Remediation of contaminated soils by enhanced nanoscale zero valent iron

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Abstract

The use of nanoscale zero valent iron (nZVI) for in situ remediation of soil contamination caused by heavy metals and organic pollutants has drawn great concern, primarily owing to its potential for excellent activity, low cost and low toxicity. This reviews considers recent advances in our understanding of the role of nZVI and enhanced nZVI strategy in the remediation of heavy metals and persistent organic contaminants polluted soil. The performance, the migration and transformation of nZVI affected by the soil physical and chemical conditions are summarized. However, the addition of nZVI inevitably disturbs the soil ecosystem, thus the impacts of nZVI on soil organisms are discussed. In order to further investigate the remediation effect of nZVI, physical, chemical and biological method combination with nZVI was developed to enhance the performance of nZVI. From a high efficient and environmentally friendly perspective, biological method enhanced nZVI technology will be future research needs. Possible improvement of nZVI-based materials and potential areas for further applications in soil remediation are also proposed.

Keyword: nZVI; soil remediation; combined pollution; soil organisms; enhancement;

Content

1. Introduction

In recent years, the accelerating industrialization process, the unreasonable exploitation of mineral resources and smelting emissions, long-term wastewater irrigation on soil and sludge application, dust precipitation caused by human activities, as well as the application of chemical fertilizers and pesticides, cause the soil pollution (Zhao et al., 2016; Fayiga and Saha, 2016). Soil is a main place for accumulating heavy metals and persistent organic pollutants, thus, the management and remediation of soil is critical important.

The conventional methods of treating contaminated soil include soil washing/flushing (Dermont et al., 2008; Lemaire et al., 2013), thermal desorption (Vamerali et al., 2009), vitrification (Curiel Yuste et al., 2009), photocatalyst (Wang, H., et al. 2016; Wang, H., et al. 2017; Wu, Z., et al. 2017) and bioremediation (Barnes et al., 2010), however, these methods have a risk of relatively expensive, time consuming and secondary pollution. The presence of many nanomaterials has been a boon to soil restoration (Xiong, T., et al., 2018). However, most nanomaterials are nonmagnetic and difficult to recycle. Compared with other nanomaterials, nZVI caused extensive attention because it is non-toxic, cheap, abundant and easy to produce (Karn et al.,2011). Due to its nano size, nZVI has a higher reactivity towards a wide range of contaminants, especially heavy metal and organic pollutants (Fu et al., 2014; Mueller et al., 2012; Lefevre et al., 2016; Zhou et al., 2016; Guan, Sun, 2015; Gong et al., 2009; Xu et al., 2010), and a higher soil mobility and delivery compared to its microscale counterpart and directly injected into the pollution source area. Consequently, nZVI is deemed as a promising remediation strategy suitable to remediate the contaminated soil. Meanwhile, organism is key contributors in soil fundamental ecosystem process. Therefore, potential issues are related to an overall evaluation of the long-term effect of nZVI on soil organism, including microorganisms (Chaithawiwat et al., 2016a; Chaithawiwat et al., 2016b; Sacca et al., 2014), geobiont (El-Temsah and Joner, 2012; El-Temsah et al., 2013; Yirsaw et al., 2016; El-Temsah, Sevcu, 2016) and plants (Ma et al., 2013; Monica and Cremonini, 2009; Wu et al., 2016; Li et al., 2015) have to be considered before further in situ deployment of nZVI remediation strategies. Thus, in order to reduce the excess use of nZVI influencing the adverse effect on soil organisms, researchers employed physical (Stefaniuk et al.,2 016; Wang et al., 2015; Fukushima et al, 2000; Gomes et al., 2014) and chemical (Dermont et al., 2008; Lemaire et al., 2013; Danish et al., 2016;Zhang etal., 2007) methods to enhance the performance of nZVI.

However, these assistive technologies needed energy consumption and caused secondary pollution, which are not favorable for field application. To address these issues, in the recent years, bio-nZVI technology referred to bioremediation coupled with the amendment of nZVI nanoparticles attract great attention for remediation in contaminated soil. One is the combined remediation strategy using phytoremediation and nZVI. Hyperaccumudated plant Panicum maximum and Helianthus annuus comined with nZVI obtained the effective remediation in TNT-contaminated soil. (Jiamjitrpanich et al., 2012) . In the study of Gong et al (Gong et al., 2017b), low concentration of nZVI alleviated the oxidative damage to rumine under Cd-stress, provding the basis for combiantion phytoremedation and nZVI. Another impotant methord is combiantion microremediation with nZVI. A rapid derease of the pollutant concertration together with hydrogen evolution and redox potential shifts caused bt nZVI can finanlly lead to favorable conditions for consequent biological process (Němeček et al., 2016; Dinh et al., 2016; Xiu et al., 2010). This united process could completely mineralize organic pollutants and immobilize heavy metal in a shorter time and avoid the generation of toxic byproducts, which will be the focus of future research. In this review, firstly, the performance, the migration and transformation of nZVI affected by the soil physical and chemical properties are summarized. Secondly, physically, chemically and biologicallt enhanced nZVI strategy are propsed. Thirdly, the toxicity of nZVI to soil oganisms are discussed. Lastly, challenges and outlook of nZVI technology are well offered. With the flouring development of nZVI and enhanced nZVI strategy, their applications for soil remediation could be accessed in an effective, convenient and recyclable pathway.

2. Environment application of nZVI in soil

2.1 Removal of heavy metal contaminants by nZVI

Soil is not only an integral part of the terrestrial ecosystem but also an important reservoir of volume of pollutants. In the last few decades, soil pollution caused by heavy metals is a worldwide challenge (Wu et al., 2014). Anthropogenic activities, such as mining, military activities, manufacturing, and the long-term wastewater irrigation on soil and industrial or domestic sludge application are the main sources of metal pollution (Aminiyan et al., 2015; Fayiga and Saha, 2016; Wei and Yang, 2010; Shahid, et al., 2014; Fan, et al., 2008). To decrease heavy metal contaminant bioavailability and mobility, various strategies have been used (Hu et al., 2011; Huang et al., 2008; Tang et al., 2008; Feng et al., 2010). Among these, nZVI has emerged as an effective option for the treatment of contaminated soil (Zhang et al., 2010; Gil-Diaz et al., 2016; Mar Gil-Díaz et al., 2014; Fajardo et al., 2015; Chen et al., 2015a). Zhang et al (Zhang et al., 2010) found that bioaccessibility of As decreased by 40.4%, demonstrating good results for As immobility after supplement with nZVI. Similarly, the application of nZVI reduced the amount of As in the available fractions and increased the amount of As in the residual fraction (Gil-Diaz et al., 2016). The formation of adsorption complexes and precipitation process accounted for As immobilization (Jegadeesan et al., 2005). Except for As, nZVI had good immobilization effect on several common heavy metals in soil, including Pb, Zn, Se, Cr ,Cd and so on (Mar Gil-Díaz et al., 2014; Mele et al., 2015; Dorjee et al., 2014; Chen et al., 2016; Su et al., 2016). Interestingly, superior immobilization effect was found for Pb than Zn under the same condition (Mar Gil-Díaz et al., 2014). The presence of soil-derived humic acid influenced the heavy metal immobilization process by nZVI due to competition for adsorption sites (Dorjee et al., 2014).

In recent year, due to the high efficiency, bimetal nZVI nanoparticles used for heavy metal soil remediation has brought about widespread attention. Evidence, to date, suggested as the contaminant concentration are high up to 120mg/kg, Cr(VI) reduction efficiency exceeded 99% under weakly acidic conditions as the nZVI/Cu nanoparticles was used in the contaminated soil (Zhu et al., 2016). nZVI, as a powerful, inexpensively and environmental friendly agent, has been used for heavy metal soil remediation, and satisfactory results have been achieved not only in the laboratory but also in the field. Singh conducted the success field application for the reduction of Cr(VI) in contaminated soil with nZVI and obtained satisfactory results (Singh et al., 2012). Zhang confirmed the feasibility of nZVI as the reactive barriers (PBR) from in situ remediation of uranium-contaminated red soils. The removal capacity of U(VI) polluted soil with supplement with nZVI was significantly higher (5-10 times) than those of soil without supplement (Zhang et al., 2015). Unfortunately, the technology limitations which include poor stability and mobility of nZVI and tendency of aggregation, further reduced the reduction reactivity in soil. In conclusion, the use of nZVI to remediate polluted soils with heavy metals is a promising in situ strategy. However, additional work is required to enhance the performance of nZVI.

Table1. Removal of heavy metal contaminants by nZVI in soil

Target soil	Treatments	Pollution concentration	Main performances	Reference
As-polluted soil	nZVI	315 mg/kg	As bioaccessibility was decreased by 40.4%	Zhang et al , 2010
As-polluted soil	nZVI	5800 mg/kg	As in the residual fraction was increased.	Gil-Diaz et al. , 2016
Pb/Zn-polluted soil	nZVI	Pb 9.0 mg/kg Zn 20 mg/kg	Residual fractions of Pb/Zn was increased	Mar Gil-Díaz et al. , 2014
Pb-polluted soil	0.2g/L nZVI and 0.2M citric acid	132mg/kg	Pb efficiency removal was reached 83%.	Wang et al. , 2014
Cr(VI)-polluted soil	nZVI/Cu	120 mg/kg	Cr(VI) reduction efficiency exceeded 99% at a pH of 5.	Zhu et al. , 2016
Cr(VI) polluted soil	0.01g/L to 0.15g/L nZVI	15.84 mg/kg.	Cr(VI) reduction efficiency was increased from 14.51% to 86.83% in 120 min	Singh et al. , 2012
Cr-polluted soil	nZVI/Biochar	320 mg/kg,	Cr(VI) and Cr_{total} by inexpensive biochar-supported nZVI (nZVI@BC) was 100% and 91.94%	Su et al. , 2016
Cr-polluted soil	starch–stabilized nZVI	400 mg/kg.	An important reduction of Cr bioavailability	Alidokht et al. , 2011
Pb, Cd and Cr multi-polluted soil	nZVI/Activated carbon	Cd 360 mg/kg Pb 600 mg/kg Cr 80 mg/kg	Bioavailability and toxicity was reduced.	Chen et al. , 2015
Sb(V)-polluted soil	nZVI and Humic acid-coated nZVI	0.685 mg/kg	The observed rate constant of was decreased in the presence of HA.	Dorjee et al. , 2014
Uranium-polluted red soil	nZVI	50 mg/kg	The adsorption capacity was increased by 5-10 times	Zhang,Liu, 2015

2.2 Removal of persistent organic pollutants (POPs) by nZVI

Besides heavy metals, persistent organic pollutants also pose a serious threat to the human health and environment safety, especially in soil (Solé et al., 2013; Jwg and Meharg, 2011; Zeng et al., 2013b). Owing to these compounds of extreme persistence and recalcitrance, there is urgent to develop a cost effective and sustainable remediation technology, and nZVI is considered to be a promising alternative for reductive degradation of POPs.

Recalcitrant polycyclic aromatic hydrocarbons (PAHs) such as Benzoapyrene (BaP) and Anthracene (ANT) were completely depleted with persulfate activated by nZVI, however, Phenanthrene (PHE) showed higher resistance to degradation, achieving near 90% removal degree under the same condition (Pardo et al., 2016). In the study of Chang et al (Chang et al., 2012), the nanoparticles have been successfully applied for remediating the sites contaminated with PAHs. The removal efficiency of PAHs in soil is high up to 62% at the nZVI dosage of 0.15g/g soil, and the observed rate constant performed a linear relationship with nZVI dosage. Except for PAHs, the nZVI is also useful in the reducing degradation of various persistent organic pollutants, such as Trichloroethylene (TCE), Polychlorinated Biphenyls (PCBs), Trinitrotoluene (TNT), Dichlorodiphenyltrichloroethane (DDT) and antibiotic ibuprofen and so on (Chowdhury et al., 2015; Kustov et al., 2011; Machado et al., 2015; Jiamjitrpanich et al., 2012; Zeng etal., 2013a; Yang et al., 2010; El-Temsah et al., 2016; Han et al., 2016).

Surfactants can improve organic pollutants strongly adsorbing in soils desorption (Gharibzadeh et al., 2016). In the presence of 1% surfactant, nZVI commercial suspension obtained the maximum 83% of PCBs removal (Gomes et al., 2015). Similarly, the addition of a anionic surfactant sodium dodecyl sulfate (SDS) could improve the oxidation rate of the PAHs (Peluffo et al., 2016). Studies have shown that Tween-80 also plays a role in increased the bioavailability of pollutants (Binh et al., 2016).

Table2. Removal of POPs by nZVI in soil

Target soil	Treatments	Main performances	Reference
PAHs -polluted soil	nZVI	Completely removal of BAP and ANT, near 90% removal degree of PHE was obtained	Pardo et al., 2016
PAHs -polluted soil	nZVI	The removal efficiency of PAHs in soil are high up to 62%.	Chang et al., 2007
PAHs -polluted soil	nZVI and SDS	The highest conversions of PHE (80%) were achieved	Peluffo et al., 2016
TCE-polluted soil	CMC-nZVI	TCE concentrations decreased by over 99%	Chowdhury et al., 2015
TCE,PCB-polluted soil	starch-stabilized Fe/Pd	98% of TCE was transformed and 80% of PCBs was destroyed.	Kustov et al., 2011
PCB-polluted soil	nZVI and Saponin	The maximum 83% of PCB removal efficiency was obtained	Gomes et al., 2015
Ibuprofen-polluted soil	nZVI	The degradation efficiency of ibuprofen are up to 95%.	Machado et al., 2015
DDT-polluted soil	nZVI	Increased the degradation of DDT geometic isomer	Yang et al., 2010
DDT-polluted soil	nZVI	DDT degradation was obtained with nZVI-R (22.4%) and nZVI-T (9.2%)	El-Temsah et al., 2016
DDT-polluted soil	nZVI	The degradation half-life of p,p'-DDT is 27.6 h.	Han et al., 2016
TNT-polluted soil	nZVI	The 99.8% TNT removal was achieved.	Jiamjitrpanich et al., 2010
2,3,7,8-TCDD-polluted soil	nZVI and Tween 80	A maximum dioxin removal of about 60% was achieved.	Binh et al., 2016

3. Factors affecting reactivity of nZVI in environmental application

Following the release to the environment, aggregation of nZVI with themselves (homoaggregation) or with natural minerals and organic colloids (heteroaggreagtion) occurs spontaneously (Dwivedi, Dubey et al., 2015). The rapid aggregation resulted from the dominant magnetic attractive forces greatly hindered the environmental applications of nZVI. The aggregation behaviors of bare nZVI under the guide of the DLVO theory (He et al., 2007). Therefore, nZVI NPs dispersed and stabilized by surface coatings (e.g., surfactants, polymers, and polyelectrolytes) have been generally employed with the possible stabilization mechanisms shown in Fig 1. Anionic polyelectrolytes modified nZVI could keep the right distance from negatively charged minerals and NOM in the environment (Yan et al., 2013; Li et al., 2006). The coatings of low molecular weight polymers or surfactants, which primarily provided electrostatic stabilization, are still sensitive to ionic strength and exhibited good resistance to changing electrolyte conditions. Unlike surfactants, some polymers could irreversibly adsorb onto NPs surfaces via covalent bonds. Importantly, there are the strong interactions between polymers and NPs surfaces and few polymers desorbed from the modified nZVI (Hotze et al., 2010). Chemical transformations of nanomaterials in the environment are extremely complicated, including reduction, oxidation, dissolution, sulfidation, biodegradation, adsorption of macromolecules, as well as degradation of the surface coating (Mu et al., 2017; Dwivedi et al., 2015). Specially, the nZVI interaction with water and oxygen process is regarded as nZVI aging. The aging process could alter the thickness of the shell and composition of nZVI and thereby affect its reactivity and ecological effects, which is in turn consider as the most representative and important transformation of nZVI in the environment. (Dong et al., 2016; Wang et al., 2010). Anecdotal evidence suggests that the reactivity of nZVI in contaminated soil are affected by complicated factors. In addition to contaminant species, nZVI properties, the soil geochemical conditions (pH, temperature, NOM, moisture, dissolved oxygen) as well as the aged soils.

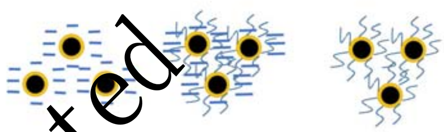

Fig.1. possible schematic stabilization mechanisms for surface coating

3.1 Contaminants species

The amendment of nZVI could simultaneously immobilize multi-heavy metal including Cd, Cr and Zn in soil with discriminative effectiveness and stability (Gil-Diaz et al., 2016). In this context, the best result was found for Cr. The specific removal mechanisms depended on the standard redox potential (E0) of both nZVI and heavy metal contaminant. Metals with (E0) much more positive than Fe0 (e.g. Cr As Cu U and Se) are removed by reduction and precipitation, however, metals has a more negative reduction potential than that of Fe0 (e.g. Cd and Zn) are removed by adsorption (Boparai et al., 2013; Li et al., 2006). The remarkable differences on removal efficiency were also observed in the the case of different organic pollutants. The conversion efficiency of phenanthrene and pyrene by nZVI are significantly higher than anthracene (ANT) and benzo[a]pyrene (BaP) , which are related to the presence of quinone type compounds, that can promote the reduction of Fe2+ into Fe3+ (Peluffo et al., 2016).

3.2 nZVI properties

The nanosize effect of nZVI played an important role in the degradation of pollutants compared with micron-scale zero-valent iron (MZVI) counterpart. nZVI has proved to have a good performance on decomposition of p-nitrophenol and was greatly superior to that of commercial iron power (Liu et al., 2015). Adding the same amount of iron, the Total Petroleum Hydrocarbons (TPH) removal activation with nZVI (60%) are slightly higher than gZVI (54 %) (Pardo et al., 2015).

In addition, to the best of our knowledge, the redox-activity of nZVI particles are strongly related to the particles size and the size distribution as well as overall morphologies and surface chemistry (Keane, 2010). Under the same experimental conditions, the best Cr(VI) removal efficiency of the prepared nZVIs using peach, pear and vine leaf extracts are significantly higher than that of using lemon leaf extracts (23%), which is due to different sizes and agglomeration tendencies of nZVI (Machado et al., 2013a). Similarly, in another study, the best ibuprofen degraded results presented using the nZVI produced by black tea leaf extracts, this can be explained by smaller nanoparticles (Machado et al., 2013b). Larger specific surface area and more active sites could accelerate the reaction.

In addition, the appropriate dosage of nZVI should be take into account in practical application. After 72 h, total removal of 1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane (p-p′DDT) increased from 78.0% to 89.9% with the increased dosage from 1.0% to 2.0% nZVI, respectively (Yang et al., 2010). This is easily explained that the higher dosage of nZVI offered more available active sites. However, excessive nZVI dosage may have an adverse effect on soil microorganisms. Therefore, the optical dosage of nZVI through comprehensively consideration of various factors is significant important.

3.3. Soil geochemical conditions

3.3.1. pH

pH play an important role in the nZVI reactivity, longevity and selectivity for the target contaminant (Jang et al., 2014). Numerous studies have shown that pH affects the immobilization effect of various heavy metals in soils. (Dong et al., 2011; Wang et al., 2014a; Begum et al., 2012). On the one hand, pH can affect the surface equipotential point of nZVI, which further affect the affinity for the metal ions (Zhao et al., 2016). On the other hand, passive layer of the nZVI surface at high pH hinders electron transfer and the competition effect of DO (Hwang et al., 2011) .

For organic pollutants, dechlorination of chlorinated organic pollutants by nZVI is often strongly hindered by increased pH because large amounts of H^+ ions were consumed during the surface reaction (Chen et al., 2015a). In addition, converting H^+ to H_2 by nZVI may generate more reactive atomic hydrogen for the degradation of pollutants especially in the presence of a noble metal catalyst (e.g.,Pd or Ni), leading to accelerate the electron transfer (Rajajayavel and Ghoshal, 2015). Wang employed an automatic pH control system to keep stable pH for efficient dechlorination of the PCBs contaminated soil by bare nZVI and Pd/nZVI (Wang et al., 2012). In the end, pH affect the interaction between humus and pollutants in soils (Zhao et al., 2016).

3.3.2. Temperature

The temperature is also an important factor influencing the activity of nZVI. The degradation of p,p′-DDT by 1.0% nZVI in flooded soil increased by increasing temperature (Han et al., 2016). Similarly, increasing temperature could enhance the persulfate oxidation pf PAHs in sediments by nZVI (Chen et al, 2015a). This is because high temperature is helpful to the desorption of organic pollutants. In contrast, the adverse effect of temperature on nZVI in the process of polluted soil reparation also have been noticed. The degradation efficiency of 1,2,3,4,5,6-hexachlorocyclohexane （γ-HCH） by nZVI obviously increased from 89.0 to 99.0 % with increasing temperature from 298 K to 303 K, but that decreased to 78.0 % with a further increase in temperature to 308 K (Singh et al., 2013). It is high temperature sterilize the microbes that influence decomposition of pollutants in the soils (Varanasi, Fullana, 2007;Liu et al., 2014). Lastly, environmental temperature may affect the respiration and metabolism of microbial organisms (Pajares and Bohannan, 2016).

3.3.3 Soil moisture

Soil moisture may affect the ionization and activation of nZVI (Kim et al., 2010). Total chlorine removal of p,p′-DDT by nZVI has increased significantly due to the increase of soil moisture, especially, removal efficiency of p,p′-DDT achieved 75.6% in flooded soil (Han et al., 2016) This may be attributed to flooded soil with water decreases the dissolved oxygen content which prevent the corrosion of nZVI. In addition, water is polar moleculer, which can provide H proton that has strong reducibility for contaminants transformation (Satapanajaru et al., 2006;Yang et al., 2010;Xie et al., 2016). However, Kim et al (Kim et al.,2010) found that the effect of moisture on the degradation of metolachlor in soil amended by nZVI was not significant. Therefore, the suitable moisture of the soil is significant in guaranteeing the reactivity of nZVI.

3.3.4. Dissolved oxygen

On one hand, soil dissolved oxygen influence microbial metabolism and activity. It also reported that when combined with anaerobic or aerobic microorganisms, nZVI enhanced the dechlorination of chlorinated organic pollutants (Lee et al., 2001; Huang et al., 2016a; Binh, Imsapsangworn, 2016; Sun et al., 2016). For example, combination of an anaerobic Desdfitobacterium sp Strain Y-51 and nZVI could reduce dechlorinate tetrachloroethylene (PCE) in soil slurry (Lee et al., 2001). The possible mechanism could be anaerobic corrosion of Fe0 and produced cathodic H2, which might react with PCE used as an electron acceptor. On the other hand, nZVI oxidized by dissolved oxygen, and it led to the formation of surface passive layer on the surface of the nZVI particles, on the other words, the electron transfer became sluggish, which could slow down the detoxication of organic pollutants (Lee et al., 2008a). Thus, daily monitoring of dissolved oxygen should take into account in the real field practice.

3.3.5 NOM

Soil organic matter (NOM) is a key factor controls the fate and mobility of nZVI in soil through adsorption, solubility and moisture interactions. NOM is an electron mediator, which facilitate electron transfer from nZVI to organic contaminants and promote fast reduction of organic compounds in soils (Kim et al., 2012a ;Kim et al., 2012b; Zhang et al., 2011; Yang et al., 2010). NOM enhance nZVI effect on organic metolachlor degradation under anaerobic soil conditions (Feitz et al., 2005). In addition, the mitigation of harmful effect of nZVI on soil microorganisms in the presence of NOM was observed by Chen et al (Chen et al., 2011). And one important point, NOM enhanced mobility of nZVI. The sorption of the NOM onto the nZVI, resulting in a reduced sticking coefficient may be the primary mechanism of enhanced mobility (Johnson et al., 2009). However, the effect of the soil organic matter on the mineralization effect of pollutants has not yet been determined. Peluffo et al reported that the addition of HA didn’t produce an improvement of the PAHs removal (Peluffo et al., 2016). Xu et al found the introduction of NOM decreased the removal of 2,4-dichlorophenol (2,4-DCP), attributed to the competition between NOM and contaminants for the surface reaction sites (Xu et al., 2013).

3.4 Aged soil

Usually, pollutants exist in stable form and difficult to desorption from soil which impeded the nZVI reactivity and degradation efficiency. Further, degradation of chlorinated compounds which have aged in soil for many years is far slower than for recently polluted and spiked soil due to lower bioavailability of the former (Moretto et al., 2005; Varanasi et al., 2007). El-Temsah et al (El-Temsah et al.,2013) reported that addition of 1 g nZVI / kg soil led to about 50% degradation of DDT in spiked soil at the end of 7 d incubation, compared to 24% in aged DDT polluted soil. This may be due to complex relationships between DDT and soil, such as desorption, solubilization and dissolution of DDT. Eggen and Majcherczyk (Eggen et al., 2006) found that DDT degradation in aged sediment achieved 93% when they added high concentrations of nZVI (1.7 g nZVI /kg sediment) for an month or so, significantly higher than macro-sized zero-valent iron counterpart.

4. Enhancing nZVI technology

4.1. nZVI combination with physically enhanced technology

4.1.1. Ultrasonic assisted nZVI technology

Ultrasonic assisted technology are not only used in the preparation of nZVI but also assisted in the removal of contaminants. On one hand, the nanoparticles can be dispersed by ultrasound which exposing more of the reaction sites, can be helpful for the reaction (Stefaniuk et al., 2016; Wang et al., 2015). Moreover, nanoparticles are broken into smaller particles in the absence of ultrasound (Jamei et al., 2014). On the other hand, acoustic cavitation led to the removal of oxide layers and impurities, accordingly, fresh Fe0 were continuously exposed for future surface reactions (Liu et al., 2007). A integrated technology of nZVI combine with ultrasound for enhanced Cr(VI) removal was proposed (Zhou et al., 2015). Samaei etal (Samaei et al., 2016) successfully employed ultrasound to enhance MTBE degradation with H2O2/nZVI. Besides, under the ultrasound assisted condition, the degradation of two kinds of dye by the rectorite-supported nanoscale zero-valent iron composite was over 93% and 97% within 20min, respectively (Yuan et al., 2016). In sum, although ultrasound assisted nZVI technology did improve the contaminants removal, however, most of the studies on the ultrasound assisted nZVI was carried out in the lab. The extensive energy loss, the noise, as well as acoustic cavitational erosion restrict application in the real practice.

4. 1.2. UV-light assisted nZVI technology

Under aerobic conditions, the corrosion of Fe^0 by O_2 can generate hydroxyl radical (•OH), which are responsible for oxidation of organic compounds (Fukushima et al., 2000). The mainly disadvantage of the Fenton process including extra H2O2 and producing large amounts of iron sludge has weaken the field application. The combined reaction of Fe0 with UV can produce Fe2+ and H2O2 from the HO2• that results from the UV irradiation of H2O, allowing a Fenton-like reaction without a requirement for extra H2O2 (Guan, et al., 2015), as shown in Fig 2. In this combined reaction, UV light can be used as the energy source for the oxidation of Fe0 and H2O2 generation.

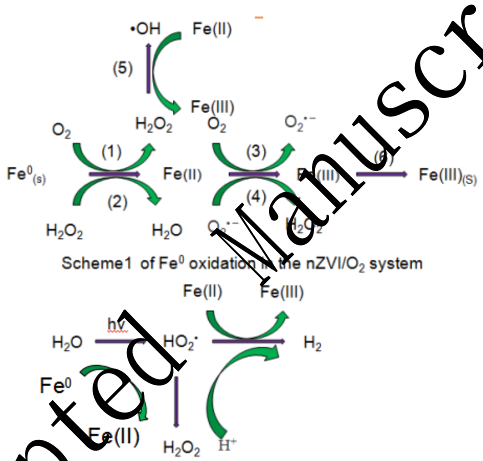

Fig 2. Scheme of Fe^0 oxidation in the nZVI /O_2 system and of Fe^0 oxidation in the nZVI/O_2 system under UV light Reproduced with permission from Ref.(Guan et al., 2015). Copyright 2015, Elsevier.

In the study of Morgada, UV light doubled As(v) removal rates with commercial iron nanoparticles attributed to the formation of multiple active species under UV irradiation, and the process being even more enhanced in the presence of HA (Morgada et al, 2009). The iron oxides present on the surface of the nanoparticles are not acted as passive material but semi-conductors which induced a photo-catalytic process under UV light. Son et al (Son et al., 2009) found that the degradation of 1,4-dioxane in the presence of UV light was significantly enhanced compared to Fe0-only. TiO2/nZVI composite improved the photo-catalytic activity for the degradation of organic contaminant azo dye Acid-Black-24 (AB-24) under UV light conditions (Hsieh et al., 2010). In the system, the concentration of Fe^{3+} decreased with time while a high level of Fe^{2+} was maintained, as a result, the increased ratio of Fe^{2+}/Fe^{3+} reduced the possibility of electron-hole pair recombination and sustained the catalytic of TiO_2 (Hsieh et al., 2010). The results represented mainly in the lab, the degradation of pollutants through the photo-catalytic process catalyzed by nZVI under visible light rather than UV light is needed to study.

4.1.3. Electronic assisted nZVI technology

nZVI technology was enhanced by electronic assisted technology. Electronic assisted nZVI technology that is faciliate for the contamination migration obtained the maximum 80% PCB removal in the PCB-contaminated soil (Gomes et al., 2015). In additon, Molinate could be also successfully degraded in soils by hybrid technology. It is Molinate can be desorped from soil to an aqueous solutions, that is help for sequential degradation of nZVI (Gomes et al., 2014). This integrated technology is also effectively for the Cr(VI) remediation. The composite technology had the prior in removing Cr(VI), which was increased to 80%, compared with electron remediation 14.78% only. Electric effect (such as electroosmosis, electricity transport, and electrophoresis) derived from electric field which triggered the heavy metal ions orient migration along the field gradient, facilitating pollutants accumulation and centralized treatment by nZVI (Ma et al., 2013). Further, Ethylenediaminetetraacetic acid (EDTA) and acetic acid solutions as alternative electrolytes in the electrokinetic (EK) process on degradation was demonstrated and remarkable differences on chromium valence state were observed. The presence of acetic acid promoted the reduction of Cr(VI) to Cr(III), while EDTA lead to more chromium immobilization. (Ma et al., 2013).

4.2. nZVI combination with chemically enhanced techniques

Although physically enhanced nZVI technology could improve the removal efficiency and rates of multi-contaminants, which could be a promising and environmental-friendly method. The cost of energy and limitation in low permeability of soil restrict these techniques employment. Recently, the use of nZVI with chemically assisted technique is attracting researchers' attention.

4.2.1 nZVI combination with ISCO technique

Although it is cost, in-situ chemical oxidation (ISCO) is effective to mineralize a wide range of contaminants. The widely usefulness of nZVI was used as a Fe^{2+} source to catalyze $S_2O_8^{2-}$ to $SO_4^{\bullet -}$ through the direct electron transfer from nZVI to $S_2O_8^{2-}$ (Liang et al., 2008; Pardo et al., 2016). The removal efficiency of PAH was up to 90% with the addition of 0.01g/L nZVI compared to that to 10.7% with unactivated persulfate (Chen, Binh, 2014). In most cases, heavy metals and organic pollutants simultaneously exist in the contaminated soils. The application of Bentonite-nZVI as a catalyst to active persulfate could remove heavy metal Cr(VI) and phenol simultaneously. Meanwhile, the heavy metal removal mainly by the radical $SO_4^{\bullet-}$, neither $HO^{\bullet}$ or $O_2^{\bullet-}$ are elucidated, as shown in Fig 3. (Diao et al., 2016). Except for persulfate, nZVI as a catalyst to active percarbonate obtained similar effect (Danish et al. 2016).

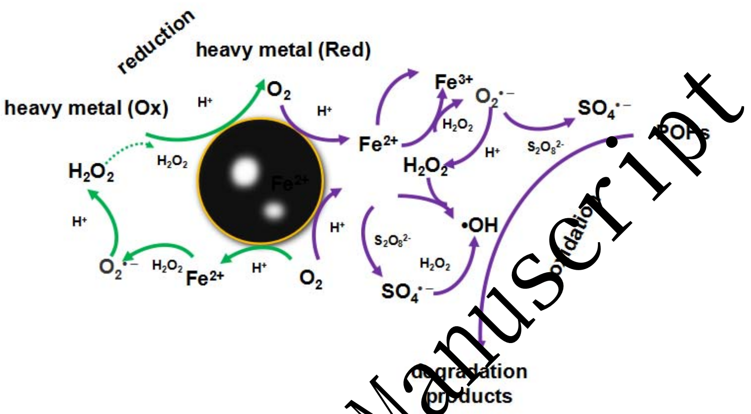

Fig 3. Proposed reaction mechanism for the simultaneous removal of heavy metal and organic pollutants by nZVI/persulfate hybrid system. Reproduced with permission from Ref.(Diao et al., 2016). Copyright 2016,Elsevier.

4.2.2. nZVI combination with soil washing technology

Soil washing technique is a a kind of chemical process with the aid of chemical reagents, trying to extract the heavy metal from contaminated soil into the liquid phase. Commonly used chemical reagents including inorganic acids, salts, cheating agents and surfactants (Dermont et al., 2008; Lemaire et al., 2013). The anionic surfactant sodium dodecyl sulfate (SDS) outstandingly improved TCE desorption and degradation rates by subsequent nZVI (Chowdhury et al., 2015). Among these agents, several synthetic chelators such as EDTA have been well studied for remediation of heavy metal contaminated soils in recent years (Arwidsson et al., 2010). Organic acid, especially short-chain organic acids (Wang, Zhang, 2014a) may form strong complexes with Fe3+ and thus could inhabit the precipitation of hydroxides iron on nZVI surfaces (Ou et al., 2016). The addition of short-chain organic acids instead of surfactant promoted pentachlorophenol

(PCP) degradation by nZVI. Although the needed quality of organic ligand is small amount, the toxicity of organic ligand on soil microorganism is a noticeable problem. The mechanism of mineralizaition in the presence of nZVI and strippant also need further study.

4.3. nZVI combination with biologically enhanced technology

Biotechnology, such as photoremediation or microremedation, is considered as an efficient technology for contaminant removal, stabilization or degradation. The above two biotechnologies share environment-friendly and cost-effective advantages over most conventional chemical and physical remediation strategies. Over the years, extensive research has certified the effectiveness of biotechnology for the remediation of soils contaminated. Currently, considerable efforts has been conducted to investigate a combined soil remediation technique using biotechnology and nZVI to deal with complex soil pollution.

4.3.1 nZVI combined with phytoremediation

4.3.1.1 The impact of nZVI on soil plants

Plants are important components of the soil, maintaining normal soil ecological function (Chang et al., 2007; Machado et al., 2013b). Thus, nZVI has been introduced to soil remediation could pose potential influence on plants (Ma X. et al., 2010; Monica and Cremonini, 2009; Wu et al., 2016; Li et al., 2015). Plants exposed to nZVI show different effects, such as stimulation of the seed germination and growth, increasing in biomass and chlorophyll (Xie et al., 2016; Libralato et al., 2016; Kim et al., 2010). For example, Li et al found that the exposure of peanut seed to nZVI at low concentration (10-320 μmol/L) stimulated the seed germination and development. At certain concentrations, the nZVI processed samples were even better than a commonly iron nutrient solution. This positive effect may probably due to the internalization of nZVI by the plants (Li et al., 2015).

Roots are important part of underground planting, which are also the first part of the contact with nZVI. A recent study by Kim showed that exposure of plants to 500 mg/L nZVI can enhance Arabidospis thaliana root elongation because nZVI induces cell wall loosening (Kim et al., 2014). In addition, plant root cell walls are affected by nZVI supplyment and thus affect the respiration of plants. After the nZVI are internalized by plants, the nZVI moved along the plant pipeline. The metabolism of plants is disturbed by nZVI. The superoxide dismutase, peroxidase and catalase activities decreased by 12%, 6.1% and 5.9%, respectively, suggesting protecting plant from oxidative damage in the nZVI-treated soil sample (Wu et al., 2016). The leaves are the most important organ of the plant on the floor. Interestingly, they further found that exposure of kindred plant to nZVI enhances stomatal opening by inducing the activation of plasma membrane H+-ATPase, leading to possibility of increased CO2 uptake (Kim et al., 2015).

However, the effect of nZVI on plants has not yet been concluded. On the contrary, nZVI slow down the germination and development of lettuce seeds, and seed germination decreased to 45% and root elongation shorten around 80% (Rede et al., 2016). nZVI exhibited strong negative impact on Typha and hybrid poplas at high concentrations may attributed to uptake of nZVI by poplar root cells (Ma et al., 2013). Visible iron deficiency symptoms were observed in plants, which was due to the blocked transshipment of nutrient element iron from the root to shoot related to the internalization of nZVI in the presence of higher concentration of nZVI (Ma et al., 2013). In addition, due to oxidation of nZVI, resulting in O2 deficiency and excess strong reductive Fe(II) in soil, which had negative impact on the plants in the context of soil (EI-Temsah et al., 2016). The possible impact of nZVI on plants as shown in Fig 4. The above results indicated that nZVI at low concentrations can be used with scarcely adverse effects on plants and thus be suitable for combination with plants remediation.

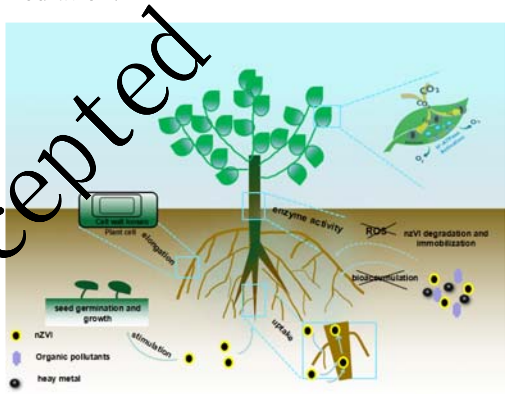

Fig 4. The possible impact of nZVI on plants

4.3.1.2 Phytoremediation impacted by nZVI nanoparticles

There are various remediation technologies for soil remediation (Gong et al, 2017a). However, most remediation techniques merely stay the stage of transformation soil pollutants into their less toxic forms rather than thorough removal of toxic substances. By comparison, phytoremediation is a plant-based acceptable alternative technique for soil remediation, which could remove the extract, degrade, sequester, and stabilize a wide range of soil pollutants. The efficiency of phytoremediation strongly depends on the uptake ability of plants and the bioavailability of pollutants. However, the biological availability of pollutants and the endurance capacity of certain plants are limited. To solve these problems, the combined remediation strategy using phytoremediation and nZVI is an emerging technology (Jiamjitrpanich et al., 2012; Gil-Diaz M etal, 2016; Gong et al, 2017b).

Germination, transplanting and preliminary test of tolerance study of plant with TNT and nZVI suggested that both Panicum maximum and Helianthus annuus had low rates of germiantion in TNT-contaminated soil. The results showed that Panicum maximum and Helianthus annuus could survive at higher rates of transplanting than that of germination. It indicated that transplanting was more suitable as a method for nano-phytoremediation of Panicum maximum and Helianthus annuus in TNT-contaminated soil. Notably, Panicum maximum should be selected as a hyperaccumulated plant because it could survive for a longer period of time in TNT and nZVI-contaminated soil. Maximum tolerance dosage of Panicum maximum to TNT-contaminated soil was at least 320 mg/kg and nZVI-contaminated soil was at least 1000 mg/kg in the transplantation method (Jiamjitrpanich et al, 2012).

Gil-Díaz et al. (Gil-Diaz M. et al., 2016) investigated the influence of nZVI treatment on soil recovery of As-polluted soils. The authors found that the application of 10% nZVI significantly reduced the uptake of As in plant shoots and roots, and increased the height and dry weight of barley plants under metal stress. However, the amplified phytotoxicity of the contaminants by the addition of nZVI had also been certified. Similarly, Cd content in cell wall of plants reduced, and its concentration in cell organelle and soluble fractions increased by S-nZVI supplyment. Importantly, low concentration of nZVI alleviated the oxidative damage to ramie under Cd-stress, while high concentration of nZVI played an aggravated role. These findings demonstrate that nanoparticles at low concentration can improve the efficiency of phytoremediation. This study herein develops a promising novel technique by the combined use of nanotechnology and phytoremedaiation in the remediation of heavy metal contaminated sites (Gong et al., 2017b).

Therefore, further investigations should be conducted in order to understand the different effects of nZVI on plants under certain contaminated conditions before using the combined technique of phytoremediation and nZVI to remove pollutants from the contaminated soil.

4.3.2. Micro-remediation impacted by nZVI nanoparticles

4.3.2.1 The impact of nZVI on soil microorganism

Remediating soil with nZVI is deemed as the largest stream of engineering nanoparticles into the environment (Huang et al., 2015). The reason that makes nZVI useful for environment remediation such as enhanced surface area and high active reactivity also made them potential harmful to living microorganisms (Lefevre et al., 2016). These microorganisms can be main contributors to soil remediation and it is important to understand how they are affected by nZVI. In the last decade, an increasing amount of studies evaluating the toxicity of nZVI on soil microorganisms have been carried out (El-Temsah et al., 2016; Chaithawiwat et al., 2016a; Chaithawiwat et al., 2016b; Sacca et al., 2014). Two types of nZVI have negative impact on the Escherichia coli due to oxidation of nZVI, resulting in O2 consumption and excess ferrous ions in soil (El-Temsah et al., 2016). On the other hand, the presence of nZVI in soil gradually released H2 required for microbiological process, facilitating microbial growth and metabolism (Sacca et al., 2014). Natural organic matter and humic acids, as common soil components, could also alleviate nZVI toxicity. Chen et al (Chen et al., 2011) reported a mitigation of the bactericidal toxicity of nZVI towards E.coli and B.subtilis in the presence of humic acids as they adsorbed onto nZVI particles and bacterial cells, which hindered direct contact between nZVI and cells.

Although a majority of toxicity studies have been carried out with bare-nZVI, nZVI particles used for in situ remediation are typically surface stabilized, and the type of stabilizers used not only increase mobility of nZVI but also attenuate nZVI toxicity. Carboxymethylcellulose (CMC) coated on nZVI surface could prevent the direct contact likely by increasing electrostatic repulsions, which prevented cell death and lysis (Wang et al., 2014b). Most of the literature on the mechanism of microbial toxicity suggests that generation of Fe^{2+} and ROS when exposed to nZVI, and induced the cell structure disruption (Lee et al., 2008b) or increased the permeability of member (Chen et al., 2012), proving the channel for Fe^{2+} in to the cell. Once internalization, Fe^{2+} could react with the H_2O_2, leading to oxidative stress and impeded transport of nutrients (Naseem and Farrukh, 2015). In addition, Bacillus species counteract to nZVI toxicity by forming spores, preventing direct contact between nZVI and bacterial. Klebsiella oxycota's high cellular defenses against nZVI toxicity was attributed to a signaling molecule produced indole which used to induce sporulation (Sacca, Fajardo, 2014). Finally, the production of extracellular polymeric substances (EPS) developed by microbial species can also effectively mitigate nZVI toxic effects (Ševců et al., 2011). The mechanism of microbial toxicity when exposed to nZVI was proposed as shown in Fig 5.

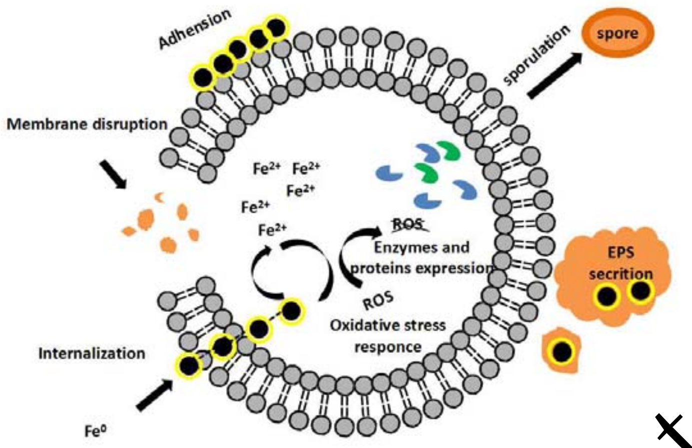

Fig 5. Proposed reaction mechanism of microbial toxicity when exposed to nZVI

4.3.2.2 Micro-remediation impacted by nZVI nanoparticles

Bioremediation using microorganisms has emerged as a potentially useful alternative technology for the cleanup of contaminated sites (Barnes et al., 2010). Particular attention has been paid to exploring the combination microremediation with nZVI for reductive dehalogenation of organic pollutants. A rapid decrease of the pollutant concentration together with hydrogen evolution and redox potential shifts caused by nZVI can finally lead to favorable conditions for consequent biological processes (Němeček et al., 2016; Binh et al., 2016; Xiu et al., 2010). Both white foot fungi and Sphingomonas sp. PH-07 combination with bimetallic Fe/Pd rapidly reduce degradation of target pollutants (Murugesan et al., 2011). Firstly, the oxidation-deoxidation environment of the soil is changed by the injection of nZVI. The CMC-nZVI coupled with biological treatment efficiently degrade 2,3,7,8-Tetrachlorodibenzo-p-dioxin in soils, which is related to a reducing conditions was achieved after injection of nZVI facilitating the biodegradation (Binh et al., 2016). Similarly, the use of PAA stabilized nZVI coupled with bioremediation for successfully mineralizing 1,2-dichloroethane (1.2-DCA) (Wei et al., 2012), attributed to conditions conductive to microbial activities when nZVI as supplements. Recently, Lv and Zhang et al (Lv et al., 2016b) developed a novel three stage hybrid nanobimetallic reduction/oxidation/biodegradation treatment to achieve completely mineralization of BDE47 in 90min. The redox potential of the soil supplied by nZVI promoted the propagation of microorganisms which contributed to debromination. Interestingly, the SiO_2-nZVI/Pd exhibited much lower toxicity to the P.putid strain and higher reactivity in debromination than nZVI/Pd. Secondly, the bioavaliability of pollutants has changes when nZVI as supplements. Halogenated organic compounds first dehalogenate by nZVI, and increased biological availability were facilitate to bio-degradation (Jiang et al., 2015). In addition, the production of H_2 from the corrosion of nZVI as electron donor stimulated microbial growth and dechlorination (Wei et al., 2012). The use of bioargumentation of an anaerobic baterical Desulfitobacterium sp.strain and addition of nZVI effectively reductive dechlorination of tetrachloroethylene (PCE) by maintaining the proper pH and redox potential by producing H_2 (Lee et al., 2001). Studies have shown that biodegradation of TCE can be enhanced by the addition of nZVI combination with indigenous dechlorinating bacterial community (Barnes et al., 2010). Thirdly, nZVI is used as a soil supplement to change the composition and structure of the soil. The enrichment of iron-reducing bacterial can influence nZVI longevity by reducing Fe^{3+} to Fe^{2+}, which become available for reduction of chlorinated organic compounds (Němeček et al., 2016). In situ remediation application of nZVI suspension in stabilization Cr(VI) combing subsequent biotic reduction are up to a year. nZVI oxidized to Fe^{3+} and then reduced back to Fe^{2+} by iron-reducing bacterial, which played an important role in the stabilization process. Barnes proposed combining bimetallic Fe/Ni nanoparticles and indigenious dechlorinating bacteria for the remediation of Chlorinated Aliphatic Hydrocarbon (CAH) contaminated sites due to the stimulation of the microbial growth. Lastly, the oxidation of Fe(II) could also afford energy for the microorganism co-metabolic dehalogenation reaction. The proposed reaction mechanism of nZVI-bio technology is as shown in Fig 6.

However, the effect of micro-remediation has not been concluded. In contrast, bacterial dechlorinating TCE were bio-inhibited by nZVI for treatments with 1g/L nZVI (Xiu et al., 2010). The degradation efficiency of TCE progressively decreased in the presence of increasing Fe^0 dosage, which ranged from 0.01 to 0.1 g/L, and cease completely at the dosage of 0.3g/L or above (Barnes et al., 2010), this is related to excessive nZVI may have adverse effect on dechlorination microbes (Huang et al., 2016). Obviously, there is a trade off between degradation of pollutants and microbial growth. Thus, in the real application, the appropriate dosage of nZVI should be taken into account. This is essential in guaranteeing that the injected nZVI nanoparticles could biostimulate microorganisms and remove contaminants efficiently.

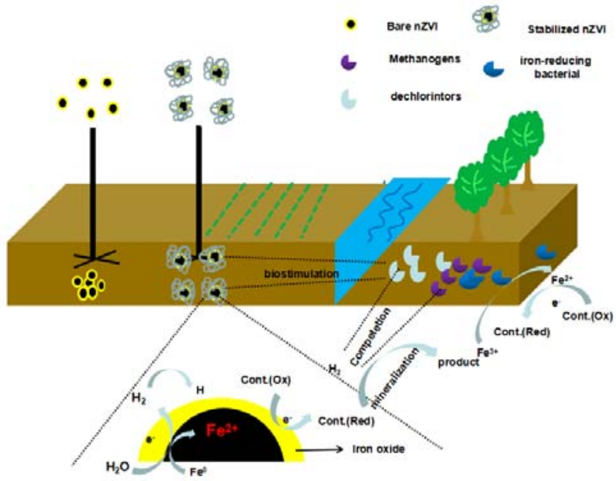

Fig 6.proposed reaction mechanism of nZVI combination with micro-remediation

7. Conclusions and future challenges

Nano-remediation using nZVI could be applied for the transformation and detoxification of combined pollutant from soil. However, the complex and variable soil environment affect the performance of nZVI. Physical, chemical and biological method combination with nZVI was developed to enhance the performance of nZVI. However, the negative impact of nZVI on organisms will inevitably induce adverse effects on the soil bio-remediation process. Although, several impressive results have been achieved in nZVI for remediation of polluted soil, researches towards nZVI combined bio-remediation still remain in its infancy, and significant improvements are still required to make these systems fully competitive.

1. Even if nZVI are extensively used, large-scale preparation is still costly. Existing producing methods for preparing nZVI are complex and time-consuming, more work is needed to reduce the preparation costs and explore new preparation methods that will produce nZVI with high quality and improved performance.

2. Although significant progress has been achieved in the combined application of nZVI and biotechnology for pollutant removal, the exact mechanisms have not yet been clearly elucidated. Complicated reaction between nZVI and soil pollutants appeared, which affect the transformation, migration, performance of nZVI. In order to improve the soil remediation efficiency, the likely fate of nZVI themselves, and the potential impact of nZVI on environmental pollutants, and how the soil remediation is influenced by the combined application of nZVI and biotechnology need to be carefully taken into consideration.

3. Risk assessment research on the combined application of nZVI and biotechnology is in its

infancy. It is clear that additional models on this issue are required to further estimate nZVI-induced potential risks to the plants/microorganisms/soils in the presence of contaminants.

4. In addition, up to now, majority studies using nZVI and the enhanced nZVI strategy to remove pollutants from soil have been conducted only at the laboratory scale. Field applications are needed since the natural environment is quite complex and difficult to imitate.

Acknowledgments

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