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Review

Microbes team with nanoscale zero-valent iron: A robust route for degradation of recalcitrant pollutants

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ABSTRACT

Integrating nanoscale zero-valent iron (nZVI) with biological treatment processes holds the promise of inheriting significant advantages from both environmental nano- and biotechnologies. nZVI and microbes can perform in coalition in direct contact and act simultaneously, or be maintained in separate reactors and operated sequentially. Both modes can generate enhanced performance for wastewater treatment and environmental remediation. nZVI scavenges and eliminates toxic metals, and enhances biodegradability of some recalcitrant contaminants while bioprocesses serve to mineralize organic compounds and further remove impurities from wastewater. This has been demonstrated in a number of recent works that nZVI can substantially augment the performance of conventional biological treatment for wastewaters from textile and nonferrous metal industries. Our recent laboratory and field tests show that COD of the industrial effluents can be reduced to a record-low of 50 ppm. Recent literature on the theory and applications of the nZVI-bio system is highlighted in this mini review.

Introduction

Biological treatment is without doubt the most important technology in wastewater treatment and environmental remediation (Rittmann and McCarty, 2000). During biodegradation, microbes grow by utilizing organic substances including various organic pollutants as carbon and energy sources. However, microbes perform poorly on many synthetic, toxic and recalcitrant compounds, such as halogenated organic compounds (HOCs), polychlorinated biphenyls (PCBs) and organic dyes. In addition, microbes are vulnerable to the toxic effect of heavy metals and metalloids such as chromium (Cr), cadmium (Cd), copper (Cu), arsenic (As) and antimony (Sb) that are commonly encountered in industrial wastewaters (Huang et al., 2018; Ling and Zhang, 2017; Wang and Zhang, 1997). The metal ions can deposit directly onto cell surfaces, damage cell membranes, even penetrate into microbial cells, thus impact the microbial growth and pollutant biodegradation (You et al., 2017).

Meanwhile, extensive studies have demonstrated that nanoscale zero-valent iron (nZVI) is effective for sorption,

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separation and transformation of heavy metals and recalcitrant pollutants including trichloroethylene (TCE), polychlorinated biphenyls (PCBs), azo dyes, and a variety of toxic metals (Huang et al., 2017; Li and Zhang, 2007; Ling et al., 2018; Wang and Zhang, 1997). For example, azo dye, a common organic contaminant in industrial wastewater, can be quickly degraded by nZVI, which also produces more biodegradable daughter products. The core-shell structure of nZVI, namely metallic iron core and iron oxide shell, bestows the nanoparticles with optimal surface chemistry and extraordinary capability to sequestrate heavy metal and metalloids. In parallel with laboratory studies on reaction mechanisms, significant progress has also been made in field applications of the nZVI technology for wastewater treatment (Li et al., 2019; Li et al., 2017; Wang et al., 2016).

Herein, we present a brief review on the combined nZVI and microbial processes for degradation of recalcitrant pollutants, with emphasis on synergic nanoparticle-cell interactions and potential large-scale applications of the combined system. A modus operandi featuring sequential nZVI and microbe combination is presented to illustrate its potential for wastewater treatment, based on recent our laboratory and field works using nZVI to treat wastewater containing heavy metal or recalcitrant organic compounds.

1. nZVI-microbe interactions

Combing nanoparticles (NP) and microbes has been shown to be a robust tool in the field of bioremediation, bioconversion and bioenergy (Chen et al., 2014; Ettwig et al., 2016; Kornienko et al., 2018; Nyström et al., 2016; Sakimoto et al., 2016). In such fusion, the NPs contribute to transmit information and signals, yield a host of complex products not feasible via purely abiotic system; the self-repair, reproduction nature of the microorganism grants NP-bio system potentially high scalability. Recent researches have recognized that the presence of NPs may play important roles in some microbial metabolisms. For example, the FeS_2 nanoparticle is widely studied about its contribution to provide iron and sulfur as nutrition element for protein building or energy generation (Jørgensen et al., 2019). Herein, we focus on the interactions which are categorized into direct and indirect pathways between nZVI and microbes (**Fig. 1**). nZVI nanoparticles have the tendency to directly attach to the surface of microbes resulted from electrostatic attractions, hydrogen bonds or other driving forces. The direct contact exerts impact through enhancing direct electron transfer, providing nutrient source of Fe, generating reactive oxygen species (ROS) that interferes cellular components (e.g., genes, proteins), while indirect impact is mainly exerted by changing geochemical conditions and via the function of corrosion products or through the interaction of iron with other elements (Melton et al., 2014).

1.1. *Effects of nZVI on microbes*

Due to the presence of metallic iron (with standard electrode potential of −0.44 V) and its diminutive size, nZVI has strong reducing power. This unique structure and physicochemical characteristics make the nZVI nanoparticle as an excellent electron donor and functional ‘nano-channel’, which is able to assist electron transfer when the microbes by themselves are limited in accessibility to electrons. Moreover, such assistance in electron transfer induces some metabolic pathways that would not have been otherwise possible. The nZVI nanoparticles can also act as a potential rich source of Fe for incorporation into enzymes.

(1) Direct contact

The nZVI particles and its oxidation products can attach directly to microbial cells via several driven force such as electrostatic attraction and/or the coulombic attraction, or even the non-coulombic interactions like dipole-dipole effects (Bosch et al., 2010), facilitating the interactions of surface protein and the nZVI‘s electron transfer via structures such as c-type cytochrome (Xiong et al., 2006), or accelerating the interspecies electron transfer processes between the microbes, and stimulating the relative abundance of bacteria such as *Magcotactic* spp. that can utilize magnetite as electron donor. Further, Fe(II) and Fe(III) released from the nZVI can participate directly in the metabolism of the microbes (e.g., through binding with specific proteins), despite that excessive Fe^{2+} uptake may cause oxidative damage to the cells (Zhao et al., 2020). Moreover, the Fe precipitation can prevent the accumulation of toxic metabolic products (e.g., H_2S) and the passing-through of the nanoparticles into the cell, so as to favor the microbe survive or induce encrustation of the microbes (Harouaka et al., 2016). Notably, it has been recognized that the direct contact is probably the major mode for the interactions between the nZVI and the microbes, because of the relative low solubility and mobility of the nZVI corrosion products (Kashefi et al., 2002).

The diminutive size of the nZVI nanoparticles further benefits their penetration into the cell through phagocytosis or membrane channels, which then leads to the production of intracellular ROS that can further react with lipids, proteins or DNA and induce offset pathways of the microbes. It is well known that the toxic effect of nanoparticles to the microbes can be implemented via the disruption of the cell structure, or through chemical damage such as inhibiting the energy transformation and changing protein structure (Lefevre et al., 2016). Series of the toxic effect have been reported including the nZVI-induced damage of membrane integrity of the microbes, reductive reaction of the functional group at the nZVI-microbe interface and even changing the life stages of the microorganism (Chaithawiwat et al., 2016). Especially, the gram-negative bacteria (e.g., E. coli) is proved to be more sensitive because of their relative thin peptidoglycan layer in the cell structure (Lee et al., 2008). Besides, fungal cells with thicker cell structure (than bacteria) are more tolerant to the toxic effect of nZVI nanoparticles. The results indicate that cell structure plays an important role to the microbes’ response to the potential toxic effect of nZVI. Although the toxic effect of nZVI to the microbes is still controversial, presence of the nanoparticles inside the cell stimulate the microbial metabolism to release the enzyme such as superoxide dismutase (SOD) and catalase (CAT), or to promote the secretion of specific protein to encapsulate the particles (Mansor and Xu, 2020).

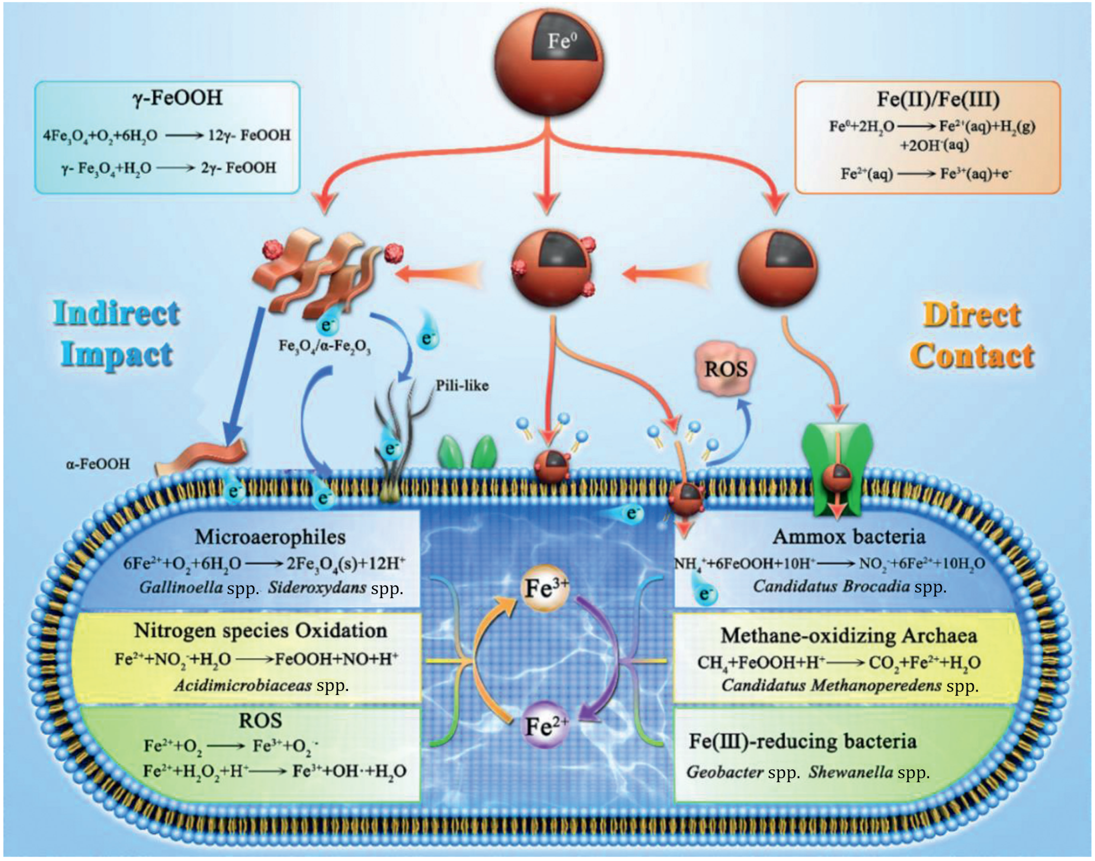

Fig. 1 – Illustration of nZVI and microbial cell interactions: direct contact and indirect impact. nZVI exerts influences to microbes directly through enhance electron transfer, disrupt of the cell membrane architectures, and generates reactive oxygen species (ROS) to interfere the gene and protein; or exerts influences indirectly through changing the geochemical conditions, utilizing electron shuttles and pili structure. The colored panels indicate possible biotic reactions. Reproduced with permission from (Kappler et al., 2021; Scheller et al., 2016; Wang et al., 2021). (Copyrights, Elsevier and Springer Nature Limited).

(2) Indirect Impact

The indirect impact is primarily caused by the changes induced by nZVI, in aspects of system geochemical conditions such as pH, H_2, redox potential and iron-based products. Some induced geochemical conditions are favorable to the microbe growth (Liu and Lowry, 2006).

The reactions of nZVI with water consume the oxygen, creating oxygen-free condition favorable for some anaerobic microbes (Eqs. (1) and (2)). For example, taking nZVI or Fe(II) as electron donor and oxygen as electron acceptor can stimulate the abundance of Microaerophiles such as *Gallinoella* spp. and *Sideroxydans* spp. (Maisch et al., 2019). The H_2 released from the nZVI corrosion is also an excellent electron donor to autotrophic microbes.

$$Fe^{o}+2H_2O \rightarrow Fe^{2+}+H_2+2OH^{-} \quad (1)$$

$$6Fe^{2+}+O_2+6H_2O \rightarrow 2Fe_3O_4+12H^{+} \quad (2)$$

The nZVI's corrosion products also affect the microbial metabolism (Bosch et al., 2010). For example, the *Geobacter metallireducens* can alternate between Fe(III) reduction and nitrate-dependent Fe(II) oxidation due to the presence of Fe-oxides. nZVI's corrosion products such as magnetite are favor for bacteria communities such *Magcotactic* spp. that can utilize magnetite as electron donors (Aulenta et al., 2013); the γ-FeOOH can act as catalyst to accelerate the microbial oxidation. Moreover, the decrease of the redox potential (E_h) caused by nZVI corrosion enhances the microbial reduction (Aeppli et al., 2019; Liu et al., 2017). In addition, the biological and chemical cycles of iron mediated by other elements such as carbon, nitrogen, sulfur may exert impact to the microbes. For example, the cycles of iron and nitrogen are commonly reported such those producing N species including NO_2^-, NO_3^-, N_2O. The formed NO_3^- is beneficial to the NO_3^- reducing Proteobacteria which is able to oxidize Fe (II). This Fe-N reactions contribute to the microbially-mediated oxidation of Fe in anoxic conditions (Melton et al., 2014).

1.2. *Effects of microbes on nZVI*

In the combination, the microbes can improve nZVI's performance in return, by regulating the nZVI's surface chemistry and intervening the product formation. For example, the microbial reduction can help to maintain low redox potential and consume the potential competing oxidants that may otherwise react with nZVI (Aeppli et al., 2019); fast microbial reduction favors the formation of amorphous products from nZVI corrosion, other than stable crystalline products (Komlos et al., 2007). Some species such as iron-reducing bacteria (IRB) directly involve into the Fe geochemical cycle occurring on or inside the cells to regulate the corrosion products (Melton et al., 2014). Besides, organic matters released by the microbes encourage the formation of the iron-ligand complexes, modify the morphology and the size of the nZVI in reaction. Another route is by generating oxidoreductases, hydrolases and transferases that can catalyze the transfer of specific functional groups such as methyl, sulfate, phosphate to affect the nZVI transformation processes. The change of solution micro-environment through microbial metabolisms also can reduce nanoparticle aggregation and thus affect the mobility of the particles (Mansor and Xu, 2020).

Certainly, the electron transfer is bidirectional processes between the NPs and microbes. Iron oxides can act as electron acceptors and the anaerobic ammonium oxidation bacteria (Anammox) as electron donor in the case of nitrogen cycle to facilitate the Fe(III) reduction and accelerate Fe-N cycle (Yang et al., 2012). The probable 'electron transfer tool' via pili-like, nanowire or electron shuttles structure (i.e., self-made redox mediators) generated from microbes contributes to the transformation of nanoparticle corrosion (Reguera et al., 2005).

Without doubt, microbes themselves have evolved strategies including biomineralization, releasing antioxidants, motility, shifting their metabolism and niching construction to maintain the balance between the positive influence and the potential inhibition (Xie et al., 2017). Examples of extracellular biomineralization induced by magnetite and goethite formation via Fe (II)-oxidizing microbes and specific protein can encapsulate the inside nZVI particles via intercellular biomineralization and export them away from the cell.

2. Applications of integrated nZVI-bio system

Reports are growing rapidly about the combined nZVI-bio process. Majority of the reported cases were direct contact and a few were operated in sequential.

2.1. *Direct contact*

For the combined nZVI-bio system, direct contact mode was frequently applied due to its simplicity. For example, a nZVI process was employed with perchlorate-reducing microorganism to treat perchlorate-contaminated wastewater. Excellent perchlorate removal performance ($\geq$ 99%) was achieved at bed residence times (BRT) ranging from 0.3 to 63 hr and an influent perchlorate concentration of 40-600 µg/L (Yu et al., 2007). In another study, nZVI integrated with microorganism for decolorization of reactive blue 13. Addition of 1.0 g/L nZVI into sludge accelerated the decolorization ratio by 29.4% after 1 hr compared to the individual technology (Li et al., 2013).

2.2. *Separated sequential mode*

Separated sequential mode of the nZVI-bio combination can reduce the potential inhibition of NPs to the microbes. For example, a three-staged hybrid nano-bimetallic-bio system, consisting of nZVI/Pd reduction, nZVI/Pd-O_2 advanced oxidation and biodegradation, was used to treat 2,2,4,4-tetrabromodiphenyl ether (BDE47); the system exhibited superior performance of fully debromination in 90 minutes, while the BDE47 was difficult to treat with single advanced oxidation and biodegradation processes (Lv et al., 2016). In another study, a separated sequential process consisting of a nZVI reactor, a flocculation reactor and a bioreactor was used to treat dye wastewater (**Fig. 2**). The operation showed that the color removal was close to 100% and the effluent COD was maintained close to 50 mg/L; both decolorization and COD reduction efficiency were much higher than those in the benchmark bioreactor of the nZVI- or bio- treatment alone (Liu et al., 2019). A large-scale two-staged nZVI treatment including nZVI reactor and a flocculation reactor was used to remove toxic heavy metals (e.g., As, Cu) from smelting wastewater first, the nZVI-treated effluent then flowed to biotreatment to remove organic substance and nitrate. The entire system showed high efficacy for all targeted contaminants. These cases showed the stability, high efficiency and low cost of the separated sequential system.

Several other technical innovations were emerging from the nZVI-bio system. For example, direct-anchoring of the NPs to the engineered biofilms, microbes or enzymes was reported to be effective to improve the performance (Kornienko et al., 2018). A new concept was proposed about the direct-mixing strategy of the anchoring of nanomaterials in the extracellular matrix of bacterial biofilms to facilitate the electron transfer between nZVI and the microbes through narrowing physical distance (Wang et al., 2019).

3. Future outlooks

Integrating nanoscale zero-valent iron (nZVI) technology to conventional biological processes has been proven to be effective for wastewater treatment and environmental remediation. The combined schemes minimize major drawbacks of biological processes such as metal cytotoxicity, low bioavailability and toxic byproducts of some organic pollutants.

Ongoing developments from both nanotechnology and recombinant DNA techniques can further expand the advantages of the nZVI-bio technology (Hennebel et al., 2009). For example, studies have been published on improving the reactivity of nZVI through surface structure modifications such as sulfidation, bimetallic doping such as Pt, Ni and coating with polymers at the surface of nZVI. The modified nZVI may have better chemical stability and lower toxicity, can stimulate microbial growth with the biodegradable surface coatings (Weon et al., 2021). Some organic dopants such as nanocelluloses can provide high quality carbon source as well as electron donors for microbial growth. Recent development of nanoparticle size reduction (e.g., to the level of single atoms) may fundamentally enhance the performance and effectiveness of nanoparticles, and is also expected to promote the

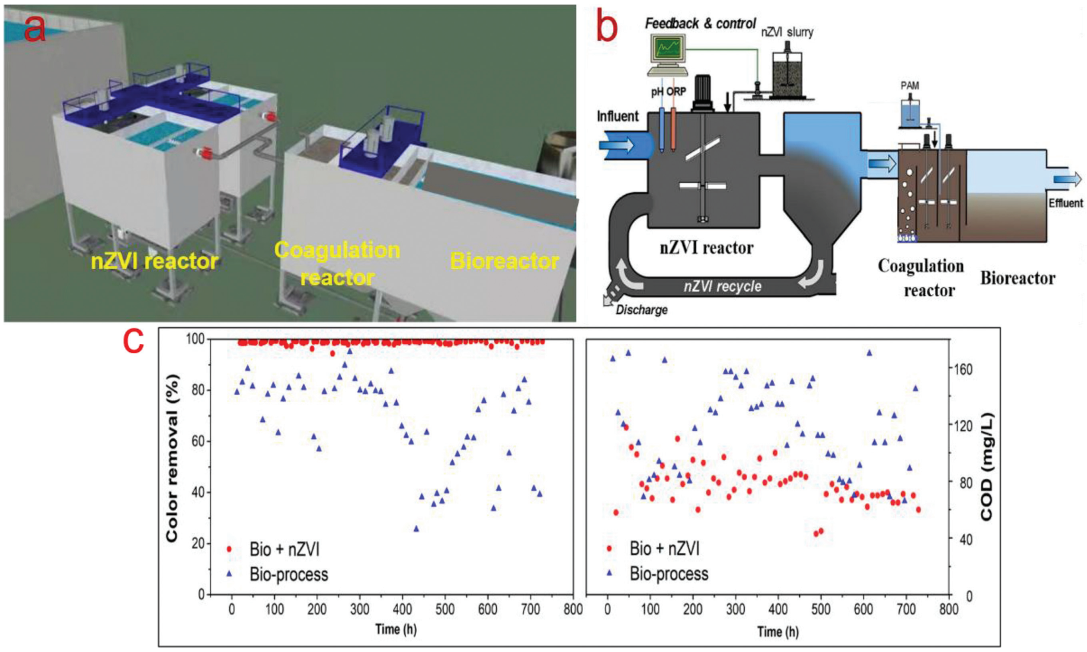

Fig. 2 – An example of the combined nZVI and biological process to treat industrial wastewater: a) the combined treatment plant showed in 3-D schematic. b) schematic process illustrated in 2-D process. c) efficiency of color removal and COD reduction.

development of nZVI-bio combination system (Li et al., 2021; Mauter et al., 2018).

Novel nZVI-bio applications have also benefitted from molecular cell biology such as metagenomics and meta-transcriptomics that could be applied to explore the underlying mechanisms of nZVI-bio processes (Vila Vich et al., 2020). For example, inserting microbial cells with metal-binding proteins via clustered regularly interspaced short palindromic repeats (CRISPR) is being investigated to replace the native genes of indigenous bacteria with specific metal-binding genes, which have high reactivity and selectivity for target pollutants. Creative researches in the bio-nano fusion are rapidly expanding our understanding on the diversity, ecology and environmental impact of the single atom nanotechnology and molecular biotechnology, and thus on the NP-bio fusion. While the iron biochemical cycle and the interactions among the nanoparticles and microbes have long been the foci of environmental and ecological sciences, the development of new tools such as gene editing and isotope tracer offers new capability to understand complex processes in the environment and will in turn promote cost-effective innovations and more sustainable environmental technologies.

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