



Review

The influences of iron characteristics, operating conditions and solution chemistry on contaminants removal by zero-valent iron: A review



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ABSTRACT

For successful application of a zero-valent iron (ZVI) system, of particular interest is the performance of ZVI under various conditions. The current review comprehensively summarizes the potential effects of the major influencing factors, such as iron intrinsic characteristics (e.g., surface area, iron impurities and oxide films), operating conditions (e.g., pH, dissolved oxygen, iron dosage, iron pretreatment, mixing conditions and temperature) and solution chemistry (e.g., anions, cations and natural organic matter) on the performance of ZVI reported in literature. It was demonstrated that all of the factors could exert significant effects on the ZVI performance toward contaminants removal, negatively or positively. Depending on the removal mechanisms of the respective contaminants and other environmental conditions, an individual variable may exhibit different effects. On the other hand, many of these influences have not been well understood or cannot be individually isolated in experimental or natural systems. Thus, more research is required in order to elucidate the exact roles and mechanisms of each factor in affecting the performance of ZVI. Furthermore, based on these understandings, future research may attempt to establish some feasible strategies to minimize the deteriorating effects and utilize the positive effects so as to improve the performance of ZVI.

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List of abbreviations

1,1,1-TCP	1,1,1-trichloropropanone	k_{SA}	Surface area normalized rate constant
124TCB	1,2,4-trichlorobenzene	k_{obs}	Rate constant of contaminants removal
2A4NT	2-amino-4-nitrotoluene	MCAA	Monochloroacetic acid
2-NT	2-nitrotoluene	mZVI	Microscale zero-valent iron
4A2NT	4-amino-2-nitrotoluene	NACs	Nitroaromatic compounds
4CINB	4-chloronitrobenzene	NB	Nitrobenzene
4-NP	4-nitrophenol	NOM	Natural organic matter
AQDS	Anthraquinone-2,6-disulfonate	nZVI	Nanoscale zero-valent iron
CAAs	Chloroacetic acids	PCE	Pentachloroethylene
CAHs	Chlorinated aliphatic hydrocarbons	PNP	<i>p</i> -nitrophenol
<i>cis</i> -DCE	<i>cis</i> -dichloroethylene	PRB	Permeable reactive barrier
CT	Carbon tetrachloride	$R_{impurity}$	Ratio of kinetic constants measured with and without impurity
DAT	2,4-diaminotoluene	$R_{pretreatment}$	Ratio of kinetic constants measured with and without pretreatment
DBPs	Disinfection byproducts	R_{NOM}	Ratio of kinetic constants measured with and without NOM
DCAA	Dichloroacetic acid	TCAA	Trichloroacetic acid
DO	Dissolved oxygen	TCA	Trichloroethane
DNT	2,4-dinitrotoluene	TCE	Trichloroethylene
HA	Humic acid	TNT	2,4,6-Trinitrotoluene
FA	Fulvic acid	TeCA	Tetrachloroethane
F_{MHD}	Lorentz force	ZVI	Zero-valent iron
$F_{\Delta B}$	Field gradient force		

1. Introduction

In the past two decades, zero-valent iron (ZVI) has attracted significant attention as a promising reactant for removal of various environmental contaminants from wastewater and groundwater due to its high reductive capacity, the environmental friendliness of iron, and the production of nontoxic iron oxides after the removal of the contaminants. ZVI is very versatile and it can act as a reductant (i.e., via Fe⁰ and surface-bound Fe(II)) for environmental contaminants, a sorbent (i.e., via the iron (hydr)oxide layer) for other metals, and a coagulant (i.e., via dissolution of Fe(II) from the ZVI surface) for various anions in wastewater and groundwater.

Therefore, various contaminants, including halogenated organics (Arnold and Roberts, 2000; Johnson et al., 1996; Roberts et al., 1996), nitroaromatics (Agrawal and Tratnyek, 1996; Keum and Li, 2004), dyes (Nam and Tratnyek, 2000), phenolic compounds (Morales et al., 2002), heavy metals (Rangsvik and Jekel, 2005; Shokes and Möller, 1999) and various oxyanions including arsenate (Neumann et al., 2013; Su and Puls, 2001a,b), arsenite (Neumann et al., 2013; Sun et al., 2014), chromate (Alowitz and Scherer, 2002; Feng et al., 2015), nitrate (Alowitz and Scherer, 2002), bromate (Xie and Shang, 2007), selenite (Liang et al., 2013), selenate (Klas and Kirk, 2013; Liang et al., 2015), and uranyl (Fiedor et al., 1998; Gu et al., 1998) could be removed by ZVI.

Table 1
Influence of iron intrinsic characteristics on the performance of ZVI towards contaminants removal.

Intrinsic iron characteristics	Effects	Mechanisms	Ref.
Surface area	Increasing iron surface area generally enhances the performance of ZVI.	Large surface area of ZVI is expected to provide more sites on which reactions occur.	(Agrawal and Tratnyek, 1996; Cope and Benson, 2009; Gillham and O'Hannesin, 1994; Wang and Zhang, 1997)
Iron impurities	Carbon	Enhancing the performance of ZVI	(Dou et al., 2010; Wu et al., 2013; Zhou et al., 2013)
		Deteriorating the performance of ZVI	(Burris et al., 1998; Lin and Lo, 2005; Velimirovic et al., 2013a)
	Sulfur	Enhancing the performance of ZVI	(Oh et al., 2002; Oh et al., 2004, 2005; Tamara and Butler, 2004; Ye and Chiu, 2006)
	Transition metals	Enhancing performance of ZVI	(Matheson and Tratnyek, 1994; O'Carroll et al., 2013)
		Deteriorating the performance of ZVI	(Tamara and Butler, 2004)
Oxide films	Deteriorating the performance of ZVI	Serving as a physical barrier to inhibit electron transfer.	(Scherer et al., 1998; Scherer et al., 2000)
	Enhancing or maintaining the performance of ZVI	Acting as a semiconductor to mediate electron transfer.	(Scherer et al., 1998; Scherer et al., 2000)
	Enhancing the performance of ZVI	Acting as a coordinating surface containing sites of Fe ²⁺ , which complexes with the contaminant and then reduces it.	(Scherer et al., 1998; Scherer et al., 2000)
		Facilitating the contaminants removal by adsorption and/or co-precipitation processes.	(Liang et al., 2014a; Sun et al., 2014; Yan et al., 2012)

Nowadays, ZVI has proven itself a promising technology for the remediation/treatment of groundwater and wastewater contaminated with a wide range of organic and inorganic contaminants (Fu et al., 2014; Guan et al., 2015b).

Many factors were believed to affect the performance of ZVI towards contaminants removal, and a huge number of studies have been conducted over the past 20 years (Johnson et al., 1996; Liu and Lowry, 2006; Tang et al., 2015). Specifically, these investigated factors can be roughly divided into three categories: iron characteristics, operating conditions and solution chemistry. Understanding their effects on the performance of the iron will provide opportunities to assess the feasibility of this technology and to adapt the engineering design to site-specific conditions. However, few review papers have summarized these factors affecting the ZVI performance (Fu et al., 2014; O'Carroll et al., 2013). Moreover, no general conclusions have been reached so far because the reported influences of each individual variable on the removal efficiency are limited to a specific contaminant, and the importance of these variables varied widely among different studies. For example, some researchers reported that the presence of dissolved oxygen (DO) could diminish the ZVI performance toward some contaminants such as bromate (Xie and Shang, 2007), bromoacetic acid (Zhang et al., 2004), and trichloropropanone (Lee et al., 2007), but others found that the existing DO could enhance the removal of chromate (Feng et al., 2015), nitrate (Westerhoff and James, 2003), dye (Wang et al., 2010), monochloroacetic and dichloroacetic acid (MCAA, DCAA) (Tang et al., 2015) by ZVI. Similarly, sulfate, one of the major anions present in natural waters, has been reported to enhance ZVI performance by destabilizing the passive surface films (Devlin and Allin, 2005), whereas a deterioration effect of sulfate on the reduction of trichloroethylene (TCE) by nanoscale zero-valent iron (nZVI) was also observed by Liu et al. (2007).

Therefore, it is important to better understand these factors to gain insight into the suitability of ZVI application for removal of

specific contaminants under certain environmental conditions. Accordingly, this review comprehensively summarizes the ZVI performance to date, with a focus on the influence of iron characteristics, operating conditions and solution chemistry on the contaminants removal by ZVI. Throughout this work, additional research needs and unresolved challenges are proposed to provide a future look to the pertinent engineering challenges of ZVI-based technologies.

2. Effect of iron intrinsic characteristics

Iron samples from different origins generally show different performance toward contaminants removal. Given that the iron intrinsic characteristics such as surface area, impurity and oxide film coating are always diverse among various iron types, they are always believed to contribute to this variation in ZVI performance. Thus, in this section, the effects of these factors on contaminants removal by ZVI will be discussed in detail, as summarized in Table 1.

2.1. Surface area

Since the process of contaminants removal by ZVI involves the reaction at the iron surface, the specific surface area of the ZVI particles has been identified as an important feature that influences the sequestration kinetics of contaminants by ZVI. In general, increasing the iron surface area, for instance by increasing the amount of iron or decreasing the particle size, was believed to enhance the contaminants removal rates (Agrawal and Tratnyek, 1996; Lien and Zhang, 2001; Wang and Zhang, 1997). For example, Gillham and O'Hannesin (1994) first reported that larger ZVI surface area could lead to greater rates of dehalogenation of chlorinated compounds. Subsequently, attempts were made to quantitatively establish a correlation between the degradation rates of a particular contaminant and the surface area of ZVI

(Alowitz and Scherer, 2002; Johnson et al., 1996; Su and Puls, 1999). Surface area concentration (ρ_a), the product of the iron solids concentration and the iron surface area, was first proposed by Matheson and Tratnyek (1994) as a general independent variable to correlate with the contaminants removal rate constants by ZVI. There were linear relationships between the rate constants of contaminants degradation (k_{obs}) and the surface area concentration of iron when carbon tetrachloride (CT) (Matheson and Tratnyek, 1994), TCE (Cope and Benson, 2009; Su and Puls, 1999), and nitro aromatic compounds (NACs) (Agrawal and Tratnyek, 1996) were degraded by ZVI. Moreover, normalization of the initial rate constants to iron surface area concentration yields a specific reaction rate constant k_{SA} (i.e., $k_{SA} = k_{obs}$ normalized to ρ_a), which is considered to be a more general descriptor of the reactivity of iron samples from different origins than k_{obs} , and is now widely used in remediation design calculations and other intersystem comparisons (Johnson et al., 1996; Kanel et al., 2006).

Although a larger surface area of ZVI is expected to provide more sites on which reactions occur, some studies had revealed that there was no particular correlation between the ZVI performance and specific surface area. For example, in order to explore the influencing factors of ZVI performance, Velimirovic et al. (2013a) prepared 13 different microscale zero-valent iron (mZVI) particles which were manufactured in a similar way but varied in particle size (D_{50} , 7–98 μm), surface area (0.04–11.4 m^2/g), and surface composition (mainly C, O and S content). Then, they evaluated the performance of these mZVI particles toward a mixture of chlorinated aliphatic hydrocarbons (CAHs) under consistent experimental conditions, and correlated the observed first order disappearance rate constants with the specific surface area of these mZVI samples (Velimirovic et al., 2013b). It was found that, although the fastest disappearance rate was achieved by the iron particles with the highest surface area, limited or no reactivity was observed for some iron samples with 4–10 times higher surface area than the others. Accordingly, the correlation analysis did not exhibit any strong association between the removal rate constants of CAHs and the specific surface area of mZVI samples, implying that there were other factors affecting ZVI performance significantly apart from the iron surface area.

2.2. Iron impurities

Different commercial ZVI particles (i.e., electrolytic vs. cast) that have been used either in laboratory studies or in full-scale applications vary widely in their composition and content of impurities (Henderson and Demond, 2007; Su and Puls, 1999; Velimirovic et al., 2013a). Cast iron, usually produced by reduction of ore (e.g., hematite ($\alpha\text{-Fe}_2\text{O}_3$) and limonite ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$)) by coke at high temperature, may contain substantial amounts of carbon and silicon, and smaller amounts of transition metals (e.g., Cu, Cr, and Ni), as well as other impurities such as sulfur. However, iron produced by electrolysis is typically more pure. Given the economic considerations, granular cast iron with a high content of impurities is typically used as the medium in field application. Thus, understanding the potential influence of impurities on iron performance is of particular interest.

2.2.1. Carbon

Carbon, a non-iron component in cast iron, has been suggested to be involved in the process of iron corrosion and/or contaminant removal, and a large portion of this carbon may occur as graphite (Ye and Chiu, 2006). It is generally agreed that aqueous Fe^0 corrosion occurs through an electrochemical mechanism. The anodic process is the Fe^0 dissolution while the cathodic process is the liberation of hydrogen as hydrogen gas under anaerobic conditions

or oxygen reduction under oxic conditions (Guan et al., 2015b; Noubactep, 2008). Carbon present in ZVI samples may act as additional cathodes to form galvanic couples with Fe^0 , and then the highly active $\text{Fe}(\text{II})$ and nascent hydrogen can be generated and released from the galvanic corrosion reaction (Zhou et al., 2013). Based on this principle, Wu et al. (2013) prepared activated carbon/nanoscale zero-valent iron (C- Fe^0) composites to induce micro-electrolysis so as to improve the removal of $\text{Cr}(\text{VI})$. Their results indicated that, compared with Fe^0 alone, the C- Fe^0 system shortened the reaction time necessary to reduce $\text{Cr}(\text{VI})$ to $\text{Cr}(\text{III})$ from 20 min to 10 min, and the reduction process was found to occur mainly on the surface of C. Further investigation showed that increasing the carbon cathode surface increased the electric current in the carbon-iron micro-electrolysis, indicating the redox reaction was enhanced by carbon. Similarly, Dou et al. (2010) investigated the $\text{As}(\text{V})$ removal by galvanic couples composed of zero-valent iron and activated carbon (Fe^0/AC). They found that the rate constant of $\text{As}(\text{V})$ removal by Fe^0/AC (1:1) was much higher than that of Fe^0 alone (0.802 versus 0.330 h^{-1}). Moreover, potentiodynamic polarization scans confirmed the promoted Fe^0 corrosion accounted for the improvement of $\text{As}(\text{V})$ removal when Fe^0 was coupled with AC.

Despite the fact that C- Fe^0 systems may improve the contaminants removal to some extent, a negative effect of carbon impurity was more extensively documented in literature. In particular, by acting as nonreactive sites, a high content of carbon present in iron may deteriorate the removal of chlorinated compounds (e.g., CT, PCE, TCE) by inducing nonreactive sorption (Burriss et al., 1998; Lin and Lo, 2005; Su and Puls, 1999; Velimirovic et al., 2013a). It has been reported that the reduction rates are proportional to the amount of chlorinated compounds sorbed onto the reactive sites, thus the nonreactive sorption by surface carbon could lead to delayed attainment of adequate steady-state pollutant removal in flow-through systems like packed beds or permeable reactive barriers (Burriss et al., 1998). Therefore, in order to obtain efficient

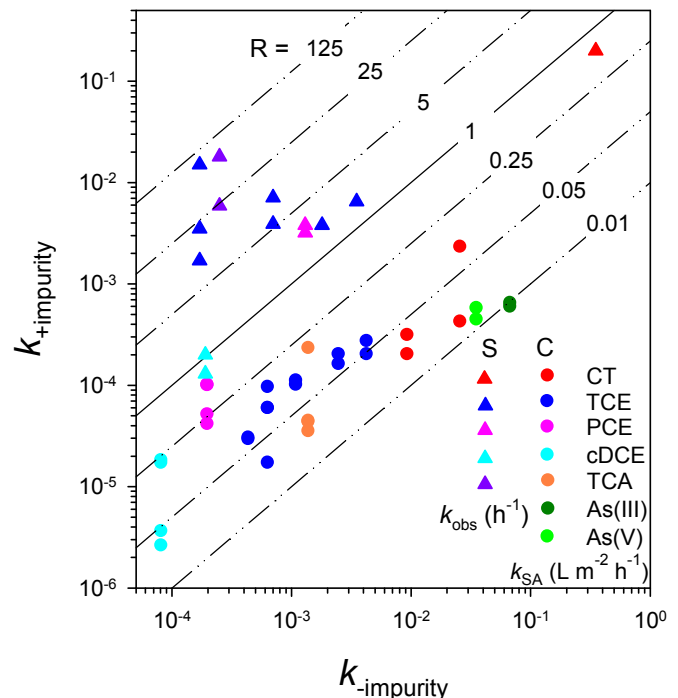


Fig. 1. Summary of the ratio of contaminants removal rate constants with low-purity and high-purity ZVI ($R_{impurity}$).

contaminant sequestration by ZVI, Velimirovic et al. (2013a) suggested that the carbon content present in iron particles should not exceed 0.5%.

In order to better elucidate the promoting or deteriorating effects of carbon, a ratio (R_{impurity} , herein R_{carbon}) of kinetic constants for contaminants removal by carbon-present Fe^0 (where the carbon content was in the range of 0.1–4%) and carbon-free Fe^0 was calculated, according to Eq. (1).

$$R_{\text{impurity}} = \frac{k_{+\text{impurity}}}{k_{-\text{impurity}}} \quad (1)$$

Note that the resulting ratios are unitless, so they should be directly comparable. Most of the data we compiled and used to calculate R_{impurity} were pseudo first order, but some were surface area normalized (i.e., reported as k_{SA}). All of the results in Table S1 (see Supporting Information) are summarized in Fig. 1 by plotting $\log k_{+\text{impurity}}$ vs. $\log k_{-\text{impurity}}$, with diagonal contours denoting selected values of R_{impurity} . As demonstrated in Fig. 1, the values of R_{carbon} generally fall in the range of 0.01–0.25, i.e., the presence of carbon impurity (0.1–4%) could retard the contaminants removal rates by a factor of 4–100. It should be specified that, although the available data for calculating the R_{carbon} were mainly relevant to chlorinated compounds, this trend may be extended to other types of contaminants (e.g., As(III) and As(V), see Fig. 1). To confirm this hypothesis and give a more practical implication, further investigation is needed by including other inorganic contaminants. On the other hand, it seemed that the roles of carbon present as impurity in iron particles were quite different from that in a C- Fe^0 system reported by Dou et al. (2010). This difference may be partially explained by the fact that the carbon content in iron particles (0.1–4%) is always much lower than that of the C- Fe^0 system (e.g., 50%) (Dou et al., 2010).

With respect to the exact role of carbon on the contaminants transformation in Fe^0 system, there was a debate on whether the carbon impurity can change the reaction pathway of some contaminants removal by ZVI (Dries et al., 2004). Some researchers claimed that, in addition to being nonreactive adsorption sites, graphite in cast iron could also mediate the reduction of nitrogenous compounds such as nitroaromatics, nitrate esters, nitrite, and heterocyclic nitramines by serving as reaction sites (Oh et al., 2002, 2004, 2005; Ye and Chiu, 2006). For example, Oh et al. (2002) investigated the reduction behaviors of 2,4-dinitrotoluene (DNT) by pure iron and cast iron (carbon content > 2%) in anaerobic conditions. They found that the reduction of DNT to 2,4-diaminotoluene (DAT) required over 2 h with scrap iron, whereas complete transformation was achieved within an hour by high-purity iron powder. More importantly, in contrast to the result with high-purity iron, 2-amino-4-nitrotoluene (2A4NT), rather than 4-amino-2-nitrotoluene (4A2NT), was observed to be the dominant intermediate in both aqueous and solid phases, suggesting that there were different mechanisms involved in the reduction of DNT by pure and cast iron. The slower DNT reduction observed with scrap iron may be attributed to the adsorption of DNT and its daughter products to graphite inclusions, which were proposed by Burris and co-workers to be nonreactive adsorption sites for chlorinated compounds (Burris et al., 1998). However, the theory of nonreactive adsorption to carbon cannot explain the disparity in distribution of the intermediates. Therefore, another possible explanation was proposed, i.e., the graphite inclusions in scrap iron can transfer reductants from iron to adsorbed nitroaromatic molecules, which represent a previously unrecognized type of reaction sites (Oh et al., 2002). This hypothesis was supported by further experiments conducted using two-compartment dialysis cells in which DNT and pure iron powder were separated by

a graphite sheet, where graphite mediated, indirect reduction of DNT occurred primarily through reduction of the *ortho* nitro group to form 2A4NT, while DNT reduction at the iron (hydr/oxide) surface occurred via *para* nitro reduction to give 4A2NT (Oh et al., 2002). With respect to the reductants in the cast iron system, it was considered that, in addition to electrons, atomic hydrogen produced through reduction of protons by elemental iron was also involved and more likely responsible for the DNT reduction (Oh et al., 2002). Based on the different intermediate distributions of DNT observed in pure and cast iron systems, Jafarpour et al. (2005) further examined the role of graphite in the reduction of DNT through numerical modeling. Their results indicated that most DNT (at least $66 \pm 2\%$) was reduced on the graphite surface despite the low graphite content and the reduction rates with graphite were generally lower than those with elemental iron. Moreover, their results suggested graphite might have the unique ability to both adsorb hydrophobic compounds and conduct electrons.

Tamara and Butler (2004) also reported that the graphite present in lower purity irons could favor the CT reaction pathway, dichloroelimination, which led to completely dechlorinated products at both pH 7.0 and 9.3. One possible explanation proposed by the authors was that increased contents of impurities such as graphite in the lower-purity irons could cause the trichloromethyl radical intermediate to sorb to the Fe^0 surface more closely or for a longer period of time, allowing a second one-electron transfer, in competition with hydrogenolysis. It is also possible that the conducting properties of graphite could facilitate a second electron transfer to the trichloromethyl radical, forming dichlorocarbene, which would then react to form completely dechlorinated products.

Summarizing this part, for the removal of many halogenated or nitrogenous compounds by cast iron, these contaminants could be adsorbed onto the embedded graphite which is relatively less reactive, resulting in a decreased remediation performance by cast iron. With regard to the removal of inorganic contaminants, the influences of carbon impurity are still unclear and deserve further investigation (Dou et al., 2010; Wu et al., 2013).

2.2.2. Sulfur

Sulfur is a common segregant that appears in cast irons. On the other hand, iron metal placed in PRBs could naturally (e.g., through the growth of sulfate-reducing bacteria) or through engineered measures (e.g., injection of sulfide) form an FeS coating (Wilkin et al., 2003). This coating had been extensively assessed as reactive medium to remove both metals and halogenated organics from groundwater (Henderson and Demond, 2013; Jeong and Hayes, 2007). Furthermore, it was evidenced that improved catalytic properties could be achieved by a combination of iron sulfides and zero-valent metals, although the exact mechanism of the process had not been fully elucidated.

For example, many studies have reported faster rates of CT (Lipczynskakochany et al., 1994) and TCE (Butler and Hayes, 2001; Hassan, 2000) degradation by Fe^0 treated with dissolved sulfide compared to the pristine Fe^0 , and one study even suggested a relationship between the S content of Fe^0 and the reductive dechlorination of TCE by Fe^0 (Hassan, 2000). Based on the kinetic results summarized in Table S1 and Eq. (1), the ratio (R_{sulfur} , $k_{+\text{sulfur}}/k_{-\text{sulfur}}$) of kinetic constants for contaminants removal by sulfur-present (or sulfide-treated) and sulfur-free Fe^0 was calculated. As illustrated in Fig. 1, the values of R_{sulfur} generally fall in the range of 1–125, which means the dissolved sulfide pretreatment of iron (sulfur contents range from 0.2% to 6.4%) could increase the contaminants removal rates by 1–125 fold. Accordingly, for iron particles containing appreciable amounts of sulfur impurities, ferrous sulfide may be formed *in situ* (following Eqs. (2)–(4)) and thus

improve the ZVI performance by acting as a catalyst (Hassan, 2000). The main reactions involved in ferrous sulfide formation can be written as:



Nonetheless, a comparison of iron performance between pure iron and cast iron in batch or field tests indicated that, little if any positive influence of sulfur content was always reported. For instance, contrary to the significant positive results of many studies, Tamara and Butler (2004) revealed that S contents (~0.1%) in cast irons did not increase the iron performance with respect to reductive dechlorination on a surface-area-normalized basis at constant pH, and they attributed this difference to the various pH conditions adopted in different studies. However, in our opinion, it seemed more likely the enhancing effect of sulfur was interfered or masked by the deteriorating effect of carbon, partially because the sulfur content (~0.1%) typical of cast irons was always much lower than that of carbon (2–4%). Therefore, in order to improve the ZVI performance by taking advantage of the enhancing effect of sulfur, iron pretreatment with dissolved sulfide may be necessary.

2.2.3. Transition metals

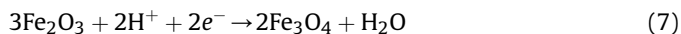
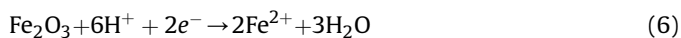
Localized corrosion can occur when two different metals are in contact. Therefore, the presence of transition metal impurities, like Cu, Cr, Ni and Co, is expected to influence the extent of Fe^0 corrosion, which in turn will affect the rates of contaminant removal. In most of the electrochemical couples, Fe^0 is considered to behave as an anode, becoming sacrificially oxidized to protect the noble metal, while the noble metal acts as a catalyst and increases the rate of reduction. These aspects have prompted the researchers to apply the so-called bimetals based on Fe^0 to enhance contaminants removal (Choi et al., 2008; Matheson and Tratnyek, 1994). This positive effect has been widely investigated and discussed in greater detail elsewhere (O'Carroll et al., 2013). Generally, based on the properties of metal additives, two types of catalytic mechanisms of the bimetallic reductants have been proposed: (1) the improved performance is related to the ability of the transition metal to enhance iron corrosion rates through formation of a galvanic couple (Lien and Zhang, 2002); (2) the reactivity of the reductant might be expected to scale with a metal additive's capacity to generate and store adsorbed atomic hydrogen (Cwiertny et al., 2006).

2.3. Oxide films coated on the iron surface

Depending on the formation time, the oxide films coated on ZVI surface could be divided into two categories: (1) an air-formed film that forms as a result of the commercial ZVI production and storage process (Gheju, 2011; Ritter et al., 2002); (2) an authigenic film that forms when ZVI contacts with water and contaminants. Both of them are believed to play important roles in determining the ZVI performance.

Specifically, the pre-existing oxide film is considered to consist of an inner film of Fe_3O_4 and an outer film of Fe_2O_3 . Electrons can migrate almost freely in the magnetite layer (a semiconductor with a band gap of 0.11 eV) (Huang and Zhang, 2005) and thus the magnetite layer will allow processes such as electron transfer to occur. However, the outer hematite and maghemite layers could passivate the iron surface, and greatly hinder the mass and electron

transport, resulting in a low performance of pristine ZVI in the initial reaction stage since it takes time to eliminate the oxide layer (Guan et al., 2015b; Huang and Zhang, 2005). Fortunately, upon contact with water, the breakdown of the protective film (i.e., autoreduction of Fe_2O_3) can occur, whereby water and electrons from iron metal participate in the reduction process (Odziemkowski and Simpraga, 2004). The related reactions can be written as:



It should be noted that the observed removal of original Fe_2O_3 from the iron surface does not necessarily indicate a thinning of the total film thickness. In contrast, this film may remain roughly the same in thickness, for example, as a result of conversion of the Fe_2O_3 to Fe_3O_4 (Eq. (7)), or it may have thickened, for example, due to the continuous formation of corrosion products.

Actually, oxide film formation is intrinsic to iron corrosion in water. Immersion can trigger processes including oxidation of the freshly exposed surface coupled with reduction of reactive solutes (e.g., oxygen, target contaminants), and aggregation of particles and subsequent cementation by formation of authigenic mixed-valent Fe(II)-Fe(III) phases. Long-term batch and column studies have shown that the surface layer of corrosion products evolves with time into a complex mixture of amorphous and crystalline iron oxyhydroxides (Fe_3O_4 , Fe_2O_3 , FeOOH , $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, etc.) (Noubactep, 2008, 2010a). As mentioned above, the oxide layer may be passivating, and its development could further decrease the reactivity of ZVI and reaction potential, despite the overall performance of the particle should be a function of morphology, distribution, and type of precipitates.

Given the mechanisms of contaminants removal by ZVI, three possible roles of the universal oxide film in reduction reactions at the $\text{Fe}^0/\text{H}_2\text{O}$ interface were proposed (Scherer et al., 1998, 2000): (1) the oxide film serves as a physical barrier deteriorating electron transfer from Fe^0 to the electron acceptor (contaminant) and the electron transfer may occur from the metal to the dissolved substance through defects in the metal such as pits; (2) the oxide film mediates electron transfer from Fe^0 to the contaminant by acting as a semiconductor; (3) the oxide film acts through coordinating surface sites of Fe^{2+} , which form complexes with the contaminants and then reduce them. However, Noubactep et al. (2009) claimed that, although this model was well-accepted, it overlooked the fact that some contaminants could also be adsorbed on to nascent or aged iron oxyhydroxides (adsorption) and would be entrapped in their structure (co-precipitation). Indeed, ZVI has been shown to remove a wide variety of contaminants from water by a mixture of transformation, adsorption, and co-precipitation processes. In cases where contaminants are not degraded, but rather are removed by transfer from the aqueous to solid phase, the overall treatment process is referred to as sequestration (Liang et al., 2014a, 2014b; Yan et al., 2012). The sequestration of contaminants (e.g., heavy metals) in $\text{Fe}^0/\text{H}_2\text{O}$ systems is generally favored by the growth and accumulation of iron oxides—and other iron-containing solid phases—that are formed by the Fe^{2+} that is released during corrosion of Fe^0 (Noubactep, 2009). However, the specific effects of these authigenic phases are multiple and variable, so the relative importance of specific effects is not always clear, despite many relevant studies have been conducted. For example, although thicker passive films (and the formation of secondary authigenic

Table 2
Influence of operating conditions on the performance of ZVI towards contaminants removal.

Operating conditions	Effects	Mechanisms	Ref.	
pH	Enhancing the performance of ZVI at low pH	Acceleration of iron corrosion and dissolution of the passivated oxide layers on ZVI surface; Direct involvement of H ⁺ in the contributing reactions.	(Matheson and Tratnyek, 1994; Song and Carraway, 2005)	
	Enhancing the performance of ZVI at high pH	An increase in the amount of surface-bound Fe(II); Slow loss of Fe phases; Favor the adsorption or precipitation of metal cations.	(Bae and Hanna, 2015; O'Carroll et al., 2013)	
	Deteriorating the performance of ZVI at low pH	A fast loss of ZVI particles through Fe dissolution; The excessive accumulation of hydrogen bubbles at ZVI interface.	(Chen et al., 2001; Choe et al., 2004)	
	Deteriorating the performance of ZVI at high pH	Passivation by mineral precipitation which inhibits the mass transfer.	(Agrawal and Tratnyek, 1996; Dong et al., 2010)	
DO	Deteriorating the performance of ZVI	A greater chance to form protective film and/or its ability to compete for electrons.	(Huang and Zhang, 2005; Tang et al., 2015)	
	Enhancing the performance of ZVI	Increasing iron corrosion; Formation of a more reducing condition.	(Guo et al., 2016; Guo et al., 2015)	
Iron dosage	Enhancing the performance of ZVI with increasing iron loading	Proportional increase in the number of active sites and reactive surface areas.	(Deng et al., 1999; Song and Carraway, 2005)	
Pretreatment	Acid washing	Enhancing the performance of ZVI	Breakdown of passivating oxide layer; Increasing surface area; Increasing density of highly reactive sites; Increasing concentrations of adsorbed H ⁺ and Cl ⁻ .	(Agrawal and Tratnyek, 1996; Matheson and Tratnyek, 1994) (Lai et al., 2006; Lai and Lo, 2008)
		Deteriorating the performance of ZVI	More severe mineral precipitation caused by the enhancing iron corrosion at the beginning.	
	H ₂	Enhancing the performance of ZVI	Increased reactive sites number and sorption capacity per unit iron surface area; Reduction of oxide film.	(Liou et al., 2005; Lin and Lo, 2005)
	Ultrasound	Enhancing the performance of ZVI	Removing corrosion products, precipitates and other debris from iron surfaces; Increasing the percentage of active sites by pitting and cracking of metal surfaces.	(Geiger et al., 2002; Hung et al., 2000)
	Premagnetization	Enhancing the performance of ZVI	Taking advantage of magnetic memory of ZVI, i.e., the remanence kept by ZVI.	(Li et al., 2015a; Li et al., 2015b)
Mixing	Mixing types	Magnetic mixing significantly enhances the performance of ZVI compared with mechanical mixing.	Magnetic field effect, i.e., Lorentz force gives rise to convection in solution; Field gradient force tends to move paramagnetic ions (Fe ²⁺) along the higher field gradient and causing localized corrosion	(Jiang et al., 2015; Liang et al., 2014a; Liang et al., 2014b)
	Mixing rates	Enhancing the performance of ZVI with increasing mixing intensity.	Increasing mass transport of oxidizing species (e.g., O ₂ , H ⁺ , and contaminants) and products (e.g., Fe ²⁺ , OH ⁻) toward/ from the iron surface; Causing particle abrasion and keeping corrosion products suspended.	(Agrawal and Tratnyek, 1996; Epolito et al., 2008; Scherer et al., 2001)
Temperature	Enhancing the performance of ZVI with elevating temperature	Overcoming the high activation energy barrier; Accelerating mass transport; Increasing the steady-state concentration of absorbed hydrogen.	(Bransfield et al., 2007; Lai et al., 2014; Oh et al., 2006)	

phases) increase the surface area for contaminant removal by non-reductive processes, breakdown of the passive film on ZVI generally favors contaminant reduction by exposing more strongly reducing surface area (Turcio-Ortega et al., 2012; Xie and Cwiertyny, 2010). When ZVI is deployed for water treatment under oxic conditions, the role of authigenic iron oxides is even more critical because the phase transformations are more dynamic and oxidative pathways for contaminant treatment become more significant (Mylon et al., 2010).

Considering the key role that oxide/passive films play in the—short and long term—performance of ZVI in remediation applications (Calderon and Fullana, 2015; O'Carroll et al., 2013; Sarathy et al., 2008), more attention should be paid to these effects (e.g., aging effect) in future.

3. Effect of operating conditions

In Fe⁰/H₂O systems, contaminants removal is neither a purely chemical/electrochemical reduction nor a purely physical adsorption process (Noubactep, 2009). Complex interfacial reactions like dissolution, adsorption, redox reaction, and precipitation can occur simultaneously or sequentially on the iron surface during the decontamination process. Thus, in addition to the iron intrinsic properties, some operational parameters, including pH, DO, iron dosage, iron pretreatment, mixing conditions, and temperature, should also impact these reactions significantly and can ultimately affect the fate and transport of the contaminants (see Table 2).

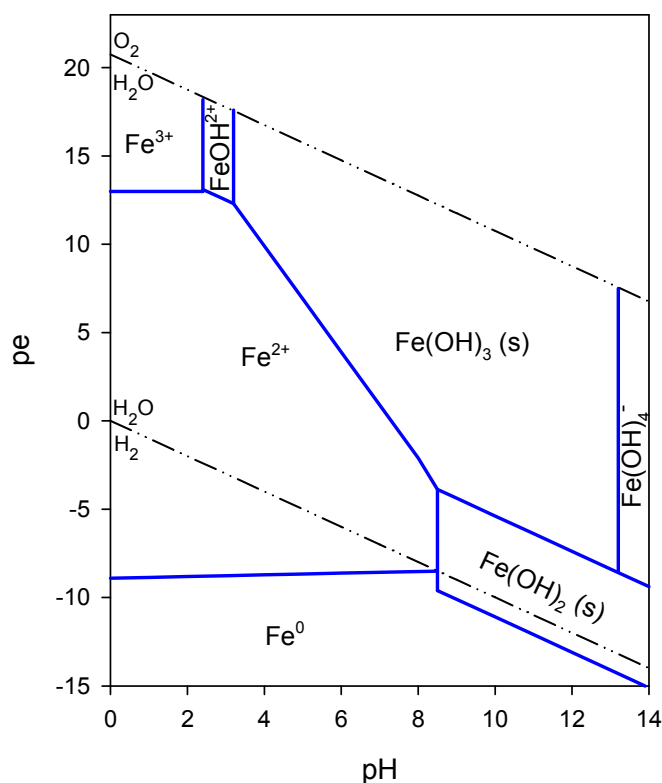


Fig. 2. pe-pH diagram for the Fe-H₂O system at 25 °C. Total Fe = 10⁻⁴ M.

3.1. pH

pH is one of the most important characteristics of natural waters that affects the rates of contaminants removal by ZVI since pH greatly affects the rate of ZVI corrosion (Bae and Hanna, 2015; O'Carroll et al., 2013). As shown in the pe-pH diagram for Fe-H₂O system (Fig. 2), at $pe > -9$, Fe⁰ becomes unstable and will react with water to form Fe(II) (Bang et al., 2005), which may hydrolyze and form Fe(OH)₂ or be oxidized to Fe(III) by oxygen. The resulting Fe(III) will readily hydrolyzes, precipitates (Fe(OH)₃) and transforms to oxides. Obviously, these reactions and the resulting domains of iron species in Fe-H₂O system are pH dependent, and pH would undoubtedly cause a change in ZVI performance.

An increase in rate constants with decreasing pH for reductive removal of organic or inorganic contaminants was commonly documented in literature. For example, over the pH range from 5.5 to 10.0, the reduction rate constants of CT by ZVI was found to decrease with increasing pH, and this pH effect on k_{obs} was apparently linear with a slope of 1.08 h⁻¹/pH (Matheson and Tratnyek, 1994). Likewise, Song and Carraway (2005) revealed that the reduction of 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA) by nZVI decreased with increasing pH from 6.5 to 9.0, consistently with the results observed for CHCl₃ and TCE reduction (Choe et al., 2001; Song and Carraway, 2006). For the inorganic contaminants removal, an enhancement in the performance of ZVI was also observed with decreasing pH values (Alowitz and Scherer, 2002; Guan et al., 2015a; Jiang et al., 2015). For instance, it has been reported that the specific rate constants of Se(IV) removal by ZVI in buffered solutions dropped from 92.9 to 6.87 L h⁻¹ m⁻² as pH increased from 4.0 to 7.0 (Liang et al., 2013). The pH effect on Se(IV) removal rate was unlikely ascribed to the species variation of Se(IV) with pH but most associated with the proton consuming nature of the reaction between Se(IV) and ZVI. Given reactive oxygen

substances including H₂O₂ and HO• can be generated in the Fe⁰/H₂O/O₂ system following the Fenton reactions, a pH-dependent trend of ZVI performance has also been reported for the oxidation of various organic and inorganic compounds by ZVI where the oxidation rates increased with decreasing pH (Joo et al., 2004; Katsoyiannis et al., 2008; Sun et al., 2014). For example, at initial pH 3.0, As(III) (1000 µg/L) could be completely converted to As(V) in solution within 1 h by 0.1 g/L ZVI, while increasing the initial pH to 5.0 and above, little dissolved As(V) could be detected even after 3 h (Sun et al., 2014).

In summary, the good performance of ZVI at low pH should be mainly ascribed to the acceleration of iron corrosion and dissolution of the passivated oxide layers on ZVI surface, while a high pH deteriorates the performance of ZVI due to more mineral precipitation which inhibits the mass transfer (Bae and Lee, 2014; Dong et al., 2010). However, lowering solution pH to very acidic condition (e.g., below 3.8) might also diminish the ZVI performance, as it could cause a fast loss of ZVI particles through Fe dissolution, and/or lead to an excessive accumulation of hydrogen bubbles at the ZVI interface which may decrease the available reactive surface area for contaminants removal (Chen et al., 2001; Choe et al., 2004). In addition, the pH effect can also be complicated by the pH dependent changes of the surface charge distribution of iron hydroxides/oxides, the ionization of weak acid or bases (pK_a values), and the solubility, speciation, complex formation tendency of metal or metalloid contaminants (Noubactep, 2010b). For example, increasing solution pH to moderate basic conditions can favor some metal cations removal by improved adsorption to iron oxides or precipitation as metal hydroxides via hydrolysis (e.g., Cu, Cd, Zn, Co) (O'Carroll et al., 2013). In a recent study, Bae and Hanna (2015) even suggested that high pH values (i.e., pH 8.0–9.0) could improve the reduction rate of 4-NP in both unbuffered and buffered suspensions in the presence of low amounts of nZVI (0.010–0.075 g/L), whereas lower pH (6.0–7.0, unbuffered) with same nZVI loading slowed the 4-NP reduction. These unexpected results may be associated with the following two factors: (1) relatively lower Fe(II) dissolution at high pH values than at pH 6.0 and 7.0, leading to the preservation of solid Fe phases, and/or (2) an increase in the amount of surface Fe(II) complexed with oxide coatings and then in the electron density of the surface-bound Fe(II). Contrary to numerous previous reports using buffered pH systems, the conflicting results also highlight the potential impacts of buffering agents (e.g., Good's buffers), although these buffers are widely believed to interact weakly with iron (Alowitz and Scherer, 2002).

3.2. DO

DO is ubiquitous in shallow groundwater aquifers or industrial wastewaters where most of the ZVI systems were operated (Huang and Zhang, 2005; Shimizu et al., 2012). As a highly active oxidant, DO may exert significant influence on iron corrosion and thus the subsequent removal of contaminants. The iron corrosion process, when iron is immersed in water, can be regarded as being made up of anodic and cathodic components. Obviously, the anodic process is the iron dissolution following Eq. (5). Regarding to the cathodic reaction, the reduction of oxygen would dominate in the presence of oxygen (Eq. (8)), while in the absence of oxygen the commonly invoked cathodic reaction will become the formation of hydrogen gas via the reduction of protons (Eq. (9)).



Although several studies have been conducted to explore the

potential effects of DO on the performance of ZVI in recent years, no general conclusions have been achieved to date (Huang and Zhang, 2005; Tang et al., 2015). Some researchers stated that the presence of DO could deteriorate the performance of ZVI due to the greater chance to form protective film and/or its ability to compete for electrons, while others argued that DO may also enhance the ZVI performance by increasing iron corrosion. For example, Lee et al. (2007) found that the rate constants of 1,1,1-trichloropropanone (1,1,1-TCP) degradation decreased significantly with increasing DO concentration, possibly due to oxygen out-competing the 1,1,1-TCP for reactive sites. Yin et al. (2012) also reported a remarkable deterioration effect of oxygen on NB reduction by ZVI, where only 21.5% NB was removed by the ZVI system aerating with pure oxygen within 8 h, while aerating the system by air or nitrogen could increase the NB removal to 75.2% and 92.3%, respectively. However, some studies did not observe any significant effect of DO on the reaction rates of some disinfection byproducts (DBPs) like tri-bromoacetic acid, trichloronitromethane, and trichloroacetonitrile by ZVI (Lee et al., 2007; Zhang et al., 2004). Furthermore, interesting results have been reported on an enhancing effect of DO on the removal of some contaminants with ZVI. For instance, Westerhoff and James (2003) found that a lower initial DO (8.8 versus 0.6 mg/L) resulted in 50% less reduction of nitrate, which was contrary to the expectation that oxygen reduction would be necessary prior to an onset in nitrate reduction. Likewise, the removal of perchlorate (Im et al., 2011), dyes (Wang et al., 2010), Cr(VI) (Yoon et al., 2011a) were also demonstrated to increase with the increasing DO concentration. Recently, by taking advantage of oxygen or other oxidants such as NaClO, H₂O₂, KMnO₄ and CrO₄²⁻, Guo et al. developed a new method (i.e., ZVI/oxidants) to improve the performance of ZVI (Guo et al., 2015, 2016). Their interesting results highlighted the critical role of strong oxidant in ZVI technology (not mainly related to the Fenton's reaction despite it can be strengthened simultaneously). In particular, the presence of such strong oxidants can drive very rapid and intensive iron corrosion by oxidative attacking the iron surface, and can hence facilitate the nitrate reduction or the sequestration of many heavy metals (e.g., As(V), Sb(V), Cd(II), Hg(II)) from water. It seems that, besides accelerating the generation of iron oxides which can act as adsorption sites, the presence of oxygen may facilitate the formation of a more reducing condition partially due to the rapid

production of dissolved and/or surface-bound Fe(II) (Huang and Zhang, 2005; Liang et al., 2014b).

With respect to the discrepancies in the role of DO, one possible explanation was considered to be related with the formation of various iron corrosion products (Huang and Zhang, 2005), which can serve as a physical barrier, a semiconductor or a coordinating surface, as mentioned in Section 2.3. In the presence of DO, a two-layer structure with an inner layer of magnetite and an outer layer of lepidocrocite may be formed, which would deteriorate the performance of ZVI. While with DO being depleted, the outer lepidocrocite layer may be transformed to magnetite, which is not expected to impede the ZVI performance even in a substantial thickness. From the other perspective, some researchers suggested the aqueous and adsorbed/structural Fe(II) involved in ZVI system could also account for the effect of oxygen. Tang et al. (2015) investigated the performance of ZVI for CAAs (e.g., MCAA, DCAA and TCAA) removal under controlled dissolved oxygen conditions (0, 0.75, 1.52, 2.59, 3.47 or 7.09 mg/L DO). They found that the removal of CAAs increased first and then decreased with increasing DO concentration. Compared with anoxic condition, the presence of oxygen substantially enhanced the reduction rates of MCAA and DCAA, which reached a peak at 1.52 mg/L DO, while for the TCAA reduction, DO significantly deteriorated its removal rates especially when the oxygen concentration was above 2.59 mg/L. Depending on the change of reducing agents and corrosion coatings, it was suggested that accumulation of aqueous ferrous iron (~7.28 mM) under anoxic conditions deteriorated the corrosion of iron and thus reduced the available reductants for CAAs degradation; under the low oxidic condition (e.g., below 2.59 mg/L), the reduction of O₂ by ferrous iron was dominating, with the formation of green rust which was expected to be powerful for removal of CAAs; while under highly oxidic conditions, the excess oxygen would markedly compete for reducing agents, resulting in a drop in the CAAs rate constants.

In our opinion, the role of oxygen in the performance of ZVI may be case/pollutant specific, namely this effect may significantly depend on the removal mechanisms of contaminants. As demonstrated in Fig. 3, for contaminants removal via adsorption or oxidation process, an enhancing effect of DO could be safely concluded. However, for contaminants removal where a reduction process was involved, the presence of oxygen could induce a trade-

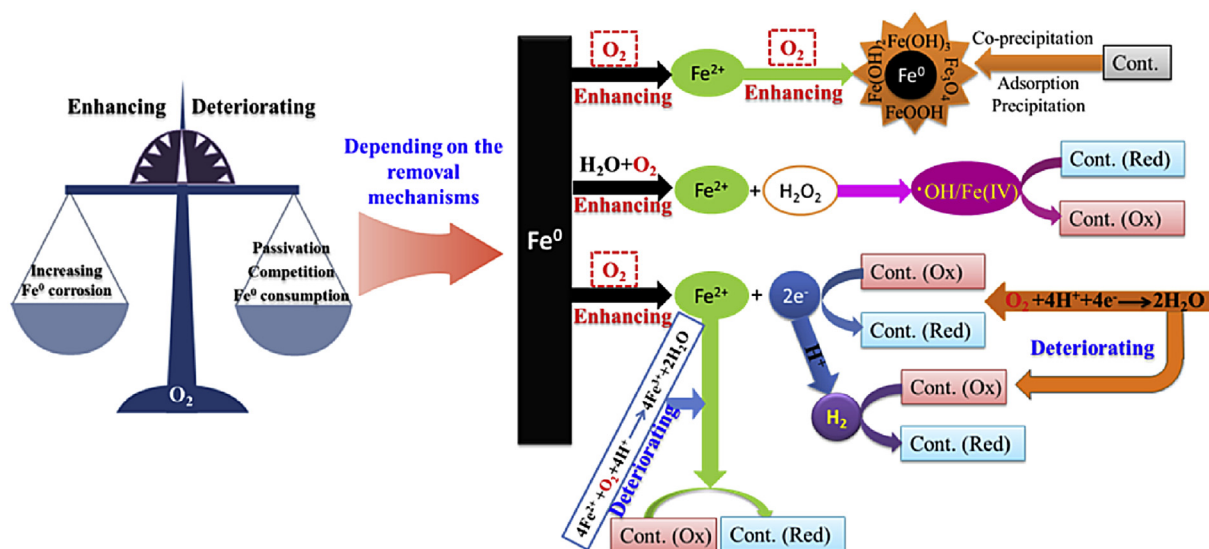


Fig. 3. Illustration of the multiple roles of DO in the process of contaminants removal by ZVI.

off between the increased iron corrosion and the competition for reducing species (Fe^0 , Fe^{2+} , H_2). Given that these multiple roles always occur independently or in combination, the net effect of oxygen on contaminants reduction by ZVI would be difficult to predict. Nevertheless, future attempts could be made to find some feasible methods either to minimize the deterioration effects of oxygen or to enhance the ZVI performance taking advantage of its promotion effect.

3.3. Iron dosage

It is obvious that an increase of ZVI dosage will exert a positive effect on the performance of ZVI due to the proportional increase of the number of active sites and reactive surface area. For example, Matheson and Tratnyek (1994) demonstrated that regression of the CT dehalogenation rate constants versus iron concentration gave a linear relationship with $R^2 = 0.96$. Deng et al. (1999) also observed that the rates of vinyl chloride (VC) reduction by metallic iron and ethylene production were accelerated by increasing amounts of iron. Similarly, for TCA reduction by nZVI, the corresponding pseudo-first-order rate constant was found to increase linearly up to at least a loading of 0.32 g/L (Song and Carraway, 2005).

Although many studies have concluded the observed rate constant increased in a linear fashion with increased iron loading, conflicting results have also been documented in literature. For instance, Bae and Hanna (2015) systematically studied the effect of nZVI concentration on the reduction of 4-NP, solution pH, oxidation and reduction potential (ORP) and dissolved Fe(II) in unbuffered pH systems. It was found that an exponential rather than a linear relationship between the rate constant and the nZVI concentration was obtained despite the reduction kinetics of 4-NP was inevitably accelerated with the increasing nZVI concentration. This suggested that not only the nZVI concentration but also additional factors (e.g., a higher pH induced by a high nZVI loading, see Section 3.1) may contribute to the improvement in the degradation kinetics of 4-NP (Bae and Hanna, 2015).

3.4. Pretreatment of iron

As mentioned in Section 2.3, non-pretreated commercial ZVI is usually covered with a discontinuous passive layer of iron oxides, which can hinder the mass transport of oxidizing species and products to/from the iron surface, resulting in a low contaminant removal performance. Therefore, in order to maintain or enhance the ZVI performance, iron pretreatment by manipulating the properties of the oxides before the initial reaction stage was conducted in some studies (Guan et al., 2015b). The commonly used iron surface pretreatment strategies include acid washing, H_2 -pretreatment, ultrasound-pretreatment, and recently premagnetization. All of them are believed to exert influence on the ZVI performance to some extents.

Acid washing, one of the earliest examples used to pretreat virgin ZVI, can remove the passive oxide layer and thus increase the contaminant reduction rates in laboratory tests (Clark et al., 2003; Matheson and Tratnyek, 1994). As proposed by Agrawal and Tratnyek (1996), the positive effect induced by HCl pretreatment should be associated with one or more of the following mechanisms: (1) cleaning of the surface by dissolution of the metal and breakdown of the passivating oxide layer, (2) increasing the metal surface area by etching and pitting through corrosion, (3) increase in the density of highly reactive sites consisting of steps, edges, and kinks, following corrosion by the acid, and (4) increased concentrations of adsorbed H^+ and Cl^- that persist after pretreatment with HCl. However, compared with the unwashed ZVI, some researchers had reported that acid washing may deteriorate the performance of

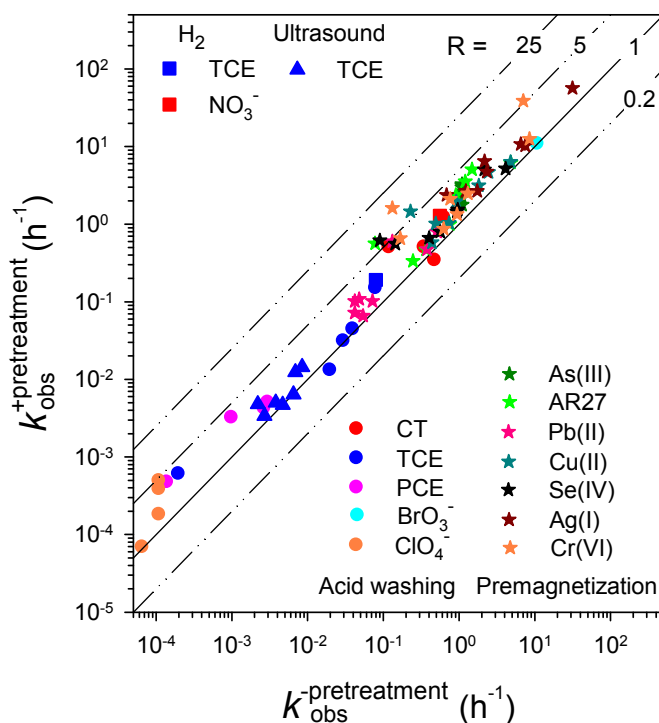


Fig. 4. Summary of the ratio of kinetic constants with and without pretreatment ($k_{\text{pretreatment}}^+$) for currently available data on contaminants removal by ZVI.

ZVI toward contaminants removal (e.g., Cr(VI), TCE) in long-term column tests (Lai et al., 2006; Lai and Lo, 2008). One possible explanation is that the accelerated iron corrosion rate at the beginning might subsequently result in more severe mineral precipitation on the ZVI surface, which would lead to more severe and rapid loss of the acid-washed ZVI reactivity.

Pretreatment with H_2 was also observed to have the ability to improve nitrate (Liou et al., 2005) and TCE (Lin and Lo, 2005) removal by ZVI. It was believed that both the number of reactive sites and the sorption capacity per unit iron surface area were increased through the H_2 -reducing pretreatment. Similarly, as a direct approach, the application of ultrasonic energy has been shown to change the iron surface physically and chemically and thus restore the reactivity of ZVI (Ruiz et al., 2000). Specifically, besides removing corrosion products, precipitates and other debris from iron surfaces, ultrasound-pretreatment can also alter the ratios of surface species (such as adventitious carbon to carbonyl carbon and iron to oxygen) to make the iron more reactive (Geiger et al., 2002; Hung et al., 2000).

ZVI is ferromagnetic, so it can be magnetized in an external magnetic field and remains magnetized even after the external field is removed. Recently, premagnetization of iron by taking advantage of its magnetic memory was employed in our laboratory to improve the ZVI performance (Li et al., 2015b). It was surprisingly observed that, compared to the pristine ZVI, a greater As(III) elimination rate was obtained by the premagnetized ZVI over the initial pH range of 4.0–9.0, and the reaction rate increased progressively with increasing the intensity of the magnetic field for premagnetization. Moreover, from a broad perspective, premagnetization could enhance the performances of multiple ZVI samples for the sequestration of various oxidative contaminants (including amaranth (AR27), Pb(II), Cu(II), Se(IV), Ag(I) and Cr(VI)) with rate constants that were 1.2- to 12.2- folds greater than those by pristine ZVI under well-controlled experimental conditions (Li et al., 2015a). Further investigation indicated that the improved

performance of premagnetized ZVI was not induced by the physical squeezing effect of the ZVI grains during magnetization, but more likely ascribed to the remanence kept by the magnetized ZVI. The remanence kept in the ZVI particles after premagnetization makes each magnetized ZVI particle a small magnet, which can generate an inhomogeneous magnetic field around the surface of magnetized ZVI particle. Thus, being analogous to applying an external weak magnetic field (WMF), an enhancing effect of premagnetization on ZVI performance was observed (the relevant mechanisms were further discussed in Section 3.5.1).

Based on the kinetic results summarized in Table S2, the ratio ($R_{\text{pretreatment}}$, $k_{+\text{pretreatment}}/k_{-\text{pretreatment}}$) of kinetic constants with and without pretreatment for currently available data on contaminants removal by ZVI was calculated and illustrated in Fig. 4. A comparison of the $R_{\text{pretreatment}}$ values relevant to the different pretreatment methods revealed that, premagnetization was a little more efficient (1.2–12.2 vs. 0.7–4.5) than the other three methods in improving the performance of ZVI. More importantly, given that employing premagnetization possesses many other merits such as chemical-free, ease of operation and environmentally friendliness, this method will definitely count much in the field of ZVI-based technology.

3.5. Mixing

3.5.1. Mixing methods

In batch tests, the commonly used mixing methods to overcome the limitation of mass transport include shaking with orbital shaker or end-over-end tumbler and stirring with mechanical or magnetic stirrer. Despite all of them can mix the iron slurry conveniently, different ZVI performance would be obtained by different mixing devices. For example, Epolito et al. (2008) reported that the Reactive Blue 4 (RB4) decolorization rate using an end-over-end tumbler at 4 rpm was almost as fast as that obtained with the orbital shaker at 300 rpm, indicating that mixing characteristics may be more important than the mixing speed.

Moreover, the WMF introduced by a magnetic stirrer should not be neglected when ZVI was used to sequester contaminants. However, until recently few studies have recognized and addressed the potential effect of WMF on the performance of ZVI. In our lab, it was found that replacing the magnetic stirrer with a mechanical stirrer considerably decreased Se(IV) removal by ZVI. Careful examination of the literature implied that this phenomenon may be ascribed to the WMF (<70 mT) supplied by the magnetic stirrer and the magnetic rotor (Liang et al., 2014b). Further investigation confirmed this hypothesis and demonstrated that the application of a WMF can accelerate the ZVI corrosion and thus enhance the removal of many organic and inorganic contaminants (e.g., Orange II (Xiao et al., 2016), Se(IV) (Liang et al., 2014a, 2014b), As(V)/As(III) (Sun et al., 2014), Cu(II) (Jiang et al., 2015), Cr(VI) (Feng et al., 2015)).

With respect to the mechanisms of WMF-induced enhancement on ZVI performance, it appears to be mainly associated with the Lorentz force (F_{MHD}) and the field gradient force ($F_{\Delta B}$) involved in ZVI/WMF system. In particular, the Lorentz force can give rise to convection in the solution which narrows the diffusion layer and enhances mass transport across the passive film at the metal-solution interface (Hinds et al., 2001; Lioubashevski et al., 2004). The field gradient force tends to move paramagnetic ions (Fe^{2+}) along the higher field gradient at the ZVI particle surface, which creates localized galvanic couples and electromagnetic forces that stimulate the migration of ions, breakdown of the passive film and eventually localized corrosion (Sueptitz et al., 2011; Waskaas and Kharkats, 2001). Numerical simulations were performed to evaluate the flux density distribution near the ZVI sphere surface, by assuming a 10 μm diameter spherical particle of pure ZVI in an

externally-applied magnetic field with homogeneous flux density (B_{appl}) of 10 mT. It was found that, at the point of peak field gradient, the calculated magnetic forces acting on Fe^{2+} are $F_{\text{MHD}} = 0.17 \text{ N m}^{-3}$ and $F_{\Delta B} = 64.4 \text{ N m}^{-3}$ (with a molar magnetic susceptibility of $14750 \times 10^{-9} \text{ L mol}^{-1}$ and assuming a Fe^{2+} concentration of 0.01 M) (Liang et al., 2014b). Accordingly, the field gradient force seems to play a more important role in inducing the WMF effects since a much higher $F_{\Delta B}$ could be achieved.

3.5.2. Mixing rate

Depending on the characteristics of contaminant and operating conditions of the system, many studies have shown that the contaminant removal process by ZVI is mass transport limited, where the reaction rate increases with increasing mixing intensity (e.g., rpm). Indeed, Agrawal and Tratnyek (1996) pointed out that, for a reaction that is completely mass transport limited, a linear relationship should exist between the reaction rate coefficient and the square root of the batch mixing rate ($\text{rpm}^{1/2}$). Using a ZVI rotating disk electrode, Scherer et al. (2001) further revealed that the current densities varied linearly with $\text{rpm}^{1/2}$ (electrode rotation rates below 4900 rpm) in the nitrobenzene reduction process. On the other hand, nonlinear increasing relationships between reaction rate and $\text{rpm}^{1/2}$ were also observed by some researchers. For example, Epolito et al. (2008) conducted a series of decolorization assays with an orbital shaker at the following rotational speeds: 0, 4, 25, 50, 100, 200, 300 and 400 rpm. It was found that RB4 decolorization rate did not exhibit an expected linear pattern but more likely an exponential increase with respect to $\text{rpm}^{1/2}$, which was considered to be associated with the inefficient mixing by the orbital shaker at or below 60 rpm, as well as the ZVI surface site saturation effect (Nam and Tratnyek, 2000).

In summary, since the mass transfer resistance in the diffusion boundary layer and iron oxides film of a ZVI particle plays a crucial role in the process of contaminants removal by ZVI, any mixing operation that can accelerate the transport of oxidizing species (e.g., O_2 , H^+ , and contaminants that can accept electrons) and products (e.g., Fe^{2+} , OH^-) toward/from the iron surface, will enhance the performance of ZVI. In addition, by causing particle abrasion and keeping corrosion products suspended, the mixing process could also facilitate the accessibility of iron surface for contaminants and thus improve the performance of ZVI.

3.6. Temperature

Temperature, an important parameter for both laboratory batch tests and field treatment units design, is always considered to have a positive impact on the performance of ZVI when it is elevated. For example, to evaluate the temperature effect on the arsenic removal by ZVI in geothermal waters (where high temperature can occur naturally), batch kinetic studies were carried out by Tyrovala et al. (2006) at three different temperatures at 20, 30 and 40 °C. It was found that a 20 °C temperature increase caused 89.5% increase in the pseudo-first-order constant for the experiment with As(III) and 60.9% for the experiment with As(V). In addition, the increase in temperature also resulted in a significant increase in the elimination rate constants of co-present nitrate and phosphate by ZVI. Elevating temperature had also been used to increase the reduction of perchlorate, which reacts with iron slowly under ambient conditions. Oh et al. (2006) revealed that with elevating the temperature to 200 °C by a microwave digester, 98% of aqueous perchlorate could be removed by ZVI in 1 h and complete removal was achieved after 2 h. Similarly, at a moderately elevated temperature (75 °C), complete NO_3^- removal could be obtained within 30 min retention time in a Fe^0 -packed column (Ahn et al., 2008). Recently, Lai et al. (2014) systematically investigated the influence

Table 3
Influence of co-existing solutes on the performance of ZVI towards contaminants removal.

Co-existing solutes		Effects	Mechanisms	Ref.
Anions	Cl ⁻	Enhancing the performance of ZVI Deteriorating the performance of ZVI	Formation complexes with iron centers to breakdown the protective oxide film; Causing pitting corrosion. Competitive sorption with respect to perchlorate or nitrate reduction.	(Devlin and Allin, 2005; Hernandez et al., 2004; Johnson et al., 1998) (Hwang et al., 2015; Moore et al., 2003)
	SO ₄ ²⁻	Enhancing the performance of ZVI	Increasing the surface reactivity or sorption capacity; Formation complexes with iron centers to breakdown the protective oxide film.	(Bi et al., 2009; Devlin and Allin, 2005; Jeong et al., 2015; Zhu et al., 2013)
	NO ₃ ⁻	Deteriorating the performance of ZVI	Rapid iron consumption; Alternation of surface properties by Fe-anion complexes.	(Liu et al., 2007; Su and Puls, 2004; Yu et al., 2013)
		Deteriorating the performance of ZVI	As a reactant, it competes for reactive sites with target contaminants; As a passivating agent, it generates passive oxide film.	(Farrell et al., 2000; Klausen et al., 2001; Xie and Cwiertny, 2013)
	HCO ₃ ⁻	Enhancing the performance of ZVI	Not well established.	(Liu et al., 2007; Su et al., 2014)
		Deteriorating the performance of ZVI	Passivation caused by carbonate-bearing minerals; Passivation of reactive sites by forming Fe-anion complexes.	(Köber et al., 2002; Klausen et al., 2003; Phillips et al., 2000)
	SiO ₃ ²⁻	Enhancing the performance of ZVI	Not well established but it is depending on concentration (relatively low) and exposure time (short-term).	(Agrawal et al., 2002; Bi et al., 2009)
Cations	Fe ²⁺ , Mg ²⁺ , Mn ²⁺ , Co ²⁺ , Ni ²⁺ , Zn ²⁺ , Cu ²⁺ , Pb ²⁺	Deteriorating the performance of ZVI	Physically blocking access of the contaminants to the reactive sites by forming a protective layer; Chemically alter the reactivity of the interfacial region by changing the speciation of the surface-associated iron	(Klausen et al., 2003; Kohn and Roberts, 2006; Su and Puls, 2001a,b)
		No apparent influence	Acting as an inert supporting electrolyte under ambient conditions.	(Devlin and Allin, 2005; Moore et al., 2003)
	Ca ²⁺ , Mg ²⁺	Potential deteriorating or enhancing effects Enhancing the performance of ZVI	Reduction by ZVI in long term applications or at elevated temperatures. Serving as electron donor; Enhancing electron transfer; Formation of bimetallic system; Depassivation of aged Fe ⁰ .	(Lim and Zhu, 2008; Im et al., 2011) (Bae and Hanna, 2015; Huang et al., 2012; Tang et al., 2014b; Xu et al., 2012)
NOM		Deteriorating the performance of ZVI	Masking the reactive sites on the Fe ⁰ surface by accumulation of precipitates such as CaCO ₃ Competing for or blocking of reactive sites; Decreasing mass transfer to/from the reactive surfaces; Changing the surface electrostatic and reductive potentials.	(Bennett, 1997; Dong et al., 2013; Mak et al., 2009) (Johnson et al., 2009; Klausen et al., 2003; Tsang et al., 2009)
		Enhancing the performance of ZVI	Enhanced adsorption; Serving as electron shuttle.	(Tratnyek et al., 2001; Xie and Shang, 2005)

of operating temperature on the reduction behavior of refractory *p*-nitrophenol (PNP) by ZVI, as well as on the relevant parameters like iron dosage, pH, and stirring speed. According to their results, elevated temperature (e.g., 85 °C) could significantly improve the reduction efficiency of the concentrated PNP (1000–10,000 mg/L) in industrial wastewater by ZVI. Furthermore, due to the employment of high temperature, the necessary iron dosage and stirring intensity could be reduced, meanwhile the working solution pH could be broadened from <5.0 to 6.7 (Lai et al., 2014).

With respect to the mechanism of the enhancing effect of temperature, it should be mainly ascribed to three aspects: (1) elevating temperature helps to overcome the high activation energy barrier; (2) elevating temperature can increase the steady-state concentration of adsorbed atomic hydrogen for contaminant removal (Bransfield et al., 2007); (3) elevating temperature can accelerate mass transport by enhancing the average kinetic energy and thermal motion of the molecules.

4. Effect of solution chemistry

Apart from the iron properties and operating conditions, there are many other factors that affect the ZVI performance under realistic conditions and, one of the most widely recognized and thoroughly studied factors was solution chemistry, including pH, DO and water constituents, etc. The effects of pH and DO have been discussed in Section 3. Thus, in this section, the water constituent effects will be discussed.

Typical co-solutes present in natural water include a wide range

of anions (such as chloride, sulfate, nitrate, carbonate, silicate and perchlorate) and cations (such as Fe²⁺, Co²⁺, Ni²⁺) including those controlling hardness (e.g., Ca²⁺, Mg²⁺), as well as natural organic matter (NOM). Many studies had reported that the types and amounts of co-solutes in aqueous matrix would dictate the performance of ZVI (Klausen et al., 2003; Liu et al., 2007; Wilkin et al., 2003). Generally, as shown in Table 3, some solutes are redox-active species that can consume ZVI through cathodic attack and some are inert species that may deposit on the iron surface resulting in the formation of water-solid interfacial barrier to mass transfer or deactivation of surface reductive sites through mineralogical modification. In contrast, some other solutes may enhance the performance of ZVI either by facilitating the breakdown of passivating Fe(III) (hydr)oxide coatings or by enabling the formation of new reactive phases. Individual solutes may concurrently serve different roles, and the net effect could vary with concentration, exposure time and also contaminant type.

4.1. Coexisting anions

4.1.1. Cl⁻

Chloride is generally considered to be a corrosion promoter capable of destabilizing the passive oxide film, and thus can enhance the performance of ZVI. For example, using a glass-encased magnet (GEM) reactor, Devlin and Allin (2005) investigated the Cl⁻ effect on the performance of granular iron toward 4-chloronitrobenzene (4CINB). It was found that, relative to ClO₄⁻, the presence of 8 mM Cl⁻ significantly enhanced the 4CINB reduction,

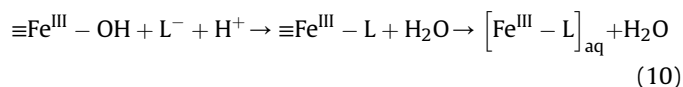
and this positive effect was proposed to be associated with either increased surface reactivity or sorption capacity. Likewise, Hernandez et al. (2004) demonstrated that the surface area normalized pseudo-first-order rate constant of 2,4,6-Trinitrotoluene (TNT) degradation by ZVI increased from 6.5 L/(m²·h) in the absence of Cl⁻ to 37 L/(m²·h) in the presence of 3 mM Cl⁻.

In general, the reaction enhancement by chloride can be attributed to two factors. Firstly, the addition of chloride anions can enforce the breakdown of the protective oxide film coated on ZVI surface. Hard Lewis base ions (such as Cl⁻, Br⁻) were reported to be especially aggressive toward the passivating oxide layers to form strong complexes with iron centers (Johnson et al., 1998). As the oxide layers were broken down by these diffusing anions, more bare metal was exposed and available for water, oxygen or target contaminants. Secondly, chloride can promote localized corrosion on iron with irregular pit shapes, and pitting on the iron surface provides new reactive sites for reaction of organic and inorganic species adsorbed onto the metal surface (Gotpagar et al., 1999; Hernandez et al., 2004).

Nonetheless, conflicting results about the effects of chloride on the performance of ZVI had also been reported. For instance, during long-term experiments, it was observed that the promoting effect of Cl⁻ on degradation of 2-nitrotoluene (2-NT) (Klausen et al., 2001) or TCE (Klausen et al., 2003) by ZVI decreased over time, indicating that the rate-enhancing effect of Cl⁻ may be relatively short lived. Moreover, the deterioration effects of Cl⁻ have been reported by some researchers, such as in the reduction of perchlorate (Moore et al., 2003) or nitrate (Hwang et al., 2015). This negative impact was believed to be associated with the competitive sorption at the metal surface, which could limit the surface sites available for perchlorate or nitrate reduction.

4.1.2. SO₄²⁻

Sulfate is another common anion associated with an enhancement of the performance of ZVI (Devlin and Allin, 2005; Johnson et al., 1998), although the exact mechanism by which it enhances the performance of ZVI has not been conclusively established. For example, it has been reported that the degradation of CT (Lipczynskakochany et al., 1994), 4CINB (Bi et al., 2009; Devlin and Allin, 2005), NB (Yin et al., 2012) and the sequestration of As(V) (Biterna et al., 2007) could be accelerated in the presence of SO₄²⁻. Sulfate is not expected to act as aggressively toward the oxides as chloride does, while many studies have reported metal oxide dissolution promoted by SO₄²⁻ (i.e., ligand-promoted dissolution, Eq. (10)).



Specifically, SO₄²⁻ can strongly adsorb onto oxide surfaces by displacing the surface hydroxyl groups and forming monodentate or bidentate complexes with surface iron (Ali and Dzombak, 1996; Jeong et al., 2015; Zhu et al., 2013). Therefore, the presence of SO₄²⁻ may destroy the protective oxide film and thus help to maintain or accelerate the iron corrosion. This was partially evidenced by the study of Yu et al. (2013), wherein the pH variation in unbuffered Fe⁰/H₂O system with and without SO₄²⁻ was compared. It was observed that the solution pH increased from 6.0 to 8.4 in the absence of SO₄²⁻, whereas upon the addition of 50 mM SO₄²⁻, a higher final solution pH value (from 6.0 to 9.7) was obtained, indicating the iron corrosion was enhanced by SO₄²⁻ (Guan et al., 2015b; Noubactep, 2008). Being a divalent ion, SO₄²⁻ tends to show stronger affinity on iron oxide surfaces and promote more

proton adsorption compared to monovalent anions (Rietra et al., 2000). Therefore, SO₄²⁻ may be more efficient in de-passivating aged ZVI compared to monovalent ions, and this could be one possible explanation for the observation that SO₄²⁻ enhanced the performance of ZVI toward 4CINB to a greater extent than Cl⁻ did (Devlin and Allin, 2005).

On the other hand, the deterioration effects of SO₄²⁻ on the reduction of TCE (Liu et al., 2007) and 1,1,1-trichloroethane (TCA) (Yu et al., 2013) were reported by some researchers. These differences may have a distinct implication on the application of ZVI technology in practice. According to Eq. (10), the Fe-anion complexes ($\equiv\text{Fe}^{\text{III}}-\text{L}$) could be formed and accumulated on the iron surface when $\equiv\text{Fe}^{\text{III}}-\text{L}$ did not convert rapidly to $(\text{Fe}^{\text{III}}-\text{L})_{\text{aq}}$. In that case, the reactive sites on the iron surface and its corrosion products may be blocked by these Fe-anion complexes (Liu et al., 2007; Su and Puls, 2004). Fourier Transform Infrared (FTIR) spectroscopic investigation on SO₄²⁻ adsorption did provide evidence that SO₄²⁻ formed monodentate surface complexes on hematite (Eggleston et al., 1998) and goethite (Peak et al., 1999). In addition, the presence of SO₄²⁻ may change the route of Fe⁰ dissolution, as revealed by Yu et al. (2013). In their study, sulfate transformed the intermediate form Fe(OH)_{ads} to Fe₂(SO₄)_{ads}, which weakened the affinity between Fe and TCA, and thus depressed the degradation of TCA by Fe⁰.

4.1.3. NO₃⁻

Nitrate, as an iron reducible anion (Alowitz and Scherer, 2002), was reported to impact the performance of ZVI significantly (Liu et al., 2007). In particular, the deteriorating role of NO₃⁻ in reduction reactions with ZVI has been well documented. Ritter et al. (2003) showed that, in the presence of NO₃⁻, little TCE was reduced to end-products ethene and ethane despite TCE was already adsorbed onto the iron. Similarly, Liu et al. (2007) reported that the presence of 3 mM NO₃⁻ decreased the TCE reduction rates by 3-fold compared to that of DI water, and the degree of deterioration increased with the increasing NO₃⁻ concentration (e.g., a 7-fold decrease at 5 mM NO₃⁻). Devlin and Allin (2005) showed that, relative to ClO₄⁻, the presence of 8 mM NO₃⁻ impeded the reduction of 4CINB by granular iron. Furthermore, Klausen et al. (2001) found that nitrate could not only reduce reaction rates when it was the sole anion in solution, but it could also interfere strongly with the performance enhancing effect of chloride, when the two anions were present together. It appears that nitrate impacts the performance of ZVI in two aspects: (1) as a reactant, it slows the reduction of target contaminants by competing for reactive sites on the iron; (2) as a passivating agent, it generates passive ferric (Fe(III)) (oxyhydr)oxides that dampen reactivity and shorten longevity (Xie and Cwiertny, 2013). The latter role has been confirmed electrochemically, where a smaller corrosion current was obtained compared to chloride, indicating a greater degree of surface passivation in nitrate solution (Farrell et al., 2000).

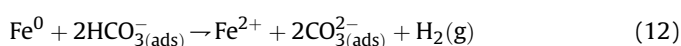
Although negative effects were always involved in ZVI system when NO₃⁻ was present, nitrate was also reported to enhance the performance of ZVI under some conditions. For instance, Liu et al. (2007) reported that an initial NO₃⁻ concentration ≤ 1 mM slightly enhanced the reduction of TCE compare to DI water. However, the related mechanism is not clear yet. For Pb²⁺ removal by nZVI, Su et al. (2014) found that the immobilization of Pb²⁺ was accelerated in the presence of NO₃⁻ compared to the case of nitrate-free system (5 min versus 15 min). It was considered that nitrate reduction led to the increase of solution pH, which significantly enhanced Pb²⁺ precipitation.

4.1.4. HCO₃⁻

Bicarbonate (and carbonate), one of the most common and

abundant inorganic anions in groundwater, has been extensively investigated, and its influence was found to be typically dependent on its concentration and exposure time (Agrawal et al., 2002). For example, the presence of 5 mM bicarbonate was reported to initially enhance TCA removal rate, but after a 24 h exposure time no further enhancement was evident (Agrawal et al., 2002). Similarly, Klausen et al. (2003) observed that the performance of ZVI toward organohalides and nitroaromatic compounds was initially enhanced (first 90 days) at a high bicarbonate concentration (total of 20 mM, and relative to 2 mM of carbonate species), but was ultimately deteriorated due to formation of passive iron carbonate precipitates. Recently, Bi et al. (2009) systematically investigated the mechanisms of the deteriorating and promoting effects of carbonate toward the performance of ZVI. It was observed that 4ClNB removal by ZVI was enhanced due to the presence of carbonate of low concentration (<0.8 mM), where it was hypothesized that amorphous Fe(OH)₂ was formed preferentially relative to passive FeCO₃, allowing free CO₃²⁻ to promote iron corrosion. However, when the carbonate concentration was higher than 0.8 mM, FeCO₃ would form preferentially, which could passivate the iron surface depending on the kinetics of mineral precipitation.

It was generally accepted that the presence of carbonate could lead to the precipitation of mineral phases such as carbonate green rust, siderite (FeCO₃), calcite (CaCO₃), or aragonite (CaCO₃) (Klausen et al., 2003). This property is critical for the carbonate effect on the performance of ZVI because (1) these precipitates may reduce the porosity of the permeable media (Yabusaki et al., 2001); (2) they could inhibit contaminant access to the iron surface by forming an insulating film (Köber et al., 2002; Klausen et al., 2003; Phillips et al., 2000); (3) some precipitates like carbonate green rust, was reported to be a redox-active phase (Agrawal et al., 2002; Klausen et al., 2003; Phillips et al., 2000; Williams and Scherer, 2001). On the other hand, although the exact mechanism by which carbonate species enhance the performance of ZVI is unclear, it was reported that adsorbed H₂CO₃ and HCO₃⁻ in ZVI system could react as oxidants, providing cathodic reactions and help drive iron dissolution transiently:



It should be noted that, although these properties of carbonate may allow it to accelerate the iron reaction rates at early time, carbonate species will eventually deteriorate the performance of ZVI by formation of passive iron carbonate precipitates over the longer term when they are present in sufficient amounts (Agrawal et al., 2002).

4.1.5. SiO₃²⁻

Silica, commonly present in natural water, is a known corrosion inhibitor that could depress ZVI performance. Column studies conducted by Klausen et al. (2003) demonstrated that the presence of silica species greatly diminished the degradation of TCE and nitroaromatic compounds by ZVI. Kohn et al. (2003) further investigated the effect of silica on the reduction of 1,1,1-TCA by granular iron as a function of added silica concentration, pH, and duration of iron exposure to dissolved silica. According to their results, the higher the silica loading, the greater extent performance diminished (i.e., 0.17 mM silica produced 30% reduction in reaction rate while 0.83 mM produced 65–75% reduction). During a long-term column study, Kohn and Roberts (2006) indicated that the dissolved silica species could also result in the generation of a less desirable product *cis*-dichloroethylene (*cis*-DCE) during the

process of TCE sequestration by ZVI.

It was hypothesized that silica most likely forms monomeric surface complexes ($\equiv\text{FeH}_3\text{SiO}_4$, $\equiv\text{FeH}_2\text{SiO}_4^-$, and $\equiv\text{FeHSiO}_4^{2-}$) initially, and a silica film or gel is formed on the iron surface eventually, which prevents anodic dissolution of the iron and thereby hinders the transfer of electrons to the contaminant or may alter the electronic environment of reactive sites (Klausen et al., 2003; Kohn et al., 2005). In addition, the presence of silica species can also compete for adsorption sites with some contaminants (e.g., As(V) and As(III)), and thus depress their sequestration by ZVI (Su and Puls, 2001a). Therefore, the deterioration effect of silica on the performance of ZVI can be attributed to the result of different physical and chemical processes. Specifically, silica could either physically block access of the contaminants to the reactive sites by forming a protective layer, or could chemically alter the reactivity of the interfacial region by changing the speciation of the surface-associated iron (Kohn and Roberts, 2006).

4.1.6. ClO₄⁻

Perchlorate is always considered to be inert and interact minimally with ZVI surfaces, and thus was always designated as the null solution and the benchmark for comparisons of different anions effects in Fe⁰ systems (Devlin and Allin, 2005). However, thermodynamically, perchlorate can be reduced to chlorate or to chloride depending upon the utilized reductant. Actually, the perchlorate reduction at various metal and metallic electrode surfaces has been reported, contrary to the previous assumption that perchlorate behaves as an inert electrolyte (Ujvári and Lang, 2011). Similarly, many studies have also observed the perchlorate reduction on ZVI surfaces despite the reaction rate may be relatively slow for immediate use in remediation system design. For instance, Moore et al. (2003) investigated the ClO₄⁻ removal by several commercial iron filings (size = 20–100 mesh, surface area = 0.08–5.65 m²/g) under anoxic conditions. About 66% of ClO₄⁻ (initial concentration 0.1 mM) was reductively removed within 2 weeks at neutral pH, with the iron dosage as high as 1250 g/L. Im et al. (2011) reported that the oxygen could improve the perchlorate removal by ZVI, where almost all ClO₄⁻ (0.016 mM) could be removed within 12 h under oxic conditions with the iron dosed at 10 g/L (size = 325 mesh). Decreasing the size of ZVI particles to the nanoscale had been reported to enhance the reaction rates for ClO₄⁻ reduction greatly. For example, Xiong et al. (2007) showed that ~90% of ClO₄⁻ was destroyed within 7 h by nZVI at an iron dosage of 1.8 g/L and at moderately elevated temperatures (90–95 °C).

Given the abovementioned statements, the presence of ClO₄⁻ in ZVI systems may not only act as an inert supporting electrolyte in practice but would also compete for reactive sites and thus diminish the target contaminants removal, especially in long term applications or at elevated temperatures. This has been partially evidenced by the studies of Lim and Zhu (2008), where they investigated the influence of ClO₄⁻ on dechlorination of 1,2,4-trichlorobenzene (124TCB) by nanoscale Pd/Fe particles, and their results showed that the presence of 0.2–2 mM ClO₄⁻ had a moderate deterioration effects on 124TCB dechlorination rate compared with that of ultrapure water (~0.05 versus ~0.09 min⁻¹). Therefore, during the design and operation processes of a ZVI system, the potential interactions between ClO₄⁻ and iron surfaces should not be overlooked, and this issue deserves further investigation in future.

4.2. Coexisting cations

4.2.1. Enhancing effect of cations

A variety of cations present in contaminated water, such as Fe²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and so on, were believed to have the

ability to improve the ZVI performance. For example, previous studies indicated that addition of a certain amount of Fe^{2+} (e.g., 50 mg/L) could significantly accelerate the nitrate (Huang et al., 2003; Xu et al., 2012) and molybdate (Huang et al., 2012) reduction, probably due to the enhanced iron corrosion. Selenate, one of the most stable and mobile species, was difficult to be removed by Fe^0 alone (Yoon et al., 2011b). Indeed, negligible selenate removal (~4%) was obtained within 24 h in the presence of Fe^0 alone (Tang et al., 2014b). However, upon the addition of a small amount of Fe^{2+} (e.g., 0.1 mM), 72% selenate was removed after 24 h, implying the presence of Fe^{2+} was essential for selenate removal. Specifically, regarding to the enhancing mechanisms, Fe^{2+} could directly react with selenate by serving as partial electron donor (e.g., Fe^{2+} was found to be consumed with a $\text{Fe}^{2+}:\text{Se}$ stoichiometry of ~1:1) or facilitate the transformation of a passive ferric coating on the iron surface to Fe_3O_4 and thus enhance electron transfer between Fe^0 core and selenate. On the other hand, when Fe^{2+} was adsorbed onto the iron oxide surface, it might become a more reductive agent than Fe^0 and thereby play an important role in the pollutants reductive transformation (Bae and Hanna, 2015; Klausen et al., 1995).

Slight amounts of manganese and cobalt are usually incorporated into iron materials during smelting. They will dissolve simultaneously during iron corrosion and release Mn^{2+} and Co^{2+} into solution. Considering the similar chemical characters as Fe^{2+} , Tang et al. (2014a) investigated the effect of Co^{2+} and Mn^{2+} on selenate removal by ZVI. Their results showed that Co^{2+} and Mn^{2+} did promote selenate removal by ZVI due to the combined effects of redox reaction and indirect catalysis (the formation of a $\text{Fe}^0\text{-Co}^0$ system and/or the incorporation of Co^{2+} or Mn^{2+} into the magnetite crystal structure) role of Co^{2+} and Mn^{2+} (Tang et al., 2014a). It was also found that Co^{2+} exhibited a more significant impact on the performance of ZVI toward selenate removal than Mn^{2+} , possibly because Co^{2+} promoted Fe^{2+} release and the formation of a bimetallic ($\text{Fe}^0\text{-Co}^0$) system to catalyze selenate reduction by ZVI.

With respect to the formation of bimetallic system, Doong and Lai (2006) also indicated that the added divalent metal ions such as Cu^{2+} , Co^{2+} , Ni^{2+} could be reduced by Fe^0 to zero-valent metals, thereby forming bimetallics that accelerate the dechlorination rate of PCE.

In addition to improving the performance of pristine ZVI toward contaminants removal, many cations could also recover the reactivity of passivated ZVI. For example, in a series of studies on the depassivation of aged Fe^0 by divalent cations (Liu et al., 2013a, b; Liu et al., 2014), it was observed that the degradation of TCE by aged iron was markedly enhanced with the addition of Fe^{2+} , Mg^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cu^{2+} , or Pb^{2+} , and the rate constants of TCE removal in the presence of particular cations were positively correlated to the log K representing the affinity of the cations for hydrous ferric oxide surface sites. Therefore, the authors proposed that the surface oxide layer dissolution induced by the addition of some divalent cations accounted for the recovery of aged Fe^0 with respect to TCE degradation. In particular, the depassivation process is proposed to involve (1) surface complexation of cations on surface coatings of aged Fe^0 , (2) dissolution of the hydrated surface as a consequence of magnetite exposure, and (3) transport of electrons from underlying Fe^0 via magnetite to target contaminants.

4.2.2. Deteriorating effects of cations

Hardness (e.g. Ca^{2+} , Mg^{2+}), one of the most prevalent constituents in groundwater, is always considered to be negative to the performance of ZVI. For example, Lo et al. (2006) demonstrated that there was a 17% drop in the Cr(VI) removal capacity when Mg^{2+} (1–2 mM) was present whereas Ca^{2+} (1–2 mM) caused a slight decrease in Cr(VI) removal. Furthermore, when carbonate and hardness ions were present together, the Cr(VI) removal capacity of Fe^0 was further decreased to 33%. Dong et al. (2013) also showed that the presence of 6 mM Ca^{2+} could decrease the NB reduction rates from $2.0 \times 10^{-4} \text{ s}^{-1}$ to $8.3 \times 10^{-5} \text{ s}^{-1}$. It was found that, in a long term Fe^0 based PRB application, Ca^{2+} and Mg^{2+} concentrations decreased from the front part to the end of PRB and it was most likely a consequence of the precipitation of these ions in the treatment zone (Keith et al., 2005; Lo et al., 2006). With the accumulation of these precipitates over time, the permeability of the treatment zone or the residence time of the porous walls would be consequently decreased. On the other hand, the passivated precipitates (e.g. CaCO_3) could mask the reactive sites on the Fe^0 surface where electron transfer occurred and thereby result in a decrease of the ZVI performance (Mak et al., 2009).

4.3. Natural organic matter

NOM is one of the most abundant materials on earth and is ubiquitous in shallow aquifers (it usually occurs in the range of a few mg C/L to a few hundred mg C/L) where Fe^0 based technologies are most applicable (Chen et al., 2011). NOM always includes a skeleton of alkyl and aromatic units with functional groups such as carboxylic acids, phenolics, hydroxyls, and quinones (Tratnyek et al., 2001; Xie and Shang, 2005). Accordingly, NOM can readily adsorb to mineral surfaces such as iron oxides coatings present on the surface of corroded ZVI (Johnson et al., 2009; Keum and Li, 2004; Klausen et al., 2003). The adsorption of NOM, even at low surface coverage, may block the surface sites of Fe^0 where the remediation of contaminants takes place. Based on the chemistry of Fe^0 , NOM, quinonoid models for NOM, and anthropogenic surfactants, Tratnyek et al. (2001) have proposed a variety of ways that the kinetics of contaminant transformation by Fe^0 might be influenced: (1) solubilization of contaminants by partitioning to micelles or other surfactant aggregates in the solution phase, (2) enhanced absorption of contaminants by partitioning to the

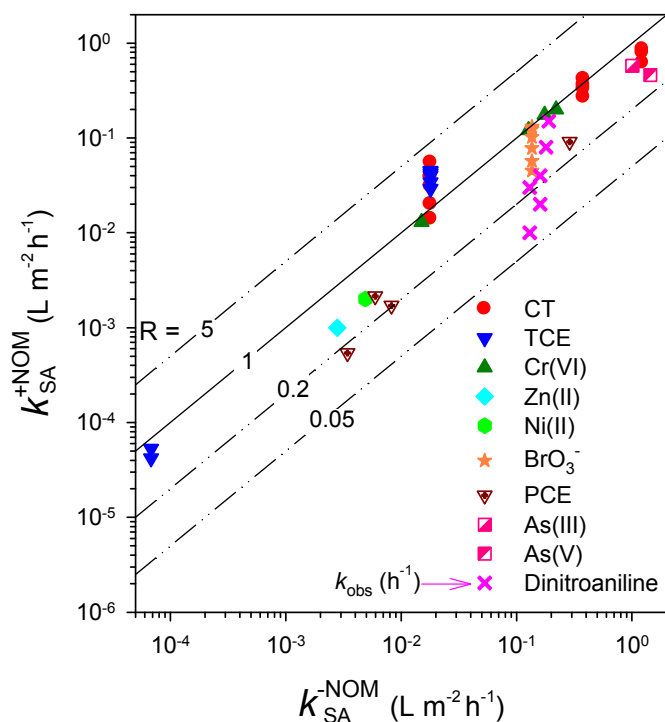


Fig. 5. Summary of the ratio of kinetic constants with and without NOM (R_{NOM}) for currently available data on contaminants removal by ZVI.

hydrophobic layer formed by surfactants that adsorb to Fe^0 particle surfaces, (3) competition between surfactants and contaminants for the surface sites where reaction occurs, and (4) “catalysis” of contaminant reduction by redox active surfactants that act as mediators of electron transfer at the particle–water interface. Most of these effects have been observed by many researchers through batch or column studies. While considering the effects may occur independently or in combination, it is difficult to predict their net outcome on contaminant removal kinetics.

Fig. 5 calculated and summarized the ratios (R_{NOM} , $k_{+\text{NOM}}/k_{-\text{NOM}}$) of rate constants of contaminants removal by ZVI with and without NOM for some available data (Table S3) by plotting $\log k_{+\text{NOM}}$ vs. $\log k_{-\text{NOM}}$ with diagonal contours denoting selected values of R_{NOM} . As shown in Fig. 5, the values of R_{NOM} generally fall in a range of 0.05–5, which means the overall effect of NOM on ZVI performance may be negative, positive or negligible, depending the type and concentration of NOM and/or the target contaminants. For example, Tratnyek et al. (2001) found that the reduction rates of CT and TCE by ZVI were decreased by 1–2 times due to the competitive sorption of humic acid (HA, a major component of NOM) onto the surface of ZVI, whereas fulvic acid (FA) seemed to exert marginal influence on the removal of NB and CT by ZVI. On the other hand, upon the addition of two quinonoid electron transfer mediators (i.e., lawsone and anthraquinone-2,6-disulfonate (AQDS)), the rates of NB and CT reduction appeared to be accelerated. The role of HA to transfer electrons from the inner Fe^0 to Fe(III) was also observed in the bromate reduction, where the Fe(III) -HA complexes formed on the outer oxide layer or in solution could regenerate reactive Fe(II) to reduce bromate (Xie and Shang, 2005). Liu et al. (2009) also revealed that the TCE removal could be enhanced in the presence of HA, but more likely by partitioning into newly formed HA aggregates, where these aggregates seemed to be readily deposited on the Fe^0 surfaces through interception and gravitational sedimentation. Nonetheless, in the long term, the continuous deposition of these aggregates on iron surface may eventually lead to a noticeable blocking of reactive sites and flow paths. Therefore, despite the sometimes promoting influence of NOM, more research is required before determining whether there is potential for using this effect to improve the performance of ZVI in field.

Besides adsorption onto mineral surfaces, NOM is well known to have a strong binding capacity with cation ions and to form stable aqueous complexes, which may also impact the contaminant removal (Dries et al., 2005). Additionally, the corrosion rates of ZVI may also be reduced in the presence of HA, which in turn could reduce the formation of new sorption sites for contaminant removal (Giasuddin et al., 2007). For instance, Dries et al. (2005) revealed that Zn^{2+} and Ni^{2+} could complex strongly with HA, which prevented the removal of Zn^{2+} and Ni^{2+} in batch experiments and delayed the removal of both metals in a long-term continuous flow column test. Furthermore, dissolved iron released from corrosion could also complex with HA, resulting in the formation of colloids and aggregates in solution. It was reported that the formation of Fe-humate complex significantly promoted the amount of dissolved iron in batch and column studies when Fe^0 was employed to treat Cr(VI) (Liu et al., 2008, 2009). With continuous release of dissolved iron due to the corrosion of Fe^0 systems, HA aggregates larger than 0.45 μm comprising metal precipitates and/or hydrolyzed species would eventually be formed in solution, especially when HA coexists with calcium or magnesium (Tsang et al., 2009). These aggregates may affect the sorption and/or the reduction of contaminants in Fe^0 systems. For example, Rao et al. (2009) reported that the removal rate of arsenic by Fe^0 was diminished in the presence of HA probably because of the formation of soluble Fe-humate in the groundwater which hindered the formation of iron precipitates.

In summary, the presence of NOM in natural water would impact the efficiency and lifetime of ZVI, and thus should be considered in the design and operation of a ZVI based system. In order to predict the impact of NOM, further investigations are needed to quantitatively elucidate the role of the different organic fractions.

5. Conclusions

The current review systematically summarized the effects of iron intrinsic characteristics, operating conditions, and solution chemistry on contaminants sequestration by ZVI and the possible involved mechanisms. All of them exert significant influences on the ZVI performance toward contaminants removal, negatively or positively. However, many of these influences have not been well understood or otherwise cannot be individually isolated in experimental or natural systems. Thus, further study is required in order to elucidate the exact roles and mechanisms of these factors in determining the performance of ZVI. A detailed understanding on this issue will benefit the design and operation of *in situ* ZVI-based PRBs or other low-cost ZVI-based water and wastewater treatment systems. In particular, future research should be carried out to work out some feasible guidelines for improving the performance of ZVI in real practice. In these guidelines, the deteriorating effects can be overcome (e.g., pretreating natural water to remove deteriorating constituents) and the positive effects can be taken advantage of (e.g., bimetals developed previously and ZVI/WMF, ZVI/oxidants proposed recently).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.05.031>.

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