Chapter 2
Nanoscale Zero-Valent Iron Particles for Water Treatment: From Basic Principles to Field-Scale Applications

Tanapon Phenrat, Petra Skácelová, Eleni Petala, Adriana Velosa, and Jan Filip

Abstract Reductive technologies of groundwater and soil treatment, based on nanoscale zero-valent iron (nZVI) particles, have been recognized and generally accepted as modern remediation tools for elimination of broad range of both organic and inorganic environmental contaminants, mainly at sites where fast and efficient removal of persistent and emerging organic and inorganic pollutants is needed. In this chapter, we summarize the basic principles and chemical pathways of the nZVI interaction with water and contaminants, recent approaches to nZVI modifications enhancing their reactivity and longevity (including electrostatic and steric stabilization of nZVI, synthesis and applicability of bimetallic particles and nZVI-based nanocomposites, emulsification of nZVI particles, and combination of nZVI with electrokinetics), and present an overview on field-scale applications of nZVI for remediation purposes all over the world. The main aim is to demonstrate the diverse properties of nZVI particles and their possible limitations for water treatment.

Keywords Nanoparticles · Iron · nZVI · Groundwater · Surface and chemical modification · Nanocomposites · Reaction mechanisms · Field-scale applications

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Overview of contaminants affecting soil

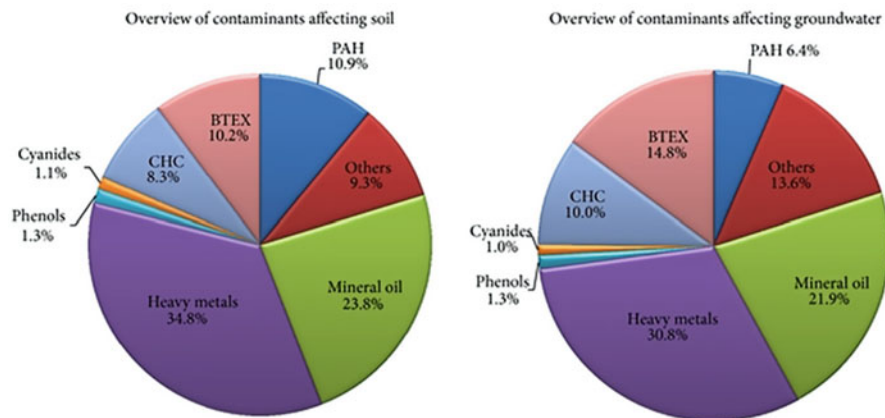Overview of contaminants affecting groundwater

Fig. 2.1 Prevalence of soil and groundwater contaminants in Europe (adapted from Panagos et al. 2013 with permission)

2.1 Groundwater and Soil Contamination as a Worldwide Problem and Opportunity for Nanotechnologies

Groundwater and soil contamination caused by various toxic substances has posed a serious threat to human and ecological health while it has been of great concern to the general public worldwide for more than 40 years. In 2011, approximately 1.17 million potentially contaminated sites and 0.127 million contaminated sites were identified in the European Economic Area (European Environment Agency 2014). Figure 2.1 illustrates the statistics on the prevalence of soil and groundwater contaminants in Europe (Panagos et al. 2013). Over the last three decades, several European countries have introduced national policies and practices for the management of contaminated sites (Rodrigues et al. 2009). Although, in 2002, the EU Thematic Strategy for Soil Protection was proposed by the European Commission with the objective to protect soils across the EU, no specific regulations for soil protection at the EU level have been introduced so far. 'While the Commission in May 2014 decided to withdraw the proposal for a Soil Framework Directive, the Seventh Environment Action Programme, which entered into force on 17 January 2014, recognizes that soil degradation is a serious challenge (European Commission 2019). However, remediation activities in European countries are still going on. By 2018, 58,340 sites had been remediated (European Environment Agency 2014). A substantial budget is used for contaminated site management. For example, annual national expenditures for managing contaminated sites are, on average, EUR 10.7 per capita (an average of 0.041% of the national gross domestic product—GDP). Out of this, 42% comes from public budgets and around 81% is used for remediation measures, while 15% is used for sites.

Similarly, in the US, soil and groundwater contamination is a serious issue. Infamous contamination cases, such as Times Beach, Love Canal, Woburn, and the Valley of Drums, as well as their health effects (US EPA 2000, 2018a; Swartjes

Table 2.1 Prevalent contaminants of concern (COC) at National Priorities List (NPL) sites (adapted from Siegrist et al. 2011 with permission)

Contaminant of concern (COC)	Priority as a COC at US hazardous waste sites (ATSDR[a] ranking)	Prevalence at US NPL sites		US drinking water standard (μg/L)
		Number of NPL sites with COC present	Sites with COC present as a % of total NPL sites	
Arsenic	1	1149	68	10
Lead	2	1272	76	15
Mercury	3	714	49	2
Vinyl chloride	4	616	37	2
Polychlorinated biphenyls	5	500	31	0.5
Benzene	6	1000	59	5
Cadmium	7	1014	61	5
Polycyclic aromatic hydrocarbons	8	600	42	–
Benzo(*a*)pyrene	9	–	–	0.2
Chloroform	11	717	50	100
Trichloroethene	16	852	60	5
Chromium	18	1127	68	100
Tetrachloroethene	33	771	54	5
Pentachlorophenol	45	313	20	1
Carbon tetrachloride	47	425	26	5
Xylene (total)	58	840	51	10,000
Toluene	71	959	60	1000
Methylene chloride	80	882	56	5
1,1,1-trichloroethane	97	823	50	200
Ethylbenzene	99	829	49	700

[a]*ATSDR* Agency for Toxic Substances and Disease Registry

2011) generated environmental cleanup regulations, including the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) for abandoned sites and corrective action of the Resource Conservation and Recovery Act (RCRA) for active sites and generated remediation engineering (Applegate and Laitos 2006; US EPA 2018a). Progressively, hundreds of thousands of sites with different degrees of contamination have been identified in the US. Table 2.1 summarizes prevalent contaminants of concern (COCs) at National Priorities List (NPL) sites. In 2018, the NPL featured 1566 contaminated sites. 381 of them have been sufficiently restored, posing a minimal risk, and proposed for site deletion (US EPA 2018b). Nevertheless, over the next decades, cleanup research and business will still be active in restoring the remainder as well as newly spilled sites. The US EPA

(2011) estimated that between the years 2004 and 2033 the cost for remediation may be as high as US$209 billion, while the number of cleanup sites could be as high as 294,000.

For Asian countries, remediation is at an infant stage, although soil and groundwater contamination has long been threatening the quality of life. For example, in China, according to the Ministry of Land Resources, in 2007, over 10% of cultivated land was substantially contaminated with heavy metals from mining and metallic smelting (approx. two million ha), oil extraction and refining (approx. five million ha), solid-waste stockpiles (i.e., open dumps; approx. 50,000 h.), improper handling of industry gaseous emission, wastewater discharge, and processing residue (approx. ten million ha), and sewage irrigation (approx. 3.3 million ha) (Li et al. 2015). In 2014, the Chinese government published a national soil survey report showing that 16.1% of all soil and 19.4% of cultivated land was contaminated with both organic and inorganic chemical contaminants. The total area of contaminated soil was roughly 25 million ha, while 3.5 million ha of farmland was so contaminated that no agriculture should be allowed on it (The Economist 2017). Cadmium and arsenic were found in 40% of the affected land. China undertook 28, 40, and 32 remediation projects for the years 2013, 2014, and 2015, respectively. The government estimated that, with 3.33 million ha of contaminated farmland already identified, the total budget remediation could reach as much as US$ 157,000 million (based on 2018 USD) (Gu and Stanway 2017).

Currently, more than 59 remediation technologies based on at least one of 14 different types of treatment processes are available in various stages of development and application (Van Deuren et al. 2002). Nevertheless, there is always enough room for nanotechnology to step in as an innovative in situ remediation technology. This gives birth to nanoscale zerovalent iron particle (nZVI), one of the nanotechnologies that is most frequently applied for groundwater and soil remediation. The primary utilization of ZVI is a passive remediation technology called permeable reactive barrier (Fig. 2.2). For this technique, bulk zerovalent iron (ZVI) in the form
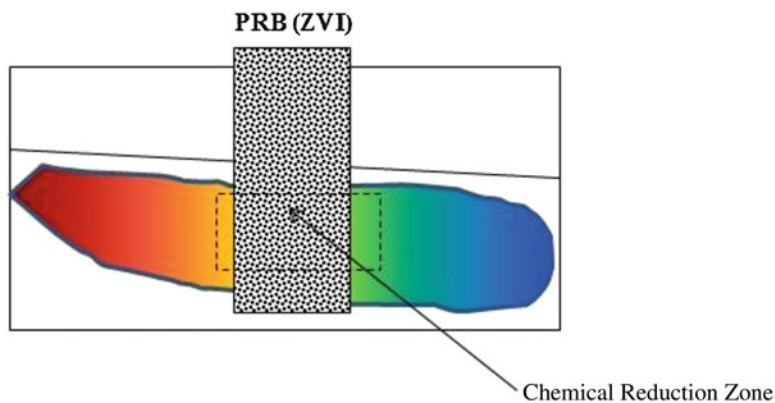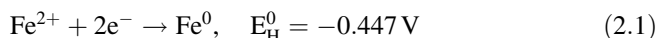

Fig. 2.2 Permeable reactive barrier using bulk ZVI

Table 2.2 Contaminants of concern amendable by ZVI and nZVI as well as their standard redox potentials (E^0) in aqueous solution at 25 °C (Bard et al. 1985; O'Carroll et al. 2013)

Aqueous solution	Half reactions	E^0 (V)
Chromium (Cr)	$CrO_4^{2-} + 8H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O$	1.51
Chromium (Cr)	$CrO_7^{2-} + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 7H_2O$	1.36
Platinum (Pt)	$Pt^{2+} + 2e^- \leftrightarrow Pt$	1.19
Palladium (P)	$Pd^{2+} + 2e^- \leftrightarrow Pd$	0.92
Mercury (Hg)	$Hg^{2+} + 2e^- \leftrightarrow Hg$	0.86
Silver (Ag)	$Ag^+ + e^- \leftrightarrow Ag$	0.80
Arsenic (As^V)	$H_3AsO_4 + 2H^+ + 2e^- \leftrightarrow HAsO_2 + 4H_2O$	0.56
Copper (Cu)	$Cu^{2+} + 2e^- \leftrightarrow Cu$	0.34
Uranium (U)	$UO_2^{2+} + 4H^+ + 2e^- \leftrightarrow U^{4+} + 2H_2O$	0.27
Arsenic (As^{III})	$H_3AsO_3 + 3H^+ + 3e^- \leftrightarrow As + 3H_2O$	0.24
Copper (Cu)	$Cu^{2+} + e^- \leftrightarrow Cu^+$	0.16
Lead (Pb)	$Pb^{2+} + 2e^- \leftrightarrow Pb$	−0.13
Nickel (Ni)	$Ni^{2+} + 2e^- \leftrightarrow Ni$	−0.25
Cadmium (Cd)	$Cd^{2+} + 2e^- \leftrightarrow Cd$	−0.40
Iron (Fe)	$Fe^{2+} + 2e^- \leftrightarrow Fe$	−0.44
Zinc (Zn)	$Zn^{2+} + 2e^- \leftrightarrow Zn$	−0.76
Barium (Ba)	$Ba^{2+} + 2e^- \leftrightarrow Ba$	−2.92
1,2-Dichloroethane	$ClH_2C - CH_2Cl + 2e^- \leftrightarrow H_2C = CH_2 + 2Cl^-$	0.74
Carbon tetrachloride (CT)	$CCl_4 + H^+ + 2e^- \leftrightarrow CHCl_3 + Cl^-$	0.67
Tetrachloroethylene (PCE)	$Cl_2C = CHCl + H^+ + 2e^- \leftrightarrow Cl_2C = CH_2 + Cl^-$	0.57
Trichloroethylene (TCE)	$Cl_2C = CHCl + H^+ + 2e^- \leftrightarrow Cl_2C = CH_2 + Cl^-$	0.53
Vinyl chloride (VC)	$ClHC = CH_2 + H^+ + 2e^- \leftrightarrow H_2C = CH_2 + Cl^-$	0.45
1,1-Dichloroethane (1,1-DCE)	$Cl_2C = CH_2 + H^+ + 2e^- \Leftrightarrow ClHC = CH_2 + Cl^-$	0.42

of iron filings has been used as a reducing agent to build permeable reactive barriers (PRB) since 1994 (Reynolds et al. 1990; Gillham and O'Hannesin 1994).

The fundamental chemistry of ZVI in an aqueous environment from a reaction viewpoint is summarized in Eqs. (2.1–2.3). For environmental remediation purposes, Fe^0 can be oxidized by contaminants of concerns (COCs) (such as trichloroethene—TCE) in Eq. (2.1)) (as electron acceptors) as long as COCs have an E_H^0 greater than −0.447 V (see Table 2.2 for more examples of COCs treatable by ZVI and nZVI). As a result of the electron transfer, in most cases, ZVI transforms such COCs to more environmentally benign by-products or immobilized state. This transformation involves reductive dechlorination of chlorinated organics (trichloroethylene [TCE], tetrachloroethylene [PCE], and vinyl chloride [VC]) and immobilization of metals. In the meantime, Fe^0 can also react with water (or H^+) to produce H_2 gas (Eq. 2.3), which is a competing reaction to the reductive treatment and is strongly controlled by the availability of H^+ (i.e., pH).

$$Fe^{2+} + 2e^- \rightarrow Fe^0, \quad E_H^0 = -0.447\,V \qquad (2.1)$$

$$TCE + ne^- + (n-3)H^+ \rightarrow product + 3Cl^- \tag{2.2}$$

$$H^+ + e^- \rightarrow H* \rightarrow \tfrac{1}{2}H_2 \tag{2.3}$$

Although the oxidation of Fe^0 to Fe^{2+} (Eq. 2.1) is usually assumed, in environmentally relevant applications (i.e., groundwater at a natural pH), the transformation of Fe^0 core to the iron oxide shell, such as magnetite (Fe_3O_4) (Eq. 2.4) and maghemite (Fe_2O_3), is often observed (Liu et al. 2005; Reinsch et al. 2010).

$$3Fe^0 + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 8e^- \tag{2.4}$$

PRB is an established and effective technique to intercept contaminant plume; however, it is a passive technique meaning that the site owner has to maintain the PRB as long as the contaminant source exists and keeps generating toxic plume, which can last decades or even a century. This situation called for an active technique which can actively manage the source zone and expedite site closure. As shown in Fig. 2.3, the nanoscale conceptually allows ZVI to become an active technique that can be intentionally delivered to attack the source zone, thus speeding up the remediation.

The small size of nZVI not only offers the potential for injection into the subsurface for in situ remediation (Elliott and Zhang 2001; Schrick et al. 2004) but also results in an increasing fraction of atoms at the surface, excess surface energy, and high surface area (Wang and Zhang 1997). These properties lead to higher contaminant degradation/immobilization rates per mass of the remediation agents compared to bulk materials. Moreover, polymeric surface modification and supporting materials can be used to modify nZVI in order to enhance dispersion stability as well as to selectively target some specific COCs such as dense non-aqueous phase liquid (chlorinated organics). NZVI-focused research has progressed, over the past two decades, from laboratory development to field scale applications. This historical perspective has recently been reviewed by Phenrat and Lowry (2019). They divide the nZVI research and development into eight major topics, including (1) nZVI synthesis and reactivity, (2) aggregation/agglomeration, (3) transport/delivery/deposition, (4) polymer modification, (5) CMC modification, (6) toxicity, (7) sulfidation, and (8) weak magnetic/electromagnetic field, all of which are essential vehicles for effective in situ subsurface remediation. Figure 2.4 shows statistical results of peer-reviewed journal papers and the total citations of each major field. Noticeably, the number of peer-reviewed papers and citations in this field has increased quadratically so far. In 2017 alone, there were 262 peer-reviewed journal papers and 8094 citations in the nZVI field of study. Obviously, nanotechnology for subsurface remediation has been an active field of study for two decades and will continue to be active as long as contamination exists.

This chapter aims to summarize the recent development of nZVI technology including chemical pathways of pollutants treated by nZVI, modification and enhancement of nZVI, and pilot applications of nZVI as published in the scientific literature before 2018. For more details on nZVI research and development see the recently published book dealing with this topic Phenrat and Lowry (2019).
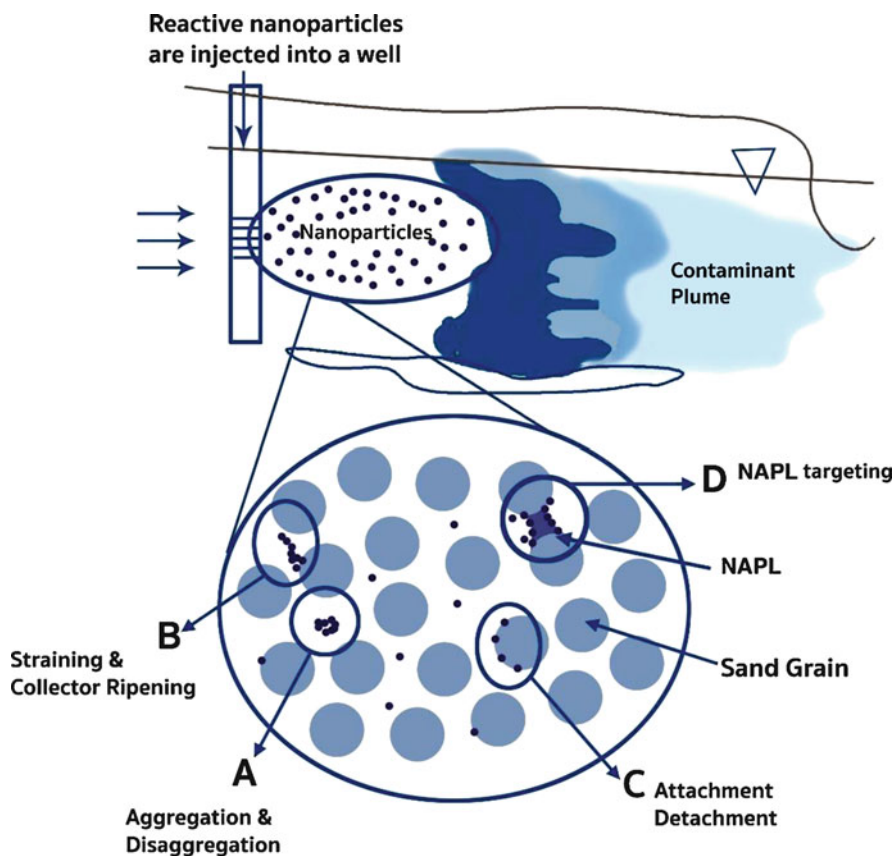
Fig. 2.3 Idealized conceptual mode of delivering nZVI for in situ non-aqueous phase liquid (DAPL) source-zone remediation. Particle mobility and contaminant targetability are needed for effective remediation (adapted from Phenrat and Lowry 2019 with permission)
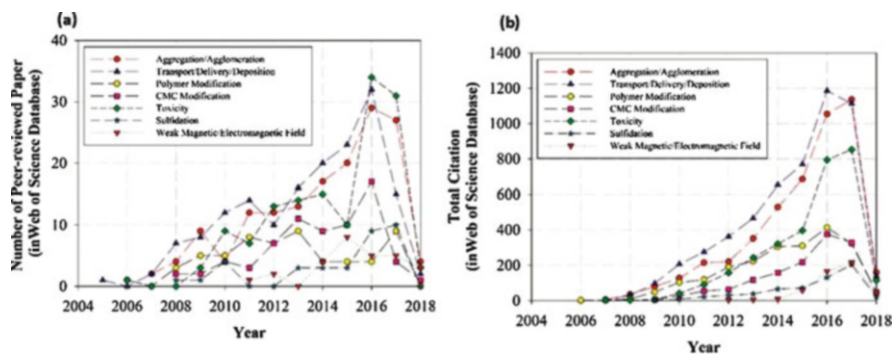

Fig. 2.4 (**a**) Total number of peer-reviewed papers and (**b**) total citations per year for each major field of nZVI research based on the Web of Science Database from 2001 to 2018 (February)

2.2 Chemical Pathways of Pollutants Removal by Zerovalent Iron

Under anaerobic conditions, Fe^0 can be oxidized by H_2O or H^+ yielding Fe^{2+} and H_2, both of which are also potential reducing agents for contaminants. There are two main dehalogenation reactions by which the organic compounds can be reduced by ZVI: hydrogenolysis (replacement of a halogen atom by a hydrogen) and reductive elimination, in which two halide ions are released. In both reactions, there is a net transfer of two electrons and they can be mediated either by atomic hydrogen transfer or by direct electron transfer.

The mechanism and reactivity of chlorinated compounds reduction by ZVI is somewhat controversial and still not very well understood. While some papers show an increased reactivity with an increasing number of halogen atoms in the organic compounds, others show the opposite trend. It seems that these conflicting data result from differences in the materials—ZVI produced by borohydride reduction versus ZVI produced by hydrogen reduction from iron minerals—as well as from differences in the experimental conditions (Elsner and Hofstetter 2011).

Wang and Farrell (2003), for example, observed that TCE reduction occurred almost exclusively by atomic hydrogen transfer at low pH values and by atomic hydrogen transfer and direct electron transfer at neutral pH values, while PCE reacted mainly via direct electron transfer at both low and neutral pH values. However, in acid conditions and micromolar concentrations, TCE reaction rates were faster than those of PCE due to faster reduction of TCE by atomic hydrogen transfer, while in neutral environment and millimolar concentrations, PCE reaction rates were faster than those of TCE. This variation of relative reaction rates was explained by a lower contribution of the atomic hydrogen reaction mechanism with increasing pH values and pollutant concentrations.

In the case of chlorinated methanes, the degradation pathways by reaction with zerovalent iron may differ from the chlorinated ethenes. Song and Carraway (2006), for example, observed that CCl_4 (CT), $CHCl_3$, and CH_2Cl_2 degradation rates were not affected by changing the hydrogen concentration in water or reaction atmosphere. So, in contrast to TCE degradation by nano ZVI synthesized by borohydride (Liu et al. 2005), no catalytic hydrogenation was found to be the degradation route for any of these compounds. Actually, CH_2Cl_2 is the main degradation product during CCl_4 reduction by ZVI and it is considered a as the final product since no degradation was observed by ZVI reaction. However, CH_4 is also produced but in very low amounts and is claimed to be generated directly through CCl_4 via a concerted elimination steps mechanism mediated by carbon radicals and carbanions.

Li and Farrell (2001) published an electrochemical investigation of the rate limiting mechanisms for TCE and CCl_4 reduction and concluded that rates of CT reduction were limited by the rate of outer-sphere electron transfer, while rates of TCE reduction were not limited by rates of electron transfer. Reduction via an outer-sphere mechanism requires only physical adsorption of CT on or near the ZVI surface. Then the production of chlorinated byproducts from chloroalkanes would

be explained by a stepwise dechlorination process in which a brief interaction of this compound with the ZVI surface would promote an electron transfer one at time. On the other hand, the TCE reduction mechanism starts with a chemisorption step that controls the overall rate of reaction before the electron transfer.

The degradation of chlorinated ethanes has been observed to be dependent on the number of chlorine atoms as well as on their position in the molecule. Song and Carraway (2005) studied the degradation of a series of chlorinated ethanes and observed that the reactivity increased by increasing chlorination. They also reported that among tri and tetrasubstituted compounds, the reactivity was higher for compounds with chlorine atoms more localized in only one carbon, e.g., 1,1,1-TCA > 1,1,2-TCA. The proposed explanation for this difference in the reactivity is the shifting of the mechanism, in which the 1,1,1-TCA reacts by a concerted pathway involving α-elimination and hydrogenolysis, while 1,1,2-TCA reduction would proceed by β-elimination.

With the aim of increasing the reactivity; mobility; and transport in subsurface, along with the inhibition of ZVI passivation, many research groups have been studying the effect of adding metal catalysts (Schrick et al. 2004); coating nanoparticles with polymers/surfactants (Wang et al. 2010); supporting nanoparticles on different substrates (Jia et al. 2011); and applying ZVI in water-in-oil emulsions (Berge and Ramsburg 2009).

Schrick et al. (2004), using Fe^0/Ni bimetallic nanoparticles, observed a TCE degradation rate constant that was 50 times faster than pure ZVI, indicating that the bimetallic nanoparticles were more efficient in degrading TCE when compared to the monometallic iron nanoparticles.

The introduction of a second catalytic metal could also prevent toxic byproduct formation by dehalogenating TCE via hydrogen reduction rather than via electron transfer and even enables the reduction of persistent compounds like monochlorophenols, which cannot be reduced by ZVI itself (Morales et al. 2002). On the other hand, the presence of different metals increases water promoted corrosion of iron, which can result in lower reactivity and lifetime. Yan et al. (2010) observed that Pd-doped ZVI nanoparticles immersed in water for 24 h did not exhibit any metallic iron component in the XPS spectrum, while the Fe^0 peak, although with decreased intensity, remained observable for pure ZVI nanoparticles kept on the same conditions. Besides, in a reactivity TCE reduction study with Pd-ZVI nanoparticles, the apparent reaction rate constant decreased from 5.7 1/h for the fresh particles to 0.96 1/h upon 24 h aging.

In bimetallic systems, the atomic hydrogen adsorbed on the reductant surface (H_{ads}) is postulated to be responsible for bimetal reactivity and the generation of H_{ads} species has been proposed by different ways. It could be produced by the dissociative chemisorption of H_2, itself generated by water reduction, or as an intermediate to H_2 generation. It is also suggested that absorbed atomic hydrogen (H_{abs}) within the metal additive lattice, instead of surface-adsorbed atomic hydrogen (H_{ads}), would represent the reactive entity in iron-based bimetallic systems (Cook 2009).

ZVI can also be used for oxidative degradation of organic compounds, either providing Fe^{2+} to Fenton process (Eq. 2.5) or by reacting with oxygen itself through

a superoxide radical ($O_2^{-\bullet}$) intermediate leading to the production of hydrogen peroxide in situ (Eq. 2.6).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH \tag{2.5}$$

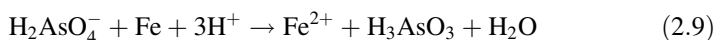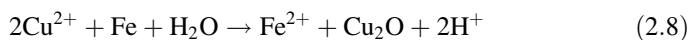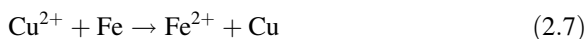$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \tag{2.6}$$
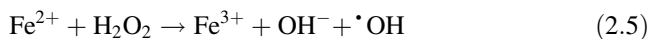
It is expected that during the oxidative process the compounds are not only dehalogenated but mineralized as well. The degradation process at this time is claimed to be promoted by hydroxyl radical (${}^\bullet OH$), which is a non-specific and powerful oxidant ($E^0 = 2.73$ V).

Keenan and Sedlak (2008) evaluated the effect of different ligands (oxalate, nitrilotriacetic acid (NTA), or ethylenediaminetetracetic acid (EDTA) on nZVI/H_2O/O_2 system and observed that all of them promoted an increase in the oxidant yield by limiting iron precipitation and accelerating the rates of key reactions like ferrous iron oxidation by oxygen and hydrogen peroxide.

On the other hand, Correia de Velosa and Pupo Nogueira (2013) also evaluated the effect of some ligands (EDTA, glycine, citrate, oxalate and DTPA) on 2,4-Dichlorophenoxyacetic acid (2,4-D) degradation by nZVI/H_2O/O_2 and reported that the only effective ligands on the catalysis of 2,4-D oxidation were EDTA and DTPA. They also postulate that the catalysis process is run by the ligand-Fe(II) species at pH values lower than 5 and by Fe(II) species at pH higher than this.

Presenting a standard potential of -440 mV, ZVI is considered a potential reductant agent for any other metal holding reduction potentials more positive than it. This property makes ZVI an interesting material for removal of heavy metals like Ni(II), Cu(II), Cr(VI), Pb(II), e.g., from groundwater or wastewater matrices.
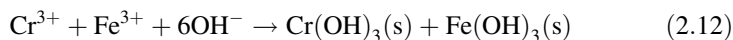
The main mechanisms by which heavy metals are removed from solution in the ZVI/H_2O system are reduction, adsorption, and precipitation/co-precipitation, according to the metal. For example, the reduction of Cu(II) (Eqs. 2.7 and 2.8) or As(V) (Eq. 2.9) by ZVI is more thermodynamically favorable than precipitation and sorption, as well as it is less affected by pH change and the presence of ligands (Li et al. 2017).

$$Cu^{2+} + Fe \rightarrow Fe^{2+} + Cu \tag{2.7}$$

$$2Cu^{2+} + Fe + H_2O \rightarrow Fe^{2+} + Cu_2O + 2H^+ \tag{2.8}$$

$$H_2AsO_4^- + Fe + 3H^+ \rightarrow Fe^{2+} + H_3AsO_3 + H_2O \tag{2.9}$$

On the other hand, if the metal/metalloid is present like an oxyanion, such as AsO_4^{3-} or SeO_4^{2-}, then the precipitation by Fe^{2+} (Eq. 2.10) becomes important. This can be even the main cause of As removal, for example.

$$3Fe^{2+} + 2HAsO_4^{2-} \rightarrow Fe_3(AsO_4)_2(s) + 2H^+ \tag{2.10}$$
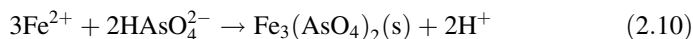
It is postulated that the Cr(VI) removal by ZVI occurs via immediate adsorption on the surface of the materials followed by electron transfer (reduction) through the oxidation of Fe^0 to Fe^{3+} (Eq. 2.11). The just generated ions (Fe^{3+} and Cr^{3+}) are then removed from the solution by precipitation of mixed hydroxides (Eq. 2.12) (Fu et al. 2014).

$$Cr_2O_7^{2-} + 2Fe + 14H^+ \rightarrow 2Cr^{3+} + 2Fe^{3+} + 7H_2O \qquad (2.11)$$

$$Cr^{3+} + Fe^{3+} + 6OH^- \rightarrow Cr(OH)_3(s) + Fe(OH)_3(s) \qquad (2.12)$$
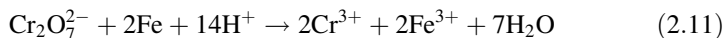
Ling et al. (2017) followed the removal of several metals (Ag(I), Ni(II), Cr(VI), As(V), Cs(I) and Zn(II)) by nZVI via high-sensitivity X-ray energy-dispersive spectroscopy-scanning transmission electron microscopy (XEDS-STEM). Since the studied metals presented very different electrochemical and coordination properties, they were used like probes, in order to understand the reactive pathways. Some of their conclusions are the following: strong oxidizing agents like Cr (VI) react by diffusion and encapsulation in the core of nZVI, while metal cations with a reduction potential close to or more negative than that of ZVI, such as Cs (I) and Zn(II), are removed by sorption or surface-complex formation.

From the application point of view, it is important to evaluate the effect of common ions on metal/metalloid removal by ZVI. Smedley and Kinniburgh (2002), for example, reported that high concentrations of phosphate in groundwater can inhibit As(V) removal by sorption since phosphate competes for sites on hydrous ferric oxides. The presence of Ca^{2+} or humic acid alone did not affect the Cr (VI) removal by ZVI in batch studies; however, the presence of bicarbonate ions increased it (Liu et al. 2009b).

The presence of nitrate, an oxidant usually reduced by ZVI, on Pb^{2+} solutions influences drastically its removal. At a low concentration of nitrate, the removal of Pb^{2+} by precipitation is increased by the pH increase promoted by nitrate reduction. However, in excess of nitrate (in relation to ZVI), the ferrite particles responsible for adsorption of Pb^{2+} are dissolved by the nitrate driven oxidation of Fe^{2+} and Pb^{2+} cations are remobilized to solution (Su et al. 2014).

Actually, nitrate can impact the performance of ZVI-driven reductions by two main ways: since it can also be reduced by ZVI, it competes with the target compounds for the reactive sites on iron particles and it works like a passivating agent, which leads to the generation of an Fe(III) (oxyhydr)oxide shell that inhibits the reactivity and decreases the lifetime of ZVI. Liu et al. (2007), for example, reported that an increase in the nitrate concentration led to the inhibition of TCE reduction up to seven-fold when the nitrate concentration reached 5 mM.

Other anions, like silicate or bicarbonate, also inhibit the degradation processes. Although these anions cannot be reduced by ZVI, they can complex to iron surface generating compounds like FeH_3SiO_4, $FeH_2SiO_4^-$, and $\equiv FeHSiO_4^{2-}$ or $FeCO_3$, decreasing the access of target compound to iron surface by forming a film or protective layer. On the other hand, chlorine and sulfate ions play corrosive roles in attacking and breaking the iron oxide layers and exposing the bare metal to the target compounds. Then, these anions usually increase the reactivity of ZVI system (Sun et al. 2016).

2.3   Modification of nZVI Particles and Enhancement of Their Reactivity

In spite of their high surface activity and remarkable environmental uptake capacity, most synthetic ZVI nanoparticles display some significant disadvantages from the technological/chemical engineering and cost/benefit perspectives. Therefore, drawbacks such as the strong tendency towards aggregation, fast oxidation, and rapid sedimentation can eliminate their long-term reactivity and decrease their maximum capacity.

Generally, it has been reported that the limited mobility of nZVI particles in saturated porous media is attributed to two reasons; firstly, nZVI can be filtered from the solution by attaching to aquifer materials and secondly, agglomeration and aggregation remarkably immobilize the particles (Phenrat et al. 2007). Agglomeration and aggregation phenomena decrease the specific surface area, and in turn, affects the reactivity and mobility in the subsurface and porous media, such as sand and soil (Ponder et al. 2000; Sun et al. 2007). The strong tendency towards nZVI aggregation is to a large extent attributed to their unstable colloidal nature and long-ranged attractive magnetic interactions between the particles (Phenrat et al. 2009).

Gravitational sedimentation of nZVI particles is a result of the aggregation effect and can be a good indicator of the colloidal stability of the particles. When nanoparticles are dispersed in a media, they can remain stable for very long time under some conditions. These conditions demand that the diffusion flux of nanoparticles overcomes the sedimentation flux. The diffusion flux of nanoparticles, that opposes gravity, is inversely proportional to the particle size, while the sedimentation flux is proportional to the square of the particle radius (Phenrat et al. 2008). When nanoparticles start to aggregate to bigger clusters in the range of micrometers, they settle as a result of the fact that the sedimentation flux turns to be bigger than the diffusion flux. Thus, their delivery and mobility is limited.

The effects of the fast oxidation of nZVI particles include a gradual loss of reactivity and permeability (Keum and Li 2004). While metallic iron exists in an aqueous environment, dissolved oxygen (DO) and water initialize its oxidation-dissolution. The whole reaction involves the formation of soluble ionic products or insoluble oxides/hydroxides. In other words, in aqueous environment, the nZVI oxidation creates species such as soluble $Fe^{2+}_{(aq)}$, H_2 and various precipitates, e.g., $Fe(OH)_2$, $Fe(OH)_3$, Fe_3O_4, Fe_2O_3, $FeOOH$, $Fe_5HO_8 \cdot 4H_2O$, and green rusts (Crane and Scott 2012). In this manner, when the precipitates are formed as a layer on the surface of nZVI and reach a critical thickness, the reactivity of nZVI is inhibited. In this point, the reactivity is eliminated while the surface of metallic iron is blocked to interact with any media or with the pollutants. These factors concerning the oxidation of the particles can be critical for the overall efficacy of this material since nZVI can react, be oxidized, consumed, or blocked before it reaches the target and remediates a desired site.

For all the above-mentioned reasons, the modification and/or stabilization of the nZVI nanoparticles, which can lead to steady or even enhanced remediation ability

and improved mobility, is deemed necessary. In the past few years, different approaches and a large number of research works have led to a new field of modification of nZVI particles. Therefore, new various methods have been developed in order to synthesize more active (Wu and Ritchie 2006), stable (Sun et al. 2007; Siskova et al. 2012), and mobile nZVI particles (Tiraferri et al. 2008; Kim et al. 2009) to simplify the synthetic procedure; reduce the cost; and finally enhance the efficacy (Zhang et al. 2012; Alessi and Li 2001), availability, and applicability to large-scale (Chen et al. 2012) and delivery capabilities (Kanel and Choi 2007).

Surface modification by electrostatic and steric stabilization, such as coating with polyelectrolytes or nonionic surfactants (Alessi and Li 2001), dispersing the particles in oil–water emulsions (Quinn et al. 2005), use of a support material for their synthesis (Wu et al. 2012; Ponder et al. 2001) and bimetallic particles with iron and a second less reactive metal, are strategies that have been investigated thoroughly. These methods have proved that it is possible to overcome the magnetic attraction between the iron nanoparticles, change the surface or interfacial properties, increase mobility and stability, minimize aggregation, and significantly increase the reactivity.

2.3.1 Electrostatic and Steric Stabilization

Surface modification by electrostatic and steric stabilization can provide conditions that overcome the magnetic attraction between the iron nanoparticles and change the surface or interfacial properties (Fig. 2.5), thus enhancing the colloidal stability and mobility. By electrostatic stabilization the surface charge is changed and repulsive forces overcome the affinity of aggregation. On the other hand, steric stabilization is typically attained by the adsorption of long-chain hydrophilic polymers whose long loops and tails extend out into the solution (e.g., surfactants) (Tiraferri et al. 2008). Combined electro-steric stabilization is also promising in terms of the use of ionic polymeric molecules that provide good dispersion and high efficacy (Sun et al. 2007). Such ionic polyelectrolytes have been applied successfully in the past (see Fig. 2.6) including polyaspartate (PAP), carboxymethyl cellulose (CMC), and polystyrene sulfonate (PSS). The modified nZVI particles in these cases have exhibited mobility in porous media due to slow desorption of polymeric surface modifiers. Every time, according to the contaminant that is targeted, the election and usage of

Fig. 2.5 Schematic representation of electrostatic, steric and electrosteric stabilization of nanoparticles (adapted from Tang and Lo 2013 with permission)
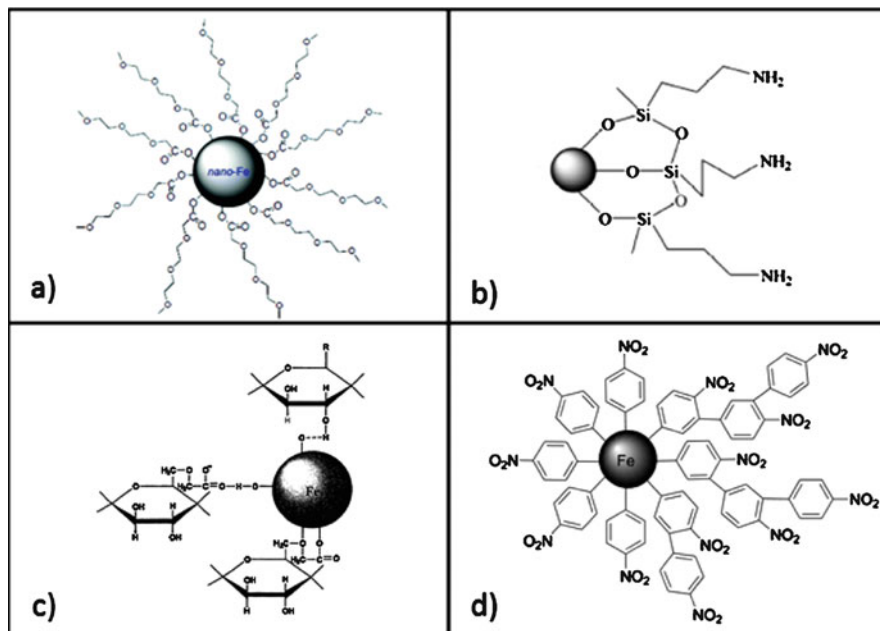
Electrostatic   Steric   Electrosteric
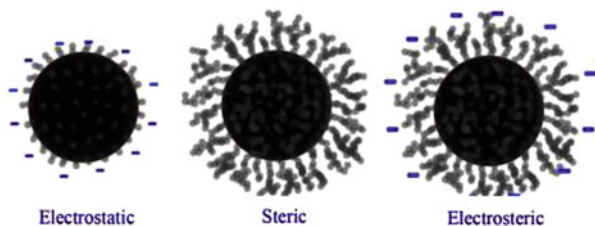
Fig. 2.6 Examples of nZVI surface modified by different surfactants (**a**) methoxyethoxyethoxyacetic acid (MEEA) (adapted from Kharisov et al. 2012 with permission), (**b**) 3-aminopropyltriethoxysilane (APS) (adapted from Liu et al. 2009a with permission), (**c**) carboxymethyl cellulose (CMC) (adapted from Zhao and He 2011 with permission), (**d**) aromatic diazonium salts (ADSs) (adapted from Guselnikova et al. 2015 with permission)

the appropriate surfactant can dramatically enhance the capacity and the colloidal stability. The higher efficiency is attributed not only to the lower extent of agglomeration of the iron particles, but also to the increased local concentration and sorption of the contaminant on the surface of iron (Alessi and Li 2001; Zhang et al. 2002). It has been reported that even the hydrodynamic diameter of the modified particles was increased after modification, their colloidal stability was enhanced, and the activation energy in the transformation of toxic compounds was decreased (Li et al. 2006; Saleh et al. 2005; Lien and Zhang 1999).

2.3.2 Bimetallic Particles

Bimetallic particles of iron with a second less reactive, i.e., usually noble, metal, e.g., Pd/Fe, Ni/Fe, Pt/Fe, Ag/Fe, Cu/Fe, have exhibited a significantly high efficacy for the degradation of many compounds (Chen et al. 2008). The incorporated metal, even in a small amount, can substantially enhance the overall nZVI reaction rate by acting as a catalyst for electron transfer and hydrogenation (Li et al. 2006). The additive metal lowers the activation energy of the reaction and increases the reaction

rate. Thus, bimetallic particles have been involved in applications where bare nZVI usually shows a slow reaction rate, e.g., aromatics and polychlorinated biphenyls (PCBs) (O'Carroll et al. 2013). The doped metals that are chosen in these systems have a much higher redox potential (E^0) than iron. In that way a galvanic cell is formed, i.e., iron acts as an anode, and electron release reactions are accelerated, i.e., the reduction of pollutants is promoted in a higher rate (Elliott and Zhang 2001). Moreover, the additive metal can play an important role in prevention of the surface precipitation of iron oxide products, thus hindering the inhibition of the reactivity of iron. Thereby, iron particles can be more stable on air while those that have lost their surface activity by the degradation of toxic contaminants can be reactivated.

Bimetallic particles can be formed through different methods and different structures can be obtained as it is depicted in the Fig. 2.7. Among the most popular ways of synthesis are counted coating and growing of metal ions around nZVI particles by co-reduction, electrochemical synthesis and inverse micelles, independent nucleation and growth of two kinds of metal species, and the deposition of the noble metal onto the surface of nZVI particles (Liu et al. 2014; Ferrando et al. 2008).

However, a critical point in their application is their potential structural change over the time and the potential environmental risk concerning the addition of one more metal in the aquifer horizon, especially in the case of Ni/Fe nanoparticles.

2.3.3 Emulsification

When there is a need of nZVI application to treatment of dense nonaqueous phase liquid (DNALP) source zones, the best way to be delivered is in emulsified oil–water suspensions (Fig. 2.8). Emulsified nano zerovalent iron (EnZVI) is a biodegradable emulsion, composed of a surfactant, biodegradable vegetable oil, water, and

Fig. 2.7 (**a**) Schematic representation of bimetallic NPs with severe possible structures (*1*) core–shell segregated structures (*2*) heterostructure (*3*) intermetallic or alloyed structures and (*4*) multishell structures (adapted from Liu et al. 2014; Ferrando et al. 2008 with permission) and examples of dimetallic particles based on nZVI (**b**) Si/Fe (adapted from Fernández-Pacheco et al. 2006 with permission), (**c**) Ag/Fe (adapted from Marková et al. 2013 with permission)
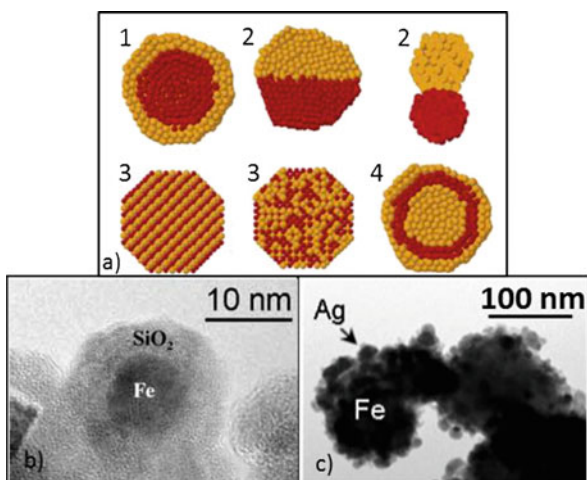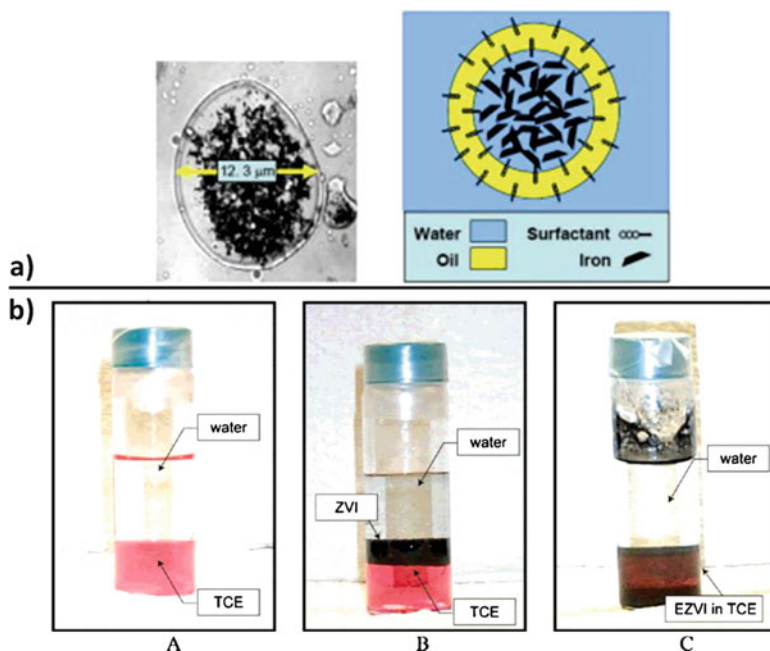
Fig. 2.8 (**a**) Magnified image and schematic illustration of EnZVI (Su et al. 2012) (**b**) Photos showing the dispersion of ZVI and EnZVI in a mixture of water and trichloroethene, TCE, solution dyed with Sudan IV, (*A*) are shown the two distinct phases of water and TCE, (*B*) distinct phases of water and TCE while the ZVI that was added remains separated from the TCE phase, (*C*) distinct phases of water and TCE but EZVI is dispersed in the TCE phase (adapted from Quinn et al. 2005 with permission)

nanoscale or micro-scale zerovalent iron particles in an emulsion (Su et al. 2012; Yang and Chang 2011). In that case, nZVI dispersed in water is surrounded by a liquid oil membrane forming droplets; the droplets then shield nZVI from direct contact with the media into which it is applied to. EnZVI possesses hydrophobic properties, making it miscible with DNALP contaminants. In that context, when the oil emulsion droplet comes in contact with DNALP, DNALP can easily diffuse into the interior place of the droplet where it can interact with nZVI and be degraded. The degradation by-products subsequently diffuse from the droplet out to the aqueous phase (O'Hara et al. 2006). In these systems, vegetable oil and surfactants sequesters some of the organic contaminants and can further serve as electron donors facilitating the total degradation process (Su et al. 2012; Singh and Misra 2015). Application of EnZVI on a large scale has been reported in several real cleanup scenarios mainly focused on organochlorine contaminants. For example, volatile organic compounds, e.g., trichloroethylene (TCE) and tetrachroroethylene (PCE) (Lee et al. 2007), and pesticides, e.g., atrazine and cyanazine (Waria et al. 2009), have been successfully and efficiently removed from subsurface aqueous systems. Namely, in USA almost 10% of the applied nZVI processes is related to the EnZVI, while, in Europe, no such a field application has been reported so far (Mueller et al. 2012). Su et al. (2012)

described the pneumatic and direct injection as two different delivery methods of EnZVI, providing promising results relating to the dechlorination and reductive dechlorination of chlorinated ethenes. Extensive tests by O'Hara et al. (2006) revealed the synergetic removal effect of EnZVI, while the combination of sequestration and abiotic degradation mechanisms driven by the oil emulsion and nZVI, respectively, was found. Moreover, there have been promising results relating to the stability and targetability of nZVI (Sheu et al. 2015). Dong et al. (2015) showed that nZVI in emulsion appears to form fewer aggregates in comparison with bare nZVI, while the oil concentration can be optimized, which leads to an efficient and long-term reactivity toward toxic compounds removal. Furthermore, in a pilot-scale study where a nZVI-emulsified colloidal substrate was used for PCE degradation, Sheu et al. (2016) not only observed the efficient dechlorination after 130 days of operation, but also noticed that the use of the nZVI-emulsified colloidal substrate increased the popolutation of *Dehalococcoides* spp. (DHC) and *Desulfitobacterium* spp. (DSB). The increase of DHC and DSB population promotes the PCE dechlorination process (Grostern and Edwards 2006). It has to be noted that there are some challenges that have to be dealt with in relation to the injection of such particles to a subsurface, e.g., due to the viscosity of these emulsions (Bhattacharjee and Ghoshal 2016). The type of surfactant and the concentrations of all the components, e.g., oil, could be tuned in order to maintain the highest remediation performance. For instance, it was found that ionic surfactants are more preferable than nonionic surfactants since they can lead, to some extent, to the enhancement of the degradation ability of nZVI (Cook 2009).

2.3.4 Using Electrokinetics

Electrokinetic (EK) remediation technology has been applied successfully to many pilot-scale sites for soil and underwater treatment of various organic and inorganic contaminants (Virkutyte et al. 2002; Gomes et al. 2012). An electrokinetic system includes a pair of electrodes and direct-current power imbedded in the soil. A low intensity electric current passes between a cathode and an anode. In that way, different ions, charged particles, and water are moving towards the opposite charged electrode. Mechanisms such as electro-migration, electro-osmosis, electrophoresis, and electrolysis take place (Mulligan et al. 2001; Weng et al. 2006). The contaminants and their byproducts can be collected by electroplating or precipitation/co-precipitation at the electrodesby the generated H_2 and OH^-. In Fig. 2.9a are depicted the electrokinetic phenomena that can occur involving the movement of electricity, charged particles and fluids.

The integration of both techniques, electrokinetics and nZVI, can couple the advantages and increase the benefits regarding water remediation. Among the overall reactions that occur during the application of the electrokinetics, electrolysis reaction of water causes the creation of H^+ and OH^- ions, with the first one to be more mobile. The protons (H^+) are very beneficial to the reaction with ferrous ions
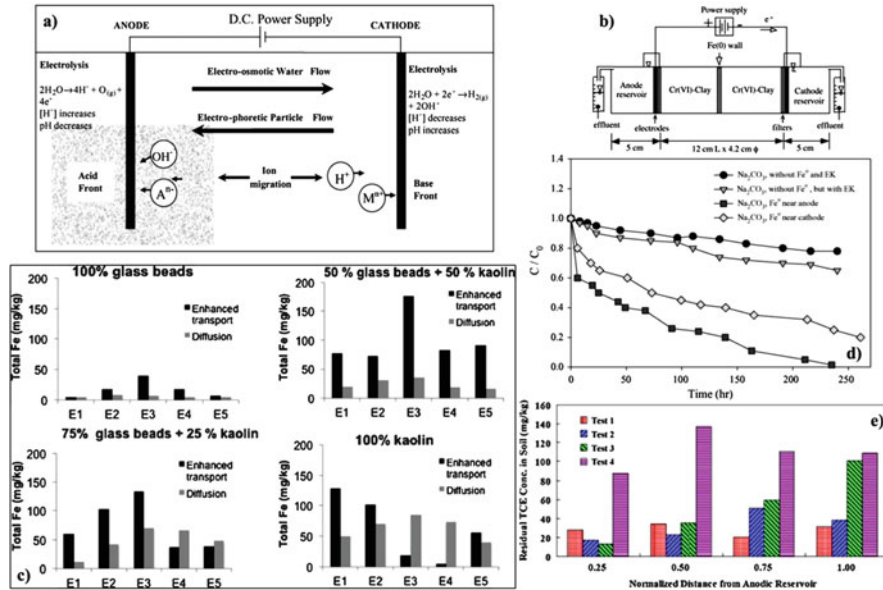
Fig. 2.9 (**a**) Basics of electrokinetic phenomena (adapted from Glendinning et al. (2007) with permission), (**b**) Model of the combination of nZVI and electrokinetics process setup (adapted from Weng et al. (2007) with permission), (**c**) Total iron distribution on the electrophoretic cell (adapted from Gomes et al. (2013) with permission) (**d**) The effect of electrokinetics on water chemistry (adapted from Chang and Cheng (2006) with permission) (**e**) The effect of electrokinetics on TCE removal (adapted from Yang and Chang (2011) with permission)

and in that way they eliminate formation of the iron oxide-passivation layer on nZVI surface, thus extending the operational life of nZVI (Chang and Cheng 2006). Moreover, electro-migration phenomena provide inhibition of sedimentation and aggregation of nZVI, i.e., their mobility and advection is increased (Černík et al. 2019). Subsequently, long-term and high reactivity of nZVI is guaranteed. In Fig. 2.9b is depicted a model example of the merge of the two techniques for hexavalent chromium (Cr(VI)) removal, where nZVI is positioned as a reactive wall and constant electric potential gradient was applied in order to move the electrolyte solution within the soil cell. Weng et al. (2007) showed the successful incorporation of nZVI and EK by presenting the synergetic effect of this combination in hexavalent chromium reduction. Chowdhury et al. (2012) investigated the impact of an external electric field on nZVI mobility in two different porous media. Due to the surface properties of nZVI, the nZVI injection into the media was preferably applied near the cathode. The obtained results revealed the potential of the minimization of nZVI oxidation and the enhancement of nZVI migration when electrokinetics was applied.

Moreover, electrokinetics offers the flexibilty to involve any nZVI based material in such processes. For instance, Reddy et al. (2011) studied the transport and reactivity of aluminum lactate modified nZVI in dinitrotoluene contaminated soils under applied electric potential, showing the altered properties both in mobility and

reactivity terms. Yang and Chang (2011) analyzed the removal efficiency of emulsified nZVI combined with electrokinetic remediation technique, providing promising insights into the application of such integrated methods. Gomes et al. (2013) tested the transport properties of polymer coated nZVI when it is combined with EK, indicating that nZVI mobility in various porous media can be enhanced with the use of direct current.

2.3.5 nZVI Supported on Various Materials

Immobilization and stabilization of highly active nZVI can be achieved by synthetically entrapping them onto a matrix. Aggregation phenomena are reported to be considerably reduced when a matrix or the support material is used for the synthesis of nZVI. In this case, nZVI possesses a higher specific area, colloidal stability, homogeneous dispersion, and narrower size distribution (Ponder et al. 2000). Therefore, supported nZVI display higher activity compared with non-supported systems (Ponder et al. 2001). Additionally, a support material can serve as a "host" for the byproducts that are formed during the nZVI reaction with the pollutants, e.g., degraded pollutant/Fe(III) hydroxides precipitates. Thus, the surface of nZVI remains longer and highly active.

The synthesis and investigation of the stability and mobility of nZVI has been achieved with great results in the presence of various support materials such as clays (Zhang et al. 2012; Üzüm et al. 2009; Wu et al. 2012; Olson et al. 2012), polymer resins (Ponder et al. 2000, 2001), amorphous silica and silica sand (Oh et al. 2007; Dorathi and Kandasamy 2012), exfoliated graphite (Zhang et al. 2006), water-soluble starch (He and Zhao 2005), cationic exchange membranes (Kim et al. 2008), cellulose acetate membranes (Meyer et al. 2004), alginate bead (Kim et al. 2010), activated carbon (Mackenzie et al. 2012), mesoporous silica (OMS) (Li et al. 2011), mesoporous silica microspheres (Qiu et al. 2011), nanostructured silica SBA-15 (Saad et al. 2010), zeolites (Zhang et al. 2002), chitosan (Geng et al. 2009; Liu et al. 2012), graphene, and ordered mesoporous carbon (Ling et al. 2012). In Table 2.3 are listed some of the support materials and their functions that have been used according the literature; in Fig. 2.10 are shown some results that compare the efficacy of bare nZVI with supported nZVI.

Besides the benefits that arise from limiting the aggregation of nZVI, synergetic effects can boost the total degradation ability of these materials even more (Table 2.4). When an appropriate support material is used, absorption; reduction; or photocatalytic properties can be added and multiply the effects. Thus, the use of a support material is a matter of high technological importance because it can extend the use and sustainability of nZVI. Moreover, the range of the targeted pollutants can be widened, involving nZVI in a larger variety of environmental scenarios.

Table 2.3 Various nZVI support materials and their function (Zhou et al. 2016)

| Modified material	Function
Silica	Protect the particles from intersystem dipolar interactions; provide numerous hydroxyl groups on the surface as active sites
Quercetin	Form complexes with some metal ions
Silver zeolite	High reactivity (e.g., antimicrobial activity) and good thermal stability; cation exchange and adsorption
Bifunctional polymer (outer PEO and inner PPO)	Outer hydrophilic region for colloidal stability and an inner hydrophobic region for solubilization of organic compounds
AMT-TMSPT	To form a stable complex with soft transition metal ions (e.g., Ag and Cd).
CTAB and CPC	Retain analytes by strong hydrophobic and electrostatic interactions
PV3A	Reduce particle size, ζ-potential, isoelectric point
Graphene	Have excellent mechanical, electrical, thermal, and optical properties and very high specific surface area; to form a strong π-π stacking interaction with the benzene ring
PDA	Offer biocompatibility, dispersibility in water, multifunctional groups (amino and catechol groups), and provide π-π stacking interaction to targets
PDMS	Full of functional groups such as hydrocarbyl, high biocompatibility, hydrophobic
PNIPAM	Thermosensitive, change the morphology by controlling temperature to accomplish the release of target compounds
MOFs	Possess extremely large surface area, low density, microporosity, easily designed or modified to have different pore sizes, and regarded as promising candidates for storage, separation, and catalysis
Chitosan	Hydrophilic, biocompatible, and biodegradable; full of amino groups, can form a chelate complexes with heavy metal ions
Clay	Large surface area, hydrophilic, widely available, inexpensive and safe
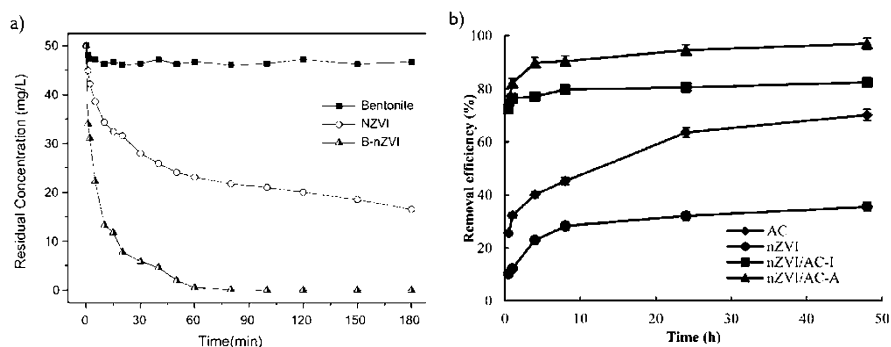
Fig. 2.10 Enhanced removal ability of nZVI (**a**) towards Cr(VI), B-nZVI: nZVI supported on bentonite (adapted from Shi et al. 2011 with permission), (**b**) towards hexachlorobenzene (HCB), nZVI/AC: nZVI supported on activated carbon (I and A refer to different processes followed for loading of iron on activated carbon) (adapted from Chen et al. 2014 with permission)

Table 2.4 Summary of examples of the nZVI modifications and their properties

Modified nZVI	Beneficial features/added properties
nZVI supported on mesoporous silica (Petala et al. 2013)	Elimination of agglomeration, high surface area and reactivity
nZVI supported on biochar (Dong et al. 2017)	Alleviation of passivation, biochar acts as a scavenger for byproducts such as Cr(III)/Fe (III) hydroxides, enhanced remediation ability
nZVI modified with sodium dodecyl sulfate (SDS, an anionic surfactant) (Huang et al. 2015)	High stabilization (less aggregation and sedimentation), higher remediation ability
nZVI/chitosan (Jin et al. 2016)	Avoidance of agglomeration and air-oxidation
nZVI/titanium oxide (Petala et al. 2016)	Synergetic photocatalytic and reductive properties
nZVI/activated carbon (Tseng et al. 2011)	Combination of physical adsorption capacity and dechlorination destructive capacities
nZVI/amphiphilic polysiloxane graft copolymers (Krajangpan et al. 2012)	Higher remediation ability, higher dispersibility, colloidal stability

2.4   Remediation Using nZVI

While nZVI has been widely used for site remediation in USA since the beginning of the new millennium, the number of full-scale remediations employing nZVI is lower in Europe (Mueller et al. 2012). Nevertheless, there is an increasing tendency to use nZVI as a novel in situ reduction technology and this material has become a well-known reagent for many environmental consultants. Although RNIP particles (Toda Kogyo Corp., Japan) have been applied to a few pilot-scale applications over the past 20 years, NANOFER nZVI (NANO IRON s.r.o., Czech Republic) is the only commercially produced nanoscale ZVI used for groundwater remediation in Europe nowadays. It has been used to treat over twenty sites, mainly in Belgium, France, Switzerland, Spain, Portugal, Italy, Denmark and the Czech Republic (Bardos et al. 2018).

Despite the great number of laboratory studies focused on pollutant removal by nZVI published in the form of scientific papers, the number of the articles documenting the full-scale or at least pilot-scale applications of nZVI is much smaller. Their summary is provided in Table 2.5. What can account for such a lack of literary sources could be the (hydro)geological as well as geochemical complexity of groundwater and soil on site (i.e., leading to much higher degree of uncertainty than in case of laboratory tests under the well-defined conditions) complicating interpretation of the observed results (Litter et al. 2018).

The first documented pilot application of nZVI (in form of Fe/Pd bimetallic nanoparticles) was performed by the pioneers of this technology, D. W. Elliott and W. Zhang, in 2001 (Elliott and Zhang 2001). In the area of an active industrial zone in Trenton, New Jersey, 1.7 kg of nZVI was fed by gravity through infiltration wells within 2 days. The concentration of PCE (target contaminant; initial concentration up to 800 μg/L) was reduced by 96% in 1 month after the application. Since that time, bimetallic or bare nZVI has been used in plenty of pilot tests in USA but only

some of them have been summarized with the results published in scientific journals (see Table 2.5). In most cases, nanoparticles were prepared directly on site using reduction of ferric salt by borohydride and only small amount of nZVI (less than 20 kg) was applied. The researchers focused not only on the remediation efficiency of nanoparticles (Glazier et al. 2003; Bennett et al. 2010; Chowdhury et al. 2015) but also on their migration ability and influence on microbial communities (Bennett et al. 2010; Kocur et al. 2014, 2015).

A pilot-scale application of nZVI in Marine Corps Depot former dry cleaners on Parris Island, South Carolina, was unique by its scale among other published pilot tests. Total amount of 275 kg of RNIP nZVI was emulsified with corn oil and surfactant in order to enhance its mobility in the subsurface. The emulsion was applied deploying two methods—pneumatic injection and direct injection. The authors described the effects of nZVI on CHCs levels in the first paper (Su et al. 2012), and transport and transformation of the nanoparticles in the second one (Su et al. 2013).

The use of nZVI for Cr(VI) reduction in a pilot in situ remediation was recently reported (Němeček et al. 2015). The polluted site is located in the northern part of the Czech Republic where potassium dichromate spread from the leather processing plant. Prior to the treatment of the site, the Cr(VI) concentration in the soil, accounting for up to 46 mg/kg, prevailed over those in the groundwater (3 mg/L). The contaminated aquifer is situated in the quaternary sands and gravels with clayey admixtures and the water table was found 4.5–5.5 m bgl (aquifer thickness about 5 m). The groundwater flows with a velocity 0.2–2 m per day and discharges into a river 500 m away. In August 2012, 120 kg of nZVI (NANOFER 25 from NANO IRON s.r.o., Czech Republic) was applied to the saturated contaminated zone through three injection wells situated perpendicularly to the groundwater flow with spacing of 2.8 m (i.e., configuration of the injected geochemical barrier). Another four monitoring wells (1 of them up-gradient and 3 down-gradient) has been drilled at the site and the evolution of selected physico-chemical parameters and changes in Cr(VI) contamination level were monitored before and after the nZVI. The nZVI application resulted in an immediate decrease in the redox potential down to −484 mV (within 1 day), followed by a rapid decrease in the concentration of both Cr(VI) and total Cr. The rapid reductive effect of nZVI was observed at a distance of 7 m down-gradient.

A similar approach, which seems to be highly promising due to the partial regeneration of the applied nZVI through successive abiotic and biotic reduction steps, was applied by the same authors at another site in the Czech Republic (Němeček et al. 2016). In this case, the aquifer is located in quaternary sandy gravel with silty admixtures and overlaid by clay and clayey loam. It is approx. 4 m thick and drained by the groundwater flow equal to 1.5 m per day into a river at the distance of 430 m. The groundwater was contaminated with Cr(VI) (4–57 mg/L) and TCE/cis-DCE (400–6000 µg/L of sum of CHCs) as a consequence of the historical chromium coating industrial activities. Two types of nZVI particles (20 kg of NANOFER STAR followed by another 20 kg of NANOFER 25S, both from NANO IRON s.r.o., Czech Republic) were applied by direct push technology during

Table 2.5 Summary of the pilot applications of nZVI as published in the scientific literature before 2018

Year of publication	Name of the site	State, province	Type of nZVI (additional substrate)	Amount of ZVI	Application method	Target contaminant	Aquifer description	Reference
2001	Trenton	New Jersey, USA	Borohydride-nZVI with palladium	1.7 kg	Fed by gravity through infiltration wells	TCE		Elliott and Zhang (2001)
2003	Research Triangle Park	North Carolina, USA	Borohydride-nZVI	11.2 kg	Pressure injection through permanent well	CHCs	Distinct, stacked, and repeating sedimentary packages consisting of sandstone grading and fining upward into siltstone	Glazier et al. (2003) and Zhang (2003)
2010	San Francisco Bay	California, USA	Borohydride-nZVI and borohydride-Fe/Pd (0.1 wt%) (CMC)	0.248 kg	Single well push-pull test	TCE	Holocene and Pleistocene alluvial sediments, predominantly silts and clays, and coarse-grained sediments	Bennett et al. (2010)
2010	Kaohsiung	Taiwan	Borohydride-Fe/Pd (1 wt%), Fe/Pd (1 wt%) from Lehigh nanotech, LLC	60 kg	Fed by gravity through infiltration wells	VC	Unconfined aquifer, composed of medium to coarse sand and few silt	Wei et al. (2010)
2012, 2013	Parris Island	South Carolina, USA	RNIP (corn oil)	275 kg	Pneumatic injection and direct-push	CHCs	Shallow, unconfined aquifer generally consisting of permeable, fine to medium, Pleistocene age sand	Su et al. (2012, 2013)
2014, 2015	Sarnia	Ontario, Canada	Borohydride-nZVI (CMC)	0.75 kg	Fed by gravity through infiltration wells	CHCs	Brown weathered clay, underlain by gray clay	Kocur et al. (2014, 2015)

Table 2.5 (continued)

| Year of publication	Name of the site	State, province	Type of nZVI (additional substrate)	Amount of ZVI	Application method	Target contaminant	Aquifer description	Reference
2015	London	Ontario, Canada	Borohydride-nZVI (CMC)	0.142 kg	Fed by gravity through infiltration wells	TCE	Sand and gravel fill or brown reworked silty sand containing sand and silt	Chowdhury et al. (2015)
2014, 2015	Hrádek nad Nisou	Czech Republic	NANOFER 25 (whey)	120 kg	Pressure injection through permanent wells	Cr(VI)	Quaternary sands and gravels with clayey admixtures	Němeček et al. (2014, 2015)
2016	—	Czech Republic	NANOFER 25S, NANOFER STAR (whey)	40 kg	Direct-push	Cr(VI), CHCs	Quaternary sandy gravels with silty admixture	Němeček et al. (2016)
2016	Wonju	South Korea	NANOFER 25S	30 kg	Injection through a packer	TCE	Unconsolidated soil layer, weathered rock, and an intact Jurassic biotite granite bottom zone	Ahn et al. (2016)
2017	Hruševo	Slovenia	NANOFER 25, NANOFER STAR, borohydride-nZVI	From 0.5 to 5 g/L in a dynamic operation mode	Treatment of effluent from an existing waste water treatment plant	Heavy metals, nitrogen in various forms, bacteria	—	Oprčkal et al. (2017)
2017	Jiangxi	China	Borohydride-nZVI	Approx. 0.462 g/L in a continuous operation mode (running for 120 days)	nZVI reactors connected to the existing waste water treatment plant	Heavy metals	—	Li et al. (2017)
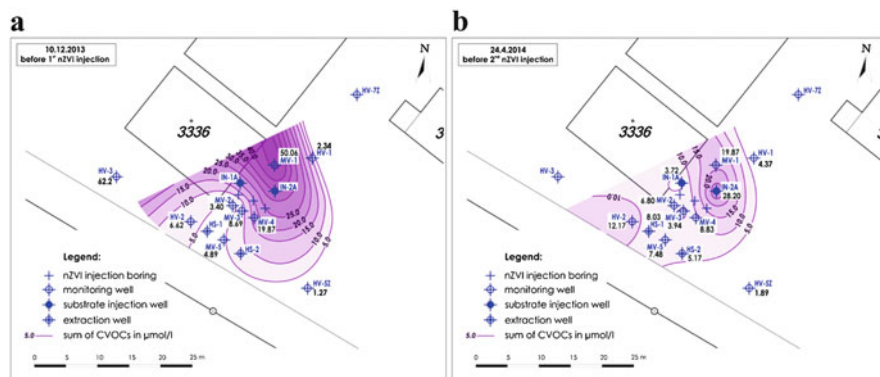
Fig. 2.11 Evolution of chlorinated VOCs (CHCs) concentration in the groundwater (**a**) before and (**b**) after the first nZVI application (adapted from Němeček et al. 2016 with permission)
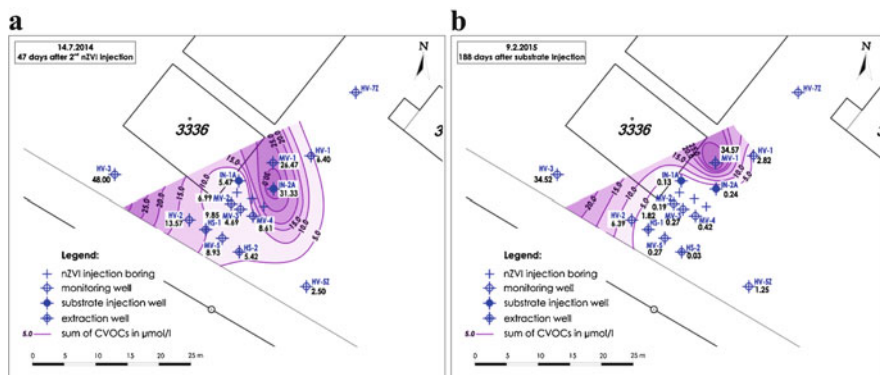

Fig. 2.12 Evolution of CVOCs (CHCs) concentration in the groundwater (**a**) before and (**b**) after the second nZVI application (adapted from Němeček et al. 2016 with permission)

the period of 4 months into the three boreholes situated perpendicularly to the groundwater flow. In the second step, the whey was applied a few months later using a circulation system resulting in 60 mg/L of TOC in the groundwater. The application of nZVI caused a decrease in the redox to below −400 mV, subsequently stabilized at 50–100 mV after the injection of whey. The evolution of chlorinated volatile organic compounds concentration during the pilot test is presented in Figs. 2.11 and 2.12.

Another pilot application of NANOFER particles was performed in South Korea (Ahn et al. 2016). nZVI was injected into the groundwater in order to treat TCE source in the aquifer of the Road Maintenance Office. Except the evaluation of the nZVI effectivity in the groundwater, the authors focused on the effect of nitrate and DO on TCE reduction and studied also reactive lifetime of injected nZVI particles. The application resulted in removal of >95% of the total TCE in 60 days. The

undesirable reactions of nZVI with dissolved oxygen and nitrates were identified as contributing to Fe(0) consumption to a large extent. The reactive lifetime of the nanoparticles at the site was found to be at least 103 days but some residual Fe (0) was proved to be present on site even after 165 days.

Not only were pilot trials on the in situ groundwater remediation reported, but also the usage of nZVI for waste water treatment was documented. A Slovenian research team investigated the effects of different nZVI particles (NANOFER 25, NANOFER STAR and borohydride-nZVI) on metal, bacteria and content of nitrogen in a real effluent water from a small biological wastewater treatment plant (Oprčkal et al. 2017). This work showed that there can be a risk of releasing trace elements into the water if these are bound to nZVI particles. Therefore, careful optimization of the iron load, and of the mixing and settling times, is necessary for the efficient process optimization. Despite in-house nZVI being the most efficient at inactivating pathogenic bacteria, these nanoparticles are not appropriate for remediation since it was found that the high levels of B and Na, originating from the $NaBH_4$ used for their synthesis, contaminated the remediated water. The NANOFER 25 slurry most effectively removed potentially toxic elements and at optimal mixing and settling times (400 and 180 min, respectively) effectively disinfected effluent water at a low (0.5 g/L) iron load.

In another study, a full-scale application of nZVI for heavy metal removal from waste water of the Jiangxi Copper Company, China, has been reported (Li et al. 2017). The waste water was contaminated predominantly with Cu, Ni, Zn, Pb, As, Se and Sb. Borohydride-reduced nZVI was applied in 5 m × 5 m × 3 m separated modules connected to the existing waste water treatment plant. The performance of the technology over 120 days proved that nZVI acted as a highly efficient reagent (>99.5% removal of key metals with capacities of 245 mg and 226 mg of As and Cu per 1 g of nZVI, respectively) providing a low redox potential and subsequent separation of metals. The advantage of such a technology lies in the fact that nZVI keeps a low redox condition in the closed reactors, lowering the required nZVI demand over time (>12 months) with partial recycling of nZVI.

References

Ahn J-Y, Kim C, Kim H-S, Hwang K-Y, Hwang I (2016) Effects of oxidants on *in situ* treatment of a DNAPL source by nanoscale zero-valent iron: a field study. Water Res 107:57–65. https://doi.org/10.1016/j.watres.2016.10.037

Alessi DS, Li Z (2001) Synergistic effect of cationic surfactants on perchloroethylene degradation by zero-valent iron. Environ Sci Technol 35(18):3713–3717. https://doi.org/10.1021/es010564i

Applegate JS, Laitos JG (2006) Environmental law: RCRA, CERCLA, and the management of hazardous waste. Foundation Press, New York

Bard AJ, Parsons R, Jordan J (eds) (1985) Standard potentials in aqueous solution, 1st edn. CRC Press, New York

Bardos P, Merly C, Kvapil P, Koschitzky H-P (2018) Status of nanoremediation and its potential for future deployment: risk-benefit and benchmarking appraisals. Remediat J 28(3):43–56. https://doi.org/10.1002/rem.21559

Bennett P, He F, Zhao D, Aiken B, Feldman L (2010) In situ testing of metallic iron nanoparticle mobility and reactivity in a shallow granular aquifer. J Contam Hydrol 116(1–4):35–46. https://doi.org/10.1016/j.jconhyd.2010.05.006

Berge ND, Ramsburg CA (2009) Oil-in-water emulsions for encapsulated delivery of reactive iron particles. Environ Sci Technol 43(13):5060–5066. https://doi.org/10.1021/es900358p

Bhattacharjee S, Ghoshal S (2016) Phase transfer of palladized nanoscale zerovalent iron for environmental remediation of trichloroethene. Environ Sci Technol 50(16):8631–8639. https://doi.org/10.1021/acs.est.6b01646

Černík M, Nosek J, Filip J, Hrabal J, Elliott DW, Zbořil R (2019) Electric-field enhanced reactivity and migration of iron nanoparticles with implications for groundwater treatment technologies: proof of concept. Water Res 154:361–369. https://doi.org/10.1016/j.watres.2019.01.058

Chang J-H, Cheng S-F (2006) The remediation performance of a specific electrokinetics integrated with zero-valent metals for perchloroethylene contaminated soils. J Hazard Mater 131 (1–3):153–162. https://doi.org/10.1016/j.jhazmat.2005.09.026

Chen L-H, Huang C-C, Lien H-L (2008) Bimetallic iron–aluminum particles for dechlorination of carbon tetrachloride. Chemosphere 73(5):692–697. https://doi.org/10.1016/j.chemosphere.2008.07.005

Chen L, Jin S, Fallgren PH, Swoboda-Colberg NG, Liu F, Colberg PJS (2012) Electrochemical depassivation of zero-valent iron for trichloroethene reduction. J Hazard Mater 239-240:265–269. https://doi.org/10.1016/j.jhazmat.2012.08.074

Chen W-F, Pan L, Chen L-F, Wang Q, Yan C-C (2014) Dechlorion of hexachlorobenzene by nano zero-valent iron/activated carbon composite: iron loading, kinetics and pathway. RSC Adv 4(87):46689–46696. https://doi.org/10.1039/C4RA06760F

Chowdhury AIA, O'Carroll DM, Xu Y, Sleep BE (2012) Electrophoresis enhanced transport of nano-scale zero valent iron. Adv Water Resour 40:71–82. https://doi.org/10.1016/j.advwatres.2012.01.014

Chowdhury AIA, Krol MM, Kocur CM, Boparai HK, Weber KP, Sleep BE, O'Carroll DM (2015) nZVI injection into variably saturated soils: field and modeling study. J Contam Hydrol 183:16–28. https://doi.org/10.1016/j.jconhyd.2015.10.003

Cook SM (2009) Assessing the use and application of zero-valent iron nanoparticle technology for remediation at contaminated sites. Report for the U.S. Environmental Protection Agency. Available via https://clu-in.org/download/studentpapers/Zero-Valent-Iron-Cook.pdf. Accessed 13 Jul 2019

Correia de Velosa A, Pupo Nogueira RF (2013) 2,4-Dichlorophenoxyacetic acid (2,4-D) degradation promoted by nanoparticulate zerovalent iron (nZVI) in aerobic suspensions. J Environ Manag 121:72–79. https://doi.org/10.1016/j.jenvman.2013.02.031

Crane RA, Scott TB (2012) Nanoscale zero-valent iron: future prospects for an emerging water treatment technology. J Hazard Mater 211–212:112–125. https://doi.org/10.1016/j.jhazmat.2011.11.073

Dong J, Wen C, Liu D, Zhang W, Li J, Jiang H, Qin C, Hong M (2015) Study on degradation of nitrobenzene in groundwater using emulsified nano-zero-valent iron. J Nanopart Res 17:31. https://doi.org/10.1007/s11051-014-2829-9

Dong H, Deng J, Xie Y, Zhang C, Jiang Z, Cheng Y, Hou K, Zeng G (2017) Stabilization of nanoscale zero-valent iron (nZVI) with modified biochar for Cr(VI) removal from aqueous solution. J Hazard Mater 332:79–86. https://doi.org/10.1016/j.jhazmat.2017.03.002

Dorathi PJ, Kandasamy P (2012) Dechlorination of chlorophenols by zero valent iron impregnated silica. J Environ Sci 24(4):765–773. https://doi.org/10.1016/S1001-0742(11)60817-6

Elliott DW, Zhang W-X (2001) Field assessment of nanoscale bimetallic particles for groundwater treatment. Environ Sci Technol 35(24):4922–4926. https://doi.org/10.1021/es0108584

Elsner M, Hofstetter TB (2011) Current perspectives on the mechanisms of chlorohydrocarbon degradation in subsurface environments: insight from kinetics, product formation, probe molecules, and isotope fractionation. In: Tratnyek PG, Grundl TJ, Haderlein SB (eds) Aquatic redox

chemistry, ACS symposium series, vol 1071. American Chemical Society, Washington, DC, pp 407–439. https://doi.org/10.1021/bk-2011-1071.ch019

European Commission (2019) Soil – Environment – European Commission. http://ec.europa.eu/environment/soil/index_en.htm. Accessed 13 July 2019

European Environment Agency (2014) Progress in management of contaminated sites. European Environment Agency, Copenhagen

Fernández-Pacheco R, Arruebo M, Marquina C, Ibarra R, Arbiol J, Santamaría J (2006) Highly magnetic silica-coated iron nanoparticles prepared by the arc-discharge method. Nanotechnology 17:1188–1192. https://doi.org/10.1088/0957-4484/17/5/004

Ferrando R, Jellinek J, Johnston RL (2008) Nanoalloys: from theory to applications of alloy clusters and nanoparticles. Chem Rev 108(3):845–910. https://doi.org/10.1021/cr040090g

Fu F, Dionysiou D, Liu H (2014) The use of zero-valent iron for groundwater remediation and wastewater treatment: a review. J Hazard Mater 267:194–205. https://doi.org/10.1016/j.jhazmat.2013.12.062

Geng B, Jin Z, Li T, Qi X (2009) Kinetics of hexavalent chromium removal from water by chitosan-Fe^0 nanoparticles. Chemosphere 75(6):825–830. https://doi.org/10.1016/j.chemosphere.2009.01.009

Gillham RW, O'Hannesin SF (1994) Enhanced degradation of halogenated aliphatics by zero-valent iron. Groundwater 32(6):958–967. https://doi.org/10.1111/j.1745-6584.1994.tb00935.x

Glazier R, Venkatakrishnan R, Gheorghiu F, Walata L, Nash R, Zhang W (2003) Nanotechnology takes root. Civ Eng 73(5):64–69. https://cedb.asce.org/CEDBsearch/record.jsp?dockey=0136224

Glendinning S, Lamont-Black J, Jones CJFP (2007) Treatment of sewage sludge using electrokinetic geosynthetics. J Hazard Mater 139(3):491–499. https://doi.org/10.1016/j.jhazmat.2006.02.046

Gomes HI, Dias-Ferreira C, Ribeiro AB (2012) Electrokinetic remediation of organochlorines in soil: enhancement techniques and integration with other remediation technologies. Chemosphere 87(10):1077–1090. https://doi.org/10.1016/j.chemosphere.2012.02.037

Gomes HI, Dias-Ferreira C, Ribeiro AB, Pamukcu S (2013) Enhanced transport and transformation of zerovalent nanoiron in clay using direct electric current. Water Air Soil Pollut 224:1710. https://doi.org/10.1007/s11270-013-1710-2

Grostern A, Edwards EA (2006) Growth of *Dehalobacter* and *Dehalococcoides* spp. during degradation of chlorinated ethanes. Appl Environ Microbiol 72(1):428–436. https://doi.org/10.1128/AEM.72.1.428-436.2006

Gu H, Stanway D (2017) China needs patience to fight costly war against soil pollution: government. Reuters

Guselnikova OA, Galanov AI, Gutakovskii AK, Postnikov PS (2015) The convenient preparation of stable aryl-coated zerovalent iron nanoparticles. Beilstein J Nanotechnol 6:1192–1198. https://doi.org/10.3762/bjnano.6.121

He F, Zhao D (2005) Preparation and characterization of a new class of starch-stabilized bimetallic nanoparticles for degradation of chlorinated hydrocarbons in water. Environ Sci Technol 39 (9):3314–3320. https://doi.org/10.1021/es048743y

Huang D-L, Chen G-M, Zeng G-M, Xu P, Yan M, Lai C, Zhang C, Li N-J, Cheng M, He X-X, He Y (2015) Synthesis and application of modified zero-valent iron nanoparticles for removal of hexavalent chromium from wastewater. Water Air Soil Pollut 226:375. https://doi.org/10.1007/s11270-015-2583-3

Jia H, Gu C, Boyd SA, Teppen BJ, Johnston CT, Song C, Li H (2011) Comparison of reactivity of nanoscaled zero-valent iron formed on clay surfaces. Soil Sci Soc Am J 75(2):357–364. https://doi.org/10.2136/sssaj2010.0080nps

Jin X, Zhuang Z, Yu B, Chen Z, Chen Z (2016) Functional chitosan-stabilized nanoscale zero-valent iron used to remove acid fuchsine with the assistance of ultrasound. Carbohydr Polym 136:1085–1090. https://doi.org/10.1016/j.carbpol.2015.10.002

Kanel SR, Choi H (2007) Transport characteristics of surface-modified nanoscale zero-valent iron in porous media. Water Sci Technol 55(1–2):157–162. https://doi.org/10.2166/wst.2007.002

Keenan CR, Sedlak DL (2008) Ligand-enhanced reactive oxidant generation by nanoparticulate zero-valent iron and oxygen. Environ Sci Technol 42(18):6936–6941. https://doi.org/10.1021/es801438f

Keum Y-S, Li QX (2004) Reduction of nitroaromatic pesticides with zero-valent iron. Chemosphere 54(3):255–263. https://doi.org/10.1016/j.chemosphere.2003.08.003

Kharisov BI, Rasika Dias HV, Kharissova OV, Jiménez-Pérez VM, Olvera Pérez B, Muñoz Flores B (2012) Iron-containing nanomaterials: synthesis, properties, and environmental applications. RSC Adv 2(25):9325–9358. https://doi.org/10.1039/C2RA20812A

Kim H, Hong H-J, Lee Y-J, Shin H-J, Yang J-W (2008) Degradation of trichloroethylene by zero-valent iron immobilized in cationic exchange membrane. Desalination 223(1–3):212–220. https://doi.org/10.1016/j.desal.2007.03.015

Kim H-J, Phenrat T, Tilton RD, Lowry GV (2009) Fe^0 nanoparticles remain mobile in porous media after aging due to slow desorption of polymeric surface modifiers. Environ Sci Technol 43 (10):3824–3830. https://doi.org/10.1021/es802978s

Kim H, Hong H-J, Jung J, Kim S-H, Yang J-W (2010) Degradation of trichloroethylene (TCE) by nanoscale zero-valent iron (nZVI) immobilized in alginate bead. J Hazard Mater 176 (1–3):1038–1043. https://doi.org/10.1016/j.jhazmat.2009.11.145

Kocur CM, Chowdhury AI, Sakulchaicharoen N, Boparai HK, Weber KP, Sharma P, Krol MM, Austrins L, Peace C, Sleep BE, O'Carroll DM (2014) Characterization of nZVI mobility in a field scale test. Environ Sci Technol 48(5):2862–2869. https://doi.org/10.1021/es4044209

Kocur CMD, Lomheim L, Boparai HK, Chowdhury AIA, Weber KP, Austrins LM, Edwards EA, Sleep BE, O'Carroll DM (2015) Contributions of abiotic and biotic dechlorination following carboxymethyl cellulose stabilized nanoscale zero valent iron injection. Environ Sci Technol 49 (14):8648–8656. https://doi.org/10.1021/acs.est.5b00719

Krajangpan S, Kalita H, Chisholm BJ, Bezbaruah AN (2012) Iron nanoparticles coated with amphiphilic polysiloxane graft copolymers: dispersibility and contaminant treatability. Environ Sci Technol 46(18):10130–10136. https://doi.org/10.1021/es3000239

Lee Y-C, Kwon T-S, Yang J-S, Yang J-W (2007) Remediation of groundwater contaminated with DNAPLs by biodegradable oil emulsion. J Hazard Mater 140(1–2):340–345. https://doi.org/10.1016/j.jhazmat.2006.09.036

Li T, Farrell J (2001) Electrochemical investigation of the rate-limiting mechanisms for trichloroethylene and carbon tetrachloride reduction at iron surfaces. Environ Sci Technol 35 (17):3560–3565. https://doi.org/10.1021/es0019878

Li X-Q, Elliott DW, Zhang W-X (2006) Zero-valent iron nanoparticles for abatement of environmental pollutants: materials and engineering aspects. Crit Rev Solid State Mater Sci 31 (4):111–122. https://doi.org/10.1080/10408430601057611

Li J, Li H, Zhu Y, Hao Y, Sun X, Wang L (2011) Dual roles of amphiphilic triblock copolymer P123 in synthesis of α-Fe nanoparticle/ordered mesoporous silica composites. Appl Surf Sci 258 (2):657–661. https://doi.org/10.1016/j.apsusc.2011.07.037

Li XN, Jiao WT, Xiao RB, Chen WP, Chang AC (2015) Soil pollution and site remediation policies in China: a review. Environ Rev 23(3):263–274. https://doi.org/10.1139/er-2014-0073

Li S, Wang W, Liang F, W-x Z (2017) Heavy metal removal using nanoscale zero-valent iron (nZVI): theory and application. J Hazard Mater 322:163–171. https://doi.org/10.1016/j.jhazmat.2016.01.032

Lien H-L, Zhang W-X (1999) Transformation of chlorinated methanes by nanoscale iron particles. J Environ Eng 125(11):1042–1047. https://doi.org/10.1061/(ASCE)0733-9372(1999)125:11(1042)

Ling X, Li J, Zhu W, Zhu Y, Sun X, Shen J, Han W, Wang L (2012) Synthesis of nanoscale zero-valent iron/ordered mesoporous carbon for adsorption and synergistic reduction of nitrobenzene. Chemosphere 87(6):655–660. https://doi.org/10.1016/j.chemosphere.2012.02.002

Ling L, Huang X, Li M, Zhang W (2017) Mapping the reactions in a single zero-valent Iron nanoparticle. Environ Sci Technol 51(24):14293–14300. https://doi.org/10.1021/acs.est.7b02233

Litter MI, Quici N, Meichtry M (eds) (2018) Iron nanomaterials for water and soil treatment, 1st edn. Pan Stanford Publishing, Singapore

Liu Y, Majetich SA, Tilton RD, Sholl DS, Lowry GV (2005) TCE dechlorination rates, pathways, and efficiency of nanoscale iron particles with different properties. Environ Sci Technol 39 (5):1338–1345. https://doi.org/10.1021/es049195r

Liu Y, Phenrat T, Lowry GV (2007) Effect of TCE concentration and dissolved groundwater solutes on NZVI-promoted TCE dechlorination and H2 evolution. Environ Sci Technol 41:7881–7887. https://doi.org/10.1021/es0711967

Liu Q, Bei Y, Zhou F (2009a) Removal of lead(II) from aqueous solution with amino-functionalized nanoscale zero-valent iron. Cent Eur J Chem 7(1):79–82. https://doi.org/10.2478/s11532-008-0097-1

Liu T, Rao P, Lo IMC (2009b) Influences of humic acid, bicarbonate and calcium on Cr (VI) reductive removal by zero-valent iron. Sci Total Environ 407(10):3407–3414. https://doi.org/10.1016/j.scitotenv.2009.01.043

Liu T, Wang Z-L, Zhao L, Yang X (2012) Enhanced chitosan/Fe^0-nanoparticles beads for hexavalent chromium removal from wastewater. Chem Eng J 189–190:196–202. https://doi.org/10.1016/j.cej.2012.02.056

Liu W-J, Qian T-T, Jiang H (2014) Bimetallic Fe nanoparticles: recent advances in synthesis and application in catalytic elimination of environmental pollutants. Chem Eng J 236:448–463. https://doi.org/10.1016/j.cej.2013.10.062

Mackenzie K, Bleyl S, Georgi A, Kopinke F-D (2012) Carbo-iron – an Fe/AC composite – as alternative to nano-iron for groundwater treatment. Water Res 46(12):3817–3826. https://doi.org/10.1016/j.watres.2012.04.013

Marková Z, Šišková KM, Filip J, Čuda J, Kolář M, Šafářová K, Medřík I, Zbořil R (2013) Air stable magnetic bimetallic Fe–Ag nanoparticles for advanced antimicrobial treatment and phosphorus removal. Environ Sci Technol 47(10):5285–5293. https://doi.org/10.1021/es304693g

Meyer DE, Wood K, Bachas LG, Bhattacharyya D (2004) Degradation of chlorinated organics by membrane-immobilized nanosized metals. Environ Prog 23(3):232–242. https://doi.org/10.1002/ep.10031

Morales J, Hutcheson R, Cheng IF (2002) Dechlorination of chlorinated phenols by catalyzed and uncatalyzed Fe(0) and Mg(0) particles. J Hazard Mater 90(1):97–108. https://doi.org/10.1016/S0304-3894(01)00336-3

Mueller NC, Braun J, Bruns J, Černík M, Rissing P, Rickerby D, Nowack B (2012) Application of nanoscale zero valent iron (NZVI) for groundwater remediation in Europe. Environ Sci Pollut Res 19(2):550–558. https://doi.org/10.1007/s11356-011-0576-3

Mulligan CN, Yong RN, Gibbs BF (2001) Remediation technologies for metal-contaminated soils and groundwater: an evaluation. Eng Geol 60(1–4):193–207. https://doi.org/10.1016/S0013-7952(00)00101-0

Němeček J, Lhotský O, Cajthaml T (2014) Nanoscale zero-valent iron application for in situ reduction of hexavalent chromium and its effects on indigenous microorganism populations. Sci Total Environ 485–486:739–747. https://doi.org/10.1016/j.scitotenv.2013.11.105

Němeček J, Pokorný P, Lacinová L, Černík M, Masopustová Z, Lhotský O, Filipová A, Cajthaml T (2015) Combined abiotic and biotic in-situ reduction of hexavalent chromium in groundwater using nZVI and whey: a remedial pilot test. J Hazard Mater 300:670–679. https://doi.org/10.1016/j.jhazmat.2015.07.056

Němeček J, Pokorný P, Lhotský O, Knytl V, Najmanová P, Steinová J, Černík M, Filipová A, Filip J, Cajthaml T (2016) Combined nano-biotechnology for in-situ remediation of mixed contamination of groundwater by hexavalent chromium and chlorinated solvents. Sci Total Environ 563–564:822–834. https://doi.org/10.1016/j.scitotenv.2016.01.019

O'Carroll D, Sleep B, Krol M, Boparai H, Kocur C (2013) Nanoscale zero valent iron and bimetallic particles for contaminated site remediation. Adv Water Resour 51:104–122. https://doi.org/10.1016/j.advwatres.2012.02.005

Oh YJ, Song H, Shin WS, Choi SJ, Kim Y-H (2007) Effect of amorphous silica and silica sand on removal of chromium(VI) by zero-valent iron. Chemosphere 66(5):858–865. https://doi.org/10.1016/j.chemosphere.2006.06.034

O'Hara S, Krug T, Quinn J, Clausen C, Geiger C (2006) Field and laboratory evaluation of the treatment of DNAPL source zones using emulsified zero-valent iron. Remediat J 16(2):35–56. https://doi.org/10.1002/rem.20080

Olson MR, Sale TC, Shackelford CD, Bozzini C, Skeean J (2012) Chlorinated solvent source-zone remediation via ZVI-clay soil mixing: 1-year results. Groundwater Monit Remediat 32 (3):63–74. https://doi.org/10.1111/j.1745-6592.2011.01391.x

Oprčkal P, Mladenovič A, Vidmar J, Mauko Pranjić A, Milačič R, Ščančar J (2017) Critical evaluation of the use of different nanoscale zero-valent iron particles for the treatment of effluent water from a small biological wastewater treatment plant. Chem Eng J 321:20–30. https://doi.org/10.1016/j.cej.2017.03.104

Panagos P, Van Liedekerke M, Yigini Y, Montanarella L (2013) Contaminated sites in Europe: review of the current situation based on data collected through a European network. J Environ Public Health 2013:158764. https://doi.org/10.1155/2013/158764

Petala E, Dimos K, Douvalis A, Bakas T, Tucek J, Zbořil R, Karakassides MA (2013) Nanoscale zero-valent iron supported on mesoporous silica: characterization and reactivity for Cr (VI) removal from aqueous solution. J Hazard Mater 261:295–306. https://doi.org/10.1016/j.jhazmat.2013.07.046

Petala E, Baikousi M, Karakassides MA, Zoppellaro G, Filip J, Tuček J, Vasilopoulos KC, Pechoušek J, Zbořil R (2016) Synthesis, physical properties and application of the zero-valent iron/titanium dioxide heterocomposite having high activity for the sustainable photocatalytic removal of hexavalent chromium in water. Phys Chem Chem Phys 18(15):10637–10646. https://doi.org/10.1039/C6CP01013J

Phenrat T, Lowry GV (eds) (2019) Nanoscale zerovalent iron particles for environmental restoration: from fundamental science to field scale engineering applications, 1st edn. Springer, Cham. https://doi.org/10.1007/978-3-319-95340-3

Phenrat T, Saleh N, Sirk K, Tilton RD, Lowry GV (2007) Aggregation and sedimentation of aqueous nanoscale zerovalent iron dispersions. Environ Sci Technol 41(1):284–290. https://doi.org/10.1021/es061349a

Phenrat T, Saleh N, Sirk K, Kim H-J, Tilton RD, Lowry GV (2008) Stabilization of aqueous nanoscale zerovalent iron dispersions by anionic polyelectrolytes: adsorbed anionic polyelectrolyte layer properties and their effect on aggregation and sedimentation. J Nanopart Res 10 (5):795–814. https://doi.org/10.1007/s11051-007-9315-6

Phenrat T, Kim H-J, Fagerlund F, Illangasekare T, Tilton RD, Lowry GV (2009) Particle size distribution, concentration, and magnetic attraction affect transport of polymer-modified Fe[0] nanoparticles in sand columns. Environ Sci Technol 43(13):5079–5085. https://doi.org/10.1021/es900171v

Ponder SM, Darab JG, Mallouk TE (2000) Remediation of Cr(VI) and Pb(II) aqueous solutions using supported, nanoscale zero-valent iron. Environ Sci Technol 34(12):2564–2569. https://doi.org/10.1021/es9911420

Ponder SM, Darab JG, Bucher J, Caulder D, Craig I, Davis L, Edelstein N, Lukens W, Nitsche H, Rao L, Shuh DK, Mallouk TE (2001) Surface chemistry and electrochemistry of supported zerovalent iron nanoparticles in the remediation of aqueous metal contaminants. Chem Mater 13 (2):479–486. https://doi.org/10.1021/cm000288r

Qiu X, Fang Z, Liang B, Gu F, Xu Z (2011) Degradation of decabromodiphenyl ether by nano zero-valent iron immobilized in mesoporous silica microspheres. J Hazard Mater 193:70–81. https://doi.org/10.1016/j.jhazmat.2011.07.024

Quinn J, Geiger C, Clausen C, Brooks K, Coon C, O'Hara S, Krug T, Major D, Yoon W-S, Gavaskar A, Holdsworth T (2005) Field demonstration of DNAPL dehalogenation using emulsified zero-valent iron. Environ Sci Technol 39(5):1309–1318. https://doi.org/10.1021/es0490018

Reddy KR, Darko-Kagya K, Cameselle C (2011) Electrokinetic-enhanced transport of lactate-modified nanoscale iron particles for degradation of dinitrotoluene in clayey soils. Sep Purif Technol 79(2):230–237. https://doi.org/10.1016/j.seppur.2011.01.033

Reinsch BC, Forsberg B, Penn RL, Kim CS, Lowry GV (2010) Chemical transformations during aging of zerovalent iron nanoparticles in the presence of common groundwater dissolved constituents. Environ Sci Technol 44(9):3455–3461. https://doi.org/10.1021/es902924h

Reynolds GW, Hoff JT, Gillham RW (1990) Sampling bias caused by materials used to monitor halocarbons in groundwater. Environ Sci Technol 24(1):135–142. https://doi.org/10.1021/es00071a017

Rodrigues SM, Pereira ME, Ferreira da Silva E, Hursthouse AS, Duarte AC (2009) A review of regulatory decisions for environmental protection: part I — challenges in the implementation of national soil policies. Environ Int 35(1):202–213. https://doi.org/10.1016/j.envint.2008.08.007

Saad R, Thiboutot S, Ampleman G, Dashan W, Hawari J (2010) Degradation of trinitroglycerin (TNG) using zero-valent iron nanoparticles/nanosilica SBA-15 composite (ZVINs/SBA-15). Chemosphere 81(7):853–858. https://doi.org/10.1016/j.chemosphere.2010.08.012

Saleh N, Phenrat T, Sirk K, Dufour B, Ok J, Sarbu T, Matyjaszewski K, Tilton RD, Lowry GV (2005) Adsorbed triblock copolymers deliver reactive iron nanoparticles to the oil/water interface. Nano Lett 5(12):2489–2494. https://doi.org/10.1021/nl0518268

Schrick B, Hydutsky BW, Blough JL, Mallouk TE (2004) Delivery vehicles for zerovalent metal nanoparticles in soil and groundwater. Chem Mater 16(11):2187–2193. https://doi.org/10.1021/cm0218108

Sheu YT, Chen SC, Chien CC, Chen CC, Kao CM (2015) Application of a long-lasting colloidal substrate with pH and hydrogen sulfide control capabilities to remediate TCE-contaminated groundwater. J Hazard Mater 284:222–232. https://doi.org/10.1016/j.jhazmat.2014.11.023

Sheu YT, Lien PJ, Chen KF, Ou JH, Kao CM (2016) Application of NZVI-contained emulsified substrate to bioremediate PCE-contaminated groundwater – a pilot-scale study. Chem Eng J 304:714–727. https://doi.org/10.1016/j.cej.2016.06.126

Shi L-N, Lin Y-M, Zhang X, Chen Z-L (2011) Synthesis, characterization and kinetics of bentonite supported nZVI for the removal of Cr(VI) from aqueous solution. Chem Eng J 171(2):612–617. https://doi.org/10.1016/j.cej.2011.04.038

Siegrist RL, Crimi M, Simpkin TJ (eds) (2011) In situ chemical oxidation for groundwater remediation, SERDP ESTCP environmental remediation technology, vol 3, 1st edn. Springer, New York. https://doi.org/10.1007/978-1-4419-7826-4

Singh R, Misra V (2015) Stabilization of zero-valent iron nanoparticles: role of polymers and surfactants. In: Aliofkhazraei M (ed) Handbook of nanoparticles. Springer, pp 1–19. https://doi.org/10.1007/978-3-319-13188-7_44-1

Siskova K, Tucek J, Machala L, Otyepkova E, Filip J, Safarova K, Pechousek J, Zboril R (2012) Air-stable nZVI formation mediated by glutamic acid: solid-state storable material exhibiting 2D chain morphology and high reactivity in aqueous environment. J Nanopart Res 14:805. https://doi.org/10.1007/s11051-012-0805-9

Smedley PL, Kinniburgh DG (2002) A review of the source, behaviour and distribution of arsenic in natural waters. Appl Geochem 17(5):517–568. https://doi.org/10.1016/S0883-2927(02)00018-5

Song H, Carraway ER (2005) Reduction of chlorinated ethanes by nanosized zero-valent iron: kinetics, pathways, and effects of reaction conditions. Environ Sci Technol 39(16):6237–6245. https://doi.org/10.1021/es048262e

Song H, Carraway ER (2006) Reduction of chlorinated methanes by nano-sized zero-valent iron. Kinetics, pathways, and effect of reaction conditions. Environ Eng Sci 23(2):272–284. https://doi.org/10.1089/ees.2006.23.272

Su C, Puls RW, Krug TA, Watling MT, O'Hara SK, Quinn JW, Ruiz NE (2012) A two and half-year-performance evaluation of a field test on treatment of source zone tetrachloroethene and its chlorinated daughter products using emulsified zero valent iron nanoparticles. Water Res 46(16):5071–5084. https://doi.org/10.1016/j.watres.2012.06.051

Su C, Puls RW, Krug TA, Watling MT, O'Hara SK, Quinn JW, Ruiz NE (2013) Travel distance and transformation of injected emulsified zerovalent iron nanoparticles in the subsurface during two and half years. Water Res 47(12):4095–4106. https://doi.org/10.1016/j.watres.2012.12.042

Su Y, Adeleye AS, Zhou X, Dai C, Zhang W, Keller AA, Zhang Y (2014) Effects of nitrate on the treatment of lead contaminated groundwater by nanoscale zerovalent iron. J Hazard Mater 280:504–513. https://doi.org/10.1016/j.jhazmat.2014.08.040

Sun Y-P, Li X-Q, Zhang W-X, Wang HP (2007) A method for the preparation of stable dispersion of zero-valent iron nanoparticles. Colloids Surf A Physicochem Eng Asp 308(1–3):60–66. https://doi.org/10.1016/j.colsurfa.2007.05.029

Sun Y, Li J, Huang T, Guan X (2016) The influences of iron characteristics, operating conditions and solution chemistry on contaminants removal by zero-valent iron: a review. Water Res 100:277–295. https://doi.org/10.1016/j.watres.2016.05.031

Swartjes FA (ed) (2011) Dealing with contaminated sites: from theory towards practical application, 1st edn. Springer, Dordrecht. https://doi.org/10.1007/978-90-481-9757-6

Tang SCN, Lo IMC (2013) Magnetic nanoparticles: essential factors for sustainable environmental applications. Water Res 47(8):2613–2632. https://doi.org/10.1016/j.watres.2013.02.039

The Economist (2017) The most neglected threat to public health in China is toxic soil. The Economist Newspaper Limited

Tiraferri A, Chen KL, Sethi R, Elimelech M (2008) Reduced aggregation and sedimentation of zero-valent iron nanoparticles in the presence of guar gum. J Colloid Interface Sci 324 (1–2):71–79. https://doi.org/10.1016/j.jcis.2008.04.064

Tseng H-H, Su J-G, Liang C (2011) Synthesis of granular activated carbon/zero valent iron composites for simultaneous adsorption/dechlorination of trichloroethylene. J Hazard Mater 192(2):500–506. https://doi.org/10.1016/j.jhazmat.2011.05.047

US EPA (2000) Superfund: 20 years of protecting human health and the environment. Office of Solid Waste and Emergency Response, Washington, DC

US EPA (2011) Beneficial effects of the superfund program. Office of Superfund Remediation and Technology Innovation, Washington, DC

US EPA (2018a) Superfund: CERCLA Overview. https://www.epa.gov/superfund/superfund-cercla-overview. Accessed 10 Dec 2018

US EPA (2018b) Superfund: National Priorities List (NPL). https://www.epa.gov/superfund/superfund-national-priorities-list-npl. Accessed 10 Dec 2018

Üzüm Ç, Shahwan T, Eroğlu AE, Hallam KR, Scott TB, Lieberwirth I (2009) Synthesis and characterization of kaolinite-supported zero-valent iron nanoparticles and their application for the removal of aqueous Cu^{2+} and Co^{2+} ions. Appl Clay Sci 43(2):172–181. https://doi.org/10.1016/j.clay.2008.07.030

Van Deuren J, Lloyd T, Chhetry S, Liou R, Peck J (2002) Remediation technologies screening matrix and reference guide, version 4.0. FRTR. https://frtr.gov/matrix2/top_page.html. Accessed 10 Dec 2018

Virkutyte J, Sillanpää M, Latostenmaa P (2002) Electrokinetic soil remediation — critical overview. Sci Total Environ 289(1–3):97–121. https://doi.org/10.1016/S0048-9697(01)01027-0

Wang J, Farrell J (2003) Investigating the role of atomic hydrogen on chloroethene reactions with iron using Tafel analysis and electrochemical impedance spectroscopy. Environ Sci Technol 37 (17):3891–3896. https://doi.org/10.1021/es0264605

Wang C-B, Zhang W-X (1997) Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. Environ Sci Technol 31(7):2154–2156. https://doi.org/10.1021/es970039c

Wang W, Zhou M, Jin Z, Li T (2010) Reactivity characteristics of poly(methyl methacrylate) coated nanoscale iron particles for trichloroethylene remediation. J Hazard Mater 173(1–3):724–730. https://doi.org/10.1016/j.jhazmat.2009.08.145

Waria M, Comfort SD, Onanong S, Satapanajaru T, Boparai H, Harris C, Snow D, Cassada DA (2009) Field-scale cleanup of atrazine and cyanazine contaminated soil with a combined

chemical-biological approach. J Environ Qual 38(5):1803–1811. https://doi.org/10.2134/jeq2008.0361

Wei Y-T, Wu S-C, Chou C-M, Che C-H, Tsai S-M, Lien H-L (2010) Influence of nanoscale zero-valent iron on geochemical properties of groundwater and vinyl chloride degradation: a field case study. Water Res 44(1):131–140. https://doi.org/10.1016/j.watres.2009.09.012

Weng C-H, Lin TY, Chu S-H, Yuan C (2006) Laboratory-scale evaluation of Cr(VI) removal from clay by electrokinetics incorporated with Fe(O) barrier. Pract Period Hazard Toxic Radioact Waste Manage 10(3):171–178. https://doi.org/10.1061/(ASCE)1090-025X(2006)10:3(171)

Weng C-H, Lin Y-T, Lin TY, Kao CM (2007) Enhancement of electrokinetic remediation of hyper-Cr(VI) contaminated clay by zero-valent iron. J Hazard Mater 149(2):292–302. https://doi.org/10.1016/j.jhazmat.2007.03.076

Wu L, Ritchie SMC (2006) Removal of trichloroethylene from water by cellulose acetate supported bimetallic Ni/Fe nanoparticles. Chemosphere 63(2):285–292. https://doi.org/10.1016/j.chemosphere.2005.07.021

Wu P, Li S, Ju L, Zhu N, Wu J, Li P, Dang Z (2012) Mechanism of the reduction of hexavalent chromium by organo-montmorillonite supported iron nanoparticles. J Hazard Mater 219–220:283–288. https://doi.org/10.1016/j.jhazmat.2012.04.008

Yan W, Herzing AA, Li X-Q, Kiely CJ, Zhang W-X (2010) Structural evolution of Pd-doped nanoscale zero-valent iron (nZVI) in aqueous media and implications for particle aging and reactivity. Environ Sci Technol 44(11):4288–4294. https://doi.org/10.1021/es100051q

Yang GCC, Chang Y-I (2011) Integration of emulsified nanoiron injection with the electrokinetic process for remediation of trichloroethylene in saturated soil. Sep Purif Technol 79(2):278–284. https://doi.org/10.1016/j.seppur.2011.03.004

Zhang W-X (2003) Nanoscale iron particles for environmental remediation: an overview. J Nanopart Res 5(3–4):323–332. https://doi.org/10.1023/A:1025520116015

Zhang P, Tao X, Li Z, Bowman RS (2002) Enhanced perchloroethylene reduction in column systems using surfactant-modified zeolite/zero-valent iron pellets. Environ Sci Technol 36(16):3597–3603. https://doi.org/10.1021/es015816u

Zhang H, Jin Z-H, Han L, Qin C-H (2006) Synthesis of nanoscale zero-valent iron supported on exfoliated graphite for removal of nitrate. Trans Nonferrous Metals Soc China 16:s345–s349. https://doi.org/10.1016/S1003-6326(06)60207-0

Zhang Y, Li Y, Li J, Sheng G, Zhang Y, Zheng X (2012) Enhanced Cr(VI) removal by using the mixture of pillared bentonite and zero-valent iron. Chem Eng J 185–186:243–249. https://doi.org/10.1016/j.cej.2012.01.095

Zhao D, He F (2011) Preparation and application of stabilized iron nanoparticles for dechlorination of chlorinated hydrocarbons in soils, sediments, and ground water. United States Patent

Zhou Q, Li J, Wang M, Zhao D (2016) Iron-based magnetic nanomaterials and their environmental applications. Crit Rev Environ Sci Technol 46(8):783–826. https://doi.org/10.1080/10643389.2016.1160815