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REVIEW

Application and development of zero-valent iron (ZVI) for groundwater and wastewater treatment

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Abstract
Zero-valent iron has been used for more than 130 years for water treatment. It is based on redox reactions as well as on sorption to the corrosion products of iron. It is successfully applied for the removal of metals and organic pollutants from groundwater and wastewater. There are different variations how zero-valent iron can be used, especially (i) permeable reactive barriers, (ii) fluidized bed reactors and (iii) nanoscale zero-valent iron. Permeable reactive barriers are used for in situ treatment of groundwater in trench-like constructions or in a funnel and gate system. Their advantages are low maintenance cost, inexpensive construction and prevention of excavation wastes, and their disadvantages are surface passivation and clogging of pores by corrosion products. Zero-valent iron nanoparticles are injected directly in contaminated soil or groundwater. Their advantages are a higher reactivity than coarse-grained zero-valent iron and their mobility in the subsurface to reach the contaminated areas. However, they also have some major disadvantages like fast ageing in the system, phytotoxicity, agglomeration during migration and high costs. The latest development is a fluidized bed process ("ferrodecont process") which avoids the passivation and clogging observed in permeable reactive barriers as well as the high costs and toxicity issues of nanoscale zero-valent iron. First results of this technology for Cr(VI) and organically contaminated groundwaters and metal removal from industrial wastewaters are highly promising.

Keywords Zero-valent iron · Environmental remediation · Fluidized bed reactors · Ferrodecont process

Introduction

Due to increasing industrial activities and economic growth all around the globe, environmental pollution is getting more and more severe, thus becoming a major problem. The input of certain contaminants in the environment through wastewaters and the pollution of groundwater makes their remediation of critical importance (Fu et al. 2014). In some cases, the traditional methods like excavation and disposal of the contaminated soil to landfill and pump-and-treat methods for groundwater remediation are not adequate (Cundy et al. 2008).

Metallic or zero-valent iron (ZVI) has been used in a variety of different approaches for the treatment and remediation of wastewater and groundwater since 1857 (Devonshire 1890). Prior to 1990, there had already been studies that described the use of ZVI for the removal of inorganics (Gould 1982). The underlying mechanism for ZVI remediation was discussed in a number of articles (Makota et al. 2017; Noubactep 2015).

ZVI can be used in remediation application and metal removal as granular iron in permeable reactive barriers or fluidized bed reactors (Müller et al. 2014), scrap iron (Gheju and Balcu 2017) and nanoscale zero-valent iron (nZVI) (Li et al. 2006) including bimetallic nanoscale zero-valent iron (O'Carroll et al. 2013). There are already several of reviews on ZVI for environmental remediation which focus on the reaction mechanisms (Noubactep 2015) and removable contaminants (Fu et al. 2014), but do not consider more recent developments such as fluidized bed processes (Müller et al. 2014).

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Materials and Methods

This study presents a review of studies dealing with ZVI in its two most applied forms, granular iron and nanoscale iron. In contrast to previous reviews, it focuses more on the practical application of ZVI, rather than the exact mechanism, and considers fluidized bed processes. The review has been carried out from October 2019 to February 2020 at Leoben, Austria. National and international publications have been screened and compared using criteria such as the scale of experiments and the treated material.

Results Basic principles

ZVI particles have a Fe^0 core and an outer shell of iron oxides (Sun et al. 2006). The core acts as an electron donor and promotes the reduction of contaminants (Crane and Scott 2012) while the shell acts as an adsorbent (Calderon and Fullana 2015). Makota et al. (2017) described the responsible effects that make ZVI a suitable remediation tool. In an Fe^0/H_2O system, a contaminant can be adsorbed, oxidized and/or reduced depending on its affinities to available mineral phases and its chemical reactivity with other species, as it contains (1) oxidizing agents (e.g. Fe^{3+} species), (2) reducing agents (e.g. H_2, Fe^{2+}, Fe_3O_4) and (3) adsorbing agents (e.g. hydroxides and oxides) acting in synergy. It can also act as a coagulant for various anionic species when exposed to water, and Fe^0 can also be specifically used to generate Fe(II)/Fe(III). The reaction pathways have already been extensively described in the literature (Yan et al. 2013; Zhang 2003; Weber 1996). Main reactions of relevant redox pairs for contaminant of Fe^0/H_20 systems are given in Table 1.

Table 1 Electrode potential of redox couples relevant removal in Fe0/H2O

Electrode reaction	E^0 (V)
$Fe^{2+} + 2e^- \rightleftharpoons Fe^0$	− 0.44
$Fe^{3+}{}_{(s)} + e^- \rightleftharpoons Fe^{2+}{}_{(s)}$	− 0.34 to − 0.65
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Fe^{3+}{}_{(aq)} + e^- \rightleftharpoons Fe^{2+}{}_{(aq)}$	0.77
$O_2 + 2H^+ + 2e^- \rightleftharpoons 2OH^-$	0.81
$Fe^0 + O_2 + 2H^+ \rightleftharpoons Fe^{2+} + OH^-$	–
$Fe^0 + Fe^{3+}{}_{(aq)} \rightleftharpoons 3Fe^{2+}{}_{(aq)}$	–
$Fe^0 + 2H^+ \rightleftharpoons Fe^{2+} + H_2$	–
$Fe^0 + Fe^{3+}{}_{(s)} \rightleftharpoons 3Fe^{2+}{}_{(aq)}$	–
$Fe^{2+}, Fe^{3+}, H_2O, O_2 \rightleftharpoons Fe^{II}Fe^{III}$(hydr)oxides	–

Electrode potential values are given versus the standard hydrogen electrode (Makota et al. 2017)

ZVI can be applied to adsorb and chemically reduce metals as well as for the removal of organic contaminants. ZVI systems have successfully treated pollutants such as cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), selenium (Se), technetium (Tc) and uranium (U) in batch and column studies through reduction, precipitation and adsorption (Makota et al. 2017). Hence, ZVI is a suitable tool for the treatment of water contaminated by several pollutants. The removal of organic contaminants occurs via the reductive degradation of the chemical, i.e. the contaminant is physically destroyed into smaller less toxic compounds (Crane and Scott 2012). The chlorinated compounds are partially or totally dechlorinated in a reductive environment to ethane and chloride (Mueller et al. 2012). Even tetracycline (TC), one of the most widely used antibiotics for human and veterinary applications, can be degraded with nZVI into smaller organic compounds (Gopal et al. 2020).

Permeable reactive barriers

Principles

PRBs are executed by placing an appropriate hydraulically permeable medium in the aquifer and remediate the contaminated plume (ITRC 2005). Constructive methods of PRBs normally include excavation and installation of continuous walls (trench style) or so-called funnel-and-gate systems to ensure an inexpensive construction, long operating time and low maintenance cost, while using reactive material efficiently (ITRC 2011; Köhler 2004). Other advantages include the possibility of in situ treatment, avoiding the wastes and costs associated with the above-ground handling of large volumes of water with low contaminant concentrations. (Han et al. 2016). A reactive medium is selected by considering factors such as activity, sufficient permeability, hydraulic conductivity, environmental compatibility, availability, cost efficiency and long-term stability (Han et al. 2016). A broad range of different materials such as limestone, zeolite or activated carbon may be used, but granular ZVI is the most used material for PRBs (U.S. Environmental Protection Agency 2002).

Applications

PRBs are the main application of ZVI and represent a widely used in situ technology for contaminated groundwater remediation and are considered to be the most practicable approach for treating a variety of contaminants such as organics, metals or even radionuclides. Developed in the 1990s, over 200 PRBs were installed worldwide by 2004, of which 120 are iron based (ITRC 2005; Puls et al. 1999).

Table 2 Overview of selected worldwide installed PRBs with Fe-based remediation material targeting metal pollution

Pollution cause	Location	Reactive medium	Contaminant	Application mode	Results	Cost	Date of installation	References
Wood impregnation site	Willisau, Switzerland	Grey cast iron, gravel	Chromium	Pile construction	–	–	–	Köhler (2004)
Electroplating industry	Elizabeth City, USA	ZVI	Chromium, TCE	Continuous trench	Cr was removed, TCE below maximum contaminant level for most wells, plume seems to have dipped after wall installation; Pore volume was reduced after 5 years	675 000 $	1996	(Wilkin et al. (2014), Wilkin et al. (2003), U.S. Environmental Protection Agency (2002)
Industrial site	Monticello, USA	ZVI	U, As, Mn, Se, V	Funnel and Gate	PRB effective in reducing contaminants	800 000 $	1999	U.S. Environmental Protection Agency (2002)
Waste disposal site	Oak Ridge, USA	ZVI, gravel	U (mixed waste plume	Trench style	Remediation not effective	–	1997, extended 2002	Liang et al. (2005)
Diesel fuel spill	Casey Station, Antarctica (Australian territory)	ZVI, sand (for metal remediation) plus 2 other remediation zones for organics	Hydrocarbons, heavy metals	Funnel and Gate	Assessment was inconclusive	–	2005 redesigned in 2012/2013	Statham et al. (2016)

Even though ZVI is a state-of-the-art technology, only a few studies asses the long-term field application of granular metallic iron in PRBs, especially for the removal of inorganic contaminants such as metals, as given in Table 2 (Henderson and Demond 2013; ITRC 2005; Obiri-Nyarko et al. 2014; Wilkin et al. 2014). The longest available assessment of an implemented PRB extends over a period of 15 years. Results from that study suggest that the implemented PRB in Elisabeth City is perhaps the first one to have reactive performance that surpasses the lifetime of the contaminant plume, which in this case consist of chromium and trichloroethylene (TCE). Main key factors might be (1) pH and redox conditions, (2) groundwater chemistry low in dissolved solids, (3) low influent dissolved oxygen loading and (4) the velocity of the groundwater (Wilkin et al. 2014). On the contrary, a 5-year study of a ZVI PRB at the Oak Ridge Y-12 site in the USA highlighted geochemical and mineralogical changes in material performance. Drilling tests showed cementation and reduction in the porosity of the reactive material of up to 41.7%. A decrease in the pore volume of 2.5% each year is predicted. The authors stated that performance loss was more severe than at other PRBs and was caused by extremely high iron corrosion due to high nitrate concentration in groundwater (Liang et al. 2005).

To investigate the removal of both heavy metals and hydrocarbons, a field trial PRB was modified in Antarctica. It was executed as a sequenced PRB consisting of three sections, one containing a mixture of ZVI and sand. Even though the authors claim that the tested construction might be appropriate for other locations, the effectiveness of pollutant removal was inconclusive as a hydrocarbon contamination source had been excavated and inflowing heavy metal concentrations were insignificant. Phosphorus concentrations only were referenced and reduced through the ZVI section (Statham et al. 2016).

Advantages

PRBs represent an in situ method for contaminated site remediation which avoids excavation and landfilling of material. In contrast to pump-and-treat methods such as granular bed reactors, no pumping is required. The production of granular ZVI for PRBs is cheap and it occurs as a by-product of pig iron production. Its application in the groundwater flow does not release chemicals or nanoparticles into the environment.

Disadvantages and optimization

As a result of iron corrosion processes, several solid iron phases, such as iron oxides and hydroxides and other minerals, may precipitate and lead to a decrease in barrier porosity and subsequently decrease permeability and reactivity of ZVI. In addition, microbial activity and gas production may also cause a restriction of the functions. Flow circumvention of the barrier will be the result and lead to failure of contaminant remediation. Monitoring of PRB performance and contaminant fate is therefore necessary to understand mechanisms of limitation, whereby parameters such as pH value and flow rate are crucial (Kamolpornwijit et al. 2003; Moraci and Calabrò 2010; Puls et al. 1999). In addition, ZVI is a strongly reductive species and promotes the bonding of metals. These properties may be the cause for the reduction of species (e.g. nitrate or oxygen) not targeted for remediation at contaminated sites, which might be another potential problem (Henderson and Demond 2013). On the contrary, Henderson and Demond (2007) stated that imperfect hydraulic characterization is the main cause of failure. Therefore, the key aspect for the design of PRBs is adequate site characterization (Obiri-Nyarko et al. 2014).

For the above-mentioned reasons, a variety of studies dealt with solving the problem of limited ZVI reactivity due to passivation and clogging. It must be considered that there are only a handful of studies that cover the long-term field application of ZVI. Most studies focused on short-term experiments in laboratory scale. Parameters of the following mentioned experiments are presented in Table 3.

One simple improvement to deal with the decrease in the pore volume in PRBs due to precipitation of secondary minerals is replacing a portion of ZVI by an inert porous constant volume material (Noubactep and Caré 2010). This effect was examined by Calabro et al. (2012) by mixing granular iron with pumice. Not only does pumice increase permeability, but it might also enhance ZVI effectiveness by storing corrosion products, which leads to higher removal rates of nickel than ZVI alone. In contrast, it is also stated that a compromise between reactivity and hydraulic conductivity must be made.

Jun et al. (2009) investigated the impact of adding zeolite to a mixture of ZVI and sand for remediation of landfill leachate polluted groundwater in a laboratory-scale sequenced PRB reactor consisting of multiple layers ((1) quartz; (2) simulated aquifer; (3) different mixtures of sand, ZVI and zeolite and (4) oxygen releasing compounds (ORC)). As zeolites exhibit high sorbent potentials and high cation exchange capacity for contaminants, removal efficiency of mixed media for pollutants was higher than that of ZVI alone. Therefore, laboratory-scale studies were effective and the authors propose the concept of sequenced multilayer PRB as an alternative method for remediation of groundwater contaminated by a variety of organics, ammonia and heavy metal pollutants. However, the ORC layer lost its effectiveness entirely after 60 days, so that results might not be realizable in long-term studies.

Han et al. (2016) investigated the effect of mixing ZVI with zero-valent aluminium (ZVAl). In addition, ZVI

Table 3 Selection of laboratory-scale studies using iron-based materials

Contaminant	Remover	Parameters	Type of experiment	Flow rate	Initial concentration of contaminant	Removal efficiency (%)	Removal time	Comment	References
Ni, Cu	ZVI alone, ZVI and pumice in different mixtures, ZVI and pumice in series	–	Column tests (5 × 50/100 cm)	0.5 ml/min	Copper (50 or 500 mg/L) Nickel (50 mg/L)	Depending on mixture	1032 to 1404 h	High concentrations compared to max. groundwater val., best performance was observed when using the 30:70 ZVI/pumice granular mixture	(Moraci and Calabrò, 2010)
Cd, Ni, Cu, Zn, Cr	Acid washed ZVI/ZVAl (2:1) Sand, activated carbon	–	Laboratory-scale studies in plexiglass column (50 × 450 mm)	1.0 mL/min	–	99.5	300 h	–	(Han et al., 2016)
Molybdate	Hybridized ZVI/magnetite/Fe(II)	50 g/L ZVI, various concentrations of Fe^{2+} pH increased gradually from initial 6.1–6.3 to 6.8–7.2 after 48 h	Batch tests in sealed reactors	–	0.25 mM	52% (0.1 mM Fe^{2+}) 97% (0.5 mM Fe^{2+})	48 h	Conventional ZVI-only system could not effectively remove molybdate, as removal was stagnant after 36 h in all three tests;	(Huang et al., 2012)
Cr(VI)	Basic oxygen furnace slag (BOFS) and sand (70:30)	pH 5.5 total solid mass: 1607 g	Column tests (5 × 50 cm)	0.15 L/h	50 mg/L	Exhaustion of reactive medium	Var	Reactive media used was able to remove 0.213 mg Cr (VI) per gram of residue Present calcium may cause clogging and decrease in the hydraulic conductivity	(Frade et al., 2018)
	Basic Oxygen Furnace Slag (BOFS)	255 L of Cr(VI) aqueous solution injected, total mass of 12.75 g Cr(VI)	Bench reactor test (100 × 40 × 30 cm)	3.6 L/d	50 mg/L	100% until day 27 95% after day 71	71 d	pH rose from 5 to 9 at the end of operation phase, possibly du to Ca release	

Table 3 (continued)

Contaminant	Remover	Parameters	Type of experiment	Flow rate	Initial concentration of contaminant	Removal efficiency (%)	Removal time	Comment	References
Ni, Cu, Zn	First column: ZVI/pumice or ZVI/granular activated carbon (GAC)	pH 6.5–7 in first column	Column tests (5 × 100 cm)	0.5 mL/min	Ni and Zn 50 mg/L	Higher than Cu 98	70 d	GAC not necessary for contaminant removal	(Bilardi et al. 2018)
	Second column:					Ni 94			
	Zeolite/GAC					Zn 90			
	ZVI/lapillus mixture	pH 5	Column tests (5 × 50 cm)		Cu 500 mg/L	–	–	Effectiveness assessed over “break-through times”	(Bilardi et al. 2019)
Zn, Mn, Ca, Mg, Cd, Cr, Sr, Al	Reactor A:	Maximum dissolved oxygen (DO): 7.64 mg/L	Plexiglass columns (15 × 90 cm)	–	Zn 82.8 mg/L	Zn 93.2	–	ORC lost its effectiveness entirely after 60 days	(Jun et al. 2009)
					Mn 13.8 mg/L	Mn 90.2			
					Ca 555.9 mg/L	Ca 77.4			
					Mg 186.4 mg/L	Mg 52.6			
					Cd 0.08 mg/L	Cd 88.0			
	Quartz (40%)				Cr 0.2 mg/L	Cr 67.4			
					Sr 1.2 mg/L	Sr 62.9			
	ZVI (60%)				Al 16.2 mg/L	Al 46.7			
						Zn 97.2			
	Reactor B:	Maximum dissolved oxygen (DO): 6.78 mg/L				Mn 99.6			
						Ca 81.7			
	Quartz (34.78%)					Mg 95.9			
	ZVI (43.48%)					Cd 95.2			
	Zeolite (21.74%)					Cr 70.7			
						Sr 90.5			
						Al 58.7			

and ZVAl were treated with H_2SO_4. Results showed that $Fe(OH)_3$ and $Al(OH)_3$ precipitates form. On the one hand, these hydroxides act as sorbents for heavy metals; on the other hand, they stop the further oxidation of ZVI or ZVAl. Therefore, the treated ZVI/ZVAl was more effective to remove heavy metal ions than nontreated material.

In a more recent study, possible mixing ratios of granular ZVI and lapillus were studied by Bilardi et al. (2019) for the removal of zinc, copper and nickel cations. The ZVI/lapillus mixture at higher iron content showed the higher removal rate but also the higher reduction in the hydraulic conductivity in the long run.

Huang et al. (2012) used a new approach to avoid the effect of the passivation of ZVI. A so-called hybridized ZVI/magnetite (Fe_3O_4)/Fe(II)system (hZVI) was produced and compared to a common ZVI system. ZVI grains were coated with magnetite by employing a nitrate-Fe^{2+} treatment method, and discrete Fe_3O_4 particles were created through a rapid ZVI nitrate reaction. The co-presence of ZVI, Fe_3O_4 and Fe(II) species created a highly reactive system. Results showed that molybdate was not removed with a common ZVI system, but could be removed by hZVI.

Apart from the above-mentioned problems, ZVI is quite expensive in comparison with other reactive materials, as one ton of granular ZVI costs around 400 $, and might not be an option, especially in developing countries (Lee et al. 2003). Waste materials such as fly ash and red mud could be potential cost-effective alternatives (Komnitsas et al. 2004; Wantanaphong et al. 2005). Another study investigated the application of oxygen furnace sludge, which holds high values of elemental iron, for Cr(VI) remediation. While column tests lead to passivation of the surface, bench reactor tests modelling a PRB turned out to be effective (Frade et al. 2018). Henderson and Demond (2013) assessed iron sulphide (FeS) as a possible alternative reactive medium to ZVI. Like ZVI, FeS is strongly reductive in aqueous solution, but the main difference is that FeS does not necessarily undergo anoxic corrosion in water, and therefore, thermodynamic stability of FeS and ZVI differs. As a result, a loss of permeability may not be a problem with FeS.

ZVI in fluidized bed reactors

Principles

The use of ZVI in PRBs is already state of the art, but the above-mentioned disadvantages such as precipitation, surface passivation and clogging effects at the wall make other processes necessary (Müller et al. 2014). Therefore, the ferrodecont process, using granular ZVI in a fluidized bed reactor (FBR), was developed between 2006 and 2012. This method can be used as a pump-and-treat method for groundwater remediation (Müller et al. 2014; Sedlazeck et al 2020). The water is pumped upwards through columns filled with ZVI. This creates a fluidized bed. The collisions of the iron granules abrade the formed corrosion products and liberate fresh ZVI surfaces which avoids clogging. The corrosion products are transported from the column with the water flow and separated from the solution via filter presses. The filter cake is either disposed of or subjected to further treatment for metal recovery.

Applications

In the last years, the application range of the ferrodecont process has been extended to the destruction of organic pollutants (Sedlazeck et al. 2019) and to metal recovery from industrial wastewaters (Vollprecht et al. 2019). The latter application was a novelty compared to traditional water treatment technologies which concentrate on disposal and removal of metals from wastewater and groundwater rather than recovering and recycling. Main focus was directed to the removal of critical metals, defined as metals with growing economic importance, such as molybdenum (Mo), vanadium (V), tungsten (W), cobalt (Co) and with industrial wastewaters. Experiments with synthetic aqueous solutions showed that more than 99% of many critical metals could be removed, whereby optimum pH values depended on the intended metal to be removed. Batch experiments with six industrial wastewaters mostly confirmed the above-mentioned results and verified the effectiveness of the ferrodecont process, as more than 90% of Cr, V, In, Co and Ni were removed (Vollprecht et al. 2019).

Similar to fluidized bed reactors, Bilardi et al. (2018) investigated the pre-treatment of landfill leachate prior to its co-treatment in the municipal wastewater plants by a mixture of ZVI and pumice or granular activated carbon (GAC) in a first column and a zeolite and GAC mixture in a second column. The contribution of the GAC section to the overall contaminant removal was negligible, but altogether removal efficiency for copper, zinc and nickel was very promising. The authors propose an alternative application to PRBs, as the reactive material could be placed in a tank and act as a filter for the leachate.

Advantages

In contrast to PRBs, FBRs do not tend to clogging effects. The ex situ character of the treatment allows easier maintenance. The efficiency of the process is very high due to the intense fluid–solid interaction in the turbulent flow.

Disadvantages and optimization

FBRs are not an in situ measure and require pumping of the groundwater to the treatment plant. The resulting filter cake needs further treatment, if metals shall be recycled, or disposal. Hydro- and pyrometallurgical methods are required in the latter case (Vollprecht et al. 2020).

Nanoscale zero-valent iron

Principles

To enhance the efficiency of ZVI, nanoscale zero-valent iron (nZVI) was invented. Nanomaterials are defined as those materials whose key physical characteristics are defined by the nano-objects they contain (Kharisov et al. 2012). nZVI ranges from 10 to 100 nm (Li et al. 2006).

For laboratory-sized applications, the generally used method for nZVI manufacturing is the boron hydride reduction of ferrous salts (Crane and Scott 2012; Chekli et al. 2016; Sun et al. 2006). But for the production of a bigger amount, there are many different methods, e.g. chemical vapour deposition, pulsed laser ablation, sputtering gas aggregates, thermal decomposition, thermal reduction of oxide compounds and many more (Crane and Scott 2012).

An enormous advantage of nZVI is that it can be directly injected into the contaminated groundwater plumes or source zones without the need for ex situ methods or intensive digging and without clogging of pores (Cundy et al. 2008). nZVI is generally injected into the subsurface as a slurry or as an emulsion with a hydrophobic fluid, this should prevent the agglomeration of particles and enhance the reactivity and mobility (Cundy et al. 2008). Due to this method, the injection wells can be installed at almost any location and depth with minimal disturbance to the area above (Chekli et al. 2016; Hashim et al. 2011). Even areas that are unreachable with most other conventional technologies, including those underneath surface barriers, where only in situ methods are feasible, can be treated (He et al. 2010). The injected nanoparticles should be virtually immobile once the external injection pressure is released and they should pose no adverse environmental effect (Zhao et al. 2016).

Applications

The application of nZVI for environmental remediation (groundwater, wastewater, soil) has extensively been studied in the last 15–20 years (Calderon and Fullana 2015; Guan et al. 2015; Vanzetto and Thomé 2019; Li et al. 2017). Contaminated sites often contain a complex and varied mixture of contaminants from heavy metals to organic pollutants (Cundy et al. 2008; Li et al. 2017). Because of such complex contaminations, it is highly important that nZVI can perform fast and concurrent removal of different heavy metal ions (Li et al. 2017). There are already some field applications of nZVI, most sites are located in the USA, and only a small number of pilot studies have been conducted in Europe (Karn et al. 2009).

The zero-valent iron nanoparticles age rapidly in water due to interaction with dissolved compounds and corrosion, and this results in structural and chemical changes of the nZVI depending on the environment (Calderon and Fullana 2015). Calderon and Fullana (2015) studied the ageing of nZVI with Zn, Cd, Ni, Cu and Cr as typical contaminants found in groundwater and wastewater. The removal efficiency of all elements in the first 3 h was ≥99.9%, but only Cr showed no remobilization after an extended period, because it was the only element that was incorporated into the nZVI core. Cd and Ni showed the maximum remobilization with 65% and 27% after 21 days. Crane et al. (2011) and Dickinson and Scott (2010) showed similar results in the removal of uranium with nZVI, with a partial release of 20% of the retained uranium after one week and 60% after 3 weeks. At a Portuguese metal contamination site, Gonçalves (2016) applied nZVI and observed that at first the concentration was reduced to 60% below initial concentration, but within 4 weeks the elevation of the contaminants was close to the initial values. In contrast, Gonçalves (2016) attributed this effect to groundwater recharge and not to some kind of ageing effect of the nZVI. Calderon and Fullana (2015) also proved that mainly the pH changes of the solution were responsible for the release of metal ions into the water; this also shows that some metals are only in equilibrium with the shell of the nZVI and not entrapped in the core.

The different factors (e.g. mobility, reactivity, tendency to aggregate) determining the feasibility of nZVI depend heavily on properties such as particle size, surface charge, surface chemistry and bulk composition (Chekli et al. 2016). The particle size of nZVI has a major influence on the reactivity and mobility of the nanoparticles (Hassellöv et al. 2008; Christian et al. 2008). In comparison with highly dispersed nanoparticles, highly aggregated particles have reduced available reactive surface sites (Nurmi et al. 2005). The composition of the oxide shell and the metallic iron content of the implemented nZVI has a substantial influence on the efficacy of the nZVI treatment (Grieger et al. 2010; O'Carroll et al. 2013). The composition of the outer shell is dependent on the method of synthesis and the nanoparticle environment (Nurmi et al. 2005).

Factors affecting the reactivity of nZVI are diverse and include surface area, nZVI stabilizer, pH, soil organic matter, soil type, temperature, dissolved oxygen, soil moisture and aged soil (Jiang et al. 2018; Xue et al. 2018; Zhao et al.

2016). The reactivity of some pollutants with ZVI depends also on the age of the pollutants in the soil, and El-Temsah and Joner (2013) reported that the degradation of dichlorodipenyltrichloroethane (DDT) in spiked soil was 50%, whereas the removal efficiency in aged DDT polluted soil was only at 24%. This could be due to desorption, solubilization and dissolution of DDT in the soil. A weakly acidic soil increases the dechlorination rate of polychlorinated biphenyls (Wang et al. 2012). The pH also has an impact on the reactive lifetime due to corrosion effects and the reactivity towards the target contaminant (Zhao et al. 2016; Dickinson and Scott 2010). The pH is also a key parameter for metal transfer in soil, e.g. the As availability is lower in acidic soils than in calcareous ones (Xue et al. 2018; Gil-Díaz et al. 2017). The soil organic matter has many different contrary effects; for example, the organic matter can coat the nZVI and form a barrier for electron transfer which inhibits the reactivity towards the contaminants, but the same effect leads to a prolonged reactive lifetime of the nZVI (Zhang et al. 2011). Zhao et al. (2016) also concluded that the soil organic matter can form complexes with heavy metals and thus change the adsorption and immobilization of metals. Stabilizers for nZVI lead to a better soil mobility due to less particle agglomeration (Jiang et al. 2018). It was also proved that the efficiency of nZVI in soil is related to the leachability and bioavailability of contaminants, higher leachability and bioavailability are beneficial, but those factors depend heavily on the soil type (Xue et al. 2018; Chen et al. 2014). For example, a higher sand content in comparison with a high clay content was shown to be preferable for a high removal rate (Chen et al. 2014).

Advantages

Even though the chemistry behind nZVI and ZVI or mZVI (macroscale ZVI) is much the same, nZVI, due to the large surface area, is more reactive than ZVI, shows higher reductive efficiency and is also able to migrate in the underground to some extent, which allows active remediation not only of the plume but also of the source of contaminants (Mueller et al. 2012). nZVI holds even some more advantages, as summarized by Guan et al. (2015): (1) it can successfully remove some aqueous contaminant species due to its large surface area that mZVI cannot remove, (2) it degrades some contaminants more rapidly and (3) it avoids the formation of some undesirable by-products due to a more complete degradation.

nZVI has been proved to be a feasible method to transform a wide range of contaminants to low toxicity or inert compounds (Crane and Scott 2012; Xue et al. 2018), including all kinds of metals and metalloids like chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), nickel (Ni), zinc (Zn), cadmium (Cd), arsenic (As), selenium (Se) and actinides such as uranium (U) and plutonium (Pu) (e.g. Table 4). Also some organic compounds like chlorinated pesticides, organophosphates, nitroamines, nitroaromatics, *p*-chlorphenol and some inorganic anions such as nitrate could be removed (e.g. Table 4), whereas nitrate was reduced to ammonia (Sohn et al. 2006).

Disadvantages and optimization

Even though nZVI seems to be already more feasible than ZVI for environmental remediation, the enhancement of nZVI has been thoroughly studied (Jiang et al. 2018; Zhao et al. 2016), especially since bare nZVI has a limited soil mobility and deliverability (Crane and Scott 2012). Thus, in order to enhance the feasibility of nZVI and decrease the toxic effects on soil micro-organisms and the entire biosphere, chemical and physical methods were developed to improve the performance (Jiang et al. 2018). Physical enhanced technologies include dispersion and acoustic cavitation of nZVI using ultrasonic technology for nanoparticle, UV light or electric forces (Jiang et al. 2018). The nanoparticles can also be combined with another metal, bound onto a support or the surface modified (Xue et al. 2018). For example, to improve the reduction reactions nZVI has been coated with a catalyst, such as platinum (Pt), nickel (Ni), gold (Ag), palladium (Pd) or copper (Cu), and those products are then called bimetallic nanoparticles (Guan et al. 2015). nZVI could also be deployed in a combination with biotechnology, such as phytoremediation or microbial remediation, which would be an environmental-friendly and cost-effective remediation strategy (Jiang et al. 2018).

Stabilized nZVI has three significant advantages: (1) the stabilizers prevent the aggregation through electrostatic and/or steric repulsion, (2) they may offer a greater reactivity and (3) due to different physical and chemical properties the dispersibility, chemical reactivity, reactive longevity and toxicity of nZVI may be better controlled (Zhao et al. 2016; Xue et al. 2018). The coating of stabilizers onto nanoparticles may also passivate the reactive particle surface from reaction with the media (e.g. H_2O and dissolved oxygen) (Zhao et al. 2016).

Zhao et al. (2016) categorized possible stabilizers for nZVIs into the following five groups: (I) surfactants, (II) synthetic or natural macromolecules or polyelectrolytes, (III) viscosity modifiers, (IV) oil emulsifiers and (V) micro-scale solid supports or coatings. Stabilized nZVI shows promising results for the degradation of redox-active organics and reductive immobilization of many metals, metalloids and radionuclides (Zhao et al. 2016). Cao et al. (2018) tested the feasibility of nZVI in combination with organic acids. The removal efficiency of heavy metals was improved

Table 4 Compilation of different studies regarding the application of nZVI

Contaminant	Remover	Medium	Condition of removal	Type of experiment	Initial concentration of contaminant	Removal efficiency (%)	Removal time	References
Antibiotics (Tetracycline (TC))	nZVI-CU	Contamination of natural water	pH7, nZVI 750 mg/L	Batch experiments	10 mgL^{-1}	72 ± 0.5%	15–90 min	Gopal et al. (2020)
	B/nZVI-CU		nZVI 150 mg/L at pH 7		10 mgL^{-1}	95 ± 0.05%	15–90 min	
	nZVI	Remediation of metronidazole in aqueous solution	pH 5,6, nZVI 0,1 g per L	Batch experiments	80 mgL^{-1}	100%	5 min	Fang et al. (2011)
Polychlorinated biphenyls	nZVI and Pd/Fe bimetallic NPs	Contaminated soil from e-waste recycling area		Batch experiments				Chen et al. (2014)
Dichlordiphenyl-trichlorethane DDT	nZVI	Remediation of contaminated soil	1 to 10 g nZVI per kg	suspension incubation experiments	20 $mgkg^{-1}$	50%	7 to 30 days	El-Temsah and Joner (2013)
	nZVI-B, nZVI-T	Soil suspension	pH 5.2	Laboratory	24 $mgkg^{-1}$ soil	nZVI-B 22.4%, nZVI-T 9.2%	48 h	El-Temsah et al. (2016)
				Laboratory, vertical shaker	500 mgL^{-1}	nZVI-B 92%, nZVI-T 78%	24 h	
As, Cu	nZVI	Waste water		Treatment plant with Eh controlled reactor	As (V) ~ 108 mgL^{-1}	As ~ 99.9%	Treatment process 4–5 days	Li et al. (2017)
					Cu (II) ~ 130 mgL^{-1}	Cu ~ 99.8%		
					Zn ~ 42 mgL^{-1}	Co, Cr, Ni, Pb, Zn		
					Ni ~ 6 mgL^{-1}			
					Fe, Cr, Co, Pb, Se, Sb, Au, TI (< 20 ppb)	> 99.5% removal efficiency		
Pb, Cd, Zn	nZVI	Contaminated soil	Soil washing	Laboratory		< 10% Cd, Zn, 15% Pb		Cao et al. (2018)
	CA nZVI					Cd 34.25%, 49.50% Pb, 62.84% Zn for mine soil		
As	nZVI	Polluted soil		Batch experiments		nZVI 89.5% decrease at 2%		Baragaño et al. (2020)
U	nZVI@Zn-MOF-74		pH 3	Laboratory		High adsorption capacitiy up to 348 mg/g		Li et al. (2019)
	nZVI	Remediation of contaminated environmental water	0.1 g nZVI, pH 8.36	Sealed batch reactors	U 0,484 mgL^{-1}	> 98%	2 h	Crane et al., 2011

Table 4 (continued)

Contaminant	Remover	Medium	Condition of removal	Type of experiment	Initial concentration of contaminant	Removal efficiency (%)	Removal time	References
Pu	nZVI	Remediation of contaminated solution	Anoxic, pH 6, 0.02 g	Batch experiment	1 mgL^{-1}	77%	1 h	Crane et al. (2015)
Cr and Pb	S-nZVI (sepiolite-supported nZVI)	Remediation of groundwater	S-nZVI 1.6 g per L	Batch experiment				Fu et al. (2015)
Pb and Ni	nZVI fixed on quartz	Composted municipal waste and sewage sludge	0.2 and 0.5 g nZVI to 10 g of each organic compound	Laboratory, incubated in centrifuge tubes	Pb ~ 24 $mgkg^{-1}$ compost, Ni ~ 1.8 mg per kg compost	Pb 72.93% and Ni 23.27%	Pb 1 h, Ni 672 h	Ghasemzadeh and Bostani (2017)
Zn, Cu, Pb, As	nZVI	Soil and groundwater remediation		Field test		60%	1–3 days	Gonçalves (2016)

when nZVI was combined with organic acids, such as citric acid, tartaric acid and oxalic acids. The removal efficiency increased with increasing concentration of nZVI and solid-to-liquid ratio and decreased with increasing solution pH. Gopal et al. (2020) enhanced nZVI-Cu particles with bentonite support to overcome colloidal attraction and enhance total carbon removal. Li et al. (2019) anchored nZVI on Zn-MOF-74, thus significantly enhancing the removal of U(VI).

nZVI is extremely challenging to characterize and analyse due to their high reactivity, but it is crucial for the understanding and reproducibility of each project to report appropriate and detailed characterization of the nZVI (Chekli et al. 2016). There is also a definite lack of appropriate analytical methods for on-site detection and measurement of nZVI (Chekli et al. 2016). Natural environments and contaminations sites can vary widely from studies conducted in a closed system in the laboratory, and this can lead to a drastic overestimation of nZVI performance (Calderon and Fullana 2015; Guan et al. 2015; Li et al. 2017; Ye et al. 2019).

One of the biggest disadvantages of nZVI is its tendency for agglomeration during migration probably due to weak surface charges, and this leads to a reduced surface area and mobility as well as a deterioration of reactivity and an overall reduced efficiency (Chekli et al. 2016; Sun et al. 2006; Ye et al. 2019; Guan et al. 2015). However, sometimes lower reactivity is preferred, especially when treating slow moving groundwater, as in this case high reactivity requires more frequent injection of nZVI, which also leads to undesired cost and maintenance issues. Another one is the high reactivity of dry, bare nZVI with oxygen in the atmosphere; this leads to a passivation of the surface with a thin oxide layer (Chekli et al. 2016; Sun et al. 2006; Ye et al. 2019; Guan et al. 2015). This exothermic reaction entails also a logistic and safety problem, and there are two main approaches to make nZVI transportable: firstly as a slurry and secondly to deliberately passivate the surface (Ribas et al. 2017). To mitigate the decrease in reactivity due to the passivation, Ribas et al. (2017) invented an activation process, which degrades the oxide shell and enhances the electron transfer and increases the specific surface area of the nZVI.

Cundy et al. (2008) reasoned that nZVI could not be employed in a permeable reactive barrier (PRB) system or a similar flow-through application due to their lack of durability and extremely high pressure drops. Seven years later, Zhang et al. (2015) confirmed the feasibility of nZVI as the reactive medium in PRB on the basis of in situ remediation of uranium-contaminated red soils, even though there are still major influences (poor stability, mobility of nZVI and tendency for aggregation), limiting the reduction reactivity in the soil. This technology may not be suited for sites with a slow contaminant desorption rate, as a result of the relative short reactive lifetime (Zhao et al. 2016).

Table 5 Short overview of the costs of nZVI, ZVI and granular iron

	nZVI	ZVI	Granular iron	Literature
Cost	30–40 USD lb^{-1}	1–5 USD lb^{-1}	0.25–0.75 USD lb^{-1}	Bardos et al. (2011)
	15–100 £ per kg	Less than 1 £ per kg	Less than 1 £ per kg	2004 according to Crane and Scott (2012),
	50–150 £ per kg			Crane and Scott (2012)

nZVI that was injected during the in situ treatment of a contaminated site was left in the underground (Crane and Scott 2012). The contaminants that were not destroyed by chemical reactions were trapped in an immobile state and were not extracted from the groundwater or soil (Calderon and Fullana 2015). If those metastable systems gradually reverse towards a pre-injection state, a significant remobilization can occur (Calderon and Fullana 2015; Crane et al. 2011; Crane and Scott 2012). nZVI also has the disadvantage of relatively high costs in contrast to macro-ZVI and granular iron (Table 5).

Many toxicological concerns derive from the beforehand desired properties of nZVI like the small size, high reactivity and mobility (Cundy et al. 2008). Most research works regarding the toxicity of nZVI have shown a negative impact on many micro-organisms, especially for gram-negative bacteria (Fajardo et al. 2013). According to Vanzetto and Thomé (2019), USA and China are the leading nations in research regarding the toxicological impact of nZVI. The cytotoxicity includes disruption to the cell membrane integrity, interference with respiration and oxidative damage of DNA or enzymatic proteins by the generation of reactive oxygen species (ROS) (Vanzetto and Thomé 2019; Xie et al. 2017; Xue et al. 2018). The general trend was that with increasing nZVI concentration the toxicity to bacterial cells also increases (Fajardo et al. 2012), even though some researchers found the inverse trend that high concentrations were less toxic (Fajardo et al. 2013). Some surface stabilizers like CMC (carboxymethyl cellulose) are able to decrease the damages to cell membrane integrity, whereas the modification with other metals increases the toxicity (Xue et al. 2018). The treatments of aquifer sediments with nZVI showed a long-term adverse impact on the micro-organism (Vanzetto and Thomé 2019). It was found that fungal cells have a higher tolerance for nZVI than bacteria cells (Xue et al. 2018). It was observed that the organic matter decreases the toxicity of nZVI (Navarro et al. 2008; Pawlett et al. 2013). Aged nZVI also had a reduced toxic effect, probably due to the formation of the iron oxide layer (El-Temsah and Joner 2013). Baragaño et al. (2020) found the best results of removal rate of 89.5% at a dose of 2% nZVI (also tested 0.5%, 2%, 5% and 10%), with no negative effects on soil parameter and the soil phytotoxicity was also reduced. Dong et al. (2019) summarized the effect of nZVI on three types of functional anaerobic bacteria in the remediation of contaminated groundwater. The study proved that nZVI could create suitable environmental conditions for cell growth, but that it was highly dependent on the species and dosage of nZVI.

Discussion

The described approaches to utilize ZVI in environmental engineering, i.e. (i) PRBs, (ii) nZVI and (iii) fluidized bed reactors, have their specific advantages and disadvantages. Despite ongoing discussions about the mechanisms behind, their efficiency for the removal of both organic and inorganic pollutants from aqueous solution has been demonstrated. Due to their lower costs and lower toxicity, PRBs are and will be the dominant kind of application compared to nZVI. If cheaper production routes for nZVI will be developed and ecological issues turn out to be less crucial, this might change in the future. Fluidized bed reactors are the only of these three approaches which avoid passivation of the surface which decreases maintenance costs. On the other hand, their request for a pump-and-treat system is also associated with continuous costs. Increasing automation allows to run these reactors autonomously, whereas maintenance of PBRs still involves complex construction works. Therefore, it can be assumed that fluidized bed reactors will be favoured in more and more cases towards PBRs.

Conclusion

ZVI is a standard technology in environmental remediation. Its significance results from its broad and cheap application for a wide range of contaminants. There are three different variations for their application:

1. Granular ZVI is mostly used as reactive material in PRBs which have been installed all over the world. However, there are only a few studies dealing with the long-term application of this remediation technology and only one long-term assessment exceeding 15 years could be found (Wilkin et al. 2014). On the other hand, several recent studies discussed further development of ZVI in combination with different materials in laboratory scale

with controlled parameters such as high contaminant concentrations and short timescales. This makes it hard to assess the suitability of these innovation for field use, as laboratory settings often do not reflect conditions of contaminated sites, especially if there are multiple contaminants. Therefore, it will be crucial to focus research on application-based studies in the future. Moreover, literature studies show that research is moving towards nZVI, but there are also some open questions in this area.

2. Fluidized bed reactors ("ferrodecont process") are beginning to be applied as pump-and-treat system for the removal of Cr(VI) and organic contaminants from groundwater and of metals from industrial wastewater. Whereas their application in groundwater remediation is already conducted at the industrial scale, for industrial wastewater treatment the separation of the fixed nonferrous metals from the iron corrosion process still requires some upscaling.
3. The potential of nZVI for the in situ remediation for various contaminants has been shown; however, there are many site-related factors influencing the efficiency of those NPs. Due to that, it is quite challenging to select the most suitable treatment method for a specific site due to complex soil chemistry and/or aquifer characteristics; in some cases, it can be vital to combine two or more techniques to generate a better result (Hashim et al. 2011). One major aspect that needs further investigation is the environmental risk assessment, especially in regard to micro-organisms. The toxicological studies for bacterial and fungal species are still limited, that hampers the applicability because micro-organisms are different for each site. So, it is still in question if this method is truly feasible and environmentally acceptable.

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