

# Rapid and long-effective removal of broad-spectrum pollutants from aqueous system by ZVI/oxidants

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## HIGHLIGHTS

- The coupling of oxidants with ZVI overcome the impedance of ZVI passive layer.
- ZVI/oxidants system achieved fast and long-effective removal of contaminants.
- Multiple mechanisms are involved in contaminants removal by ZVI/oxidant system.
- ZVI/Oxidants did not change the reducing property of ORP in the fixed-bed system.

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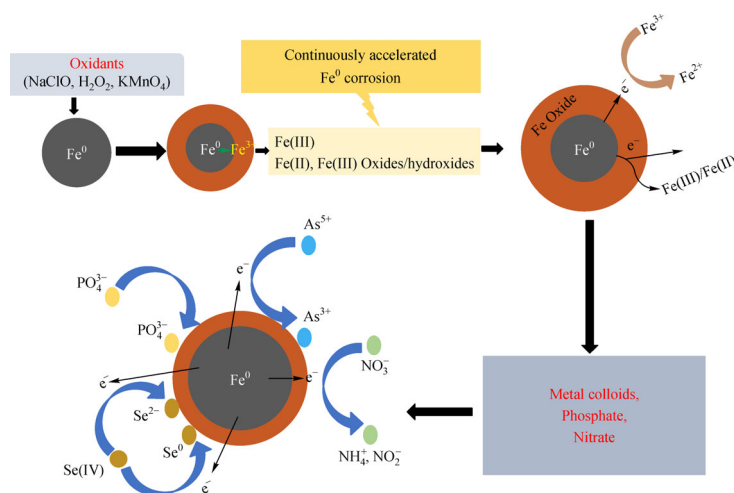
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## GRAPHIC ABSTRACT



## ABSTRACT

Zero-valent iron (ZVI) technology has recently gained significant interest in the efficient sequestration of a wide variety of contaminants. However, surface passivation of ZVI because of its intrinsic passive layer would lead to the inferior reactivity of ZVI and its lower efficacy in contaminant removal. Therefore, to activate the ZVI surface cheaply, continuously, and efficiently is an important challenge that ZVI technology must overcome before its wide-scale application. To date, several physical and chemical approaches have been extensively applied to increase the reactivity of the ZVI surface toward the elimination of broad-spectrum pollutants. Nevertheless, these techniques have several limitations such as low efficacy, narrow working pH, eco-toxicity, and high installation cost. The objective of this mini-review paper is to identify the critical role of oxygen in determining the reactivity of ZVI toward contaminant removal. Subsequently, the effect of three typical oxidants ( $\text{H}_2\text{O}_2$ ,  $\text{KMnO}_4$ , and  $\text{NaClO}$ ) on broad-spectrum contaminants removal by ZVI has been documented and discussed. The reaction mechanism and sequestration efficacies of the ZVI/oxidant system were evaluated and reviewed. The technical basis of the ZVI/oxidant approach is based on the half-reaction of the cathodic reduction of the oxidants. The oxidants commonly used in the water treatment industry, i.e.,  $\text{NaClO}$ ,  $\text{O}_3$ , and  $\text{H}_2\text{O}_2$ , can be served as an ideal coupling electron receptor. With the combination of these oxidants, the surface corrosion of ZVI can be continuously driven. The ZVI/oxidants technology has been compared with other conventional technologies and conclusions have been drawn.

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## 1 Introduction

Chemical pollution in the form of inorganic and organic pollutants is becoming a serious risk to the public health and aquatic ecosystem (Li et al., 2016; Ullah et al., 2020a). Some of the broad-spectrum pollutants in trace amounts

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are vital for human need but, long-time exposure to even smaller concentrations may cause carcinogenicity, mutagenicity, arrhythmia, diabetes, and renal disturbances (Zou et al., 2016). Several techniques are presently in use for the sequestration of As from polluted water bodies such as ion exchange, membrane filtration, coagulation-flocculation-sedimentation, and adsorption (Guo et al., 2016; Li et al., 2018; Qu et al., 2019). Zero-valent iron (ZVI) has recently attained significant attention in the efficient sequester of a wide variety of pollutants (Guan et al., 2015). The increasing attention in the use of ZVI for the treatment of polluted water is owing to its more active sites, higher reactivity, fast kinetics, non-toxicity, and stronger electron-donating ability (Liang et al., 2014). Because of its high reactive specific surface area, it has been widely applied to treat ground and wastewater contaminated by halogenated hydrocarbons (Joo and Zhao, 2008), dyes (Chen et al., 2011), heavy metals (HMs) (Guo et al., 2016), various oxyanion including arsenate and selenite (Yang et al., 2016) and  $\text{NO}_3^-$  (Huang and Zhang, 2005).

Despite its potential for treating a variety of contaminants, the application of ZVI technology for real wastewater treatment still faces some challenges. An important problem facing ZVI technology is surface passivation because of the formation of the surface passivation layer. Furthermore, when the  $\text{pH} < 4$ , the reactivity of ZVI remarkably decrease and almost remains inert under neutral and alkaline conditions (Liang et al., 2014). Because ZVI immediately reacts with  $\text{O}_2$  molecules in the water and forms a dense passivation layer (1-4 nm) of iron oxide on the ZVI surface (Guo et al., 2016). Thus, it leads to a longer hydraulic contact time between the wastewater and ZVI filter bed, which usually requires hours or even days of contact to have a remarkable effect on the removal of broad-spectrum pollutants (Fan et al., 2009). Similarly, if the concentration of metal ions is slightly higher, the contaminant remediation efficiency of ZVI becomes much inferior. This passivation of the ZVI surface seriously restricts its practical application for the remediation of broad-spectrum pollutants in water (Westerhoff and James, 2003).

To date, several modified techniques including bimetal alloying (Lee and Sedlak, 2008), nanoscale zero-valent iron strategy (Wen et al., 2014) and weak magnetic field (Feng et al., 2015) have been extensively applied to increase the efficiency of ZVI particles toward the elimination of targeted contaminants. Bimetallic particles have numerous potential benefits over conventional ZVI technology, yet it may cause ecotoxicity (Guo et al., 2016). Several studies had revealed that nanosized (nZVI) could eliminate a wide range of metal cations more efficiently than granular ZVI (Wang et al., 2018). Nonetheless, nZVI at the size range ( $< 20\text{nm}$ ) is very reactive to be efficient for in situ environmental remediations (Zou et al., 2016). Recently, it has been reported that weak magnetic field facilitates mass transport and corrosion of ZVI, alleviate

detrimental effect of the passive layer and accordingly increase contaminants elimination by ZVI (Feng et al., 2015). However, exploring a simple, economical, and eco-friendly technique to remarkably enhance the efficacy of ZVI is still critically needed.

Our research group successfully coupled common oxidants ( $\text{NaClO}$ ,  $\text{H}_2\text{O}_2$ , and  $\text{KMnO}_4$ ) with ZVI, which showed highly efficient  $\text{NO}_3^-$ ,  $\text{Cd(II)}$ ,  $\text{As(V)}$ ,  $\text{Hg(II)}$ ,  $\text{Se(IV)}$  and  $\text{P}$  removal performance compared to previously developed adsorption technologies (Guo et al., 2015; Guo et al., 2016; Li et al., 2018; Luo et al., 2020). Oxidants react with the surface of ZVI with high speed and stability, resulting in a very fast and vigorous corrosion of Fe and consequently cause the constant generation of Fe oxides and oxyhydroxides. It was found that these corrosive products thereof responsible for the steady, fast, and effective sequester of HMs via adsorption, precipitation, and coprecipitation (Li et al., 2018; Ullah et al., 2020b). Moreover, the coupling system of ZVI/oxidants has the potential to treat varied concentrations of HMs just by appropriately varying the dosing of oxidants (Guo et al., 2016).

The objective of this mini-review paper is to identify the critical role of  $\text{O}_2$  in determining the ZVI reactivity toward broad-spectrum pollutant removal. Similarly, we summarized the effects of several common oxidants ( $\text{NaClO}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{KMnO}_4$ ) on activating ZVI surfaces in removing nitrate, phosphate, and heavy metals. This paper also focuses on the sequestration efficiency and reaction mechanisms of ZVI/oxidants. Concerning ZVI/oxidants for future research, some suggestions have been proposed, a comparison with other conventional technologies has been documented and conclusions have been drawn.

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## 2 Zerovalent iron under aerobic conditions

Dissolved Oxygen (DO) can strongly influence the corrosion of  $\text{Fe}^0$  and the consequent sequestration of broad-spectrum contaminants in an aqueous system. In a  $\text{Fe}^0/\text{H}_2\text{O}$  system,  $\text{Fe}^0$  corrosion is generally regarded as an electrochemical process (Noubactep, 2008). An anodic process involves Fe dissolution; conversely, a cathodic process results in the liberation of hydrogen (H) as H gas under anoxic conditions, and  $\text{O}_2$  reduction dominates in oxygen presence (Guan et al., 2015). Oxygen oxidizes  $\text{Fe}^0$  and generates  $\text{Fe}^{2+}$  that is further hydrolyzed to  $\text{Fe(OH)}_2$  on the surface of  $\text{Fe}^0$ . The  $\text{Fe}^{2+}$  is very unstable under oxic conditions at high pH, resulting in the production of various  $\text{Fe}^{3+}$  (hydr)oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , ferrihydrite, and  $\alpha$ -,  $\beta$ -,  $\gamma$ - $\text{FeOOH}$ ) depending on DO concentration, solution pH, reaction time and temperature (Mackenzie et al., 1999). However, the involvement of oxygen may result in the formation of a dense passive oxidation layer because of water hydration and consequently inhibit mass transfer (Flury et al., 2009). The thin films of Fe oxides and

hydroxides species are insoluble in the pH range of natural water and hinder Fe corrosion. However, information regarding the effects of corrosion on the reactivity and sequestration efficacy of  $\text{Fe}^0$  with water pollutants is highly inconsistent. The corrosion of  $\text{Fe}^0$  may generate reducing agents ( $\text{Fe}^{2+}$ ,  $\text{H}/\text{H}_2$ ), removal agents such as Fe oxy(hydr)oxides for the transformation of contaminants and a coagulant through the dissolution of  $\text{Fe}^{2+}$  from the  $\text{Fe}^0$  surface (Huang and Zhang, 2005; Sun et al., 2016). Sun et al. (2016) demonstrated that the contaminants sequestration efficiency of ZVI in oxygen presence may be pollutant/case-specific, i.e. this effect can considerably rely on the removal mechanism of a given contaminant. For example, for Pollutants removed through a reduction mechanism, oxygen may promote a trade-off between the elevated corrosion of Fe and the competition of reducing species. However, the interpretation of the net effects of  $\text{O}_2$  on the removal efficiency of ZVI is very difficult to predict because these multiple roles occur independently or in combination (Sun et al., 2016).

### 3 Common oxidants and ZVI

#### 3.1 Enhanced nitrate reduction from water

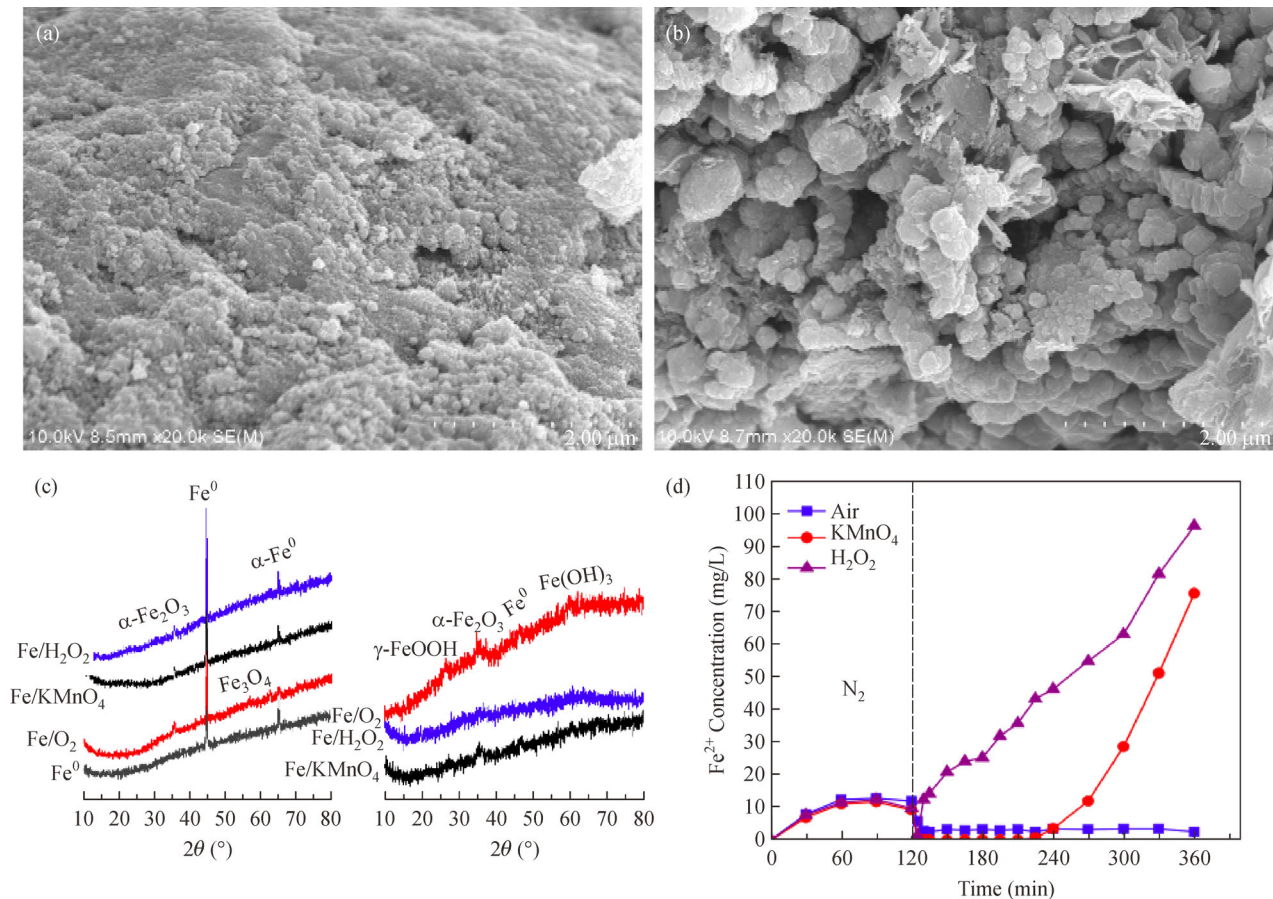
ZVI has shown great potential for the reductive transformation of various contaminants. Unfortunately,  $\text{NO}_3^-$  reduction with ZVI technology faces several drawbacks, e.g., the surface passivation layer of Fe oxide and an acidic pH requirement. The main reduction product of  $\text{NO}_3^-$  over  $\text{Fe}^0$  is ammonium, which needs to be considered (Noubactep, 2010). Since the 1990s, studies have been carried out on remediating  $\text{NO}_3^-$  by using  $\text{Fe}^0$ -promoted processes. Westerhoff and James (2003) observed that the sequester efficacy of  $\text{NO}_3^-$  reduction reached 81% after 3 h at an initial DO concentration of 8.8 mg/L and pH 8.3–8.5 in a laboratory continuous-flow ZVI packed bed columns; conversely, its efficiency decreased to 39% at an initial DO concentration of 0.6 mg/L. Yang and Lee (2005) revealed that the reduced DO concentration drives the intensive corrosion of Fe and generated more dissolved and surface-bound  $\text{Fe}^{2+}$  under aerobic conditions, i.e., below 6 mg/L, thereby enhancing  $\text{NO}_3^-$  removal performance. However, Huang and Zhang (2005) found no substantial effects of DO on the reaction rate of  $\text{NO}_3^-$ . Guo et al. (2015) revealed that the maximum reduction of  $\text{NO}_3^-$ , i.e., 49.7%, occurred at pH 2 in oxygen presence. By contrast, when the two oxidants ( $\text{H}_2\text{O}_2$  and  $\text{KMnO}_4$ ) were spiked,  $\text{NO}_3^-$  reduction considerably increased to 97% ( $\text{H}_2\text{O}_2$ ) and 94% ( $\text{KMnO}_4$ ) at pH 5. At pH 7.0, the reduction rates of  $\text{NO}_3^-$  remained at 98% and 74% for  $\text{H}_2\text{O}_2$  and  $\text{KMnO}_4$ , respectively.  $\text{NH}_3$  produced with  $\text{Fe}^0$  can be removed by zeolite, which is an inexpensive and highly selective  $\text{NH}_3$  adsorbent (Guo et al., 2015).

The  $\text{O}_2$  presence resulted in the formation of a thin

passive layer of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  oxy(hydroxide) species on a ZVI surface; these species are non-soluble in acidic solutions and protects against Fe dissolution (Fan et al., 2009). Without oxidants, a Fe powder surface exhibited an extremely smooth, compact, and dense structure, which reflected the limited corrosion of the  $\text{Fe}^0$  surface, as revealed by scanning electron microscopy (SEM). On the contrary, the involvement of  $\text{O}_2$  with ZVI, the surface of  $\text{Fe}^0$  was covered with compact clusters of corrosive products with a diameter of 100–200 nm (Fig. 1(a)). In strong oxidants spiking, the structure of the  $\text{Fe}^0$  surface was very rough, irregular, and rugged, demonstrating that the rigorous corrosion process occurred (Fig. 1b). Strong oxidants induced the pitting and etching of ZVI and produced a large specific surface area, possibly resulting in a high density of crystal edges, kinks, and steps, which served as highly reactive sites for  $\text{NO}_3^-$  reduction (Guo et al., 2015). Spiked oxidants such as  $\text{H}_2\text{O}_2$  and  $\text{KMnO}_4$  facilitated the rapid release of a large amount of amorphous green-rust-like byproducts ( $\text{Fe}^{2+}/\text{Fe}^{3+}$  hydroxides) from ZVI. Unstable  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeOOH}$  and  $\text{Fe}(\text{OH})_3$  substantially enhanced abiotic reduction of  $\text{NO}_3^-$  (Fan et al., 2009; Huang and Zhang, 2005); this process probably acted as the last counter-reaction which facilitated the dissolution of ZVI with simultaneous reduction of  $\text{NO}_3^-$  (Fig. 1(c)) (Guo et al., 2015). Despite the total consumption of oxidants, concentrations of  $\text{Fe}^{2+}$  continuously increased. A high level of aqueous  $\text{Fe}^{2+}$  concentration is not produced via oxygen dosing, suggesting the limited facilitation of  $\text{NO}_3^-$  reduction compared with that of  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  (Fig. 1(d)). The increased concentration of  $\text{Fe}^{2+}$  in a solution was closely correlated with  $\text{NO}_3^-$  reduction and  $\text{Fe}^{2+}$  could substantially enhance the reduction of  $\text{NO}_3^-$  by  $\text{Fe}^0$  (Xu et al., 2012; Huang and Zhang, 2005).

#### 3.2 Rapid and highly efficient sequestration of metal colloids

Limited DO contents in natural water drive the slow corrosion of  $\text{Fe}^0$ . As such, the produced corrosive products coated on the  $\text{Fe}^0$  surface have a leading role in the partial sequestration of Cd(II), Sb(V), As(V), and Hg(II) with pure ZVI (Liang et al., 2014). The kinetics of HMs sequestered by pure  $\text{Fe}^0$  is limited and sluggish because of the inferior solubility of  $\text{O}_2$  in water, the slow diffusion of  $\text{O}_2$  through a passive layer, and the main triple state of molecular oxygen with limited reactivity with  $\text{Fe}^0$ . In a control design within the initial 30 min (jar tests) and at an empty bed contact time (EBCT) of 8.0 min (column runs), the sequestration performance of metal colloids was very inferior by  $\text{Fe}^0$  alone. These observations were in agreement with the previous study, which demonstrated that the As removal efficiency approached 98% at an EBCT of 120 min and an initial As the concentration of 0.5 mg/L (Sun et al., 2006). Even at a long residence time of



**Fig. 1** SEM images of ZVI (a) in the presence of oxygen and (b) strong oxidant (c) XRD pattern of residual ZVI powder after reduction of nitrate (d) Fe<sup>2+</sup> evolution in combine system of ZVI and oxidants. Reprinted with permission from Guo et al., Copyright (2015) Elsevier.

150 min, the total Hg concentration of 40 µg/L in an influent substantially decreased to <0.5 µg/L (Weisener et al., 2005). Similarly, at an EBCT of 180 min, the Cd(II) removal efficiency of a Fe based adsorbent was 98.3% (Genç-Fuhrman et al., 2008).

As(V) is rapidly and effectively sequestered by ZVI/oxidants, i.e., within 10 min, the average As removal performance was 99.9%. Similarly, the residual concentration of As in jar tests was decreased from the initial concentration of 1 mg/L to 1.2–1.3 µg/L, which was below the World Health Organization's standard limitation of 10 µg/L As in drinking water. Simultaneously at an initial concentration of 0.2 mg/L, Cd(II) and Hg(II) concentrations decreased to 2.41–4.40 and 4.0–5.0 µg/L, respectively, within 30 min. Similarly, no deterioration of sequester efficacy of Cd, Sb, Hg, and As was found throughout the 10 recycles of jar tests. During long-term column running, the average As concentration in wastewater decreased from 200 µg/L to approximately 1.3–1.7 µg/L at an EBCT of 8.0±0.4 min when three oxidants at 0.1 mmol/L were spiked. A coupling system of ZVI and oxidants efficiently treated 40,000 BV influent with no As

breakthrough according to the Environmental Protection Agency's maximum permissible limit of As in drinking water (Guo et al., 2016).

Small amounts of oxidants (H<sub>2</sub>O<sub>2</sub>, KMnO<sub>4</sub>, and NaClO) accelerated the corrosion of Fe and concurrently caused the production of ferrous and ferric oxides. The oxidative potentials of NaClO, KMnO<sub>4</sub>, and H<sub>2</sub>O<sub>2</sub> are higher than that of oxygen and they have been extensively applied to treat wastewater (Yang et al., 2016). Consequently, a ZVI surface is rapidly attacked and oxidized with the rapid consumption of 1 mmol/L oxidants within 10 min. The oxidation attaches of the surface of ZVI induced by KMnO<sub>4</sub>, NaClO and H<sub>2</sub>O<sub>2</sub> occurred instantly when ZVI was continuously dosed with common oxidants, which helped in continuous generation of porous Fe oxides and hydroxides. Also, the rate of Fe<sup>2+</sup> generation increased during the reaction. Subsequently, Fe<sup>2+</sup> oxidizes to Fe<sup>3+</sup> and the Fe oxides generated continuously on the surface of Fe<sup>0</sup> (Guo et al., 2016).

SEM images show that the Fe<sup>0</sup> surface without oxidants had a very smooth surface, which indicated a decreasing degree of Fe<sup>0</sup> surface corrosion (Fig. 2(a)). Nonetheless,

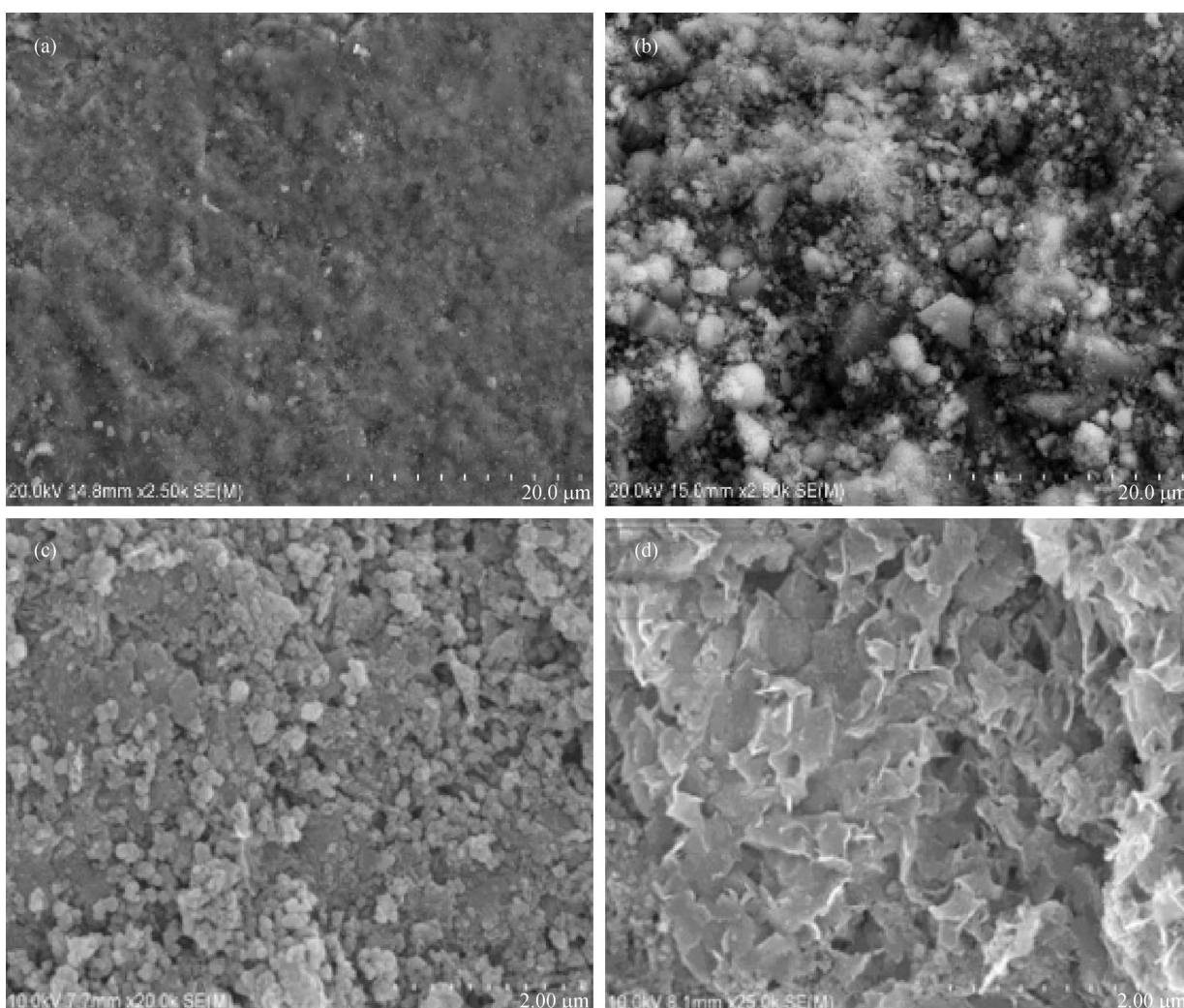
with the addition of oxidants, the  $\text{Fe}^0$  surface became irregular and rugged, suggesting that a strong electrochemical corrosion process occurred on the  $\text{Fe}^0$  surface (Figs. 2(b)–2(d)). The SEM images also exhibited that Fe oxides resembled nano- or micro-sized colloids, which presented a large specific surface area (Guo et al., 2016). These varied morphology colloids played an essential role in the removal of metal colloids through coprecipitation, precipitation, and adsorption mechanism (Neumann et al., 2013; Appelo et al., 2002). These observations were also consistent with previous spectroscopic studies, which revealed that Sb, Cd, As, and Hg was adsorbed onto Fe oxides and hydroxides via inner-sphere surface complex mechanisms (Kim et al., 2004; Randall et al., 1999). The X-ray photoelectron spectroscopy (XPS) spectra of the As peak position indicated that ZVI reduced  $\text{As}^{5+}$  to  $\text{As}^{3+}$ , even though the system was dosed with strong oxidants. Here, the spiking of common oxidants did not alter the reductive environment of the  $\text{Fe}^0$ -packed column. The

reduction of  $\text{As}^{5+}$  to  $\text{As}^{3+}$  may be possibly ascribed to the produced free hydrogen,  $\text{Fe}^{2+}$  from accelerated  $\text{Fe}^0$  dissolution, and green rust (Ullah et al., 2020b; Yang et al., 2016; Sun et al., 2011).

### 3.3 The optimum dosage of oxidants for the elimination of contaminants

A fundamental problem that must be probed was the theoretical requirement of a minimal oxidant dosage to eliminate a specific concentration of contaminants from wastewater. In the combination of ZVI with oxidants, selenium (Se(IV)) is used as an example to address the minimal oxidants dosage required at a specific concentration of HMs in a solution. Thus, the column study was designed to evaluate the long-term Se(IV) removal performance from real groundwater by using ZVI/oxidants system (Li et al., 2018).

Se(IV) can be effectively removed with suitable



**Fig. 2** SEM images of ZVI obtained after column running for metal colloids sequester ((a) pure  $\text{Fe}^0$ ; (b)  $\text{Fe}^0/\text{H}_2\text{O}_2$ ; (c)  $\text{Fe}^0/\text{NaClO}$ ; (d)  $\text{Fe}^0/\text{KMnO}_4$ ). Reprinted with permission from Guo et al., Copyright (2016) Elsevier.



oxidants spiked at a certain Se(IV) concentration. For the removal of 1M Se(IV), the minimum dosage of the required oxidant was calculated to be 3.29–3.54, 3.94–4.09, and 3.90–4.33 for  $\text{KMnO}_4$ ,  $\text{NaClO}$ , and  $\text{H}_2\text{O}_2$ , respectively. The simultaneous removal efficiency of Se(IV) was enhanced with aeration, whereas the required oxidant's dosage was reduced. By contrast, in the passivation of ZVI without oxidants, Se(IV) was effectively removed when oxidants were added to the ZVI system during long-term fixed-bed experiments with a real groundwater background. The coupling of  $\text{Fe}^0$  and typical oxidants in a fixed-bed column stably treated more than 10,000 BV of Se(IV) contaminated water. In a XANES study of the reaction of Se(IV) with ZVI, more than 85% of Se(IV) associated with Fe/Fe oxide filling comprised of  $\text{Se}^{2-}$  and  $\text{Se}^0$  (Li et al., 2018).

Selenite removal in packed column revealed that the facilitated removal of selenite by ZVI/oxidants combined system did not alter the reduction property of the oxidation-reduction potential (ORP) in the column. In our previous jar tests with oxidants dosing, ORP initially increased, i.e., 390–800 mV, but it subsequently decreased, and stably remained at  $-300$  mV (Guo et al., 2015). Previous XPS studies had also revealed that Se(IV) was reduced to  $\text{Se}^{2-}/\text{Se}^0$  on the ZVI surface (Yang et al., 2016; Yoon et al., 2011). The reduction of selenite to  $\text{Se}^{2-}$  and  $\text{Se}^0$  can be ascribed to the generation of  $\text{Fe}^{2+}$  and free  $\text{H}^+$  from the elevated dissolution and corrosion of ZVI (Yoon et al. 2011). As such, this system cannot be named advanced oxidation (Fenton system) through which  $\text{H}_2\text{O}_2$  generates an  $\text{OH}\cdot$  radical, which usually oxidizes targeted contaminants (Keenan and Sedlak, 2008; Lee and Sedlak, 2008). Whereas, the common oxidants used here facilitated the corrosion of ZVI but they were not used as an  $\cdot\text{OH}$  precursor to oxidize HMs and metalloids.

### 3.4 Phosphate sequestration by ZVI in combination with $\text{NaClO}$

In recent years, various approaches have been used to eliminate P from wastewater. Today, the main processes responsible for the elimination of P from wastewater effluent are chemical precipitation and biological treatments (Wen et al., 2014). A biological and natural system is not efficient enough to recover and remove P and meet the strict requirement of P limitation in water bodies (Zhang et al., 2006). Previous batch and column studies demonstrated the performance of ZVI in eliminating P. Sleiman et al. (2016b) observed that a ZVI/sand packed column removed 132 mgP/g Fe (Sleiman et al., 2016b). Recently, nZVI shows the potential for the efficient sequestration of P from water because of its high surface area to volume ratio, excellent magnetic properties, and surface modifiability. Wen et al. (2014) also found that using nZVI as an adsorbent may efficiently increase the

maximum adsorption capacity of P to 246 mgP/g Fe. However, the inconvenience and cost of nZVI synthesis, nZVI particles aggregation, enhanced reactivity, and limited stability are technical challenges associated with its practical application (Liang et al., 2014).

The feasibility and effectiveness of P sequestration from simulated wastewater were achieved by simply using ZVI combined with hypochlorite (ZVI/ $\text{NaClO}$ ). The behavior of two typical Fe types for the removal of P was completely different from each other. In the absence of  $\text{O}_2$ , using steel-iron (ZVI-S) alone removed only 7.3%, 19.3%, and 39.7% of P after 60 min at initial concentrations of 5, 1.0, and 0.5 mg/L, respectively. Similarly, with the involvement of oxygen, the P removal performance of ZVI-S did not improve. Conversely, the combined system of ZVI-S and  $\text{NaClO}$  significantly increased the percentage removal of P to 81.3% (anoxic) and 95.7% (oxic condition) at an initial P concentration of 0.5 mg/L. The combination of pig-iron (ZVI-P) with  $\text{NaClO}$  effectively improved the removal percentage, i.e. 94.8%–98.2% of P is removed after 12 cycles in a batch study and a fixed-bed operation at an initial P concentration of 0.5–1.0 mg/L. This observation had significant implications for P remediation in natural water bodies, where P concentration is usually below 0.1 mg/L. However, we found that P itself passivated high purity Fe (ZVI-S, steel Fe) even in the strong attack of oxidants, especially at a higher initial P concentration of 5 mg/L. These results indicated that P removal from actual wastewater should consider the raw material screening of ZVI (Luo et al., 2020).

Compared with  $\text{NO}_3^-$  and Se(IV), the insignificant effect of  $\text{O}_2$  of P removal may be attributed to the changed effects of P on a ZVI surface. Moreover, previous studies observed that the removal of P was almost negligible in a fresh-ZVI column without prior conditioning (Sleiman et al., 2016a). P itself is likely involved in the synthesis of new anti-corrosion layers of P accumulated on a steel substrate, which blocked an  $\text{O}_2$  attack on a surface of the steel. Certainly, the chemical phosphorisation of steel in  $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$  presence is an established industrial procedure for the production of uniform, thin and continuous anti-corrosion films, to protect the objected surfaces of steel from corrosion and dissolution (Simões and Fernandes, 2010; Zubielewicz and Gnot, 2004). Even the presence of a strong oxidant ( $\text{NaClO}$ ) in an aqueous system did not enhance steel (ZVI-S) corrosion, particularly at an initial P concentration of 5.0 mg/L, which resulted in inferior facilitation of P sequester by ZVI-S/ $\text{NaClO}$ . Instead, the combined system of  $\text{NaClO}$  and ZVI-P promoted the extensive and continuous ZVI-P corrosion, which yielded a substantial amount of  $\text{Fe}^{2+}$  dissolution and  $\text{Fe}^{2+}$  with limited stability oxidized to  $\text{Fe}^{3+}$  subsequently, a considerable amount of Fe oxides formed continuously on a ZVI-P surface (Luo et al., 2020).

Sleiman et al. (2016a) observed that a P solution without

prior air conditioning probably leads to the formation of an impervious and tenacious oxide-film on the surface of ZVI, which could have partly poisoned the column. This passivating film on the surface of ZVI may thwart  $O_2$  transfer to the  $Fe^0$  surface and consequently, decreased the generation of Fe oxidation products. As a result, the removal performance of P in the fresh-ZVI column was low (Sleiman et al., 2016a). Sleiman et al. (2016a) also attributed Fe passivation to the formation of a Fe oxide film, not Fe-P species. A variety of characterization approaches have been used to investigate the aging of ZVI by P and they have fully demonstrated the inhibition of ZVI-S corrosion by P itself. In simulated wastewater,  $Fe^{3+}$  partly induced the precipitation of phosphate as Fe-P species. X-ray powder diffraction (XRD) and SEM also reveal the presence of Fe-P species on a ZVI surface (Luo et al., 2020).

#### 4 Comparison of ZVI/oxidant system with conventional wastewater treatment technologies

In general, Siemens' granular ferric hydroxide (GFH) is very efficient for the elimination of As from wastewater and has an elevated treatment capability. The breakthrough of As at 0.01 mg/L from the system of GFH occurred at approximately 7200 BV water flow at an EBCE of 6.5 min and an initial concentration of 0.079 mg/L (Cumming et al., 2009). GFH's As sequester efficiency was lower than the combined system of  $Fe^0$  and oxidants. The ZVI/oxidants combine system efficiently treated 40,000 BV at a compatible flow rate when 0.1 mmol/L of three oxidants were spiked, with no indication of As breakthrough with initial As the concentration of 0.2 mg/L (Guo et al., 2016). The biggest competitor of ZVI in real wastewater applications maybe the ferrous salts. Ferrous salts are considered to be more economical choices than ZVI for contaminant removal. The operation of ferrous-aeration is very simple just by stirring and aeration/oxidation, without the phenomenon of clogging occurring as with ZVI. Nonetheless, if the wastewater contains target pollutants that need to be reduced for effective removal such as refractory COD, Cr(VI), Se(VI), Mo(VI), the coupled system of ZVI/oxidants certainly has potential advantages over ferrous aeration since the latter exhibits a relatively higher redox reactivity.

Natural Fe oxides ( $Fe_3O_4$ ,  $\gamma-Fe_2O_3$ ,  $\alpha-Fe_2O_3$ ) have a certain adsorptive capacity for the HMs, metalloids, and P, though the bulk Fe oxides usually have neither porous structures nor sufficient specific surface area. Thereby, their potential to remove those contaminants cannot be fully achieved. Preformed Fe oxides remove the metal colloids only by adsorption mechanism, with no possibility of precipitation and coprecipitation mechanisms. Further-

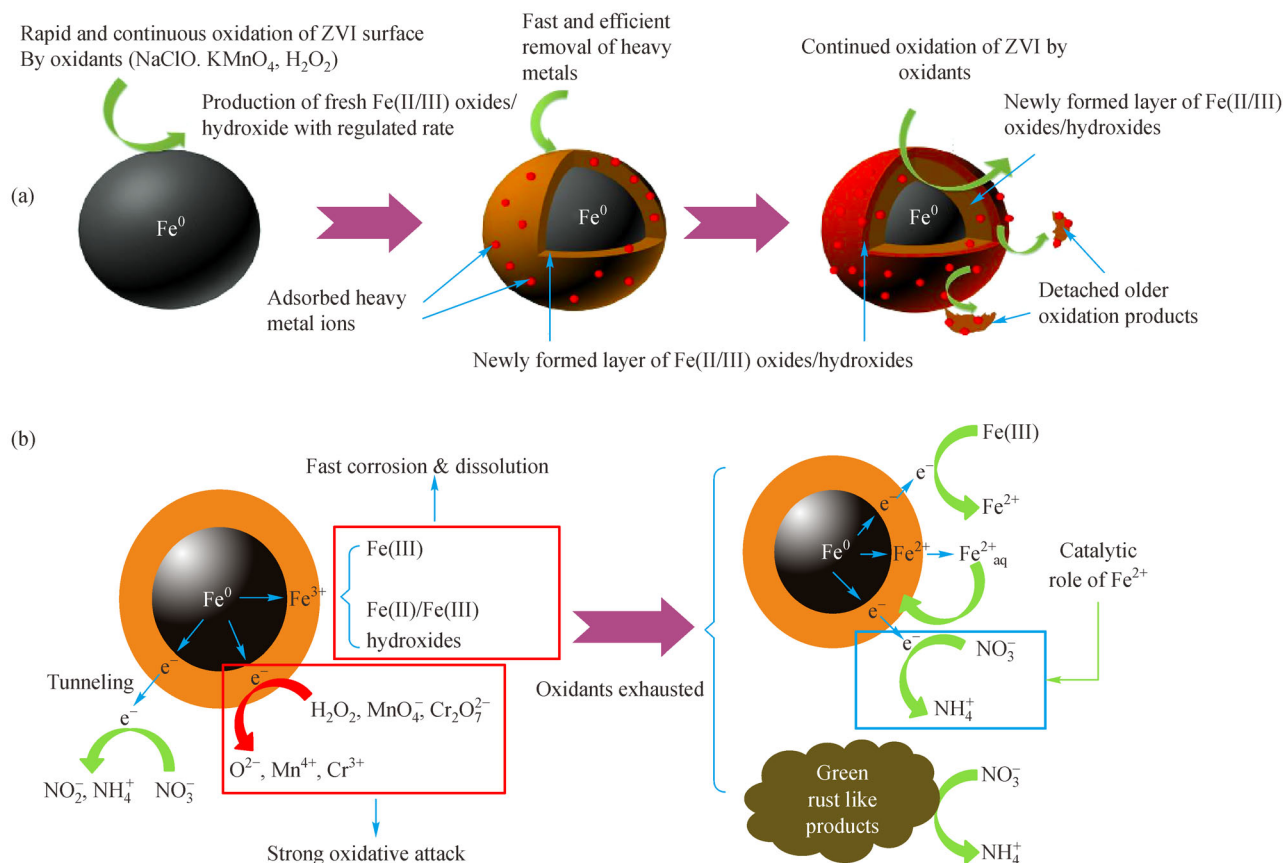
more, Fe oxides don't have reduced capability to remove Cr(VI), Mo(VII), and so on (Mercer and Tobiasson, 2008). In contrast, Fe coupling with a trace amount of common oxides, such as NaClO, is essentially a ZVI system with an accelerating generation of fresh ferric and ferrous species. In the ZVI/oxidant system, the pollutants can be removed by multiple mechanisms, such as partly reduction, precipitation and coprecipitation, and adsorption (Fig. 3). More importantly, these fresh ferric and ferrous species are continuously generated in the ZVI/oxide coupling system, make the sequestering ratio of HMs and metalloids significantly higher than natural Fe oxides materials. For example, the sequestering ratio of Fe oxides to As is usually 0.05–0.1 (Han et al., 2016), but in our ZVI/oxidant coupling system, this value may reach up to ~0.33.

#### 5 Conclusion and future perspective

In our opinion, ZVI technology is very versatile, environmental-friendly, cost-effective, and has high sorption capacity for a broad-spectrum targeted pollutant. ZVI remediation technology has a very wide application prospect in the remediation of surface and groundwater contaminants. ZVI corrosion is a crucial process governing the efficacy of  $Fe^0$  for pollution remediation in an aqueous system. Despite the spontaneous reactions of  $Fe^0$  with DO, water, (or  $H_3O^+$ ), and with the target species, these corrosion reactions are too sluggish to meet a satisfying rate of various contaminants sequester.

DO in water may result in serious passivation of the surface of ZVI. ZVI Surface passivation would lead to the low ZVI reactivity and its low efficiency in contaminant removal. The passivation of ZVI is a technical challenge that must be overcome. It is important and urgent to develop rapid, efficient, low-cost, and green technology to remove them from the aqueous system. The technical basis of the ZVI/oxidant approach is based on the other half-reaction of the cathodic reduction of the oxidants. The oxidants normally used in the wastewater treatment industry, i.e., NaClO,  $O_3$ , and  $H_2O_2$ , can be served as an ideal coupling electron receptor. With the cooperation of these oxidants, the surface corrosion of ZVI can be continuously driven. Subsequently, heavy metals, metalloids, and nitrate in water may be sequestered via multiple mechanisms e.g. precipitation, coprecipitation, adsorption, and reduction.

In the aqueous solution, the contaminant removal mechanism of ZVI comprises mainly the first transfer of an electron from ZVI to DO, water, (or  $H_3O^+$ ), and then indirectly to the target contaminants, transforming the target contaminants into less toxic species. In ZVI/oxidant system, the typical oxidants (NaClO,  $KMnO_4$ , and  $H_2O_2$ ) will consume and compete for the electrons with the targeted contaminants, which is similar to the ZVI/water system where the DO and water would consume some



**Fig. 3** Schematic model of facilitated removal of HMs (a) and nitrate (b) by ZVI/oxidants. Reprinted with permission from Guo et al., Copyright (2015 and 2016) Elsevier.

extent of the electron. The electron efficiency will reduce, and a fraction of the electron will be used for corrosion instead of attacking contaminants. All the typical oxidants reacted with the surface of ZVI with high speed and stability, drive the fast and rigorous corrosion of Fe, and hence remarkably enhanced broad-spectrum contaminants removal by ZVI. Normally, NaClO is safer and more efficient, which is permitted as a residual of natural drinking water. Normally, NaClO and ozone are safer and economical, which are probably more suitable for oxidant choices in practical use.

The academic community should focus more on the scientific issues of ZVI technology in real engineering operations. Careful selection and preparation of more reactive ZVI would be the premise of making good use of ZVI. The oxidants are certainly might be optimized when combined with some other ZVI activation approaches, i.e., ferrous and mild acid activation. The long-term reliability and stability of ZVI require the further development of integrated facilities and strategies to reduce filtering blockage. Soon, we would carry out field studies in situ to explore the processes and mechanisms of pollutants removal from actual groundwater and industrial wastewater by ZVI/oxidant. These subjects would be more

practical and truly close to people's livelihood, which would make up for the shortcomings of the previous laboratory studies.

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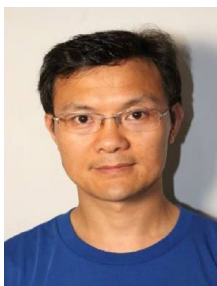


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