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Review on Nano zerovalent Iron (nZVI): From Modification to Environmental Applications

Xing Chen, Dandan Ji, Xiqing Wang and Lihua Zang*

College of Environmental Science and Engineering, Qilu University of Technology,
University Town, Changqing District, Ji'nan City, Shandong Province, China

*E-mail: zlh20151216@126.com

Abstract. Nanoscale zero-valent iron (nZVI), with its reductive potentials and wide availability, offers degradative remediation of environmental contaminants. Although nZVI particles were successfully used in wastewater treatment, there are still some drawbacks associated with the process and needs to be addressed. For example, magnetic attraction between nanoiron particles causes the rapid aggregation of particles. In addition, nZVI are more prone to react with dissolved oxygen and oxygen-rich compounds. Meantimes, nZVI could exert some degree of toxicity towards microbial species, and the effects of nZVI at the cellular and community levels are progressively being elucidated. To overcome these problems, nZVI particles were immobilized in or on suitable solid supports, and also to expand the effective pH range of the Fenton reaction. Therefore, refer to the new trends is very important when selecting nZVI for the treatment of various matrices. This review also identifies problems that may occur as a result of changes in the physicochemical properties of nZVI due to their modification (e.g. other metal doping, coating the surface, or deposition on the support). Toxicity studies suggest that cell membrane disruption and oxidative stress through the generation of Fe^{2+} and reactive oxygen species by nZVI are the main mechanisms contributing to nZVI cytotoxicity. This review highlights the application of nano-zero valent iron in treating refractory compounds.

1. Introduction

The multidisciplinary nano 'boom' has led to the evolution of a wide array of novel technologies for both domestic and industrial applications, including improved drug delivery and new methods for the treatment of contaminated water.[1] As the particle size decreases, proportion of atoms at the surface increases, raising its tendency to adsorb, interact, and react with other atoms, molecules, and



complexes to achieve charge stabilization. The potential use of nanoparticles for the treatment of contaminated groundwater has sparked a great deal of interest.

Nanoscale zero valent iron (nZVI) is the most commonly used nanomaterial in Europe and in the United States for soil and groundwater remediation. Due to its reduced size, nZVI has a higher reactivity towards a broad range of contaminants, including halogenated compounds, nitrate, phosphate, polycyclic aromatic hydrocarbons, and heavy metals, and a higher mobility compared to its microscale counterpart. Consequently, nZVI is regarded as a promising remediation strategy suitable to a broad range of applications and environments.

O'Hara et al. and Quinn et al. reported substantial reductions of trichloroethylene (TCE) in soil (greater than 80% reduction) and groundwater (60% to 100% reduction) during a fieldscale demonstration at Cape Canaveral Air Force Station (Florida), by injecting emulsified nZVI particles.

In view of the abundant published literature on the topic, this review provides an updated overview of the potential impacts of the in situ deployment of nZVI on microbial communities (summarized in Figure 1).

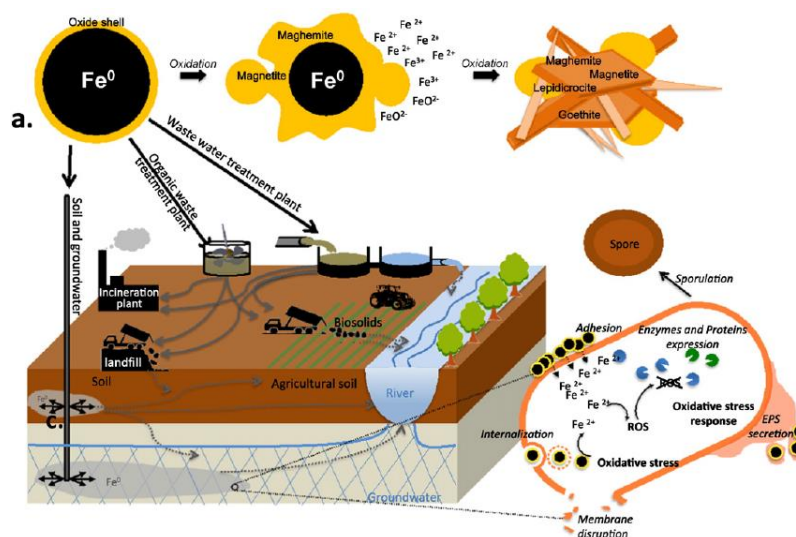


Figure 1. nZVI oxidation, cytotoxicity, cellular defense mechanisms mediated by nZVI, and potential routes of nZVI in the natural environment. Illustration of (a.) nZVI oxidation process, (b.) bacterial toxicity and defense mechanisms, and (c.) potential routes followed by nZVI in the environment. Plain gray arrows represent deliberate injection or amendment of nZVI, and deliberate transport of material potentially containing nZVI. Dashed gray arrows represent potential non-deliberate transport of nZVI in non-target environments. Abbreviations: EPS, Extracellular polymeric substances; ROS, Reactive oxygen species.

The key properties essential for the use of any engineered nanoparticle for in situ remediation includes (a) high reactivity for contaminant removal, (b) sufficient mobility within porous media, (c) sufficient reactive longevity, and (d) low toxicity. However, it should be noted that the process involved is at a sensible cost and competitive with other existing technology.[2, 3]

The practical applicability of ZVI lies in the fact that it can easily get oxidized to +2 and +3 oxidation states and in the process reduce other organic as well as inorganic impurities. Metallic iron easily acts as an electron donor:



Nanoscale iron particles are in a process to replace micro iron particles and have proven to be quite effective reductant and catalyst for a wide variety of common environmental contaminants including chlorinated organic compounds and metal ions.[4]

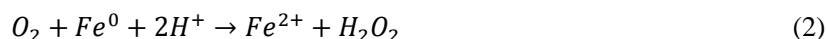
2. Application of nZVI for remediation of organic compounds

Use of nZVI particles in advanced oxidation processes (AOPs) such as the Fenton Process have shown an advantage over conventional method which requires around 40–80 ppm of ferrous ion in the solution and this value is above the standards. In addition, the application of homogeneous AOPs to treat large quantity of water may produce large amount of sludge in the final neutralization step.[5]

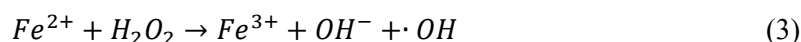
In order to avoid these disadvantages, nano-zero valent iron (nZVI) could be used as an alternative way to induce Fenton oxidation.

2.1. Fenton like reactions using nano-zero valent iron

In heterogeneous Fenton reaction, oxidation of nZVI provides an alternative means of inducing Fenton oxidation[6, 7] as shown in Eq. (2):



nZVI is the reactive reagent, and applications in vadose-zone soil or shallow groundwater rapidly oxidize nZVI to ferrous (Fe^{2+}), as shown below, and ferric iron (Fe^{3+}) leading the released electron to become available for the reduction of other compounds, whereas, through Fenton chemistry (Eqs. (2) and (3)), which produces strong oxidants capable of transforming recalcitrant environmental contaminants such as chlorinated compounds, pesticides, polychlorinated biphenyls, inorganic anions and heavy metals.[8, 9]



Use of nZVI to induce Fenton oxidation has some advantages beyond addition of Fe^{2+}/H_2O_2 [10]:

a.nZVI is able to attach or coat on large particle, therefore nZVI absorbed media could treat contaminated water passing through a sand filter or other type of filtration system.

b.nZVI injected through wells could be immobilized in/on soil grains in contaminated aquifers.

c. an increase in the reductive degradation reaction rate.

d. a decrease of the reductant dosage.

e. control over the risk of release of toxic intermediates.

f. the generation of a nontoxic end product.

Joo et al [6] studied about the ability of nZVI to induce oxidative degradation of contaminants. This study demonstrated that nZVI was capable of degrading the herbicide molinate in the presence of oxygen. In this study, it was shown that nZVI-induced Fenton oxidation could degrade over 60% of molinate at pH 8.1 and 65% at pH 4.

Bergendahl and Thies [10] have investigated the feasibility of oxidative removal of methyl-tert-butyl ether (MTBE) using ZVI. The results showed that over 99% of MTBE in water was degraded within 10 min and the major oxidation product was acetone. The addition of H_2O_2 greatly

enhanced the degradation efficiency. The rate of degradation of MTBE increases with an increase in H_2O_2 :MTBE ratio.

Although nZVI particles were successfully used in wastewater treatment, there are still some drawbacks associated with the process and needs to be addressed. For example, magnetic attraction between nanoiron particles causes the rapid aggregation of particles. In addition, nZVI are more prone to react with dissolved oxygen and oxygen-rich compounds. To overcome these problems, nZVI particles were immobilized in or on suitable solid supports, and also to expand the effective pH range of the Fenton reaction. Now widely used load materials is PVA microsphere[11, 12]. The others include calcium alginate beads [13], iron exchanged with Nafion membranes[14], iron modified clays[15, 16]. The modified supporting materials such as silica fabric[17], zeolites[18], resins [19], and cotton[20] which are used for immobilization of iron ions could be used for immobilizing nZVI.

2.2. nZVI cytotoxicity

Modifications of nZVI increased stability, reactivity, mobility, and reduced aggregation or passivation of nZVI. However, modifications of nZVI may lead to the creation of materials that not only eliminate contaminants more effectively, but also accumulate in living organisms, migrate over large distances sedimentation on bottoms of water reservoirs, or become carriers of other contaminants. Studies have demonstrated that the toxicity effects of nZVI are limited compared to other nanoparticles.[21]

The toxicity of nanoparticles can be caused by a variety of factors, largely convergent with those which are responsible for their high reactivity. The available information on nZVI is focused mainly on their effect on microorganisms and to a lesser extent, on crustaceans, fish larvae, arthropods, annelids, plants, and occasionally mammalian cells. Studies show that nZVI can be adsorbed on cell membranes of bacteria, or penetrate through them, which often leads to disturbances in the functioning of the cell. [22] Nanoparticles adsorbed on cell membranes can block cellular ducts, cause structural changes to the membranes, or inhibit mobility and nutrient intake and result in death of the bacteria. Research shows that modifications of the nZVI surface can be improved in their stabilization, reduction of aggregation, and reduction of toxicity. All forms of nZVI aggregated in soil and water in presence of a high concentration of calcium ions and thus addition of calcium salts may be improved in reducing the toxicity of groundwater due to nZVI.[23]

Another often-suggested mechanism contributing to nZVI toxicity involves the generation of highly reactive oxygen species, which accumulate in the cell environment and denature macromolecules including lipids, proteins, and nucleic acids, damaging intracellular structures and eventually leading to cell death. Because under aerated conditions, Fe^{2+} oxidizes more rapidly than it would under anaerobic conditions, the contribution of Fe^{2+} to nZVI toxicity is higher under anaerobic conditions than under aerobic conditions.[24] Modification of nZVI, e.g. as a result of nZVI coating with polyasparaginate, reduces the toxicity of nZVI by limiting direct contact of nanoparticles with cells.

3. Conclusion

The investigation of nZVI particles on organic compounds degradation is receiving more attention in the current decade. As research demonstrates, nZVI can be an effective and versatile tool for the purification of waters and soils. nZVI was successfully used for the generation of hydroxyl radicals in

AOP system. However, the potential threats resulting from the application of modified and nonmodified nZVI to various matrices are rather poorly recognized. Another important aspect in the estimation of the safety of application of nZVI is to determine how the various methods of modification will affect the fate of nZVI and their effect on living organisms.

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