohyd. Polym.*, 2016, **136**, 1085-1090.

14 S. Dutta, R. Saha, H. Kalita and A. N. Bezbaruah, *Environ. Technol. Innov.*, 2016, **5**, 176-187.

15 X. Y. Wang, M. P. Zhu, H. L. Liu, J. Ma and F. Li, *Sci. Total Environ.*,2013, **449**,157-167.

16 S. Luo, S. G. Yang, X. D. Wang and C. Sun, *Chemosphere*, 2010, **79**, 672–678.

17 N. Arancibia-Miranda, S. E. Baltazar, A. García, D. Muñoz-Lira, P. Sepúlveda and M. A. Rubio, *J. Hazard. Mater.*, 2015, **301**, 371–380.

18 D. D. Tomašević, G. Kozma, D. V. Kerkez, B. D. Dalmacija, M. B. Dalmacija and M. R. Bečelić-Tomin, *J. Nanopart. Res.*, 2014, **16**, 1-15.

19 S. S. Chen, H. D. Hsu and C. W. Li, *J. Nanopart. Res.*, 2004, **6**, 639-647.

20 M. Zdenka, S. K. Machalová, F. Jan, C. Jan, K. Milan, S. Klara, M. Ivo and Z. Radek, *Environ. Sci. Technol.*, 2013, **47**, 5285-5293.

21 H. J. Zhu, Y. F. Jia, X. Wu and H. Wang, *J. Hazard. Mater.*, 2009, **172**, 1591-1596.

22 L. Ling, B. Pan and W. X. Zhang, *Water Res.*, 2015, **71**, 274–281.

23 L. Ling and W. X. Zhang, *J. Am. Chem. Soc.*, 2015, **137**, 2788-2791.

24 F. L. Fu, D. D. Dionysiou and H. Liu, *J. Hazard. Mater.*, 2014, **267**, 194-205.

25 M. Diao and M. Yao, *Water Res.*, 2009, **43**, 5243-5251.

26 L. Changha, K. JeeYeon, L. Won II, K. L. Nelson, Y. Jeyong and D. L. Sedlak, *Environ. Sci. Technol.*, 2008, **42**, 4927-4933.

27 H. Hahn, *Nanostruct. Mater.*, 1997, **9**, 3-12.

28 C. Suryanarayana, *Prog. Mater. Sci.*, 2001, **46**, 1–184.

29 S. Li, W. Yan and W. X. Zhang, *Green Chem.*, 2009, **11**, 1618-1626.

30 C. B. Wang and W. X. Zhang, *Environ. Sci. Technol.*, 1997, **31**, 2154-2156.

31 Y. Zhao, G. R. Cui, J. J. Wang and M. H. Fan, *Inorg. Chem.*, 2009, **48**, 10435-10441.

32 M. R. Jamei, M. R. Khosravi and B. Anvaripour, *Asia-Pac. J. Chem. Eng.*, 2013, **8**, 767-774.

33 L. B. Hoch, E. J. Mack, B. W. Hydutsky, J. M. Hershman, J. M. Skluzacek and T. E. Mallouk, *Environ. Sci. Technol.*, 2008, **42**, 2600-2605.

34 S. J. Park, S. Kim, S. Lee, Z. G. Khim, K. Char and T. Hyeon, *Cheminform*, 2000, **31**, 8581-8582.

35 Z. Chen, D. Mochizuki and Y. Wada. In *Microwaves in Nanoparticle Synthesis: Fundamentals and Applications,* Wiley-VCH Verlag GmbH & Co. KGaA, 2013, pp.145-183.

36 C. J. Choi, O. Tolochko and B. K. Kim, *Mater. Lett.*, 2002, **56**, 289–294.

37 H. Sun, G. Zhou, S. Liu, H. M. Ang, M. O. Tadé and S. Wang, *Acs Appl. Mater. Inter.*, 2012, **4**, 6235-6241.

38 R. J. Joseyphus, D. Kodama, T. Matsumoto, Y. Sato, B. Jeyadevan and K. Tohji, *J. Magn. Magn. Mater.*, 2007, **310**, 2393-2395.

39 R. J. Joseyphus, K. Shinoda, D. Kodama and B. Jeyadevan, *Mater. Chem. Phys.*, 2010, **123**, 487-493.

40 C. T. Seip and C. J. O'Connor, *Nanostruct. Mater.*, 1999, **12**, 183-186.

41 L. Huang, X. Weng, Z. Chen, M. Megharaj and R. Naidu, *Spectrochim. Acta. A,* 2014, **130**, 295-301.

42 S. Machado, S. L. Pinto, J. P. Grosso, H. P. A. Nouws, J. T. Albergaria and C. Delerue-Matos, *Sci. Total Environ.*, 2013, **445**, 1–8.

43 P. Tanapon, S. Navid, S. Kevin, R. D. Tilton and G. V. Lowry, *Environ. Sci. Technol.*, 2007, **41**, 284-290.

44 J. Quinn, D. Elliott, S. O'Hara and A. Billow, in *ACS Symposium Series*, 2009, Chapter 15, pp.263-283.

45 R. Singh and V. Misra, in *Handbook of Nanoparticles, Springer International Publishing*, 2016, pp.985-1007.

46 M. Zhang, F. He, D. Y. Zhao and X. D. Hao, *Water Res.*, 2011, **45**, 2401–2414.

47 G. Fan, C. Long, W. Qin, C. Zhou, H. I. Gomes and D. Zhou, *Sep. Purif. Technol.*, 2013, **114**, 64–72.

48 B. Mohan, G. Subhasis and T. Nathalie, *Environ. Sci. Technol.*, 2013, **47**, 13355-13364.

49 T. Phenrat and G. V. Lowry, in *Nanotechnology Applications for Clean Water*, 2014, Chapter 30, pp.473-490.

50 S. R. Kanel, R. R. Goswami, T. P. Clement, M. O. Barnett and D. Zhao, *Environ. Sci. Technol.*, 2008, **42**, 896–900.

51 N. Sakulchaicharoen, D. M. O'Carroll and J. E. Herrera, *J. Contam. Hydrol.*, 2010, **118**, 117–127.

52 T. Phenrat, N. Saleh, K. Sirk, H. J. Kim, R. D. Tilton and G. V. Lowry, *J. Nanopart. Res.*, 2008, **10**, 795-814.

53 M. J. Bonder, K. L. Kiick, V. Papaefthymiou, G. C. Hadjipanayis and Y. Zhang, *J. Magn. Magn. Mater.*, 2007, **311**, 658-664.

54 W. Wei, S. Li, L. Hong, B. Pan and W. X. Zhang, *Chem. Eng. J.*, 2015, **260**, 616-622.

55 P. Tanapon, F. Fritjof, I. Tissa, G. V. Lowry and R. D. Tilton, *Environ. Sci. Technol.*, 2011, **45**, 6102-6109.

56 P. Jiemvarangkul, W. X. Zhang and H. L. Lien, *Chem. Eng. J.*, 2011, **170**, 482-491.

57 K. Sita, K. Harjyoti, B. J. Chisholm and A. N. Bezbaruah, *Environ. Sci. Technol.*, 2012, **46**, 10130-10136.

58 N. Saleh, K. Sirk, Y. Liu, T. Phenrat, B. Dufour and K. Matyjaszewski, *Environ. Eng. Sci.*, 2007, **24**, 45-57.

59 A. N. Bezbaruah, S. Krajangpan, B. J. Chisholm, E. khan and J. J. E. Bermudez, *J. Hazard. Mater.*, 2009, **166**, 1339-1343.

60 A. Tiraferri, L. C. Kai, R. Sethi and M. Elimelech, *J. Colloid Inter. Sci.*, 2008, **324**, 71–79.

61 D. V. Elena, L. Michela and S. Rajandrea, *Environ. Sci. Technol.*, 2009, **43**, 8942-8947.

62 H. Feng, D. Y. Zhao, J. C. Liu and C. B. Roberts, *Ind. Eng. Chem. Res.*, 2006, **46**, 29-34.

63 L. Zhou, T. L. Thanh, J. Y. Gong, J. H. Kim, E. J. Kim and Y. S. Chang, *Chemosphere*, 2014, **104**, 155-161.

64 H. R. Dong, Y. K. Xie, G. M. Zeng, L. Tang, J. Liang, Q. He, F. Zhao, Y. L. Zeng and Y. N. Wu. *Chemosphere*, 2015, **144**, 1682-1689.

65 M. Velimirovic, D. Schmid, S. Wagner, V. Micić, d. K. F. Von and T. Hofmann, *Sci. Total Environ.*, 2015, *In Press*, doi: 10.1016/j.scitotenv.2015.11.007.

66 P. Tanapon, T. C. Long, G. V. Lowry and V. Bellina, *Environ. Sci. Technol.*, 2009, **43**, 195-200.

67 Z. Q. Li, G. Karl, P. J. J. Alvarez, K. B. Gregory and G. V. Lowry, *Environ. Sci. Technol.*, 2010, **44**, 3462-3467.

68 I. Dror, O. M. Jacov, A. Cortis and B. Berkowitz, *Acs Appl. Mater. Inter.*, 2012, **4**, 3416-3423.

69 D. W. Elliott and W. X. Zhang, *Environ. Sci. Technol.*, 2001, **35**, 4922-4926.

70 P. G. Tratnyek, M. M. Scherer, T. J. Johnson and L. J. Matheson, In *Chemical Degradation Methods for Wastes and Pollutants: Environmental and Industrial Applications*, 2003, pp.371-421.

71 D. M. Cwiertny, S. J. Bransfield, K. J. T. Livi, F. D. Howard and R. A. Lynn, *Environ. Sci. Technol.*, 2006, **40**, 6837-6843.

72 W. X. Zhang, C. B. Wang and H. L. Lien, *Catal. Today*, 1998, **40**, 387-395.

73 F. Y. Xu, S. B. Deng, J. Xu, W. Zhang, M. Wu, B. Wang, J. Huang and G. Yu, *Environ. Sci. Technol.*, 2012, **46**, 4576-4582.

74 J. Theron, J. A. Walker and T. E. Cloete, *Crit. Rev. Microbiol.*, 2008, **34**, 43-69.

75 S. M. Hosseini, B. Ataie-Ashtiani and M. Kholghi, *Desalination*, 2011, **276**, 214-221.

76 Y. H. Liou, S. L. Lo, C. J. Lin, H. K. Wen and S. C. Weng, *J. Hazard. Mater.*, 2005, **127**, 102 -110.

77 R. S. Kalhapure, S. J. Sonawane, D. R. Sikwal, M. Jadhav, S. Rambharose, C. Mocktar and T. Govender, *Colloid. Surface. B,* 2015, **136**, 651-658.

78 R. Abazari, F. Heshmatpour and S. Balalaie, *Acs Catal.*, 2012, **3**, 139-149.

79 Z. Sun, S Zheng, G. A. Ayoko, R. L. Frost and Y. Xi, *J. Hazard. Mater.*, 2013, **263**, 768-777.

80 Z. T. Liu, C. G. Gu, Y. Mao, Y. R. Bian, Y. W. Cheng, F. Wang, X. L. Yang, Y. Song and X. Jiang, *J. Hazard. Mater.*, 2015, **298**, 328–337.

81 X. Y. Li, L. H. Ai and J. Jiang, *Chem. Eng. J.*, 2016, **288**, 789–797.

82 C. B. Wang, H. J. Luo, Z. L. Zhang, Y. Wu, J. Zhang and S. W. Chen, *J. Hazard. Mater.*, 2014, **268**, 124-131.

83 F. L. Liu, J. H. Yang, J. Zuo, D. Ma, L. L. Gan, B. M. Xie, P. Wang and B. Yang, *J. Environ. Sci.*, 2014, **26**, 1751–1762.

84 A. Azari, A. Esrafili, M. Moazzen, B. Kakavandi, A. A. Babaie and R. Rezaei-Kalantary, *J. Mazandaran Univ. Med. Sci.*, 2014, **23**, 15-27.

85 J. C. Yan, H. Lu, W. G. Gao, S. Xue and M. F. Chen, *Bioresource Technol.*, 2014, **175**, 269–274.

86 Y. Dai, Y. C. Hu, B. J. Jiang, J. L. Zou, G. H. Tian and H. G. Fu, *J. Hazard. Mater.*, 2016, **309**, 249-258.

87 S. J. Tesh and T. B. Scott, *Adv. Mater.*, 2014, **26**, 6056-6068.

88 H. Ma, Y. P. Huang, M. W. Shen, R. Guo, X. Y. Cao and X. Y. Shi, *J. Hazard. Mater.*, 2011, **211-212**, 349-356.

89 P. Puttamraju and A. K. Sengupta, *Ind. Eng. Chem. Res.,* 2006, **45**, 7737-7742.

90 A. Li, C. Tai, Z. S. Zhao, Y. Wang, Q. Zhang, G. Jiang and J. Hu, *Environ. Sci. Technol.*, 2007, **41**, 6841-6846.

91 S. Sarkar, L. M. Blaney, A. Gupta, D. Ghosh and A. K. Sengupta, *React. Funct. Polym.*, 2007, **67**, 1599-1611.

92 S. Sudipta, A. K. Sengupta and P. Prakhar, *Environ. Sci. Technol.*, 2010, **44**, 1161-1166.

93 J. L. Shi, S. N. Yi, H. L. He, C. Long and A. M. Li, *Chem. Eng. J.,* 2013, **230**, 166-171.

94 Y. C. Li, Z. M. Xiu, T. L. Li and Z. Jin, in *ACS symposium series 1124*, 2013, pp.307–326.

95 L. Wang, S. Q. Ni, C. Guo and Y. Qian, *J. Mater. Chem. A*, 2013, **1**, 6379-6387.

96 T. Y. Liu, L. Zhao, D. S. Sun and X. Tan, *J. Hazard. Mater.*, 2010, **184**, 724-730.

97 W. S. W. Ngah, L. C. Teong and M. A. K. M. Hanafiah, *Carbohyd. Polym.*, 2011, **83**, 1446–1456.

98 M. Liu, Y. Wang, L. Chen, Y. Zhang and Z. Lin, *Acs Appl. Mater. Inter.*, 2015, **7**, 7961−7969.

99 X. S. Lv, J. Xu, G. M. Jiang, J. Tang and X. H. Xu, *J. Colloid Inter. Sci.*, 2011, **369**, 460-469.

100 X. S. Lv, X. Q. Xue, G. M. Jiang, D. L. Wu, T. T. Sheng, H. Y. Zhou and X. H. Xu, *J. Colloid Inter. Sci.*, 2014, **417**, 51–59.

101 B. Yang, Z. Tian, L. Zhang, Y. P. Guo and S. Q. Yan, *J. Water Process Eng.*, 2015, **5**, 101-111.

102 Y. Wang, H. Sun, X. Duan, H. M. Ang, M. O. Tadé and S. Wang, *Appl. Catal. B-Environ.*, 2015, **172**, 73-81.

103 N. D. Berge and R. C. Andrew, *Environ. Sci. Technol.*, 2009, **43**, 5060-5066.

104 Q. Jacqueline, G. Cherie, C. Chris, B. Kathleen and C. Christina, *Environ. Sci. Technol.*, 2005, **39**, 1309-1318.

105 G. K. Parshetti and D. Ruey-An, *Chemosphere*, 2012, **86**, 392–399.

106 X. Weng, S. Lin, Y. Zhong and Z. Chen, *Chem. Eng. J.,* 2013, **229**, 27-34.

107 X. Weng, Z. Chen, Z. Chen, M. Megharaj and R. Naidu, *Colloid. Surface. A*, 2014, **443**, 404-409.

108 S. Q. Ni and Y. Ning, *J. Colloid Inter. Sci.*, 2014, **420**, 158-165.

109 J. Chang, H. Woo, M. S. Ko, J. Lee, S. Lee, S. T. Yun and S. Lee, *J. Hazard. Mater.*, 2015, **293**, 30-36.

110 Y. S. E. Temsah and E. J. Joner, *Chemosphere*, 2013, **92**,131–137.

111 X. M. Ma, A. Gurung, Y. Deng, *Sci. Total Environ.*, 2013, **443**, 844–849.

112 C. R. Keenan, G. G. Regine, L. Donald and D. L. Sedlak, *Environ. Sci. Technol.*, 2009, **43**, 4555–4560.

113 B. I. Kharisov, H. V. R. Dias, O. V. Kharissova, V. M. Jimenez-Perez, B. O. Perez and B. M. Flores, *RSC Adv.*, 2012, **2**, 9325–9358.