The colorful chemistry of nanoscale zero-valent iron (nZVI)

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Nanoscale zero-valent iron (nZVI) possesses unique chemistry and capability for the separation and transformation of a growing number of environmental contaminants. A nZVI particle consists of two nanoscale components, an iron (oxyhydr)oxides shell and a metallic iron core. This classical "core-shell" structure offers nZVI with unique and multifaceted reactivity of sorption, complexation, reduction and precipitation due to its strong small particle size for engineering deployment, large surface area, abundant reactive sites and electron-donating capacity for enhanced chemical activity. For over two decades, research has been steadily expanding our understanding on the reaction mechanisms and engineering performance of nZVI for soil and groundwater remediation, and more recently for wastewater treatment.

In this contribution, we highlight some exciting aspects of nZVI research from a number of recent papers, including those published in the Journal of Environmental Sciences (JES). A frequently-researched application of nZVI is for the treatment of wastewater containing dyes-and-pigments, especially azo dyes, through the reduction and transformation of the chromophoric azo moiety (-N=N-). Azo dyes, such as Congo Red and Direct Red 80, are organic compounds bearing the (-N=N-) bond attached to aryl, such as benzene and naphthalene. As shown in Fig. 1, the color of Congo red solution (Fig. 1A) quickly disappeared after reaction with nZVI for 3 min (Fig. 1B), and the color of filtrate of the treated solution sampled from bottle B was more transparent (Fig. 1C). In addition, the spent nZVI particles preserved high magnetization, and can be easily separated from solution with a common magnet (Fig. 1B). This experiment illustrates vividly the power of nZVI for the transformation of pollutants in water.

Nonetheless, there are still a few limitations for the large-scale application of nZVI. For example, the reactive nZVI particles often form micro- to millimeter-scale chain-like aggregates, and co-solutes (e.g., dissolved oxygen, oxidative cations, anions, and organic matters) can quickly consume nZVI and passivate nZVI surface. Li et al. (2017b) selected Hangjin #2 clay (the HJ clay) to synthesize clay-supported nZVI. The HJ clay has high surface area, relatively large pore size and porosity, also favorable cation exchange capacity and negatively charged surface. Those microstructure characteristics boosted both payload and reactivity of nZVI. For example, decolorization efficiency for methyl orange (MO) was significantly higher than that of pure nZVI. A HJ:nZVI mass ratio of 5:1 can achieve optimal reactivity by balancing nZVI aggregation and iron loading. Decolorization of MO increased with increasing the clay-modified nZVI dosage and temperature, but decreased as the MO initial concentration, pH and dissolved oxygen increased. The authors postulated that the mechanisms for MO decolorization by the clay-modified nZVI were "adsorption-enhanced reduction" (Fig. 2). The oxidative and positively charged MO was quickly sorbed, and its azo bond was subsequently reduced and transformed to sulfanilic acid (SA) and other by-products.

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decolorization process. nZVI is the main reductant and the negatively charged clay may also donate electrons for the MO reduction (Li et al., 2017b).

Similar to clay as a support, other solids and porous materials (e.g., graphite, granular active carbon, silica fume) (Xu et al., 2018; Zhang et al., 2016; Li et al., 2011) could potentially enhance the mobility and reactivity of nZVI as well. For example, nZVI particles supported on graphene (G-nZVI) with 20 wt% nZVI can remove phosphate from synthetic rainwater much more efficiently than pure nZVI (Liu et al., 2014). Silica fume supported nZVI (SF-nZVI) exhibited higher efficiency of Cr(VI) removal, and SF-nZVI distributed uniformly in both vertical and horizontal columns while unsupported nZVI particles were trapped mostly within a few centimeters (Li et al., 2011). For all the supported nZVI particles, performance is affected by the content of nZVI and composition of groundwater and/or soil. Excessive iron loading can result in aggregation, block pore tunnels of supporting materials and decrease mass transfer efficiency (Li et al., 2017b; Zhang et al., 2016; Li et al., 2011; Liu et al., 2014). The composition and concentration of ions in groundwater and soil could also modify the characteristics of electric double layer and the mobility of supported nZVI particles. For example, the stability of silica fume-nZVI decreased as concentration of Na⁺ and Ca²⁺ increased, and the surface zeta potential increased more significantly in the presence of Ca²⁺. Although the mobility and reactivity of supported nZVI particle were improved, the stability, ecological effects and costs of the supported nZVI still need to be systemically examined before it can attract any significant application (Yirsaw et al., 2016). The sorbed or reduced contaminants on supported nZVI can be remobilized as geochemical conditions of groundwater change. The supporting materials also alter the affinity of supported nZVI to microorganisms, thus affect metabolism functions of microbes (Yirsaw et al., 2016).

The reactions with nZVI are fundamentally surface-mediated; nevertheless, fundamental understanding, especially direct evidence on the surface reactions is still limited. Recent work utilizing spherical aberration-corrected scanning transmission electron microscopy (Cs-STEM) integrated with X-ray energy-dispersive spectroscopy (XEDS) and electron energy loss spectroscopy (EELS) surveyed the reactions between nZVI and a number of metal-metalloid ions (e.g., Ag, As, Cu, Cr, Cs, Ni, Se, Zn, U). This advanced analytical microscopy technique provides high-resolution and three-dimensional (3D) images and chemical reactivity information about surface sites, adsorption, surface-complexation, diffusion, and encapsulation mechanisms of metals and metalloids (Ling and Zhang, 2015; Ling et al., 2017). As exciting as viewing the near-atomic resolution (~0.1 nm) data, those
experiments were conducted under relatively pure solution and simple conditions. Effects of complex geochemical and environmental factors (e.g., major anions, cations, organic matters, suspended solids) on the spatial distribution of pollutants in nZVI particles have yet to be investigated.

For nZVI to be a continuing and vibrant topic of research, the most important undertaking is to constantly expand and accelerate its applications. This certainly requires more innovations in engineering techniques for the deployment of nZVI. The ex situ remediation technologies have successfully exploited some merits of nZVI (e.g., high reactivity, easy in situ injection, separation and recirculation) (Fig. 3). Results from recent applications of nZVI for industrial wastewater treatment show that nZVI particles could separate many metal and metalloid ions and potentially reuse the metals laden nZVI (Li et al., 2017a). However, there are still many theoretical, technical and economic challenges, for example, 1) the materials cost of nZVI is still high, 2) the longer-term reliability of nZVI in the dynamic flow system is uncertain, and 3) methods for recovery and reuse of valuable resources and appropriate disposal of spent nZVI need to be further explored. In this context, we are looking forward to seeing more high-quality studies on nZVI and its environmental applications.

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